A Textbook of
COLLOID CHEMISTRY

BY

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Second Edition

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PREFACE TO THE SECOND EDITION

This second edition of *Colloid Chemistry,* like the first, has been written with a threefold purpose: (1) to acquaint the student with the foundations of colloid chemistry and with the rôle that the classical experiments have played in the development of the modern theories and applications of the subject; (2) to formulate systematically and to correlate critically the theories underlying colloidal chemical behavior; and (3) to illustrate the widely diversified applications of the principles of colloid chemistry in such fields as the industrial arts, agriculture, and biology.

Since colloid chemistry has come of age during the time after the writing of the first edition, it might be questioned whether extended reference to the classical background should be continued in the second edition. A modern physical chemist, however, still should know of the heritage left by Nernst and Wm. Ostwald even though their classical researches are almost a century old; so too the decades-old contributions of Graham, Wo. Ostwald, Freundlich, Einstein, Svedberg, Hardy, Donnan, Perrin, Langmuir, Gortner, and Bancroft should be held up before the present-day student that he may know the solid foundations on which modern colloid chemistry is built and is still growing apace under the inspiring leadership of McBain, Flory, Debye, Williams, Mark, Hauser, and others. The systematic formulation and the critical correlation of the theories of colloidal behavior call for even more wisdom than was needed a decade ago, since the old theories are being put to the test every day and new concepts are being formulated.

In my attempt to reduce the number of pages devoted to this textbook I was confronted on all sides by new applications of the science to biology and the industrial arts. Because of the growing usefulness of the principles of colloid chemistry in most fields of human endeavor, I had considerable difficulty in limiting the number of pages devoted to applications. In order to conserve space, the references have been collected together at the ends of the chapters, and their number has been reduced by referring, when practicable, to textbooks and review articles that are replete with references which the reader may wish to consult.

Finally the new book, like the old, drew its form from the incomparable *Kapillarchemie* of Herbert Freundlich. I considered many approaches on my own and many others suggested by friends and well-wishers; but I always returned to the magnificent formulation of the subject matter by Freundlich.

From all those who helped with the first edition, I have had unselfish support in the preparation of the second edition. In addition, I have had the assistance of Dr. James Holmes of the Houdry Process Corporation in rewriting Chapter 4; of my colleague, Professor John Treanor Smith of the Rice Institute, who prepared Chapter 5; and of Dr. Henry B. Bull of Northwestern University Medical School, a pupil of our late friend, R. A. Gortner, who assisted in preparing the sections on the hydrophilic colloids. I alone, however, am responsible for any errors of omission or commission.

Students and teachers, known and unknown, throughout the country called to my attention errors and omissions in the first edition. I gratefully acknowledge this interest and hope I may continue to have their generous cooperation.

HARRY B. WEISER

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PREFACE TO THE FIRST EDITION

This textbook of colloid chemistry was written for students who have completed a general course in physical chemistry such as is commonly given in the junior year to students specializing in chemistry or chemical engineering. It is the outgrowth of twenty-five years' experience in teaching colloid chemistry as a separate course, to advanced undergraduate and graduate students. During this quarter century, the importance of colloid chemistry has come to be so generally recognized that the subject cannot be taught adequately as a part of an introductory course in general or physical chemistry. It is for this reason that most educational institutions have found it highly desirable if not essential to supplement the brief introduction to the subject with a comprehensive course on the theory and applications of colloidal behavior.

Although the science which is now called colloid chemistry is comparatively young, it has had a dramatic past which includes some of the most interesting experiments and techniques to be found in the whole history of chemistry. Moreover, the principles which are encountered in the realm of colloid chemistry are so numerous and varied that the subject has a special interest for the student of pure science who wishes to correlate and extend his scientific knowledge. Finally, in no division of chemistry are to be found more applications of scientific principles to everyday experiences in home, laboratory, and factory. This book has therefore been written with a threefold purpose: to acquaint the student with the foundations of colloid chemistry and with the rôle that the classical experiments have played in the development of the modern theories and applications of the subject; to formulate systematically and to correlate critically the theories underlying colloid chemical behavior; and to illustrate the widely diversified applications of the principles of colloid chemistry in such fields as the industrial arts, agriculture, and biology.

The plan of the book is as follows: After an introductory chapter, which is concerned with the general aspects of the colloidal state of matter, appears a section of seven chapters dealing with the phenomena of adsorption at various types of interfaces. Following this fundamental section on adsorption, ten chapters are devoted to the formation and properties of lyophobic and lyophilic sols. This discussion is followed in turn by shorter sections on gels, emulsions and foams, and aerosols and solid sols. The three concluding chapters deal in a more comprehensive way with the application of colloid chemical principles to contact catalysis, dyeing, and clay. An attempt has been made to render the presentation as clear and concise as possible by outlining the subject matter with frequent section and paragraph headings. Among the numerous references are included books and articles from which a more extended bibliography may be prepared by the student who wishes more detailed information on a specific subject.

The author takes this opportunity to acknowledge his indebtedness to the following gentlemen who have read and criticized certain portions of the manuscript: Professor Harold A. Abramson of Columbia University; Professor Wilder D. Bancroft, Professor T. Roland Briggs, and Professor Richard Bradfield of Cornell University; Professor Floyd E. Bartell of the University of Michigan; Professor Henry B. Bull of Northwestern University; Professor Charles W. Foulk and Professor Wesley G. France of the Ohio State University; Professor A. D. Garrison and Dr. W. O. Milligan of the Rice Institute; Professor William D. Harkins of the University of Chicago; Professor Harry N. Holmes of Oberlin College; Professor James W. McBain of Stanford University; Dr. Elroy J. Miller of the Michigan State College; and Professor John W. Williams of the University of Wisconsin. The suggestions so freely given by these authorities have been of very great assistance to the author in the preparation of the book. It should be stated, however, that the author alone is responsible for any errors of commission or omission. Grateful acknowledgment is also made to Mr. J. L. Flanagan for his care in checking the references and in reading the proof.

HARRY B. WEISER

MARCH 1, 1939

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CHAPTER 1

The Colloidal State

Thomas Graham,[1]* in his fundamental paper "Liquid Diffusion Applied to Analysis," showed that substances like certain inorganic salts, sugar, and glycerol, which are readily obtained in a crystalline form, will diffuse through water and certain membranes much more rapidly than substances such as albumin, gelatin, and the hydrous oxides, which are gelatinous and are obtained in the form of definite crystals with difficulty, if at all. Substances which diffuse rapidly were called *crystalloids,* and those which exhibit little or no tendency to diffuse were termed *colloids,* from the Greek *kolla,* meaning glue. Although Graham's observations led him to distinguish two classes of substances, he recognized that such a classification was arbitrary since "in nature there are no abrupt transitions," and crystalline colloids exist. Moreover, with respect to colloids Graham was the first "to speak of their peculiar form of aggregation as the colloidal condition of matter."

Although the limitations of Graham's classification were recognized by Graham himself, the important investigations of von Weimarn[2] with a definitely crystalline inorganic salt, barium sulfate, established the view that the distinction between crystalloids and colloids is not tenable and that we should speak of the colloidal state of matter just as we speak of the liquid, solid, and gaseous states of matter. Von Weimarn generalized, further, that any crystalline material can be made to assume the colloidal state under suitable conditions. A phase is said to be colloidal when it is sufficiently finely divided in at least one dimension. Strictly speaking, therefore, the term colloid should be used only as an adjective to define a physical system of matter usually made up of more than one substance. But, for convenience, we frequently refer to a finely divided phase as a colloid. This is particularly true if we are dealing with colloidal organic materials such

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* Superior numerals refer to entries in the list of references at the end of the chapter.

as gelatin, agar, and rubber which are either non-crystalline or submicroscopically crystalline.

COLLOIDAL SYSTEMS

The Colloidal Zone

A colloidal system is a heterogeneous or dispersed system of at least two phases, one of which, a finely divided or *dispersed phase,* is more or less uniformly distributed in a continuous phase, the *dispersion medium.* Wolfgang Ostwald [3] first classified dispersed systems on the basis of the size of the particles of the dispersed phase and set the limits of the colloidal zone. His most recent classification is given in Table 1.[4] The colloidal zone which Ostwald once referred to as "the land of neglected dimensions" is thus set between two arbitrarily chosen limits of particle size: 0.5 μ which is near the lower limit of the resolving power of an ordinary microscope, and 1.0 mμ which is somewhat greater than the diameters of ordinary molecules and ions.

TABLE 1

CHARACTERISTICS OF DISPERSE SYSTEMS (OSTWALD)

Type	Range of particle size	Characteristics
Coarse dispersions	$>0.5\ \mu$ $(>5 \times 10^{-5}$ cm)	Particles do not run through a paper filter; do not diffuse; do not pass through a dialyzing membrane; are microscopically visible.
Colloidal dispersions	$0.5\ \mu$ to $1\ \text{m}\mu$ $(5 \times 10^{-5} - 1 \times 10^{-7}$ cm)	Particles run through a paper filter but not an ultrafilter; are not resolved in an ordinary microscope but are usually recognizable in an ultramicroscope; diffuse and pass through a dialyzing membrane very slowly, if at all.
Molecular dispersions, solutions	$<1\ \text{m}\mu$ $(1 \times 10^{-7}$ cm)	Particles pass through both a paper filter and an ultrafilter; are not visible in microscope or ultramicroscope; diffuse and pass through dialyzing membranes quite rapidly.

The arbitrary nature of the limits is evidenced by the fact that certain substances such as egg albumin and hemoglobin may be molecularly dispersed in water, but the molecules of the compounds are so large that they come well within the colloidal range. For the most part, however, particles in the colloidal state consist of aggregates of molecules that are too small to be resolved in the ordinary microscope.

Classification and Terminology

1. Disperse systems. Classifying colloidal systems on the basis of the states of aggregation (solid, liquid, and gas), Ostwald recognized eight types of systems. These are given in Table 2, together with the name of each system and some typical examples of each.

TABLE 2

DISPERSE SYSTEMS

Dispersed phase (internal phase)	Dispersion medium (external phase)	Name	Typical examples
Solid	Liquid	Sol	Gold in water; nickel in benzene; arsenic trisulfide in water
Liquid	Liquid	Emulsion	Kerosene in water; water in benzene; milk; mayonnaise
Gas	Liquid	Foam	Froth on beer; foam on soap solutions; meringues
Solid	Solid	Solid sol	Gold ruby glass; certain gems; blue rock salt; black diamond
Liquid	Solid	Solid emulsion	Certain minerals with liquid inclusions; milk quartz; opal; pearl
Gas	Solid	Solid foam	Minerals with gaseous inclusions; pumice; lavas
Solid	Gas	Solid aerosol	Smoke; volcanic dust; ammonium chloride fumes
Liquid	Gas	Liquid aerosol	Fog; cloud; mist

The third column of Table 2 gives several terms commonly used in colloid chemistry. *Sol* is a general term usually applied to dispersions of solid in liquid, solid, or gaseous media. Since dispersions of solid in liquid are the most common examples of this class, they are called *colloidal solutions* or *sols.* If the dispersion medium is water, the system is termed a *hydrosol;* if the dispersion medium is an organic liquid, it is called an *organosol* or, more specifically, an *alcosol, benzosol,* etc. Dispersions of solid in solid are termed *solid sols,* and dispersions of either solid or liquid in gas are called *aerosols. Emulsion* is the general term for dispersions of liquid in either liquid or solid media. The liquid-in-liquid type is by far the more important.

The above classification of colloidal systems on the basis of the state of aggregation of the phases does not include the *gels.* These are solid or semi-solid systems which owe their rigidity to a kind of network structure. They have been erroneously classified by some people as liquid-in-solid systems; but, since the two phases are continuous, gel systems are of the interlacing type. The two forms of a gel are *gelatinous precipitates* and *jellies.* In general, a gelatinous precipitate comes down under such conditions that it leaves a supernatant liquid, whereas a jelly encloses all the liquid phase. *Hydrogel, alcogel,* and *benzogel* signify that the gel liquid is water, alcohol, and benzene, respectively. Certain lubricating greases from petroleum are highly viscous water-in-oil emulsions that resemble jellies superficially.

2. Difform systems. The shape of a particle as well as its size determines extent of surface. For example, a sphere may be rolled out into a disk, sheet, or film or may be drawn into a thread of any desired thickness, thereby increasing greatly the extent of surface without subdivision. Ostwald gave the name *difformation* to extreme distortion which results in a marked increase in specific surface. Colloidal phases which possess a marked surface area per unit mass because of shape rather than because of degree of subdivision were classified by Ostwald as *difform* systems. Difformation in one dimension by compression of a sphere gives plates, disks, or films. A colloidal system whose internal phase contains particles of this general shape is called a *laminar difform system.* A sphere may undergo difformation in two directions by rolling out into a thread or fiber; a colloidal system whose internal phase contains particles of this shape is called a *fibrillar difform system.* Difformation in three directions takes place when a gas is occluded within a solid rock. Von Buzágh terms such a system a *corpuscular difform system.* In Table 3 is given a classification of macrodifform systems according to the type of difformation and physical state of the internal phase and the physical state of the phases adjacent to the particle. Greater complexities may exist in highly difform systems than are illustrated in the table. Von Buzágh has summarized the principal morphological types of difform systems based on the three basic forms (films, fibers, and corpsucles) and on

TABLE 3

Difform Systems (Ostwald and von Buzágh [4])

	Laminar	Fibrillar	Corpuscular
1. Solid Films, Threads, and Corpuscles			
1. Solid-solid-solid	Slate, mica, graphite (single lamellae)	Asbestos, trichites, dendrites (single fibrillae)	Crystals in rock, single particles of powdered substance
2. Liquid-solid-liquid	Dialysing membrane, gold film between water and benzol	Textile fibers in a dye bath, etc.	Suspended particles, sol particles, single floating particles between two liquids
3. Gas-solid-gas	Films, etc., in air (normal case)	Fibers in air (normal case)	Single crystals in air (normal case)
4. Solid-solid-liquid	Electrolytic precipitate on electrode in bath	......	Particles adhering to solid walls in non-wetting liquids
5. Solid-solid-gas	Deposited layers, e.g., colored or sprayed	......	Particles adhering to solid walls
6. Liquid-solid-gas	Aged peptone skin on solution	......	Single floating particles on liquids
2. Liquid Films, Fibers, and Corpuscles			
7. Solid-liquid-solid	Films of lubricant	Capillary threads (mercury thread of thermometer)	Liquid occlusions in rock
8. Liquid-liquid-liquid	Ternary equilibrium, water-ether-succinonitrile; benzol-acetic acid-water	Pseudopodia, e.g., of Foraminifera; liquid mixtures resembling fibers of pseudopodia	Individual globules in emulsions
9. Gas-liquid-gas	Soap films	Liquid threads, e.g., molten glass, egg white, saliva, fish glue, cherry gum	Liquid droplets in air
10. Solid-liquid-liquid	Wetting films; glass-oil film water	......	Drops adhering to solid walls in liquid (oil in water on glass)
11. Solid-liquid-gas	Fresh paint and lacquer films, water film on insulators	......	Drops adhering to solid walls in air
12. Liquid-liquid-gas	Oil film on water	......	Oil drops on surface of water
3. Gaseous Films, Fibers, and Corpuscles			
13. Solid-gas-solid	Air lubrication, air film between contacting flat surfaces	Air-filled capillaries	Gaseous occlusions in minerals and rock
14. Liquid-gas-liquid	Leidenfrost effect on a liquid surface	......	Gas bubbles in liquids
15. Solid-gas-liquid	Normal Leidenfrost effect; electrolytic rectifier after Guntherschultze	......	......
16. Liquid-gas-gas	"Two-dimensional gaseous layers" after Marcelin and Adam and others	......	......
17. Solid-gas-gas	Adsorption films	......	......

increasing discontinuities. For detailed consideration of the morphology of difform systems von Buzágh's book should be consulted.

3. Lyophobic and lyophilic systems. Another classification of certain colloid systems is based on the attraction or affinity of the dispersed phase and the dispersion medium for each other. If the mutual affinity is small, the system is said to be *lyophobic;* whereas if the mutual affinity is great, the system is *lyophilic.*[5] If water is the dispersion medium, the system is termed *hydrophobic* or *hydrophilic,* as the case may be; if benzene is the dispersion medium, *benzophobic* or *benzophilic;* etc. Gold neither dissolves nor swells in water, and hence gold dispersed in water is a hydrophobic sol; similarly, arsenic trisulfide in benzene is a benzophobic sol. On the other hand, gelatin takes up water and swells to a marked degree; hence gelatin sols and jellies are hydrophilic systems. A given dispersed phase may be lyophobic in one medium and lyophilic in another. For example, starch gives lyophobic systems in alcohol and lyophilic in water, whereas rubber gives lyophobic systems in water and lyophilic in benzene.

Irrespective of the method of classification, colloid systems are dispersed systems in which at least one dimension of the dispersed phase is very small. *Colloid chemistry,* in the words of Bancroft, is therefore the "chemistry of bubbles, drops, grains, filaments, and films."

VARIATION OF CERTAIN PROPERTIES WITH PARTICLE SIZE AND SHAPE

Among the properties of matter which vary with particle size and form may be mentioned: extent of surface, surface energy, rate of solution, solubility, diffusion, Brownian movement, rate of sedimentation, color, and adsorption capacity. Most of these properties will be considered in detail in later chapters, but for purposes of illustration a few of them will be taken up at this point.

Extent of Surface

The enormous increase in extent of surface and in specific surface (area/volume) on subdividing matter in mass into small particles is shown in Table 4, which gives the results of decimally dividing a cube, 1 cm on edge, into cubical subdivisions. The 6-cm^2 surface of the original cube with a specific surface of 6 will become 60–6000 cm^2 (0.024–0.84 acre) with a specific surface of 600,000–60,000,000 when divided into cubes of colloidal dimensions. The area and specific surface of colloidal material are even greater than these figures if the mass possesses a porous or capillary structure. Thus, surface energy and surface properties predominate in colloidally dispersed material because of the relatively enormous surface presentd by a given mass. Colloid chemistry is sometimes called *surface chemistry.*

TABLE 4

DEVELOPMENT OF SURFACE BY DECIMALLY DIVIDING ONE CUBIC CENTIMETER OF SOLID

Number of cubes	Length of edge	Total surface area		Specific surface $\frac{\text{surface area}}{\text{volume}}$
		Metric units	U. S. units	
1	1 cm	6 cm^2	0.93 sq in.	6
10^3	1.0 mm	60 cm^2	9.3 sq in.	60
10^6	0.1 mm	600 cm^2	93.0 sq in.	600
10^9	0.01 mm	6,000 cm^2	6.5 sq ft	6,000
10^{12}	1.0 μ	6 m^2	64.5 sq ft	60,000
10^{15}	* 0.1 μ	60 m^2	645.8 sq ft	600,000
10^{18}	0.01 μ	600 m^2	717.6 sq yd (*ca.* 1/7 acre)	6,000,000
10^{21}	1.0 mμ	6,000 m^2	7176.0 sq yd (*ca.* 6/7 acre)	60,000,000

* Colloidal zone.

Rate of Solution

It is common knowledge that the rate of solution of a solid is increased by pulverization. Roller[6] has investigated quantitatively the effect of particle size on the rate of solution of anhydrite and has found that both the structure and the extent of exposed surface play a rôle in the process. Some of Roller's data are represented graphically in Fig. 1, in which particle size is plotted against dissolution factor. By dissolution factor is meant the relative specific rate of solution of each fraction referred to some fraction, usually the coarsest, taken as unity. In the experiments under consideration, 0.8-g samples of dry anhydrite and of dry gypsum of graded particle size were added to 100-ml portions of water at a stirring speed of 130 rpm, and the rate of solution was measured conductimetrically. The dissolution factor for particles below 50 μ in diameter rises to a maximum. For anhydrite, this maximum is 8.6 at a particle size of 7.0 μ; and for gypsum, it is 4.4 at the coarser particle size of 16.5 μ. With decrease in particle size below the maximum, the dissolution factor reaches the normal value of unity at a particle size of 2.1 μ for anhydrite and 5.1 μ for gypsum; with further decrease in particle size, the dissolution factor becomes quite low. The maximum in the dissolution factor and the subsequent decrease are attributed to the difficulty with which the solvent penetrates to the individual grains of the dry solute because of strong mutual attraction which causes the grains to adhere tenaciously to each other.

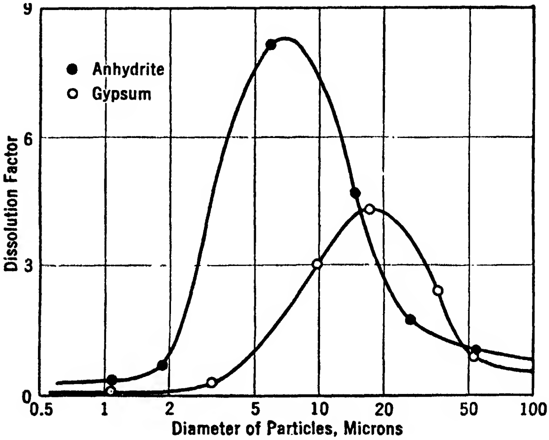

FIG. 1. Effect of particle size on the rate of solution of anhydrite and gypsum.

Surface Energy

Among the familiar phenomena at the boundary surface between liquid and vapor may be mentioned: the existence of a meniscus, the rise or fall of a liquid in a vertical capillary tube, and the tendency of a drop of liquid to assume a spherical form. To account for these and related phenomena Laplace in 1806 assumed that the molecules within a liquid exert a more or less uniform attraction on each other, whereas the molecules at the surface are attracted uniformly downward and sideways but are attracted upward much less strongly because of the smaller number of molecules in the vapor phase. From this point of view, a liquid is under a so-called internal pressure acting perpendicularly to the boundary surface. The classical investigations of van der Waals on the change from the liquid to the vapor state disclosed that this transformation is not abrupt but continuous; hence the liquid and vapor do not meet sharply in a mathematical plane.

On the contrary, certain molecules near the liquid are attracted more strongly than others farther from the surface, thereby producing a boundary layer of molecules in which a continuous density gradient exists. This density gradient in the boundary layer accounts for what is called the surface tension. The *internal pressure* is a force which acts perpendicularly to the boundary surface; associated with this is the *surface tension,* which is a force acting parallel to the boundary surface. Hence the molecules in the boundary act as though they formed a tightly stretched, elastic film over the surface of the liquid, which tends to make the surface as small as possible. The surface tension is expressed in dynes per centimeter.

Energy is required to extend the surface of a liquid since the force of surface tension opposes an increase in the amount of surface. The surface is therefore the seat of *surface energy,* which is the product of the intensity factor, *surface tension,* and the capacity factor, *area of surface.* Surface energy is expressed as the work in ergs required to increase the surface 1 square centimeter, at constant temperature. Since ergs per square centimeter is the same numerically as dynes per centimeter, surface tension is frequently expressed in the energy units.

The phenomena which manifest themselves at the boundary surface liquid-vapor exist also at the boundary surface liquid-liquid. In general, the surface tension at interfaces is termed *interfacial tension.* The methods of measuring the surface tension at the interface liquid-vapor and liquid-liquid are not given here since they are described in detail in most textbooks and laboratory manuals of physics and physical chemistry.

If a sphere of water 1 cm in diameter is dispersed into droplets 0.1 μ in diameter, Harkins[7] points out that the total free surface energy (surface tension × extent of surface) increases from 0.00009 to about 9 calories, which is nearly one-fourth the latent heat of fusion of this amount of water. If a large and small drop of water are placed side by side in an enclosed vessel, the small drop will evaporate and condense on the larger drop because of the greater surface energy (higher vapor pressure) of the smaller drop. The total surface energy is reduced by the process. Similarly, very finely divided particles of a solid might be expected to have a higher vapor pressure, a greater solubility, and a lower melting point than coarse crystals of the material.

Vapor pressure. That small crsytals have a greater vapor pressure than larger ones is well illustrated by an experiment of von Jonstorff.[8] Crystals of iodine 2–3 mm in diameter were kept in a closed vessel in the dark for 8 years, the temperature varying from 0 to 24°. In this time the smaller crystals had disappeared for the most part, and larger crystals 4–5 mm in diameter resulted.

Solubility. Curie[9] and Ostwald[9] showed that, in a system of crystals of various sizes under a mother liquor, the smaller crystals will dissolve and reprecipitate out on the larger ones (*Ostwald ripening*), thereby decreasing the total surface.

It was obserbed by Hulett[9] and confirmed by Dundon[9] that the addition of finely ground calcium sulfate or barium sulfate to saturated solutions of their respective salts causes an increase in conductivity which rises to a maximum and then decreases slowly, finally approaching that of the normally saturated solution. The changing conductivity is usually attributed to decreasing solubility with increasing particle size. Hulett observed no change in solubility of calcium sulfate crystals larger than 2 μ, but decreasing the size from 2 μ to 0.3 μ increased the solubility about 20% at 25°. Similarly, barium sulfate crystals 1.8 μ in radius had a solubility of 2.29 mg/l; but, on grinding to a radius of 0.1 μ, the solubility rose to 4.15 mg/l.

From measurements of particle size and solubility it is possible to calculate the surface tension, using the Ostwald-Freundlich[10] equation:

$$\frac{RT}{M}\ln\frac{S_2}{S_1} = \frac{2\gamma}{\xi}\left(\frac{1}{r_2} - \frac{1}{r_1}\right)$$

in which M stands for the molecular weight, ξ the density of the crystal, R the gas constant, T the absolute temperature, S_1 and S_2 the solubility of particles of radius r_1 and r_2 respectively; and γ the surface tension. Considering slightly soluble salts which are completely dissociated and whose activity coefficients may be taken as unity, the relation between increase in solubility on the one hand, and size of crystals and surface tension on the other, may be represented by a simplification of the Ostwald-Freundlich equation as given by Dundon and Mack.[9]

$$\frac{RT}{M}\ln\frac{S_r}{S} = \frac{2\gamma}{\xi r}$$

in which S_r is the solubility of small crystals of radius r, and S is the solubility of relatively large crystals.

Some calculated values of the surface tension of a number of slightly soluble salts as found by Dundon are given in Table 5. In addition to the data necessary for calculating the surface tension, the molecular volumes (M.V.) and the hardness values are included. It will be noted that molecular volume and surface tension are inversely proportional, whereas hardness and surface tension are roughly proportional.

Balarew[11] questions whether the changing conductivity on adding finely ground barium sulfate, say, to the saturated solution of the salt is due primarily to varying solubility with particle size. Balarew attributes the initial increase in conductivity to: (1) the presence of barium chloride in the sulfate, (2) the greater solubility of broken or difform crystals than of complete crystals, and (3) the breaking up of atomic aggregates. The subsequent fall in conductivity could be caused partly by the crystallizing out of barium sulfate on account of the solution of the chloride, but the velocity of crystallization is so much greater than the rate of fall of conductivity that the latter is attributed to the slow restoration of equilibrium between the complete and broken crystals. Although the greater solubility of broken crystals may be a determining factor in Hulett's experiments, there is no doubt that, below a certain size, the solution pressure of smaller particles is greater than that of larger ones. Balarew raises but does not settle the question of whether Hulett's experimental method gives a true measure of the change in solubility with crystal size.

TABLE 5

SURFACE TENSION OF CRYSTALS

Substance	M	ξ	M.V.	Diameter (μ)	Increase in solubility (%)	Temp. (°C)	γ	Hardness
$BaSO_4$ (H)	233	4.5	52.0	0.1	80	25	1250	2.5–3.5
$BaSO_4$ (D)	233	4.5	52.0	0.2	90	30	3000	2.5–3.5
$CaSO_4 \cdot 2H_2O$	172	2.32	74.2	0.2–0.5	4.4–12	30	370	1.6–2
$SrSO_4$	184	3.96	46.4	0.25	26	30	1400	3.0–3.5
Ag_2CrO_4	332	5.52	60.1	0.3	10	26	575	2 (approx.)
PbI_2	461	6.16	74.8	0.4	2	30	130	Very soft
PbF_2	245	8.24	29.7	0.3	9	25	900	2 (approx.)
CaF_2	78	3.18	24.6	0.3	18	30	2500	4

In this connection it is of interest to note that the heat of solution[12] of sodium chloride crystals, 1.3 μ average diameter, is -900 cal/mole, whereas the value for coarse crystals is -928.6 cal/mole.

Although Ostwald ripening is theoretically and experimentally established, it seems questionable whether this phenomenon is very important in the digestion of analytical precipitates. Trimble[13] showed that the solubility of barium sulfate does not change after the crystals reach 2 μ in diameter, and Kolthoff[14] found that, in general, Ostwald ripening is of subordinate influence in the aging of precipitates at room temperature. The change in filterability on digestion is attributed to perfection of very imperfectly formed crystals and to collection of smaller particles into larger clumps, followed by the cementing together of the unit particles into aggregates which are retained by the filter.

Melting point. The decrease in melting point which accompanies the very fine subdivision of crystals was first observed by Pavlov[8] with crystals of salol, antipyrine, and phenacetin. His observed lowerings of 1–7° were too high, but Meissner[8] showed that films of azobenzene, tristearin, and myristic acid 8 μ in thickness melted 0.2–0.36° lower than large crystals.

Adsorption

Adsorption consists in the concentration or accumulation of substances at surfaces or interfaces. The adsorbing phase is called the *adsorbent,* and the adsorbed phase, the *adsorbate.* If the atoms or molecules of one phase penetrate among the atoms or molecules of the second more or less uniformly, the phenomenon is termed *absorption* or solution, to distinguish it from the surface phenomenon. Since, as we have seen, matter in the colloidal state presents an enormous surface relative to the mass, adsorption is probably the most common and important phenomenon encountered in colloid or surface chemistry.

The difference between adsorption, absorption, and chemical compound formation may be illustrated by means of curves showing the variation with pressure in the amount of gas taken up by a solid phase. In Fig. 2, the amount of gas taken up x per mass of the solid m is plotted against the concentration (pressure) of the gas phase p, at constant temperature. I is a typical adsorption isotherm; II represents the absorption of a gas by a homogeneous solid phase where there is direct proportionality between the amount taken up x/m and the pressure p, as required by Henry's law; III shows the variation from Henry's law when the dissolved substance is associated; and IV represents the equilibrium between the gas and solid phases when chemical compound formation takes place.

It has been observed in some cases that the initial rapid adsorption by a solid adsorbent is accompanied or followed by a slow penetration of the adsorbed substance into the solid mass. Some people claim that the slow secondary process is absorption, whereas others consider it to be adsorption that is slowed up on account of the time required for the adsorbate to penetrate very minute pores in the adsorbent. McBain [15] recommends that the process be called *sorption* wherever there is a possibility that both adsorption and absorption are involved. In this book, the phenomenon will be termed adsorption unless secondary absorption or solid solution is known to accompany the primary process.

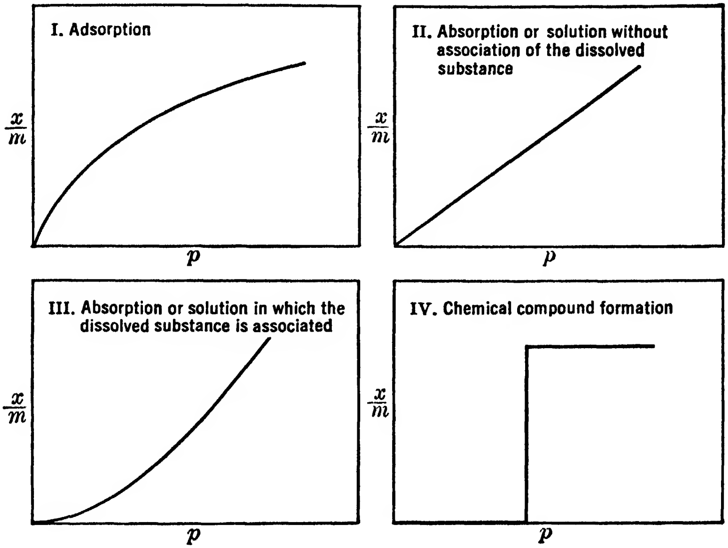

FIG. 2. Typical isotherms for adsorption, absorption, and chemical compound formation.

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PART I. ADSORPTION

CHAPTER 2

Surface Tension and Adsorption

The surface tension of a pure liquid is constant at constant temperature, but it may be changed by the addition of some other substance to the liquid. Most dissolved non-electrolytes lower the surface tension of water, some do not change it appreciably, and a few raise it slightly. In general, the surface tension of a solution lies between the surface tensions of the two constituents. Since the surface tension of water is higher than that of most other liquids, the addition of such liquids to water gives a solution with a lower surface tension.

If the surface tension of a solution is plotted against the concentration, the resulting curve approaches a straight-line relationship only when the two substances are similar chemically and when their surface-tension values are similar. For substances with quite different surface tensions, the curves pass through a minimum or exhibit a tendency toward a minimum. For example, minima were observed by Whatmough[1] with the following mixtures: acetic acid and benzene, methyl iodide, ethyl iodide, chloroform, or carbon tetrachloride; carbon disulfide and ethylene chloride; benzene and ethyl iodide; carbon tetrachloride and chloroform; ethyl acetate and amyl alcohol. On the other hand, Roentgen and Schneider[2] observed a maximum surface tension for a solution of sulfuric acid and water containing 48% H_2SO_4.

The surface tension of solutions of most salts is greater than that of water. This would seem to be in accord with the general rule since the surface tensions of salts are doubtless greater than that of water. The strong bases also increase the surface tension, but ammonia and nitric, hydrochloric, and hydrobromic acids lower it.

The surface tension of water is lowered most strongly by organic compounds with long chains of carbon atoms or with one or more benzene rings. Such compounds are said to be *surface active* or *capillary active.* Good examples of strong capillary-active compounds are the fatty acids, alcohols, and urethanes. Many colloidally dispersed substances, such as soaps, proteins, and certain dyes, likewise exhibit high surface activity. On the other hand, the salts of the lower fatty acids and hydroxy acids have little effect on the surface tension of water.

The influence of the length of the chain of carbon atoms on the lowering of the surface tension of water is illustrated in Fig. 3*a*, which gives the surface tension-concentration curves for solutions of the homologous series of fatty acids from formic to isovaleric. The higher members of the series produce a very marked lowering of the surface tension even at low concentrations.

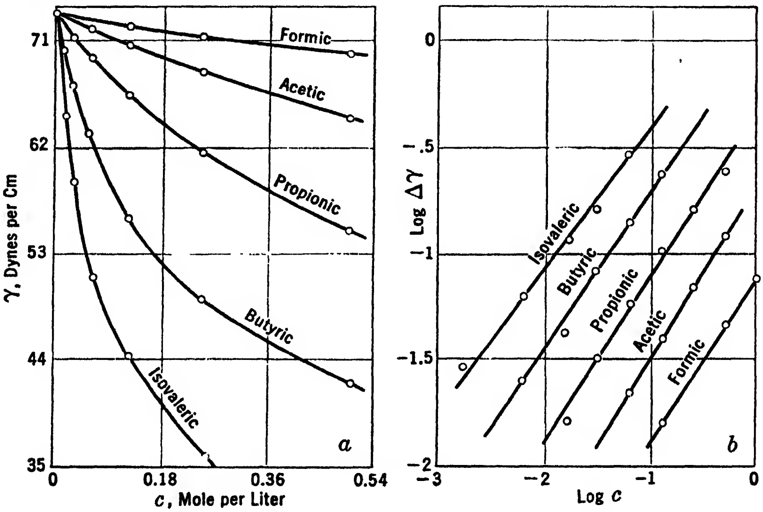

FIG. 3. Surface-tension concentration curves for solutions of certain fatty acids.

From the form of the curves in Fig. 3*a*, it is apparent that the relative lowering of the surface tension [$\Delta\gamma = (\gamma_{H_2O} - \gamma_{soln.})/\gamma_{H_2O}$] is not directly proportional to the concentration of solution c. Freundlich[3] pointed out that, for moderate concentrations, the relationship can be expressed by the empirical equation:

$$\Delta\gamma = \alpha c^{1/n} \tag{1}$$

where α and $1/n$ are constants. This equation expressed logarithmically takes the form:

$$\log \Delta\gamma = \log \alpha + \frac{1}{n} \log c \tag{2}$$

If the equation applies, the curves obtained by plotting log γ against log c should be straight lines. That this is approximately true for the results shown graphically in Fig. 3*a* is evident from the curves in *b*. Since the lines are approximately parallel, the values of $1/n$, which are given by the slopes of the lines, are practically the same for the several acids under consideration.

Surface Concentration

Gibbs's rule. In the preceding chapter, it was pointed out that the surface energy of a liquid tends to become as small as possible. Since the surface tension of a pure liquid is constant at constant temperature, the only way it can attain the minimum surface energy is for the extent of surface to become as small as possible. With solutions, there is the further possibility of decreasing the surface energy by a change in the concentration of the surface film which will decrease the surface tension. It has been found experimentally that the concentration of solute in the surface is usually different from the concentration in the body of the liquid. This was predicted in 1878 by Willard Gibbs, who formulated the rule governing the change in concentration. Gibbs's rule is usually stated in the following way: the concentration of solute in the surface film will change in such a way as to lower the surface tension. This statement goes beyond the rule as formulated by Gibbs. Gibbs's rule actually states that, regardless of the nature of either of the chemicals concerned in a two-component system, for any given slope, at a particular point on a graph of surface tension against logarithm of the activity of the solute, the adsorption is the same, irrespective of whether the surface tension at that point is higher or lower than or the same as the surface tension of the solvent.[4] It follows, therefore, that, if further addition of a solute to a solution lowers the surface tension, the surface film will be more concentrated than the body of the solution, whereas, if further addition of a solute to a solution raises the surface tension, the surface film will be more dilute than the body of the solution. The system will be in equilibrium when the change in surface tension just balances the difference in osmotic pressure between the body of the solution and the surface film.

Gibbs's surface concentration equation. The relationship between surface concentration and surface tension was first deduced thermodynamically by Gibbs[5] and later in a somewhat different form by Thomson[6] and by Milner.[7]

A solution of volume v, surface s, surface tension γ, and osmotic pressure p is passed through the following steps in the isothermal reversible cyclic process:

1. The surface s is increased by ds at constant volume. The work required W_1 is:

$$W_1 = \gamma ds$$

and the osmotic pressure changes from p to $p + (\delta p/\delta s)_v ds$.

2. The volume v is increased by dv, keeping the surface constant at $s + ds$. The work done W_2 is:

$$W_2 = -\left[p + \left(\frac{\delta p}{\delta s}\right)_v ds\right] dv$$

and the surface tension becomes $\gamma + (\delta\gamma/\delta v)_s dv$, owing to the change in concentration accompanying the dilution.

3. The surface is restored to the original area s, and the system performs the work W_3:

$$W_3 = -\left[\gamma + \left(\frac{\delta \gamma}{\delta v}\right)_s dv\right] ds$$

4. The volume is restored to the original value v, which requires the work W_4:

$$W_4 = pdv$$

The total energy changes in the process must be equal to zero, that is:

$$W_1 + W_2 + W_3 + W_4 = 0$$

From which it follows that:

$$-\frac{\delta\gamma}{dv} = \frac{dp}{ds} \tag{3}$$

This formula states that the surface tension varies with the volume, and therefore with the concentration, only when the osmotic pressure depends on the surface area.

Starting with eq. 3, an expression may be derived for the excess concentration (either positive or negative) in the surface.

If N moles of a substance are dissolved in v liters, the concentration c is:

$$c = \frac{N}{v}$$

But since a moles are withdrawn by each square centimeter of surface, the volume concentration on which γ and p alone depend is:

$$c = \frac{N - as}{v} \tag{4}$$

Equation 3 may be written as follows:

$$-\frac{d\gamma}{dc}\cdot\frac{dc}{dv}=\frac{dp}{dc}\cdot\frac{dc}{ds} \tag{5}$$

From eq. 4 it follows that:

$$\frac{dc}{dv}=-\frac{N-as}{v^2}=-\frac{c}{v};\quad\text{and}\quad\frac{dc}{ds}=-\frac{a}{v}$$

On substituting these values in eq. 5, it becomes:

$$-\frac{d\gamma}{dc}=\frac{a}{c}\frac{dp}{dc} \tag{6}$$

If the gas laws are assumed to apply, $dp/dc = RT$, where R is the gas constant and T is the absolute temperature. RT being substituted for its equivalent in eq. 6, the latter becomes:

$$a=-\frac{c}{RT}\cdot\frac{d\gamma}{dc} \tag{7}$$

or

$$a=-\frac{\alpha}{RT}\cdot\frac{d\gamma}{d\alpha} \tag{8}$$

where α is the activity of the solute.

Equation 8 is known as the Gibbs adsorption equation, since a is the amount of solute per square centimeter of surface adsorbed or concentrated in the surface or interfacial layer. From this equation it follows that the adsorption a of a dissolved substance is *positive* when $d\gamma/dc$ is negative, that is, when further addition of the solute lowers the surface tension of the solution; whereas the adsorption is *negative* when $d\gamma/dc$ is positive, that is, when further addition of the solute increases the surface tension of the solution. From the equation, it follows also that a dissolved substance may lower the surface tension to a marked degree but it can raise it only a relatively small amount. The reason is that the more a given substance lowers the surface tension, the more it is adsorbed and the greater the surface-tension change; on the other hand, if the added substance raises the surface tension, the surface concentration is relatively small because of negative adsorption and the change in surface tension is correspondingly small. As pointed out, experience has shown that relatively low concentrations of highly surface-active substances lower the surface tension of water to a marked degree.

Tests of Gibbs's adsorption equation. Quantitative tests of Gibbs's equation are not readily accomplished, partly because of the experimental difficulties encountered in determining the surface concentration. Successful qualitative experiments along this line were made by Benson,[8] who passed bubbles of air through an aqueous solution of amyl alcohol and collected and analyzed the foam. The surface concentration was found to be 0.0394 N as compared with the original mass concentration of 0.0375 N. Similar observations of Donnan and Barker[9] with nonylic acid solution showed fair agreement between observed and calculated values of the adsorption. Using the air-bubble technique, McBain[10] made accurate measurements with aqueous solutions of isoamyl alcohol, acetic, butyric, caproic, and nonylic acids, phenol, *p*-toluidine, resorcinol, thymol, camphor, and sodium chloride. In every instance 2 to 8 times as much solute was carried along by the bubble as would be predicted by the Gibbs equation. The results are essentially the same whether concentrations or activities are taken as the basis of the calculation. The amounts carried were from 2 to 4 times more than could be accommodated in a monomolecular film of closely packed, vertically oriented molecules. This suggests that the high experimental values result from the presence of chains of oriented molecules extending downward into the solution from the outermost monomolecular film.

TABLE 6

TEST OF THE GIBBS ADSORPTION EQUATION BY THE MICROTOME METHOD OF McBAIN AND HUMPHREYS

Substance	Number of experiments	Concentration g/1000 g H_2O	a, observed	a, calculated	Observed by McBain and DuBois method
p-Toluidine	11	2.00	6.1	5.2	11.8
p-Toluidine	29	1.76	4.6	4.9	....
Phenol	18	20.48	4.1	4.8	14.8
Caproic acid	30	2.59	6.8	6.3	16.2
Caproic acid	14	3.00	5.1	6.5	16.9
Caproic acid	43	5.25	6.2	6.3	20.5
Hydrocinnamic acid	33	1.50	5.6	5.1	....
Hydrocinnamic acid	19	4.5	5.4	7.9	....

Since moving surfaces may not represent equilibrium conditions or do not meet all the conditions of the Gibbs equation, McBain and Humphreys[11] made measurements of the absolute amounts of adsorption of a few substances at *static* air-water interfaces. An ingenious apparatus uses a microtome blade, traveling at a speed of 35 ft/sec, to slice off a uniform layer at the surface 0.05 to 0.1 mm in thickness, which is analyzed and compared with the bulk concentration of the solution. The results are given in Table 6, which includes, for comparison, data obtained by McBain and DuBois by the *dynamic* air-bubble method. These data show that the adsorptions determined by the static method agree quite closely with those predicted by the Gibbs equation, as compared with the high values measured by the dynamic method. It thus appears that static surfaces approach more nearly the conditions of the Gibbs equation than dynamic surfaces, indicating that the Gibbs equation represents a limiting law. But as McBain emphasizes, the concentration formula of Gibbs may not give correct results since it may not include all the components in the system and it does not include adsorption resulting from electrification at surfaces.[12]

TABLE 7

STATIC AND DYNAMIC SURFACE TENSIONS

Solution	Concentration (%)	Surface tension (dynes/cm)	
		Dynamic (capillary wave method)	Static (capillary tube method)
Water	.....	73	73
Sodium oleate	0.025	77	53
Sodium oleate	0.25	77	25
Sodium oleate	1.25	60	25
Sodium oleate	2.50	56	25
Saponin	.....	71	51
Heptylic acid	0.065	68	54

Lewis[13] investigated the adsorption of a variety of solutes at oil-water and mercury-water interfaces by dynamic methods. The observed adsorptions were found to be from 3 to 70 times greater than the values calculated with the Gibbs equation. Schofield,[14] on the other hand, claimed agreement between observed and calculated values for mercurous salts at a mercury-water interface.

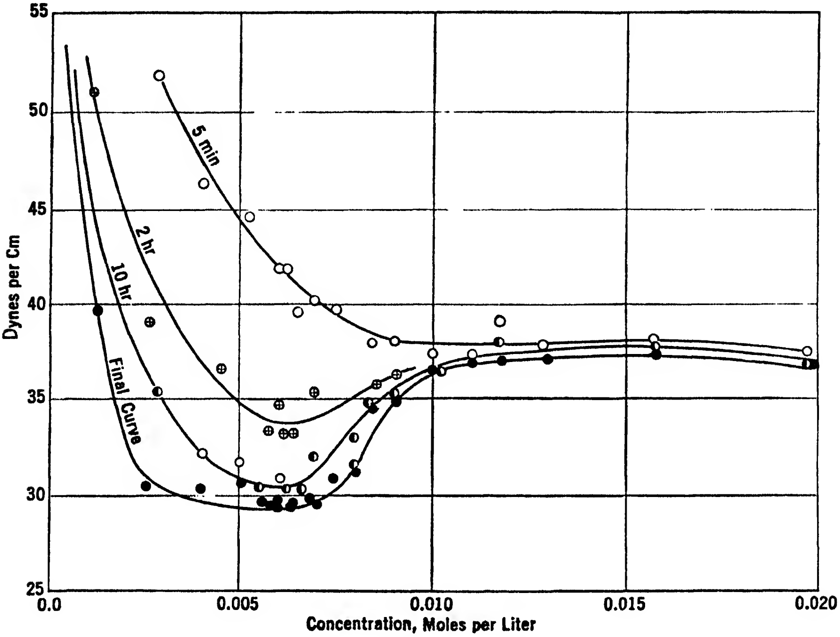

Fig. 4. Surface-tension measurements with solutions of lauryl sulfonic acid at various ages (McBain).

From the surface-tension eq. 1, Freundlich deduced the empirical adsorption equation:

$$a = \frac{x}{\Sigma s} = kc^{1/n} \tag{9}$$

where $x/\Sigma s$ is the amount adsorbed per square centimeter of surface. Like the Gibbs equation, the Freundlich equation is difficult to test experimentally for adsorption at the gas-liquid or liquid-liquid interface.

Static and Dynamic Surface Tension

When a fresh surface of a solution is produced or when an existing surface is extended, time is required for the readjustment of concentrations between the body of the liquid and the surface layer. Accordingly, different values of the surface tension would be expected, depending on whether rapid measurements are made on a fresh surface (dynamic methods) or on an old surface after equilibrium is established (static methods). This turns out to be true, as illustrated by the results of Lord Rayleigh[15] and of Freundlich.[16] The dynamic values of the surface tension given in Table 7 are always nearer to that of the solvent, whereas the static values are usually lower because most substances lower the surface tension. The dynamic value for very dilute sodium oleate solutions appears to be higher than for pure water. This is probably due to experimental error, but Bancroft[17] offers the further suggestion that the value given may be the dynamic surface tension of sodium hydroxide solution resulting from hydrolysis of the dilute sodium oleate.

The rate of change of surface tension with time is well illustrated by the results obtained with solutions of lauryl sulfonic acid by McBain and Wood[18] and shown in Fig. 4. The rate of change is fairly rapid during the first few hours, but the final curve was obtained only after the solution had stood many days.

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CHAPTER 3

Adsorption by Solid I:
General Characteristics of Adsorption of Gas or Vapor

All gases or vapors tend to be adsorbed or condensed on the surface of any solid with which they are in contact. The phenomenon was first mentioned in 1773 by Scheele, who reported the results of experiments on gases exposed to charcoal.[1] In 1777, Fontana [2] described the well-known lecture demonstration of plunging glowing charcoal under mercury and allowing it to rise into an inverted tube containing gas; as the charcoal cools, it adsorbs most of the gas and a column of mercury rises in the tube. The classical investigations of de Saussure [3] in 1814 brought forth many facts concerning adsorption phenomena. Thus, the almost universal occurrence of adsorption was indicated by his observation that all kinds of gases are adsorbed by a variety of porous substances such as meerschaum, asbestos, wood, and charcoal. He showed, further, that heat is evolved in the adsorption process and that there is a tendency for the most easily condensable gases to be taken up most strongly. Moreover, to explain the surface-condensation process, de Saussure proposed the compressed-film theory of adsorption which will be considered in the next chapter.

After giving the method of forming a few typical adsorbents, the results of more recent quantitative studies in adsorption will be considered under the following general headings: (1) the adsorption isotherm, (2) the adsorption isostere, (3) the adsorption isobar, (4) types of adsorption, (5) activation energy of adsorption processes, (6) heat of adsorption.

SOME TYPICAL ADSORBENTS

Charcoal

The application of adsorbent charcoal as a decolorizer and deodorant has been known for a long time. The fact that vegetable carbon, obtained by heating wood in a closed vessel, will remove coloring matter from solutions seems to have been known in the fifteenth century. The phenomenon received slight attention, however, until 1785, when it was rediscovered by Löwitz,[4] who was responsible a few years later for its use in the purification of raw sugar. Stenhouse[5] in 1854 used charcoal as a deodorant in a respirator; this was the forerunner of the modern gas mask.

The first adsorbent charcoals were prepared by the destructive distillation of wood; but, with the discovery in 1811 of bone charcoal which possesses superior decolorizing qualities, vegetable charcoal received a setback from which it did not recover until methods were devised for increasing greatly the adsorbing power of carbons derived from various sources. Work along this line was stimulated by the demand for highly active charcoal to be used in gas masks during World War I.

The commonest method of activating charcoal consists of heating it in a current of air under such conditions that a portion is oxidized slowly. The optimum temperature for air activation of the charcoals used in American gas masks is between 350 and 450°;[6] but higher temperatures up to 920–960° may be even more effective with redwood and sugar charcoals.[7] Carbon dioxide, chlorine, and steam may be used as oxidizing agents in place of air. The steam process, developed during World War I, is most effective at 800 to 1000°. Certain American gas-mask charcoals, e.g., Norit, are technical adsorbents prepared by the steam-activation process. German gas-mask charcoal was prepared by impregnating wood or other uncarbonized material with zinc chloride and calcining at 400–800°. Phosphoric acid, sulfuric acid, and alkalis are also used as impregnating agents.

The activation process increases the adsorption capacity of charcoal for the following reasons:

1. Removes adsorbed hydrocarbons by differential oxidation.
2. Increases the interior surface area of the charcoal as a result of (*a*) shrinkage accompanying an increase in density and (*b*) partial oxidation of the carbon itself.
3. Produces a large volume of very small capillary spaces.
4. Changes the surface from amorphous carbon to extremely minute graphite or graphitelike crystals which possess an enormous specific surface and a large surface energy resulting from loosely held electrons in the surface of the graphite lattice.[8]

The marked effect of activation on the adsorbing power of several charcoals is well illustrated by some observations of Barker[9] on the adsorption of carbon tetrachloride from its saturated vapor at 24°, as given in the second column of Table 8. In the same table are given also the granular density and a statement of the physical character of the charcoal. It will be noted, for example, that activation increases the adsorption in milligrams of CCl_4 per gram of charcoal from 11 to 1480 for commercial wood charcoal, and from 30 to 2715 for lignite semi-coke. At the same time, the granular densities decrease, and the products change from a firm to a friable physical state.

TABLE 8

Effect of Activation on the Adsorbing Power of Charcoals

Substance tested	Adsorption (mg. CCl_4/g C)	Granular density	Physical character
Ironwood	22	0.96	Fibrous, hard
Primary ironwood charcoal	30	0.89	Hard
Activated ironwood charcoal	1160	0.72	Hard, friable, granular
Commercial wood charcoal	11	0.46	Firm, fibrous
Highest activated wood charcoal *	1480	0.30	Soft, friable
Cocoanut shell	18	1.20	Hard
Primary cocoanut charcoal	47	0.96	Hard
Activated cocoanut charcoal	630	0.84	Hard
Lignite semi-coke	30	1.09	Firm
Good activated lignite charcoal	640	0.89	Firm
Highest activated lignite charcoal *	2715	0.31	Friable, granular

* Further activation reduces the granules to a fine powder.

Hydrous Oxides

Hydrous oxide gels dried under suitable conditions possess a high adsorption capacity for many gases and dissolved substances. The most familiar example is silica gel prepared[10] by pouring silicate of soda of about 1.185 sp. gr. into an equal volume of 10% HCl at 50°, under violent agitation. The resulting jelly is broken up and washed with hot water either before or after drying.[11] The rate and conditions of drying determine the porosity of the gel, and at the outset the process is carried out slowly. A temperature of 75–120° is first employed, followed by raising the temperature gradually to 300°. The most active samples are obtained by heating at 250–300° *in vacuo* for a half-hour or more.[12] The adsorption capacity may be increased by mixing silicate of soda with ferric chloride, nickel chloride, or copper sulfate, followed by drying the resulting mixed gel and dissolving out the hydrous metallic oxide with acid.[13]

Metals

Metallic adsorbents such as are used for contact catalytic agents are prepared by reduction of the oxide or of salts under suitable conditions. Nickel is obtained by reduction, with hydrogen at a temperature of 300–350°, of the oxide formed either by precipitation or by calcining the nitrate or an organic salt. Copper is obtained in the most highly active condition by reduction of the oxide at about 200°, and cobalt by reduction at around 400°. Platinum and palladium "blacks" are conveniently prepared by reduction of solutions of salts of the respective metals with an organic reducing agent such as sodium formate.

THE ADSORPTION ISOTHERM

The adsorption isotherm gives the effect of pressure on the amount of gas or vapor taken up by a solid at constant temperature. The general form of the isotherm is shown in Fig. 2, p. 13. A few of the factors influencing the adsorption will be considered in the following paragraphs.

Effect of Temperature and Pressure

For given conditions of temperature and pressure, the amount of adsorption varies with the nature of the gas or vapor and the nature of the adsorbent. But, with the same gas or vapor and the same adsorbent, the adsorption increases with increasing pressure and falls off with rising temperature. This is illustrated by Richardson's[14] data for the taking up of ammonia by cocoanut charcoal and Ryerson and Wishart's[15] data on the adsorption of chlorine by silica gel, Fig. 5. From these data, it is apparent not only that the adsorption x/m is much greater at lower temperatures but also that the isotherms are more curved. In general, the lower the temperature and pressure, the more nearly is the adsorption directly proportional to the pressure in accord with Henry's law (see Fig. 2). The adsorption may be reversed, practically all the adsorbed gases being removed by sufficient evacuation. The reversibility of the process is well illustrated by the data shown graphically in Fig. 5*b*; the points for adsorption (circles) and desorption (dots) always fall on the same curve.

Referring to Fig. 5*c* and *d*, it will be noted that an approximately linear relationship exists between the logarithm of the adsorption x/m of the respective gases and the logarithm of the pressure p.

With rise in temperature above a certain point, the nature of the adsorption may change. For example, at low temperatures oxygen, like nitrogen, is reversibly adsorbed on charcoal; [16] but at temperatures between 0 and 150°, the adsorbed oxygen is not readily removed by evacuation [17] and it has the capacity of oxidizing ethylene to carbon dioxide and water. As we shall see, the low-temperature, reversible type of adsorption is termed *physical adsorption*, whereas the high-temperature, non-reversible type is termed *chemical adsorption* or *activated adsorption.*

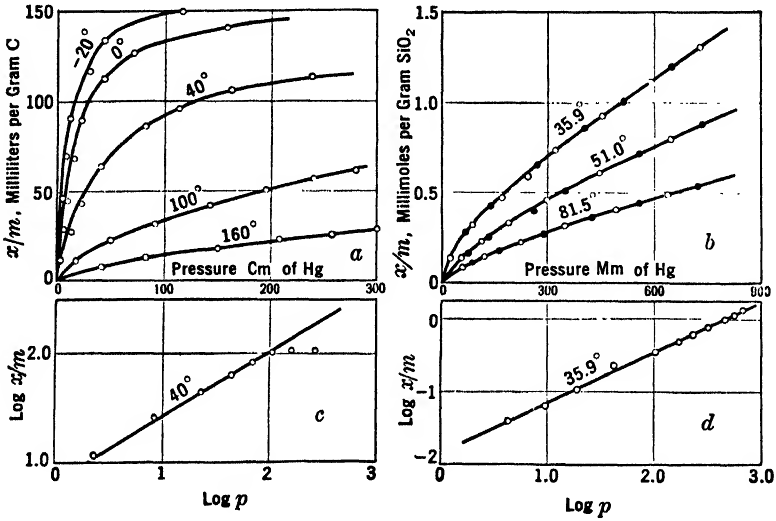


FIG. 5. Adsorption isotherms for (*a*, *c*) ammonia by charcoal and (*b*, *d*) chlorine by silica gel.

Most adsorption studies have been carried out at relatively low pressures before a maximum in the amount taken up is attained. Important observations with nitrous oxide and nitrogen at higher pressures up to 60 atmospheres were made by McBain and Britton,[18] using pure sugar charcoals activated by both the steam and air processes. The experiments were carried out with a special microbalance,[19] and particular precautions were taken to remove all foreign gases by high evacuation of the charcoal and by washing with gases whose adsorption was to be measured. Isotherms for nitrogen at 20 and −77°, using both steam- and air-activated charcoal, are shown graphically in Fig. 6. It will be noted that saturation is attained at 20° with the steam-activated charcoal but not with the air-activated adsorbent. This is not surprising in view of the fact that the adsorption value with the air-activated preparation at 20° and 60 atmospheres is only about one-half that of the saturation value at −77°.

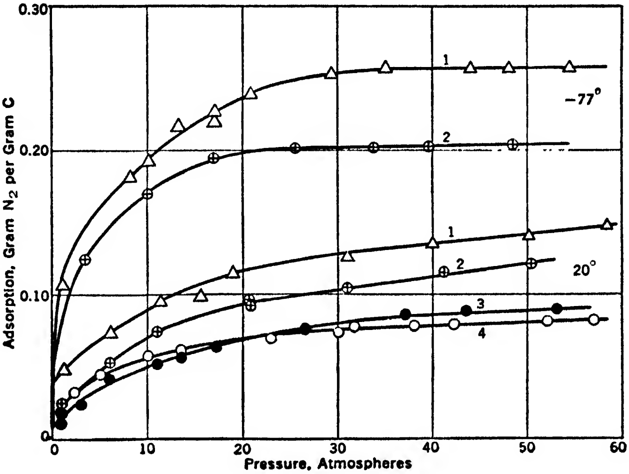


FIG. 6. Adsorption isotherms for nitrogen by air-activated (curves 1 and 2) and steam-activated (curves 3 and 4) sugar charcoals at 20° and at −77°.

The adsorption of nitrous oxide was found to attain the saturation value at pressures in the neighborhood of 20 atmospheres at temperatures of 20, 45, and 67°. The adsorption curves for all three temperatures have the same form. Since the critical temperature of nitrous oxide is 36.5°, it follows that there is no special differences between the adsorption of gas and of vapor. Nevertheless, in the consideration of adsorption in the region of the critical temperature McBain found it advantageous to express pressures not in absolute units but in terms of relative humidity, p/p_s, that is, the actual pressure, p, divided by the vapor pressure, p_s, of the corresponding liquid at the same temperature. In Fig. 7 are given some typical isotherms obtained by McBain and coworkers[20] for the adsorption of vapors on activated and highly evacuated sugar charcoal. In these curves, x/m is plotted against p/p_s. It will be noted that practically all the adsorption occurs at very low pressures, little or no increase in adsorption being observed over the whole of the remaining higher pressures. This type of curve is approached more nearly the more drastic the preliminary purification of the carbon. It therefore represents the true characteristic behavior of a pure vapor when adsorbed on pure carbon. The curves of the more usual type shown in Fig. 5 result when the charcoal employed contains more or less adsorbed impurities.

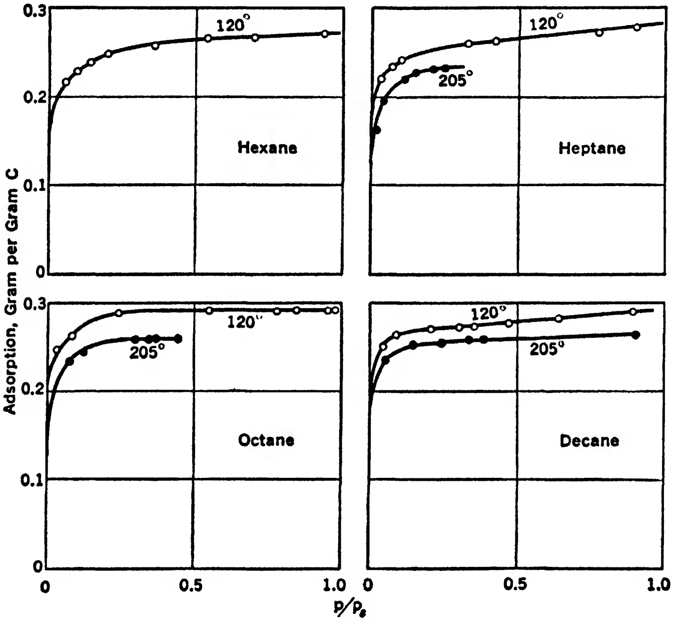


FIG. 7. Adsorption isotherms for vapors by highly evacuated sugar charcoal.

For relative humidities approaching the saturation value ($p/p_s = 1$), Coolidge[21] and Goldmann and Polanyi[22] found the simple rule, first pointed out by Gurwitsch,[23] to hold for the adsorption of various vapors at 0°, namely, that approximately equal volumes of all liquids are taken up. This is shown by the results given in Table 9, compiled by Goldmann and Polanyi.[22]

Relation between Adsorption and Physical Constants

It is frequently stated as a first approximation that a gas or vapor tends to be adsorbed more readily the easier it is to condense or the higher its boiling point. Some data of Titoff[24] shown graphically in

TABLE 9

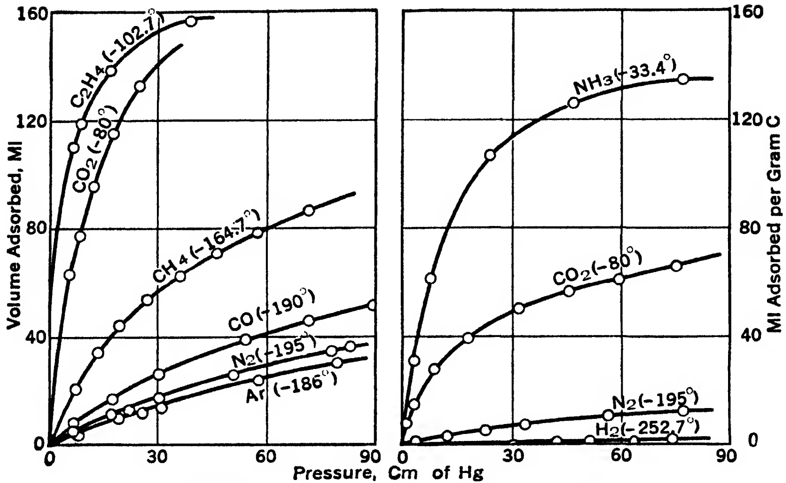
VAPORS ADSORBED BY ONE GRAM OF CHARCOAL AT 0° WHEN p/p_s IS APPROACHING UNITY

Substance	x/m			Area, spherical molecules $\frac{x}{mM}\left(\frac{M}{d}\right)^{2/3}$*
	Grams	Mole	Milliliters of liquid	
Data of Goldmann and Polanyi				
Ethyl chloride	4.98	0.0773	5.40	1.32
Ethyl ether	3.96	0.0534	5.38	1.16
Normal pentane	3.46	0.0480	5.38	1.12
Carbon disulfide	7.02	0.0923	5.42	1.40
Data of Coolidge				
Ethyl ether	3.62	0.0488	4.90	1.06
Carbon disulfide	5.81	0.0764	4.50	1.16
Ethyl formate	4.30	0.0580	4.54	1.06
Methyl acetate	4.70	0.0634	4.90	1.16
Chloroform	6.74	0.0564	4.42	1.04
Carbon tetrachloride	7.10	0.0461	4.35	0.96
Methyl alcohol	3.65	0.1139	4.50	1.32
Water	4.24	0.2358	4.24	1.62

* M, molecular weight; d, density of liquid.

Fig. 8*b* support the rule, the adsorption increasing with increasing boiling point of the several gases in the order: $NH_3 > CO_2 > N_2 > H_2$. No such regularity is to be found, however, with the series of gases studied by Homfray,[25] data for which are shown in Fig. 8*a*. Thus the order of adsorption at 0° is: $C_2H_4 > CO_2 > CH_4 > CO > N_2 > Ar$, whereas the order of boiling points is: $CO_2 > C_2H_4 > CH_4 > Ar > CO > N_2$.

Another form of the relationship between adsorption and condensability of vapors, suggested by Arrhenius,[26] connects adsorption with the constant *a* in the van der Waals equation, and the critical temperature. This is illustrated in Table 10, compiled by Arrhenius, for adsorption data of Titoff and Homfray on cocoanut charcoal at a



a (Homfray) *b* (Titoff)

FIG. 8. Adsorption isotherms at 0° for various gases by wood charcoal.

pressure of 10 cm Hg and 0°. The adsorption tends to be greater the higher the *a* value and the higher the critical temperature, but there are exceptions.

TABLE 10

RELATION BETWEEN ADSORPTION, VAN DER WAALS *a*, AND CRITICAL TEMPERATURE OF GASES

Gas	Adsorption [ml (standard conditions)/g]	$a \times 10_3$	Absolute critical temperature
Ethylene	41	8.83	284
Ammonia	71	8.08	403
Carbon dioxide	30 28	7.01	304
Methane	9.4	3.67	178
Carbon monoxide	3.2	2.80	133
Oxygen	2.5	2.69	155
Nitrogen	2.35 2.0	2.68	127
Argon	1.67	2.59	154
Hydrogen	0.227	0.42	32

Still a third relation, suggested by Schmidt,[27] states that the logarithm of gas adsorbed x/m, at 1 atmosphere pressure and at a given temperature between 0 and 150°, is a linear function of the square root of the latent heat of vaporization λ. That is, $\log x/m = k_1 \sqrt{\lambda} - k_2$, where k_1 and k_2 are constants depending on the adsorbent. This relation is about the same as that between adsorption and boiling point or critical temperature, since Trouton's rule $(ML_v/T_b = k)$ connects latent heat L_v with boiling point T_b, which, in turn, is two-thirds of the critical temperature. It follows, therefore, that all three of these interrelated generalizations are, at best, but first approximations.

Summary of regularities in adsorption of vapors. The results of the observations given above together with related data led McBain [28] to summarize the regularities observed with vapors in the form of five rules. Since all gases become vapors below their respective critical temperatures, these generalizations are quite comprehensive. The rules are as follows:

1. Adsorption is related to condensability in one or another of the ways enumerated in the preceding section. This means an enormous difference in behavior between a very low-boiling substance such as helium at one extreme, and a high-boiling liquid at the other.
2. As a first approximation, the amount of adsorption depends primarily upon the relative pressure p/p_s, or on $RT \ln p_s/p$.[22]
3. With thoroughly evacuated charcoal, the adsorption is still large (30–50% of its highest value) when the pressure is infinitesimal.
4. When p/p_s is approaching unity, equal volumes of different vapors measured in the form of the corresponding liquids are adsorbed by a given charcoal.
5. For a given value of p/p_s, the effect of temperature rise is to diminish the adsorption by somewhat less than that corresponding to an expansion of an equal weight of the free liquid. This rule applies as a first approximation even for low arbitrary values of p/p_s, or $RT \ln p_s/p$.

Rate of Adsorption

The rate of the ordinary low-temperature type of adsorption is very rapid indeed, especially on a clean, fresh surface. For example, an active charcoal at the temperature of liquid air will adsorb 100 times its own volume of air, reducing the pressure from 760 to 5 mm in a few seconds; and a gas-mask charcoal exposed to air containing 7000 parts per million of chloropicrin will adsorb 99.99% of it in

0.03 second.[6] The amount of adsorption x/m of various gases on glass in time t can be expressed by the empirical equation $x/m = kt^{1/n}$, in which k and $1/n$ are constants.[29] This is the same form as Freundlich's empirical adsorption equation (p. 49).

The presence of impurities on an adsorbent influences greatly the rate at which equilibrium is set up and even modifies the form of the isotherm (compare curves in Fig. 8 for adsorption on ordinary charcoal with those in Fig. 7 for adsorption on highly evacuated pure sugar charcoal). In any case time is required for diffusion of a gas to the more inaccessible surfaces of a porous body so that considerable time may be required to establish a final equilibrium state. Sessions in McBain's [30] laboratory showed, however, that adsorption equilibrium is definitely established on drastically evacuated charcoal within a week and thereafter remains constant year after year. The possibility is not excluded that the gas taken up slowly after the initial adsorption is dissolved in or reacts with the adsorbent. As already pointed out (p. 13), it is for this reason that McBain prefers to use the non-committal term *sorption* for the phenomenon.

The amount of adsorption usually falls off with rising temperature, but the rate of adsorption increases; hence it is frequently observed that more adsorption occurs in a short time at higher temperatures, but this is reversed for a longer interval. A sufficient rise in temperature may not only increase the amount of adsorption but may even change the nature of the phenomenon.

THE ADSORPTION ISOSTERE

The adsorption isostere shows the pressure required to give the same amount of adsorption at various temperatures. Typical isosteres for constant amounts of adsorption, when pressure is plotted against absolute temperature, are shown in Fig. 9*a*, which gives Homfray's results with carbon dioxide on charcoal. When the logarithm of the pressure is plotted against the reciprocal of the absolute temperature, linear isosteres are obtained as shown in Fig. 9*b*, which gives Coolidge's [31] data for adsorption of benzene by charcoal. This shows that the logarithm of the pressure for constant amounts of adsorption at different temperatures diminishes linearly with the reciprocal of the absolute temperature. The linear isostere corresponds to the vapor-pressure curve of a liquid; but the slope of the adsorption isostere gives the heat of adsorption, and the slope of the vapor-pressure curve gives the heat of vaporization of a liquid.

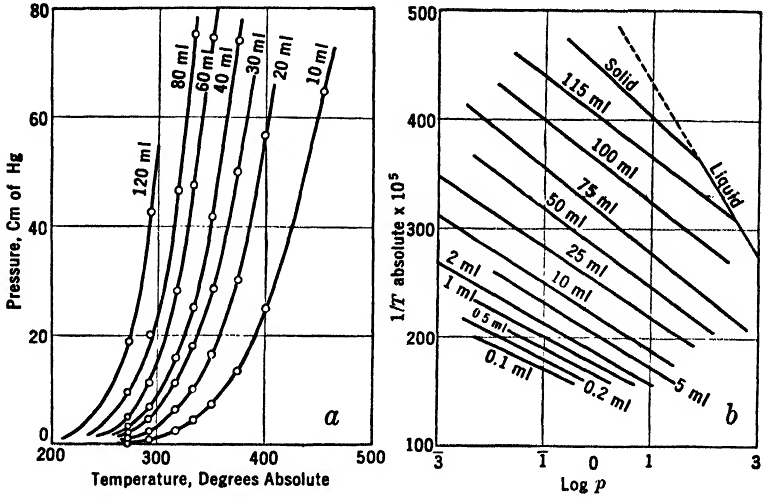


FIG. 9. Adsorption isosteres for (*a*) carbon dioxide and (*b*) benzene by charcoal.

THE ADSORPTION ISOBAR

The adsorption isobar shows the effect of temperature on the adsorption of a gas at constant pressure. Since, in general, adsorption falls off with rising temperature, the variation in adsorption with change in temperature is represented by a smooth curve of the hyperbolic type. Plotting the logarithm of the adsorption x/m against the temperature develops the relationship that the logarithm of the adsorption diminishes linearly with the temperature.[32] This empirical relationship holds as a first approximation.

In certain instances, the familiar rapid adsorption at low temperatures is followed by a slower adsorption, the rate of which increases for a time with rising temperature and then falls off. This behavior has been noted especially in the adsorption of certain gases by oxide and metallic catalysts. Typical isobars showing increase in adsorption of hydrogen with rising temperature over a certain range are given in Fig. 10. Taylor and Williamson's [33] 165-mm isobars for hydrogen on manganous-chromic oxide catalyst are shown in part *a*, and Benton and White's [34] 50-cm isobars for hydrogen on copper, in part *b*. Some solution of hydrogen in copper is recognized, and a solution isobar is included in part *b*.

From the form of the isobars, it is apparent that the adsorption at lower temperatures, labeled "physical adsorption," passes through a transition range of pseudo-equilibrium at intermediate temperatures to the higher temperature adsorption labeled "chemical adsorption." The significance of the form of the curve will be considered in the next section.

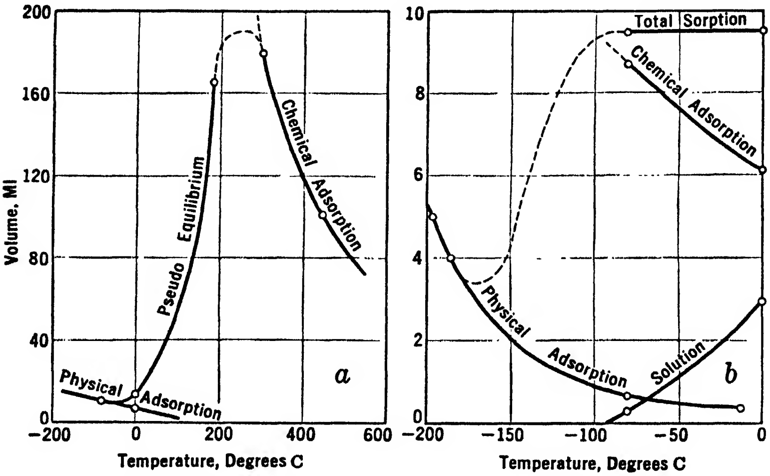


FIG. 10. Adsorption isobars for hydrogen (*a*) on manganous-chromic oxide and (*b*) on copper.

TYPES OF ADSORPTION

The term adsorption as applied to the condensation of gases on the surface of solids may involve two more or less distinct types of phenomena.[35] In the first type, the surface condensation is due to physical capillary phenomena more or less non-specific in that the adsorption parallels the physical character of the adsorbent. It has been referred to by different authors as "physical," "secondary," "reversible," and "van der Waals" adsorption. Examples of this type are illustrated in Figs. 6, 7, and 8.

The second type of adsorption, which appears to be due to primary valence forces, is relatively strong and specific, being largely independent of the physical character of the adsorbent; in other words, the adsorption is essentially of a chemical nature. This type of adsorption is encountered at certain temperatures in the taking up of such gases as hydrogen and carbon monoxide by oxide and metallic catalysts (Fig. 10). The chemical nature of the adsorption of certain gases by hot filaments has been demonstrated by Langmuir.[36] For example, he showed that the film of oxygen on a hot carbon filament was held so tenaciously that the filament had to be heated at 2000° for half an hour to remove it. Similarly, a tungsten filament, heated to 2700° in a tube cooled in liquid air and containing a low pressure of carbon monoxide, took up the carbon monoxide, probably as a result of primary valence forces, since WCO and not CO distilled off the filament at a constant rate independent of the carbon monoxide pressure. Further, at 3000° 50% of the oxygen molecules which struck a tungsten filament formed the compound WO_3 which distilled onto the glass. Since there are three atoms of oxygen in WO_3 and only two in the oxygen molecule, it follows that at least one-half the tungsten surface was covered with oxygen at 3000°. Langmuir considers that the gases are bound by primary valence forces, and he represents the phenomena diagrammatically as given in Fig. 11.

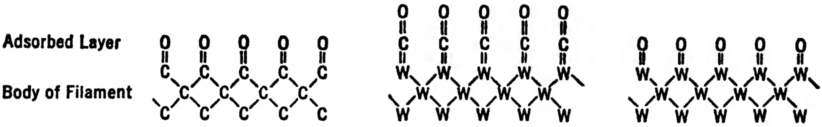


FIG. 11. Diagrammatic representation of monomolecular adsorption of oxygen by carbon and of carbon monoxide and oxygen by tungsten.

Differentiation between Adsorption Types

It is possible to differentiate more or less sharply between the so-called physical adsorption and chemical or activated adsorption. Thus, typical examples of physical adsorption are accompanied by heat effects of the order of magnitude of the heat of liquefaction, whereas in chemical adsorption the heat effects are much greater, corresponding in many instances more nearly to those of a chemical reaction (see p. 42). It is also possible to differentiate the two types by observing the effect of temperature and pressure on the adsorption. Thus, typical physical adsorption decreases rapidly and continuously with increasing temperature, whereas chemical adsorption increases at first and then falls off with rising temperature. In physical adsorption the amount of a gas taken up increases gradually with increasing pressure, and complete saturation is not obtained until the pressures are relatively high. Chemical adsorption, on the other hand, increases rapidly with increasing pressure at low pressures but soon reaches a saturation value constant for a given temperature, beyond which further pressure increase does not alter the amount adsorbed. Langmuir[37] has differentiated the two types quite sharply in adsorption studies on mica, glass, and platinum. It is obvious, however, that under certain conditions the two types will take place simultaneously, and a sharp differentiation is impossible.

Some cases of pure secondary or van der Waals adsorption have been established by London[38] in an investigation of the nature of molecular forces from the standpoint of the wave mechanics. Assuming that the adsorbed gas has the same equation of state as in the gas phase and that the forces of adsorption and van der Waals forces are related, London deduced an equation by which he calculated the heat of adsorption of helium, nitrogen, argon, carbon monoxide, carbon dioxide, and methane on charcoal, and found the results in good agreement with the observed values. This means that in these cases the adsorption is non-specific, the adsorbed gas is molecular, and the adsorption forces are van der Waals molecular forces which are sharply distinguishable wave-mechanically from electrostatic or valence forces.[39]

As noted in the above section on the adsorption isobar, direct experimental evidence by Taylor and others indicates quite conclusively that certain gases can be adsorbed at certain surfaces in two different ways characterized by the extent of adsorption and its variation with the temperature. The low-temperature adsorption which falls off with rising temperature is usually very rapid and appears to be non-specific, consisting merely in a surface condensation of a large portion of the molecules which collide with the adsorbent. At higher temperatures, on the other hand, a slow specific adsorption is sometimes observed which may result in the taking up of more gas than that adsorbed at low temperatures. The velocity with which the high-temperature type of adsorption occurs increases exponentially with the temperature. The adsorption of hydrogen by manganous-chromic oxide shown in Fig. 10 is a case in point. At $-78°$, the adsorption is rapid and practically completely reversible by evacuation at the same temperature. This is a physical condensation of the van der Waals type. At 0°, this type of adsorption is less than at $-78°$, as would be expected, but above 0° there is a very slow increase in adsorption. At 100 and 132°, there is little or no physical adsorption, and the chemical or activated adsorption is increasing until at 184 and 305° it is 15 times as great as that obtained under similar pressures at −78°. At 440° it is distinctly less than at 305° but still several times greater than the physical adsorption at −78°. Taylor observed a similar behavior with a zinc oxide adsorbent and Benton with copper, nickel, and iron adsorbents.

Further evidence of a fundamental distinction between the low- and high-temperature types of adsorption is furnished by the heats of adsorption of the gas on the same surface in the two temperature regions. It is possible by means of the Clausius-Clapeyron equation to calculate the heat of adsorption from any two isotherms on which the equilibrium pressures for a given quantity of adsorbed gas have been determined. This equation, $d \ln p/dT = \lambda/RT^2$, in its integrated form is:

$$\log p_1 - \log p_2 = \frac{\lambda}{4.58}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

where p_1 and p_2 are the equilibrium pressures for a given adsorption at temperatures T_1 and T_2, respectively, and λ is the heat of adsorption. For hydrogen adsorbed by a manganous-chromic oxide surface, λ is found to be about 1900 calories in the low-temperature range −78 to 0°, whereas λ calculated from the isotherms at 305 and 440° is greater than 19,000 calories. These data serve not only to distinguish two types of adsorption but also to account for the marked increase in the amount adsorbed in the higher temperature range.

ACTIVATION ENERGY OF ADSORPTION PROCESSES

Since the velocity with which the high-temperature type of adsorption takes place increases exponentially with the temperature, Taylor points out that one may speak of the activation energy of adsorption processes in the same way as one speaks of the activation energy of chemical reactions. The introduction of this concept leads to a modified theory of adsorption which differs from the classical theory in that the latter assumes the activation energy of adsorption to be zero and that of desorption to be λ, which is identical in magnitude with the usual heat of adsorption; the modified theory assumes an activation energy E for adsorption and, in consequence, an activation energy $E + \lambda$ for the desorption process. From this point of view the two types of adsorption which have been recognized differ in that one involves a low heat of adsorption and a low activation energy, whereas the other involves a relatively high heat of adsorption and a high activation energy. This suggests the existence in certain cases of two adsorption isobars for the same gas at a given surface, that with the higher heat of adsorption and activation energy involving greater amounts of adsorbed gas at the same temperature and pressure. At sufficiently low temperatures, the adsorption involving low activation energy will prevail chiefly; at sufficiently high temperatures, the process involving high activation energy will predominate.

Referring once more to Fig. 10, the lower adsorption isobars for hydrogen on manganous-chromic oxide and copper are chiefly of the type involving low heat of adsorption and low activation energy, whereas in the higher isobars, the process with higher activation energy predominates. Between the two, a transition region of pseudo-equilibrium adsorption values is obtained which shows an increase in the amount of gas adsorbed with increasing temperature, the velocity of adsorption at a given temperature depending on the activation energy of the high-temperature adsorption.

The magnitude of the activation energy E can be calculated by the integrated modified Arrhenius equation, $d \ln v/dT = E/RT^2$, which takes the form:

$$\log v_2 - \log v_1 = \frac{E}{4.58}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

where v_2 and v_1 are the velocities corresponding to the respective temperatures T_2 and T_1. Some data obtained with a manganous oxide and a manganous-chromic oxide adsorbent are given in Table 11. It is evident from these data that the activation energy is a function of the surface. Moreover, with increasing surface covered, the velocity of adsorption falls off, and the activation energy rises.

From these and similar adsorption data, Taylor concludes that the only essential distinction between "physical" and "chemical" adsorption is that the former normally possesses small heats of adsorption and small activation energies, whereas the latter may exhibit high heats of adsorption and moderate or large activation energies. The significance for contact catalysis of adsorption with high activation energies will be considered in Chapter 25.

It should be mentioned that, in the opinion of certain investigators, the concept of activation energies in adsorption is a delusion. A relatively slow rate of adsorption and an increase of rate with temperature are important characteristics of the activated type of adsorption; but rate alone does not distinguish the phenomenon from other slow processes. Thus Steacie[40] claims that the slow effects accompanying adsorption processes can be simply explained on the basis of existing data regarding the solubility of gases in solids. Ward,[41] on the other hand, believes that the slow process is a grain-boundary diffusion involving activation energies rather than a lattice diffusion or solution. A third possibility is that a slow displacement of strongly adsorbed gases by the adsorbate in question accounts for the increased adsorption at higher temperatures. Taylor contends, however, that solubility alone is inadequate to account for the quantitative amounts of adsorption involved at higher temperatures; that activated diffusion into the less accessible portions of the surface is indistinguishable experimentally from activated adsorption; and that the phenomena involved cannot be ascribed to displacement of adsorbed gases from the surface. It is nevertheless true that all these factors may and probably do contribute to the behavior of gases in contact with solid. To the extent that they do influence the rate of taking up of gas with temperature and are disregarded, the calculated activation energies are necessarily in error. Burrage[42] points out the difficulty of obtaining sufficiently clean surfaces to make significant measurements of rate of adsorption.

TABLE 11

ACTIVATION ENERGY OF ADSORPTION OF HYDROGEN

Adsorbent	H_2 adsorbed (ml)	Time required (min) at		E (cal/mole adsorbed)
		218°	184°	
Manganous oxide	0–2	1.8	4.6	12,400
	2–3	2.7	11.7	19,400
	3–4	4.7	21.4	20,800
		132°	100°	
Manganous-chromic oxide	0–10	3.2	6.0	5,920
	10–15	7.3	20.0	9,500
	15–20	15.9	48.0	10,400
	20–25	37.2	111.5	10,400

HEAT OF ADSORPTION

Gases on metals. The adsorption of gas or vapor by solid is always accompanied by an evolution of heat. It is sometimes stated that the heats of adsorption are somewhat greater than the heats of liquefaction of the gases taken up. Actually, they may be very much greater, as shown in Table 12, which gives (1) the heats of adsorption on certain metallic catalysts obtained by Taylor[43] and (2) the heats of liquefaction of the several gases. In some instances the heat involved corresponds more nearly to that of a chemical reaction than to condensation. The very high heat of adsorption of oxygen on platinum is probably due in part at least to oxidation;[44] in any event, the adsorption is not reversible at practicable evacuation temperatures.

TABLE 12

Heats of Adsorption and Liquefaction of Gases on Catalysts

Catalyst	Gas	Integral heat of adsorption (cal/mole)	Pressure range (mm)	Heat of liquefaction (cal/mole)
Nickel	H_2	14,960	0-760	216 (−252.8°)
	NH_3	11,240	0–90	5,100 (0°)
	O_2	98,000 *	0	1,640 (−182.9°)
Copper	H_2	9,600	0–760	
	O_2	82,000 *	0	
	CO	30,000	0–1	1,410 (−192°)
	CO_2	11,700	0–760	1,350 (0°)
	NH_3	9,200	0–155	
	H_2	11,300	0–0.01	
	C_2H_4	16,000	0–0.01	
	C_2H_6	11,000	0–0.01	
Iron	NH_3	16,000	0–10	
Platinum	H_2	32,400	0–0.01	
	O_2	161,000	0–0.15	
	CO	34,600	0–0.005	
	SO_2	35,700	0–0.02	5,900 (0°)

* Data of Russell and Bacon: *J. Am. Chem. Soc.*, **54**, 54 (1932).

In these instances, physical and chemical adsorption take place side by side; hence the above data give no indication as to what portion of the heat evolved results from chemical or activated adsorption. In the adsorption of hydrogen and perhaps of oxygen, the heat effects are probably due largely to chemical adsorption, since this apparently occurs even at quite low temperatures on metallic surfaces.

Vapors on charcoal. The heats of adsorption of eleven vapors on steam-activated sugar charcoal were obtained by Lamb and Coolidge.[45]

TABLE 13

HEATS OF ADSORPTION OF VAPORS ON CHARCOAL

Vapor	Integral heat of adsorption, h (cal/mole)	Heat of liquefaction, Q (cal/mole)	Net heat of adsorption, $h - Q$ (cal/mole)	$h - Q$/ml (cal/mole)
C_2H_5Cl	12,330	6,220	6,110	86.4
CS_2	12,630	6,830	5,800	99.1
CH_3OH	12,950	9,330	3,620	90.8
C_2H_5Br	14,330	6,850	7,480	102.0
C_2H_5I	14,250	7,810	6,440	81.5
$CHCl_3$	14,930	8,000	6,930	87.5
$HCOOC_2H_5$	15,420	8,380	7,040	90.1
C_6H_6	15,170	7,810	7,360	85.0
C_2H_5OH	14,980	10,650	4,330	76.8
CCl_4	16,090	8,000	8,090	85.6
$(C_2H_5)_2O$	16,090	6,900	9,190	80.3

In Table 13 are given their results for the molecular heats of adsorption when 1 ml of liquid is adsorbed by 10 g of charcoal. It is considered that the heat effect in the adsorption is due to two factors: the heat of liquefaction of the vapors, and the heat effect due to further compression of the liquid by the adhesive forces of the adsorbent. The latter effect, called the net heat of adsorption, is of the same order of magnitude as the heat of liquefaction. Moreover, the net heats of adsorption per milliliter, given in the last column, are almost the same. This leads to the conclusion that the heat of adsorption is due to the attractive forces of the charcoal upon the liquid and that for a given volume of liquid the heat effects are practically the same.

The results of Lamb and Coolidge are quite impressive when taken alone, but McBain[46] questions the general validity of the conclusion that net heat of adsorption is due to compression in capillaries (cf. p. 54). He points out that in the formation of a number of hydrates and hydroxides, where there is undoubted interaction between molecules, the net heats of reaction per mole of water resemble the corresponding values for adsorption given in Table 13.

APPLICATIONS

The phenomenon of adsorption of gases by solids has a number of scientific and technical applications, a few of which will be considered briefly. The rôle of adsorption in contact catalysis will be taken up in some detail in Chapter 25.

Liquefaction of gases. Many years ago, Melsens[47] liquefied chlorine, sulfur dioxide, hydrogen sulfide, hydrobromic acid, and cyanogen by placing wood charcoal, saturated with the gas in question, into one arm of a sealed V-shaped tube, dipping this end of the tube into boiling water, and placing the other end in a freezing mixture. The heat cut down the adsorption of the gas by the charcoal, and the pressure developed by its release caused liquefaction in the cold end of the tube.

High vacuum. The well-established procedure of using adsorbent carbon to facilitate the securing of a high vacuum dates back to 1874, when Tait and Dewar[48] first used the method. A 300-ml bulb filled with air at a temperature of 15° and 1.7 mm pressure was connected with another bulb containing charcoal. By immersing the charcoal in liquid air, the air in the bulb was adsorbed so strongly that the pressure was reduced to 0.00005 mm, or 1/34,000 of the original pressure. Pressures as low as 2×10^{-7} mm have been obtained by this method,[49] using activated charcoal.

Separation of gas mixtures. In view of the difference in degree of adsorption of gases by charcoal, it is possible to separate mixtures to a certain extent. For example, Ramsay[50] was able to estimate the amounts of neon, helium, and hydrogen in the air from adsorption studies with cocoanut charcoal. At 100° the charcoal adsorbs the oxygen, nitrogen, and argon, practically quantitatively, whereas the adsorption of neon and helium is slight. At the temperature of liquid air, practically all the neon is adsorbed and none of the helium. Ramsay's observations indicate that the concentration of neon in the air at sea level is about 0.00123 volume per cent, that of helium about 0.00040 volume per cent, and that of hydrogen not over $\frac{1}{500}$ of the combined volumes of neon and helium.

Krypton and xenon can be obtained[51] by passing air over charcoal at −183°, placing the charcoal tube in solid carbon dioxide at −78°, and allowing the gas which is evolved to escape. After the gas is removed from the charcoal by heating and exhausting, it is purified from carbon compounds and oxygen, leaving a mixture of nitrogen, krypton, and xenon which is separated by condensation and fractionation. Another method consists in treating liquid-air residues with charcoal, allowing the oxygen to evaporate, and separating the gases remaining on the charcoal as above described.[52]

A recent important scientific application of adsorbent charcoal is the isolation of para-hydrogen in a practically pure state by adsorption at about the temperature of liquid hydrogen.[53] In this case the charcoal acts both as an adsorbent and a catalyst which accelerates the rate at which equilibrium is reached.

The adsorptive force of silica gel for water is very great. It is therefore a good drying agent and may be employed in drying air for blast furnaces[54] and in the dehydration and purification of CO_2, H_2, O_2, N_2, He, and Cl_2. It may also be used to take up the vapor from the rapid vaporization of the liquid in the vacuum refrigeration process.[55]

The gas mask. During World War I charcoal was found to be the best all-around adsorbent for toxic gases and so was the basic material in most gas masks.[6] For this purpose the charcoal must possess a high adsorptive capacity, a high service time, and also a high velocity of adsorption, since the contaminated gas can remain in contact with the adsorbent for only a relatively short period. For effective use, the adsorbent must reduce the concentration of the toxic gas from, say, 1000 parts per million (ppm) of chloropicrin in a rapidly moving current of air to less than 1 ppm in less than the 0.1 second that the air takes to pass through the canister. The most satisfactory adsorbent for this purpose was found to be activated cocoanut charcoal. Not only did it possess the highest adsorption capacity, but also, because of its hardness, it withstood abrasion and powdering from the rough treatment to which gas masks were subjected. To increase the protection against certain volatile gases such as phosgene and hydrocyanic acid, it was found necessary to use alkaline oxidizing agents in combination with the charcoal. For this purpose granules of soda lime containing sodium permanganate were used in both British and American gas masks.

Industrial recovery of vapors. A number of types of industries use and frequently lose large quantities of valuable volatile solvents.

Among these are such industries as dry cleaning and the manufacture of artificial silk, celluloid, cordite, rubber, and artificial leather cloth, where quick evaporation of the solvent is a prime necessity for the economical success of the operations. In many of these industries, charcoal may be used to advantage for the adsorption and recovery of the solvent vapors.

An important example of the industrial adsorption of vapors is the extraction of gasoline vapors from natural gas or refinery gases.[56] This process, which was a development of World War I, utilizes activated charcoal like that used in gas masks. The technical operation consists essentially in passing gases containing gasoline vapors through a column containing the activated charcoal, distilling off the adsorbed vapors by means of steam, and subsequently condensing the vapors. Silica gel appears to be a less satisfactory adsorbent than charcoal for this purpose.[57] On the other hand, Furness [58] and Williams [59] claim that silica gel is superior both to activated carbon and to oil absorbents for the recovery of benzine and motor spirit from coke-oven gas; [60] but this is disputed by Urbain,[61] who reports that charcoal has great superiority over silica gel as a selective adsorbent of hydrocarbon vapors, especially if they are considerably diluted, as they usually are.

Adsorption by silica gel is suggested as a method for recovering the oxides of nitrogen in the arc process for the fixation of nitrogen.[62] The removal is complete from rapid air currents at low concentration, and by heating the gel, the adsorbed oxides may be recovered ready for liquefaction or for absorption in water to give concentrated nitric acid.

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CHAPTER 4

Adsorption by Solid II: Mechanism of the Adsorption of Gas or Vapor

Attempts to explain quantitatively the phenomena of adsorption awaited the development of the thermodynamic theories of Gibbs and of van't Hoff which led to a quantitative formulation of solubility, mass law, phase rule, distribution law, etc. Consideration will be given first to the empirical equation for the distribution of the adsorbed phase between the solid adsorbent and the surrounding medium, after which the following theories of adsorption will be taken up in order: (1) the monomolecular theory, (2) the polymolecular theory, and (3) the capillary theory.

I. Freundlich's Adsorption Equation

In attempting to apply the mass law to adsorption by solid, a proportionality was sought between the gas pressure p (or solution concentration c) and the amount on the solid x/m, where x grams of substance is taken up by m grams of solid. Direct proportionality would be expressed by the equation $x/m = kp$ (or kc); or by $x/m = kp^n$ (or kc^n), where n is a small integer, if association of the substance on the solid takes place. Actually, it was found that the experimental values corresponded more nearly to a modified distribution equation of the form:

$$\frac{x}{m} = kp^{1/n} \left(\text{or } \frac{x}{m} = kc^{1/n} \right)$$

where $1/n$ is not an integer but is an irrational fraction without special significance that varies with conditions between 1 and 0.1. This empirical equation, first suggested by Boedecker,[1] is usually called Freundlich's adsorption equation (*cf.* p. 22) because of the prominence which Freundlich gave to it in his books. Expressed logarithmically, the equation for gas adsorption takes the form:

$$\log \frac{x}{m} = \log k + \frac{1}{n} \log p$$

If the equation fits the data, a straight line is obtained by plotting log x/m against log p. Referring to Fig. 5, it will be seen that this is approximately true except at higher pressures of ammonia. The empirical constants k and n are evaluated by finding the slope of the line which is $1/n$ and its intercept with the $\log x/m$ axis at $\log p = 0$, which is $\log k$. To illustrate, Richardson's 0° isotherm for NH_3 on charcoal (p. 28) is reproduced in Fig. 12. The slope of the line is the tangent of the angle θ, which is 0.535; $\log k$ is 1.265. The equation for this isotherm is thus $\log x/m = 1.265 + 0.535 \log p$; hence, $1/n = 0.535$ and $k = 18.41$. More exact values of these constants may be determined by the method of least squares.

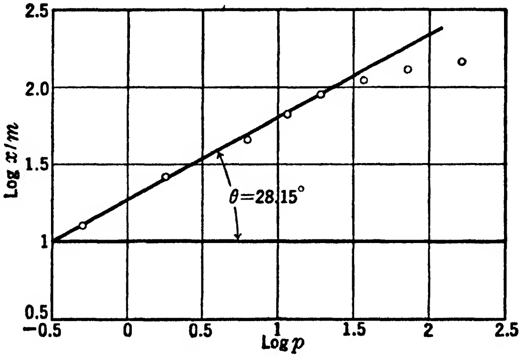

FIG. 12. Evaluation of the constants in Freundlich's adsorption equation.

McBain [2] points out that adsorption data are usually tested for conformity with the empirical Freundlich equation $x/m = kp^{1/n}$ (or $kc^{1/n}$) since it "is still the best summarized description of the approximate quantitative behavior of the extraordinary diverse instances of sorption. Such instances range from the sorption of argon at temperatures of liquid air to the gases evolved from molten glass or to the mercury sorbed even by heated carbon; from the complicated phenomena observed in the dye house to the use of the gas mask in chemical warfare; from the reactions of soil chemistry to many of those observed in living cells." At the same time, it is recognized that the equation never describes the facts accurately over any wide range of pressures or concentrations and it is useless for the portion of the curve that runs parallel to the pressure or concentration axis. Moreover, it is a purely empirical interpolation formula without theoretical foundation.

MONOMOLECULAR ADSORPTION THEORY

The theory of monomolecular and monatomic adsorption was proposed by Langmuir.[3] He assumes that adsorption is due to unsaturated forces at the surface of a crystal lattice. In the simplest case, there is a regular arrangement of uniform "elementary spaces" on the surface, each capable of holding a molecule of gas. Whenever gas molecules strike a surface, they do not in general rebound elastically but are held by the field of force of the surface atoms. The condensed molecules may evaporate subsequently, but the time lag between condensation and evaporation causes an accumulation of gas on the surface which is termed adsorption. If the surface forces are sufficiently great, the surface of the solid is covered with a layer of molecules. For true adsorption, the layer will usually be only one molecule thick since this is sufficient to saturate the surface forces. On the other hand, if the surface forces are weak, evaporation occurs soon after condensation, and only a part of the surface is covered with a single layer of adsorbed molecules.

II. Langmuir's Adsorption Equation

The expression known as Langmuir's adsorption equation may be derived as follows:

If on the surface of a solid there are N_0 spaces per square centimeter each capable of holding a molecule, then the maximum possible number of adsorbed molecules will be N_0, or N_0/N gram molecules per square centimeter, where N is the Avogadro constant.

In the simplest case, the rate of condensation S_1 on an exposed surface is proportional to μ, the number of molecules striking each square centimeter per second; to $(1 - \theta)$, the fraction of the surface not covered; and to α, the fraction of the molecular collisions which are inelastic (frequently very close to unity). The rate of evaporation is equal to $\nu\theta$, where ν is the rate when all the spaces are occupied and θ is the fraction actually occupied. When equilibrium is established, the two rates are equal, that is:

$$\mu\alpha(1 - \theta) = \nu\theta$$

from which

$$\theta = \frac{\alpha\mu}{\nu + \alpha\mu} \tag{1}$$

or, putting $\alpha/\nu = k$, a constant,

$$\theta = \frac{k\mu}{1 + k\mu} \tag{2}$$

The absorption A in gram moles per square centimeter is given by the expression:

$$A = \frac{N_0}{N}\left(\frac{k\mu}{1 + k\mu}\right) \tag{3}$$

From the kinetic theory $\mu = p/\sqrt{2\pi MRT}$, in which M is the molecular weight of the gas; μ is therefore proportional to p, the pressure, and so eq. 1 may be written in the form:

$$\theta = \frac{ap}{1 + ap} \tag{4}$$

and eq. 3 becomes:

$$A = \frac{N_0}{N}\left(\frac{ap}{1 + ap}\right) \tag{5}$$

where a is a constant. Since the values of N_0 and a in eq. 5 have to be determined empirically, this equation may be written:

$$\frac{x}{m} = \frac{abp}{1 + ap} \tag{6}$$

or in the linear form:

$$\frac{p}{x/m} = \frac{1}{ab} + \frac{p}{b} \tag{7}$$

where x/m is the number of milliliters adsorbed per gram of adsorbent, and b is a constant which is proportional to N_0/N.

These equations represent the simplest case, where there is but one kind of elementary space. If there are several kinds of spaces, equations similar to the above may be set up for each, and the total adsorption will be the sum. If the spaces are quite different, the adsorption curve will tend to consist of small steps[4] although it is really continuous. Similar formulas have been derived by Volmer[5] and by Fowler[6] from thermodynamics.

The curve corresponding to the Langmuir equation has the form shown in Fig. 15, I. It is apparent that the isotherm can be considered to consist of three parts which merge into each other: (1) At low values of p, x/m is about proportional to p, or the extent of surface covered is approximately proportional to the pressure. (2) At high values of p, x approaches the constant b, and adsorption is approximately independent of the pressure, meaning that the surface is about saturated or approximately completely covered by a monomolecular layer. At these high pressures, the adsorption is almost independent of the temperature except in so far as N_0 varies with the temperature. (3) Between these extreme conditions is an intermediate curved portion which can also be approximately represented by the expression $x/m = kp^{1/n}$, which is the Freundlich equation (Fig. 12). This emphasizes once more the limitations in the applicability of the Freundlich expression to adsorption data.

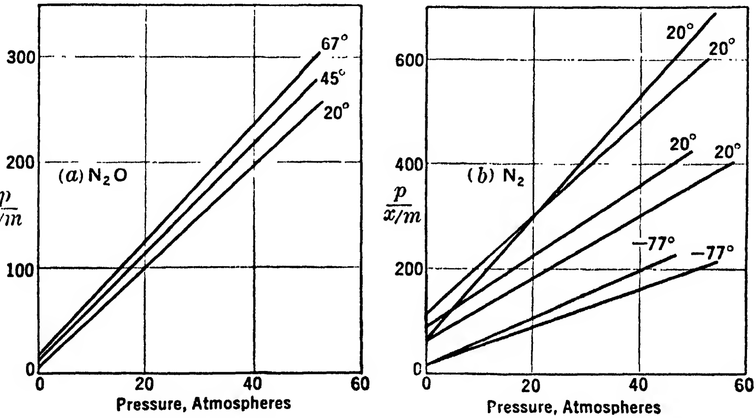

FIG. 13. Langmuir linear isotherms for the adsorption of nitrous oxide and nitrogen by carbon.

Application. The mechanism of adsorption presented by Langmuir explains in a convincing way the observations of himself and others on chemical adsorption, a few of which have already been mentioned (p. 37). Moreover, the Langmuir equation is more satisfactory than the Freundlich equation in representing the physical adsorption of gases on a variety of adsorbents whenever saturation is approached. As an illustration, the curves of McBain and Britton[7] on the adsorption of nitrous oxide and nitrogen (p. 29) by highly evacuated sugar charcoal are shown in Fig. 13. In accord with the linear equation (eq. 7), straight lines are obtained when $p/(x/m)$ is plotted against p.

The Langmuir theory has been criticized because it postulates a saturation value independent of the temperature, whereas experiment shows that the adsorption of gases and vapors falls off with rising temperature. Langmuir attributes this to a decrease in the number of elementary spaces with rising temperature; and McBain[8] suggests that it results from the expansion of closely packed matter with temperature. The Langmuir theory is also criticized because it assumes that an adsorption film on a plane surface will never be over a molecule or two[9] thick when, as a matter of fact, much thicker films have been reported on plane surfaces. Langmuir does not limit the amount taken up by porous substances to films one or two molecules thick, since capillary condensation may come in. The greater adsorption than would correspond to a monomolecular film on a so-called plane surface is attributed by Langmuir either to solution of the gas in the solid or to an underestimation of the extent of surface because of submicroscopic cracks or fissures in the adsorbent (see also p. 64).

THE POLYMOLECULAR FILM THEORY

Polanyi's Views

The hypothesis that the adsorbed gas or vapor is in the form of a thick compressed polymolecular film was proposed by de Saussure in 1815, and the concept was formulated quantitatively by Eucken[10] and Polanyi[11] a century later. It assumes the existence of long-range attractive forces extending out from the solid surface and putting the adsorbed gas or vapor under enormous pressures that may amount to as much as 37,000 atmospheres[12] near the surface, but fall off with increasing distance from the solid. Figure 14 is Polanyi's diagram showing the lines of equal potential or equal compression in the adsorption space between the surface of the adsorbent and the uniform gas space. Within this region the adsorbed gas or vapor is assumed to be in the form of a compressed fluid that obeys an

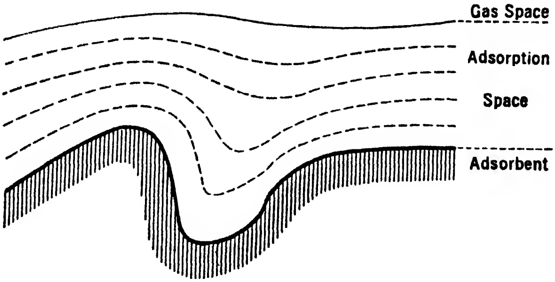

FIG. 14. Polanyi's diagram showing levels of equal adsorption potential.

ordinary equation of state such as the van der Waals equation. Accordingly, a nearly saturated vapor would condense to a liquid in the adsorption zone.

Polanyi concludes that the adsorption potential or adsorption compression is independent of the temperature over a wide range. If the attraction of the solid is independent of the temperature, it is possible to take the adsorption isotherm for any one temperature and calculate the others for the same system by applying the equation of state. This was done with considerable success by Polanyi and especially by Berenyi,[13] using the data of Titoff, Homfray, Richardson, etc. In this connection it should be mentioned, however, that these data fit the Langmuir equation even better than Polanyi's formulation.

In spite of the numerical success in testing Polanyi's theory, it is open to the objection that the forces acting between molecules are apparently of very short range, a few angstrom units. As a matter of fact, Eucken[14] has renounced the compressed-film theory, and Polanyi[15] has modified his original views by making the film two-dimensional, that is, one molecule deep.

In contrast to the original views of de Saussure and Polanyi, de Boer and Zwicker[16] and Bradley[17] assume that multilayer adsorption exists but results from polarizing effects transmitted from the first layer to successively higher layers. Brunauer, Emmett, and Teller[18] showed that such polarizing effects will be very small; they returned to Langmuir and carried out an isotherm derivation for multimolecular adsorption that is similar to Langmuir's derivation for monomolecular adsorption.

III. Brunauer, Emmett, and Teller (B.E.T.) Equation[18]

Derivation. Let $s_0, s_1, s_2, s_3, \cdots s_i, \cdots$ represent the surface area covered by 0, 1, 2, 3, $\cdots i, \cdots$ layers of adsorbed molecules. At equilibrium s_0 must remain constant; hence the rate of condensation on the bare surface is equal to the rate of evaporation from the first layer; that is:

$$a_1 p s_0 = b_1 s_1 e^{-E_1/RT} \tag{8}$$

where p is the pressure, E_1 is the heat of adsorption of the first layer, and a and b are constants. This equation states that the rate of condensation of molecules on the bare surface at equilibrium is equal to the rate of escape of molecules from the first layer. Similarly,

$$a_2 p s_1 = b_2 s_2 e^{-E_2/RT} \tag{9}$$

$$a_3 p s_2 = b_3 s_3 e^{-E_3/RT} \tag{10}$$

and

$$a_i p s_{i-1} = b_i s_i e^{-E_i/RT} \tag{11}$$

in which E_2, E_3, and E_i are the heats of adsorption in the second, third, and ith layers.

The total surface area A of the adsorbent is thus given by

$$A = \sum_{i=0}^{i=\infty} s_i \tag{12}$$

and the total volume adsorbed is:

$$V = V_0 \sum_{i=0}^{i=\infty} i s_i \tag{13}$$

where V_0 is the volume of gas adsorbed on 1 cm^2 of adsorbent surface when it is covered by a complete unimolecular film of adsorbed gas. If V_m is the volume of gas adsorbed when the entire adsorbent surface is covered with a complete monomolecular layer, it follows that:

$$\frac{v}{AV_0} = \frac{V}{V_{ni}} = \frac{\sum_{i=0}^{i=\infty} i s_i}{\sum_{i=0}^{i=\infty} s_i} \tag{14}$$

To carry out the summation indicated in eq. 14 Brunauer, Emmett, and Teller make the simplifying assumption that $E_2 = E_3 = \cdots E_i = E_L$, in which E_L is the heat of liquefaction; and that $b_2/a_2 = b_3/a_3 = \cdots b_i/a_i = g$, in which g is an appropriate constant. This is equivalent to saying that the evaporation-condensation properties in the second and higher adsorbed layers are the same as those of the liquid state. By appropriate transformation of the terms the following equation is obtained for the formation of the monolayer:

$$\frac{p}{V(p_0 - p)} = \frac{1}{V_m c} + \frac{(c-1)p}{V_m c p_0} \tag{15}$$

in which p_0 is the saturation pressure of the gas, and c is approximately $e^{-(E_1-E_L)/RT}$.

Limiting the summation of multimolecular layers to layers n molecules thick, the following relationship is obtained in place of eq. 15:

$$V = \frac{V_m c x[1 - (n+1)x^n + n x^{n+1}]}{(1-x)[1 + (c-1)x - c x^{n+1}]} \tag{16}$$

in which x is the ratio of the pressure at which the adsorption is V_0 to the saturation pressure p_0, and V_m and c have the same meaning as in eq. 8.

When $n = 1$, eq. 16 reduces to:

$$\frac{p}{V} = \frac{p_0}{cV_m} + \frac{p}{V_m} \tag{17}$$

which is the Langmuir equation (7); the usual arbitrary constants in eq. 7 are replaced by p_o, c, and V_m.

A survey of the literature discloses that all the known types of physical or van der Waals adsorption can be represented by five different types of isotherms as shown, with examples of each, in Fig. 15.

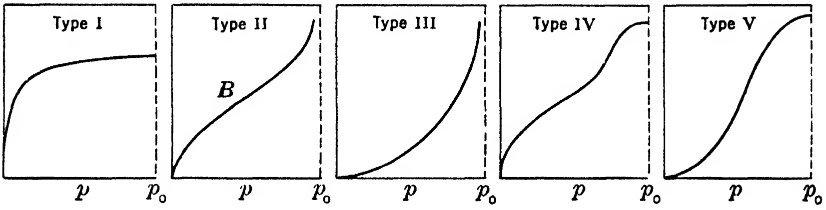

FIG. 15. Five types of van der Waals or physical adsorption isotherms with an example of each:

Type I. Adsorption of nitrogen on charcoal at −183°C.
Type II. Adsorption of nitrogen on iron catalyst at −195°C.
Type III. Adsorption of bromine on silica gel at 79°C.
Type IV. Adsorption of benzene on ferric oxide gel at 50°C.
Type V. Adsorption of water vapor on charcoal at 100°C.

Type I is the form of the Langmuir adsorption isotherm (p. 52), and Types II and IV at low pressures have the form of the Langmuir isotherm and the approximate form of the Freundlich isotherm (p. 28). The upper portion of Types II, III, IV, and V indicate capillary condensation (p. 64).

Type I is a Langmuir curve represented mathematically by eq. 10, and Type II is the common S-shaped curve represented mathematically by eq. 8. With the necessary assumptions the adsorption of bromine by silica gel (Type III) can likewise be calculated by the multimolecular adsorption equation (11). A much more complicated equation was deduced by Brunauer, Deming, Deming, and Teller[19] to represent the experimental data from which curves of Types IV and V were drawn. Thus the several types of adsorption curves are explained: Type I indicates monomolecular adsorption, and Types II, III, IV, and V indicate polymolecular adsorption at high pressures.

Application of Type II curves in determining surface area. The principle of determining surface areas from Type II adsorption isotherms involves: (1) selection from an experimental isotherm of the volume and hence of the number of molecules corresponding to a monomolecular layer and (2) multiplication of the number of molecules in the monomolecular layer by the cross-sectional area of each molecule. On the basis of accumulated evidence, the point *B* (Fig. 15, II) corresponding to the lower pressure extremity of the long linear portion of the S-shaped isotherm was selected as representing the volume of adsorbed gas necessary to form a monolayer. Later it was shown that eq. 15 could be used to evaluate V_m, the volume corresponding to a monomolecular layer, by plotting $p/V(p_0 - p)$ against

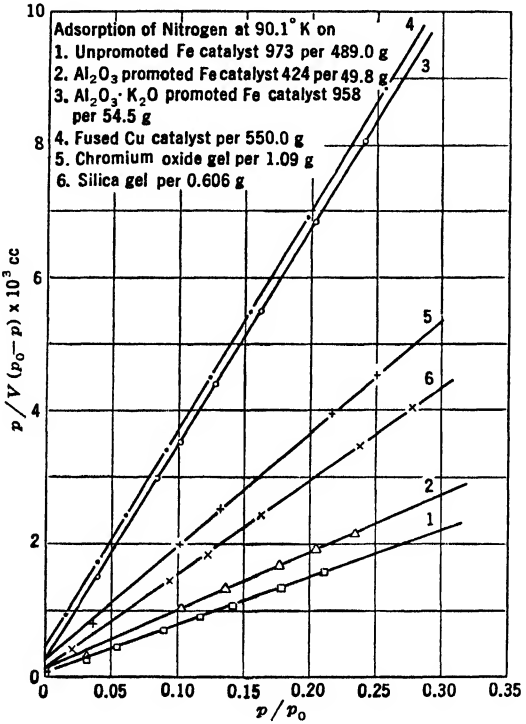

FIG. 16. Curves for adsorption of nitrogen on several different adsorbents.

p/p_0. The slope of the straight line in Fig. 16 is $(C - 1)/V_mC$, and the intercept is $1/V_mc$, from which values of the constants V_m and c are calculated.

The closeness of agreement of the values of V_m obtained by the empirical and by the graphic method is shown in Table 14.

TABLE 14

VOLUME OF ADSORBED NITROGEN (−196°C) IN A MONOLAYER ON VARIOUS ADSORBENTS (EMMETT[18])

Substance	V_m (cc/g)	Point B (cc/g)
Unpromoted Fe catalyst 973I	0.13	0.12
Unpromoted Fe catalyst 973II	0.29	0.27
Fe-Al_2O_3 catalyst 954	2.86	2.78
Fe-Al_2O_3 catalyst 424	2.23	2.09
Fe-Al_2O_3-K_2O catalyst 931	0.81	0.76
Fe-Al_2O_3 catalyst 958	0.56	0.55
Fe-K_2O catalyst 930	0.14	0.12
Fused Cu catalyst	0.05	0.05
Commercial Cu catalyst	0.09	0.10
Cr_2O_3 gel	53.3	50.5
Cr_2O_3 glowed	6.09	6.14
Silica gel	116.2	127.0

The area of the adsorbed molecule, assuming close packing, is calculated by the equation:[18]

$$\text{Area per molecule} = 4(0.866)\left(\frac{M}{4\sqrt{2}\,AD}\right)^{2/3} \qquad (18)$$

in which M is the molecular weight of the adsorbate, A is the Avogadro number, and D is the density of the liquefied or solidified gas. The calculated area per molecule is 20% greater when the density of the liquefied adsorbate[18] is employed than when the density of the solidified adsorbate[18] is used. Hence *absolute* surface area measurements are uncertain by this amount, but relative areas from adsorption measurements are reproducible to within a few per cent. The specific surfaces, in square meters per gram of various adsorbents, are given in Table 15.

TABLE 15

SPECIFIC SURFACES OF VARIOUS ADSORBENTS (EMMETT[18])

Adsorbent	Specific surface (sq m/g)
1. Fe_3O_4 catalyst (unreduced)	0.02
2. Fe catalyst 973, sample I (unpromoted): 0.15% Al_2O_3 impurity	0.55
3. Fe catalyst 973, sample II (unpromoted): 0.15% Al_2O_3 impurity	1.24
4. Fe-Al_2O_3 catalyst 954: 10.2% Al_2O_3	11.03
5. Fe-Al_2O_3 catalyst 424: 1.03% Al_2O_3, 0.19% ZrO_2	9.44
6. Fe-Al_2O_3-K_2O catalyst 931: 1.3% Al_2O_3, 1.59% K_2O	4.78
7. Fe-Al_2O_3-K_2O catalyst 958: 0.35% Al_2O_3, 0.08% K_2O	2.50
8. Fe-K_2O catalyst 930: 1.07% K_2O	0.56
9. Cecil soil, 9418	32.3
10. Cecil soil, colloid, 9418	58.6
11. Carnes soil, 10,308	44.2
12. Barnes soil, colloid, 10,308	101.2
13. Fused Cu catalyst	0.23
14. Commercial Cu catalyst	0.42
15. Pumice	0.38
16. Ni catalyst supported on pumice, 91.8% pumice	1.27
17. NiO catalyst supported on pumice, 89.8% pumice	4.28
18. Cr_2O_3 gel	228
19. Cr_2O_3 "glowed"	28.3
20. Glaucosil	82
21. Silica gel I (non-electrodialized)	584
22. Silica gel II (electrodialized)	614
23. Dried bacteria	0.17
24. Dried bacteria (pulverized)	3.41
25. KCl (finer than 200 mesh)	0.24
26. $CuSO_4 \cdot 5H_2O$ (40–100 mesh	0.16
27. $CuSO_4$ anhydrous	6.23
28. Granular Darco B	576
29. Granular Darco G	2123
30. Cement	1.08
31. Cuprene	20.7
32. Paper	1.59
33. $ZrSiO_4$	2.76
34. Graphite	30.73
35. TiO_2	9.88
36. $BaSO_4$	4.30
37. Lithopone—before calcining and grinding	34.8
Lithopone—calcined but not ground	1.37
Lithopone—calcined and ground	3.43
38. Porous glass	125.2

The reliability of the low temperature adsorption isotherm for measuring surface area is indicated by comparison of particle sizes calculated from surface area by means of the equation:

$$\text{Area} = \frac{6}{\rho d_3}$$

in which ρ is the density and d_3 the average diameter, with the diameter obtained by other methods. This comparison is illustrated in

Table 16. The discrepancies between particle sizes determined by the Brunauer, Emmett, and Teller method and by other methods probably result from irregularities in particle shape and in some instances from porosity of the particles, rather than from the inadequacy of the B.E.T. theory.

TABLE 16

COMPARISON OF SURFACE-AREA MEASUREMENTS ON ZnO PIGMENTS

	Four ZnO pigments				Sized glass beads
	1	2	3	4	
Area by adsorption of N_2	9.48	8.80	3.88	0.66	
Particle size (microns)					
Microscopic count	0.21	0.25	0.49	1.40	1.00
Ultramicroscopic count	0.135	0.16	0.26	0.82	
By adsorption of methylstearate	0.19	0.24	0.35	4.50	
By permeability	0.120	0.15	0.25	1.25	
Adsorption of N_2 (*L*) *	0.115	0.124	0.28	1.68	4.50
Adsorption of N_2 (*S*) †	0.135	0.145	0.33	1.97	5.30

* From molecular area of liquid nitrogen.

† From molecular area of solid nitrogen.

IV. The Harkins-Jura Equation

Harkins and Jura[20] point out that for any condensed film on liquids or on solids the film pressure π–area σ relationship is given by the equation:

$$\pi = b - a\sigma \tag{19}$$

in which a and b are constants, and σ is the mean area per molecule. The condensed film is monomolecular only for low values of π, but the linear relationship persists up to higher pressures where the film is several molecules thick. Because of the considerable calculation involved in obtaining the values of film pressure, eq. 1 was transformed into the equivalent relation:

$$\log p = B - \frac{A}{v^2} \tag{20}$$

or

$$\log \frac{p}{p_0} = B - \frac{A}{v^2} \tag{21}$$

in which A and B are constants, and gas pressure p and volume of adsorbed gas v are measured directly in the experimental determination of adsorption. This Harkins-Jura adsorption equation is remarkable in two respects: (1) it is the simplest adsorption isotherm known to date, and (2) it is valid over more than twice the pressure range when compared with any other two-constant adsorption equation.

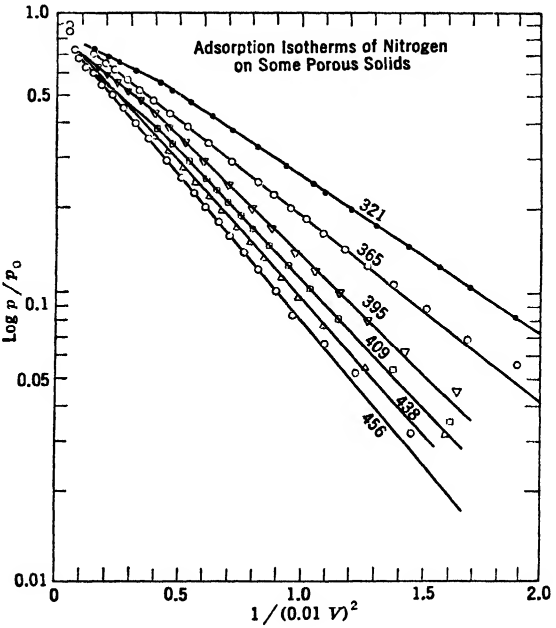

Fig. 17. Nitrogen isotherms on porous solids of areas, beginning at the top, of 321, 365, 395, 409, 438, and 456 square meters per gram. These areas are 4.06 times the square roots of the linear portion of the isotherms.

Application of the Harkins-Jura equation in determining surface area. Harkins and Jura found it possible to measure the surface area of finely divided solids without the necessity of knowing the cross-sectional area of the adsorbate molecule, which may be uncertain (see above), but which must be known in determining surface area by the Brunauer, Emmett, and Teller method. Harkins and Jura plotted the low-temperature gas adsorption data according to eq. 13, the abscissa being log p/p_0 and the ordinates being $1/V^2$. Such a plot for the adsorption of nitrogen on some porous solids is given in Fig. 17.

It was noted from such a plot by Harkins and Jura that the area of the solid Σ was proportional to the square root of the slope $\sqrt{A}$ or $\sqrt{s}$; that is:

$$\Sigma = k\sqrt{A} = k\sqrt{s} \tag{22}$$

from which:

$$k = \frac{\Sigma}{\sqrt{A}} \tag{23}$$

Harkins and Jura [21] evaluated k for nitrogen from the value of A in square meters per gram determined by an "absolute" method from the heat of immersion of titanium dioxide in liquid nitrogen at −195.8°C, and the value of A from the curve for $\log p/p_0$ against $1/v^2$. For nitrogen at 195.8°C, $k = 4.06$; hence it follows that the surface area from nitrogen adsorption measurements is given by the equation:

$$\Sigma = 4.06\sqrt{A} \tag{24}$$

The constant is different with different adsorbates and at different temperatures. For example, for water at 25°, $k = 3.85$; for *n*-butane at 0°, $k = 13.6$; and for *n*-heptane at 25°, $k = 16.9$.

In the nitrogen isotherms for different porous adsorbents as plotted in Fig. 17 the numbers represent the surface areas in square meters per gram.

Comparison of the two independent methods of determining surface area from adsorption measurements. The values of surface area calculated by the two methods described above show remarkable agreement in spite of the fact that the methods are based on two entirely different principles, the Brunauer, Emmett, and Teller method being based on a kinetic theory and the Harkins-Jura method on a thermodynamic theory. This fact is illustrated by Table 17.

The agreement between the two methods is very close, but Harkins and Jura point out that they obtain more consistent results on the assumption that the value of k is constant in eq. 15 than are obtained by the Brunauer, Emmett, and Teller procedure if a constant value is assumed for the molecular area of the adsorbed gas. The applicability and the limitations of the two methods are discussed in detail by Harkins and Jura [22] and by Emmett,[23] and the choice of method to be employed in determining the surface area of a solid should be decided only after a careful perusal of these two critical reviews. In most instances both methods are valid; in any event, either method gives a value for the surface area that is probably much more nearly the

TABLE 17

COMPARISON OF SURFACE AREA VALUES *

Solid	Absolute methods[21]	Brunauer, Emmett, Teller method[18]				Harkins-Jura method[22]			
		Adsorbate				Adsorbate			
		N_2 16.1	H_2O 14.8	*n*-Butane 56.6	*n*-Heptane 64.0	N_2	H_2O	*n*-Butane	*n*-Heptane
TiO_2 I	13.8	13.9	9.8	7.8	9.8	13.8	13.8	13.8	13.8
TiO_2-Al_2O_3	8.9	9.6	8.9			9.6	11.8		
TiO_2 II		8.7	8.3		6.1	8.7	8.4		8.7
$BaSO_4$		2.4	2.0	1.5	1.7	2.4	2.3	2.2	2.3
SiO_2		3.2	3.0		2.5	3.2	3.3		3.3
$SiO_2 \cdot Al_2O_3$		633.0				602.0			
		415.0				415.0			
		475.0				505.0			
		373.0				370.0			
		254.0				257.0			
		129.0				131.0			

* Harkins and Jura: *J. Am. Chem. Soc.*, **66**, 1370 (1944).

true value than could possibly be obtained before the applicability of Brunauer, Emmett, and Teller's and of Harkins and Jura's procedures was established.

THE CAPILLARY-CONDENSATION THEORY

V. The Zsigmondy-Patrick Equation and the Kelvin Equation

The capillary-condensation theory assumes that the vapors are condensed as liquid in pores as a result of the lowering of the vapor pressure because of surface-tension effects. The theory proposed by Zsigmondy[24] to explain the adsorption of water by silica gel assumes that each particle of the gel is covered with a monomolecular film of water and that, in addition, liquid water condenses in irregular pore spaces under suitable conditions of vapor pressure. Patrick,[25] enlarging on this concept, considers the adsorption by porous substances such as silica gel and charcoal to be due entirely to a capillary condensation that is independent of the nature of the adsorbent. From this point of view, the form of the adsorption isotherm expresses merely the distribution of the internal volume of the adsorbent as a function of the dimension of the pores. The Patrick equation for adsorption is the empirical expression:

$$V = k\left(\frac{p\gamma}{p_s}\right)^{1/n}$$

where V is the volume of adsorbed liquid, p is the pressure, p_s is the vapor pressure of the condensed gas at the temperature in question, γ is the surface tension, and k and $1/n$ are constants. For sulfur dioxide adsorbed on silica gel at various temperatures this equation is: $V = 0.1038\ (p/p_s)^{0.447}$.

The capillary condensation of vapors will take place under appropriate conditions when they are exposed to solids containing pores of suitable size and when the liquid will wet the solid. On the other hand, capillary condensation is not a general theory of adsorption, since it does not explain adsorption of gases or adsorption on plane surfaces.

The conformity of Patrick's adsorption data with the Patrick adsorption equation does not prove the correctness of the assumptions on which the equation is based. Thus Berenyi found that Patrick's data conform with Polanyi's compressed-film mechanism of adsorption.

Patrick's equation is now chiefly of historical interest. Nearly all workers at the present time make use of the Kelvin [26] equation, applying it to the desorption isotherm in order to obtain some information concerning pore size and pore-size distribution in porous solids. Kelvin's equation, assuming that condensation of a vapor takes place at a relative pressure p/p_0 in a cylindrical capillary of diameter D, is:

$$D = \frac{4\gamma V \cos\theta}{RT2.303 \log p/p_0}$$

where γ is the surface tension of the liquid, θ is the angle of wetting, V is the molal volume of the liquid, and T is the temperature. The applicability and limitations of this equation are considered, among others, by Emmett and DeWitt.[27]

The relative advantages and disadvantages of the multilayer theory and the condensation theory have been considered in detail by Emmett and his colleagues.[28] The Brunauer, Emmett, Teller theory and the Harkins and Jura theory are both quite satisfactory for representing adsorption on plane surfaces. Both may be unsatisfactory in representing the behavior in adsorption on porous solids. The present tendency of Zettlemoyer,[29] Anderson,[30] Joyner,[31] and others is to make some modifications in the basic assumptions or to carry out more rigorously some steps in the derivation of eq. 15. The real limitation in the usefulness of the multilayer adsorption equation in the case of porous solids is that both multilayer and capillary adsorption can and do take place simultaneously with such adsorbents, and at present no one can tell what part of the total adsorption is due to multilayer formation and what part is due to capillary condensation.

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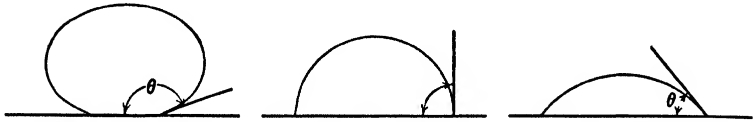
CHAPTER 5

Adsorption by Solid III: Adsorption of Liquid by Solid; Wetting

If a liquid is brought in contact with a solid that adsorbs it strongly, the liquid forms a film over the surface of the solid and is said to wet the solid. In the event that the solid does not adsorb the liquid sufficiently strongly to displace the film of air or other foreign substance on the surface, there will be an angle of contact between the liquid and the solid (see Fig. 18). For complete wetting the contact angle is zero; for no wetting the contact angle is 180°; and for partial wetting the contact angle is some value between these two extremes. Bartell[1, 2] defines wetting as that phenomenon which occurs when a solid phase and a liquid phase come in contact in any manner so as to form a solid-liquid interface.



Contact angle between 90 and 180°   Contact angle 90°   Contact angle between 0 and 90°

FIG. 18. Types of liquid-solid contact angles.

THE WETTING OF SOLIDS[*]

Surface Energy

The factors which determine the wetting behavior in a given equilibrium system are the surface and interfacial energies of the phases present. The free energy per unit area of a phase boundary, γ,[†] is

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[*] This section was prepared by Professor J. T. Smith of the Rice Institute.

[†] The following notation will be used throughout this discussion: the free energy per unit area of a given surface or interface = γ; the total energy per unit area of a given surface or interface = h; the internal energy per unit area of

equal to the work which must be done to create a unit area of the phase boundary. The numerical value of γ is dependent upon the composition and structure of the layer of atoms or molecules in which the transition from the interior of one phase to the interior of the other occurs, as well as upon the nature of the phases themselves. Interfaces adsorb any materials present in either phase which will lower the free energy of the interface. This lowering is accomplished by an alteration in the transition layer which makes the phase boundary less sharp. To use Harkins'[3] terminology, the interfacial region is thickened by the adsorption. As a result of this adsorption phenomenon, amounts of impurities which would produce no significant change in other physical properties of a substance may greatly alter the surface energy of the material or its interfacial energy with some other substance.

The total energy per unit area of a phase boundary, h, is the sum of the work which must be done and the heat which is absorbed when a unit area of the phase boundary is created. Since these changes occur at constant pressure, h represents the enthalpy of the surface or interface. However, since the change in the volume of the system is small for a change in the surface area, the internal energy of the surface, ϵ, can be assumed to be equal to the total energy or enthalpy of the surface except perhaps at very high pressures. The numerical values of h and ϵ are of course greatly affected by the adsorption of impurities, just as was mentioned for γ.

The values of γ, h, and ϵ for a solid surface or a solid-liquid interface are subject to such wide sources of variation that special mention should be made of the factors affecting them. Practically all solids adsorb gases to some extent and adsorb vapors strongly, the amount of adsorption depending of course on the relative saturation of the material in the gas phase. Thus the surface energy of a solid exposed to air may be altered slightly by the adsorption of O_2 or N_2 and perhaps greatly by the adsorption of H_2O. Furthermore air which might be considered fairly pure may contain oil as minute droplets or as vapor which will rapidly contaminate a clean solid surface upon exposure. Greases and waxes spread over solid surfaces so that contact of a clean solid surface with a contaminated one results

a given surface or interface = ϵ; these symbols will be followed by subscripts to denote the phases in contact: S indicates a solid surface, L a liquid surface, LS a liquid-solid interface.

in contamination. A solid which has been immersed in a liquid and then removed may have a film so tenaciously adsorbed on the surface that drastic treatment is necessary before all traces of the film are removed. Impurities present in very small amounts in a liquid phase may be adsorbed strongly at the interface between the liquid and a solid, thus producing a large change in the interfacial energy. In addition to variations resulting from contamination, the surface or interfacial energy of a solid may change with the exact structure of the solid atoms in the surface. Thus the energy of a polished surface may be appreciably different from that of a cleaved crystal surface, and the energy of one crystal face may be different from that of another.

Because of these sources of variation, it is evident that, in evaluating any experimental study of solid surfaces, special attention must be paid to the exact experimental techniques used in preparing and handling these surfaces. A given piece of work often has no general significance because the results may be dependent primarily upon a particular set of experimental conditions.

Relation between γ and h

The quantities γ and h are related for any surface or interface. By considering the thermodynamic properties of a system at constant pressure in which the free energy is a function of temperature and surface area, the following relation is obtained[4] for a given pressure, temperature, and surface area σ:

$$h = \gamma - T\left(\frac{\partial \gamma}{\partial T}\right)_{\sigma,p} \tag{1}$$

Actually pressure in general has only a small effect on h, γ and $(\partial\gamma/\partial T)_{\sigma,p}$, and for most systems the quantities are independent of σ. Thus the equation is generally applied without much regard for variations in pressure and surface area, and $(\partial\gamma/\partial T)_{\sigma,p}$ is usually written $d\gamma/dT$.

This equation is exactly like the Gibbs-Helmholtz equation relating the change in heat content ΔH with the change of free energy ΔF, for a chemical reaction.

The significance of the terms in the equation is apparent when one considers that the total energy per unit area of a surface is composed of two parts, the work which must be performed to create one unit area of the surface γ and the heat which is absorbed when one unit area of surface is formed, $-T(d\gamma/dT)$. Since γ in general decreases as the temperature increases, $-T(d\gamma/dT)$ is positive, and heat is absorbed by the system when the surface area is increased. Thus h is in general greater than γ.

Condition for Contact-angle Formation

Consider a system (Fig. 19) consisting of a fluid phase A in contact with a second fluid phase B on a solid surface C. Suppose that at equilibrium the interface between A and B forms the angle θ with the solid C measured through phase A. Let γ_{BC}, γ_{AB}, γ_{AC} be the free energies per square centimeter of interface for the phase boundaries BC, AB, and AC respectively.

By considering the energy changes which occur for a small reversible displacement of the line of contact of the interface between A and B along the solid C, it can be shown that:

$$\gamma_{BC} = \gamma_{AC} + \gamma_{AB} \cos \theta \qquad (2)$$

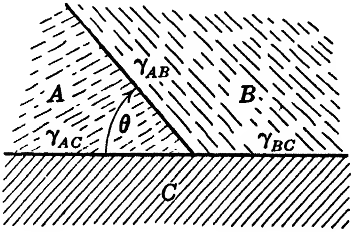

Fig. 19. A contact angle between fluid phases A and B on a solid C.

This equation, first suggested by Young,[5] shows that, in order for a contact angle different from 0° or 180° to be formed between the fluids A and B on the solid C, the values of the interfacial energies must be such that $|\gamma_{AC} - \gamma_{BC}| < \gamma_{AB}$.

This relation may be derived by regarding the surface energies as arising from forces acting parallel to and in the plane of the surfaces, and then by setting the resultant force component parallel to the solid surface equal to zero for equilibrium. It should be emphasized that this sort of reasoning is not rigorous. It involves substituting, for the condition that the free energy be a minimum, the condition that the force component parallel to the surface be zero, which gives the same results for this type of problem.

Validity of Contact-angle Relations

It must be emphasized that Young's equation holds only when true equilibrium exists. This means that in an experimental system it must be possible to cause a slight displacement of the line of contact of the interface between A and B on the solid C in either direction with the same contact angle θ. Furthermore, when true equilibrium exists, each of the phases in the system must be saturated with respect to the other two, and each of the phase boundaries must be in equilibrium with respect to all the components present in the system. As has been emphasized before, often there is a large change in phase-boundary energy caused by the adsorption of a minor constituent present in one of the phases as a result of a slight solubility or vapor pressure. This means that all the surface energies in an equilibrium system must be considered as dependent upon all the components present even though the bulk concentration of some component in the particular phase of interest may be low.

Experimental Methods for Measuring Contact Angles

Many procedures have been used for contact-angle measurements. In general the procedure used is dependent upon the physical state of the solid. If the solid can be obtained in a plate having a plane surface several millimeters in extent each way, some modification of the tilting plate apparatus originally advocated by Adam and Jessop[6] and modified by Harkins and Fowkes[7] may be employed. Bartell and coworkers[8] have used a method for measuring the contact angles on powder. The method is essentially empirical but can be used where other techniques are impossible. Bartell and coworkers have also developed techniques for the direct observation of drops or bubbles on plane surfaces.[9] By arranging a system so that the volume of the drop or bubble can be controlled, measurements may be made under advancing or receding condition.

Hysteresis in Contact-angle Systems

In general, when an attempt is made to measure a contact angle, it is found that the value may vary between two limits which may be as much as 50° or more apart. Suppose that a contact angle is observed when phase A and phase B are in contact on a solid and is measured through phase A. The upper limiting value of the angle is characteristic of measurements made when phase A is slowly displacing phase B from the surface; that is, when phase A is advancing, and the lower limiting value is characteristic of measurements made when phase A is receding, phase B is slowly displacing A. This phenomenon of the existence of a range of contact-angle values has been termed *hysteresis.* There are many factors which may have a bearing on hysteresis, such as the roughness of the surface, the presence of adsorbed films of foreign substances which are removed by the advancing fluid, and the formation of an adsorbed layer from the liquid or liquids used. One point is definite, however; that is that any system in which hysteresis is observed cannot be an equilibrium wetting process, and accordingly the familiar contact-angle equation cannot be applied without considerable reservation as to its meaning.

Values of Contact Angles of Liquids on Solids in Air

Water forms 0° contact angles on practically all clean metal and mineral surfaces.

The contact angle of water is high, 70 to 100°, on solid organic substances which have the non-polar $—CH_2$ or $—CH_3$ groups exposed on the surface. Since practically all solid surfaces become rapidly covered with a thin film of wax or grease upon exposure to air, contact angles different from 0° are often observed on such materials as glass, silica, mica, metals, and other solids which when clean would be completely wet with water. In general, organic liquids give a 0° contact angle on all solid surfaces whether clean or contaminated. Mercury and similar metallic liquids give contact angles on most surfaces, the principal exceptions being metals, with many of which complete wetting and often amalgamation occur.

In Table 18, contact-angle values are given for four materials as determined by Harkins and Fowkes.[7]

TABLE 18

CONTACT ANGLES GREATER THAN ZERO WITH WATER

Substance	*Value*
Ceylon graphite	85.7
Talc	87.8
Stibnite	84.2
Paraffin	108–111

Interfacial Contact-angle Systems

The contact angle between two immiscible liquids on a solid has been studied by a few investigators, notably Bartell.[10] Water and some organic liquid have been used in most of the studies of this type. As would be expected, hysteresis is very prominent in such systems, the angles depending in general upon which liquid wets the solid first. As one might predict, water preferentially wets strongly polar solids such as silica, glass, alumina, and fluorite, whereas organic liquids preferentially wet the non-polar type of surfaces such as the noble metals, carbon, and the sulfide minerals.

DISTRIBUTION OF SOLIDS BETWEEN TWO LIQUIDS

If a solid is added to a vessel containing two immiscible liquids, preferential adsorption or wetting takes place, and this leads to varying results, first studied by Hofmann[11] and Reinders.[12] For example, when finely divided gypsum is shaken with water and benzene or chloroform, the solid remains in the water; red lead, on the other hand, adheres to the surface of the organic liquid. Bancroft[13] states the theory of the process in the following way: In general, the solid particles tend to go into the water phase if they adsorb water to the practical exclusion of the organic liquid; they tend to go into the organic liquid if they adsorb the latter to the practical exclusion of the water; and they tend to go into the dineric interface if the adsorption of the two liquids by the solid is sufficiently great to increase considerably the miscibility of the two liquids at the surface between solid and liquid.

The behavior of the system may be explained by considering the relation between the three interfacial tensions which determine the interfacial contact angle. The following notation is used for the final equilibrium interfacial tensions in the system:

γ_{WO}' = the interfacial tension between the organic liquid and water in the presence of the solid.

γ_{WS}' = the interfacial tension between water and the solid in the presence of the organic liquid.

γ_{OS}' = the interfacial tension between the organic liquid and the solid in the presence of water.

If $\gamma_{WS}' + \gamma_{WO}' \leqq \gamma_{OS}'$, the water wets the solid with a 0° angle measured through the water phase, and the solid stays in the water phase. Similarly if $\gamma_{WO}' + \gamma_{OS}' \leqq \gamma_{WS}'$, the angle is 0° measured through the organic liquid, and the solid will stay in the organic liquid. If $\gamma_{WO}' > | \gamma_{WS}' - \gamma_{OS}' |$, a contact angle is formed between the two liquids on the solid, and the solid will tend to collect at the interface.

The above statements are of course consistent with the requirement that, other things being equal, the final state of the system will be such that the total surface and interfacial energy is a minimum.

The difference in behavior of a number of solid substances when shaken with two liquids is shown in Table 19, taken from observations by Reinders.[12] In this table the letters *w*, *o*, and *i* mean that practically all the solid goes to the water, the organic liquid, and the interface, respectively. Two letters, such as *wi*, mean that the powder goes chiefly to the water phase, but a part of it goes to the interface; *w*(*i*) means that a very little goes to the interface.

TABLE 19

Preferential Adsorption of Solids by Liquids

Suspended material	Water and				
	Paraffin oil	Amyl alcohol	CCl_4	C_6H_6	$(C_2H_5)_2O$
Kaolin	*w*	*w*(*i*)	*w*(*i*)	*w*	*w*(*i*)
CaF_2	*wi*	*wi*	*w*(*i*)	*w*(*i*)	*w*(*i*)
Gypsum	*w*	*wi*	*w*	*iw*	*w*(*i*)
$BaSO_4$	*w*(*i*)	*wi*	*wi*	*wi*	*wi*
PbO	*i*	*i*	*iw*	*i*	*iw*
Malachite	*io*	*i*	*i*	*i*	*iw*
ZnS	*i*	*i*	*i*	*i*	*iw*
PbS	*io*	*io*	*i*	*i*	*i*
C	*io*	*i*	*i*	*i*	*i*
As_2S_3 (sol)	. . .	*i*	*w*	*w*	*w*

These observations illustrate the tendency for the sulfides to go into the dineric interface and for the gangue material, such as kaolin and gypsum, to remain in the aqueous phase. Such behavior was the foundation for the obsolete Elmore bulk ore flotation process in which sulfide ores were concentrated by mixing the pulverized ore with a considerable amount of water and then shaking with a viscous oil. The tendency for carbon to concentrate at the interface has led to a flotation process for getting ash-free coal which gives a special grade of coke.[14]

It should be pointed out that the conclusions as to the way a given pair of liquids will behave with a given solid depend on the experimental conditions, such as the liquid which wets the solid first, the relative amounts of the liquids, and the time allowed for equilibrium conditions to be set up. Thus, Hofmann found that glass is wetted more readily and more rapidly by water than by xylene or petroleum but that an excess of the organic liquid will in time displace a film of water from a glass surface. Accordingly, one would expect glass powder to behave differently, depending on whether it was treated first with water or with the organic liquid. Actually, if the glass is first wetted with water and then shaken with kerosene, all the glass goes into the water phase; whereas, if the powder is allowed to stand for a long time with kerosene or heated with it to hasten the removal of the air film, part of the glass is carried into the interface and remains there for some time.

THE WORK DONE IN WETTING

In order to correlate the wetting behavior of liquid-solid systems, the decrease in free energy of the system which occurs during the wetting process is commonly used. The decrease in free energy is the same as the work done by the system for a reversible process at constant pressure. Since there are three different processes by which wetting may occur, three different free-energy changes may be evaluated and given names. The processes and terms are explained in Table 20 and are further discussed in the following sections, using the notation of Harkins.[15]

TABLE 20

WETTING PROCESSES

Process	Term used to indicate the work done by the system in the wetting process	Description of process
Adhesional wetting	Work of adhesion, W_A	A solid surface and a liquid surface are brought together to form a solid-liquid interface
Spreading wetting	Spreading coefficient or spreading pressure, $S_{L/S}$	A liquid is spread over a solid surface, forming a liquid surface and a liquid-solid interface where there previously existed only a solid surface
Immersional wetting	Free energy of emersion, F_E	A solid is immersed in a liquid, forming a liquid-solid interface from the solid surface

Expressions for the work done by the system during each of these wetting processes may readily be obtained in terms of the energies of the surfaces or interfaces whose areas change in the process.

Work of Adhesion

Adhesional wetting of 1 sq cm of surface consists of three parts: the formation of the solid-liquid interface involving a work term of $-\gamma_{LS}$, the destruction of the solid surface involving a work term of $+\gamma_S$, and the destruction of the liquid surface involving a work term $+\gamma_L$. Thus it follows that, for 1 sq cm of solid-liquid interface formed,

$$W_A = \gamma_S + \gamma_L - \gamma_{LS} \tag{3}$$

The value of W_A is subject to all the uncertainties present in the values of γ_S, γ_L, and γ_{LS}, as mentioned in the discussion of surface energies. If it is to be assigned a single value characteristic of only the solid and liquid present, it is necessary that some standard reproducible conditions be adopted. A convenient set of conditions are that γ_S be the surface energy (in a vacuum) of the pure solid freed of all surface contamination, that γ_L be the surface energy of the pure liquid in an atmosphere consisting of its saturated vapor, and that γ_{LS} be the interfacial energy between the pure solid and pure liquid. Values obtained under any other conditions are not characteristic of the solid and liquid alone. Inasmuch as there is no experimental method for a direct determination of γ_S or γ_{LS}, W_A cannot be calculated from eq. 3. In the following section, a method is described for calculating W_A by the use of contact-angle data and adsorption measurements.

Calculation of W_A From Contact-angle Measurements

Investigators have published values of W_A based upon the following interpretations of contact-angle measurements. If a liquid forms an equilibrium contact angle in air on a solid such as is indicated in Fig. 20, eq. 1 may be used to relate the various surface energies, and thus the result shown in the figure may be obtained. The primes are placed after each γ to emphasize that γ_L' and γ_{LS}' are in the presence of air, as normally measured, and that γ_S' is the surface energy of the solid in air saturated with the liquid. The work of adhesion W_A' under these conditions is given by the equation:

$$W_A' = \gamma_S' + \gamma_L' - \gamma_{LS}'$$

or

$$W_A' = \gamma_L' + \gamma_L' \cos\theta \tag{4}$$

This value, W_A', is the work of adhesion of a liquid saturated with air with a solid surface saturated with air and the vapor of the liquid. It should not be confused with the standard value of W_A, referring to the pure materials *in vacuo.*

Harkins[16] pointed out that, if the contact angle is determined for a liquid on a solid in the absence of air, and if the decrease in the surface energy of the solid π_e, resulting from adsorption of the saturated liquid vapor, is determined, then the standard value of the work of adhesion may be found. This follows since we have (see Fig. 21) that:

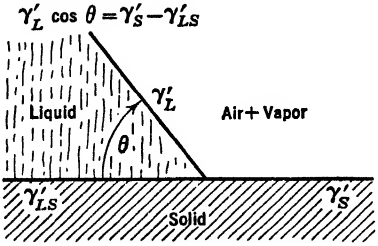

FIG. 20. Contact angle of a liquid on a solid in air.

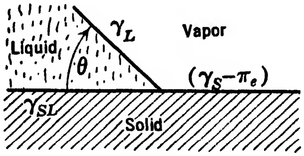

FIG. 21. Contact angle of a liquid on a solid in a liquid vapor atmosphere.

$$\gamma_L \cos\theta = \gamma_S - \pi_e - \gamma_{SL}$$

and thus

$$\gamma_S - \gamma_{SL} = \gamma_L \cos\theta + \pi_e$$

where γ_L, γ_S, and γ_{SL} refer to the standard values previously defined. Finally, combining eq. 3 with the above, the result is:

$$W_A = \gamma_L \cos\theta + \pi_e + \gamma_L \qquad (5)$$

In order to evaluate π_e, the Gibbs adsorption equation is applied to the vapor-solid adsorption isotherm. By integrating the Gibbs adsorption equation from zero pressure to the saturation pressure of the vapor, π_e may be calculated.

For the majority of systems involving a pure liquid and a pure solid, $\theta = 0°$. This generally means that the vapor is adsorbed to form a duplex film, that is, a film of sufficient thickness so that the outer surface is independent of the liquid-solid interface and is just like a pure liquid surface. However, regardless of the nature of this film, if $\theta = 0°$, $\cos\theta = 1$ and

$$W_A = \pi_e + 2\gamma_L$$

Work of Spreading

The spreading pressure (or spreading coefficient), $S_{L/S}$, is the work done per square centimeter when a liquid spreads over a solid to form a liquid layer on the solid surface. Since 1 sq cm of solid-liquid interface and 1 sq cm of liquid surface are formed while 1 sq cm of solid surface is destroyed, we have:

$$S_{L/S} = \gamma_S - \gamma_{SL} - \gamma_L \tag{6}$$

Referring to the treatment for the work of adhesion, it is evident that the standard value of $S_{L/S}$ is given by the following relation:

$$S_{L/S} = \pi_e + \gamma_L \cos\theta - \gamma_L \tag{7}$$

If $\theta = 0°$, which is the usual condition for clean solids, this relation reduces to:

$$S_{L/S} = \pi_e$$

Work of Immersional Wetting

As the name implies, the free energy of emersion f_E is the free-energy change which occurs per square centimeter of surface when a solid is removed from a liquid. This of course is the same as the work done during the immersion of a solid in a liquid, in which process 1 sq cm of liquid-solid interface is formed for each square centimeter of solid surface destroyed.

Thus, f_E is given by the equation:

$$f_E = \gamma_S - \gamma_{SL} \tag{8}$$

If this process is made to occur using pure materials in a vacuum, the standard values of γ_S and γ_{SL} are applicable, and f_E assumes a definite value characteristic of the two materials. For these conditions, as was derived for the work of adhesion,

$$\gamma_S - \gamma_{SL} = \pi_e + \gamma_L \cos\theta$$

Therefore:

$$f_E = \pi_e + \gamma_L \cos\theta \tag{9}$$

By way of review it may be noted that the work of immersional wetting f_E is the basic term occurring in the expressions for the work involved in all three wetting processes. The work of adhesion $W_A = f_E + \gamma_L$, and the work of spreading wetting $S_{L/S} = f_E - \gamma_L$.

Table 21 contains some data on the work involved in the various wetting processes for a few typical systems, as determined by Harkins and coworkers.[17]

TABLE 21

WORK OF ADHESION, SPREADING COEFFICIENT, AND FREE ENERGY OF EMERSION BETWEEN TiO_2 (ANATASE) AND VARIOUS LIQUIDS (ERG CM^{-2})

Liquid	$S_{L/S}$	f_E	W_A
H_2O	190	262	334
N_2	56	64	72
nC_4H_{10}	43	58	73
nC_7H_{16}	46	66	86

TOTAL ENERGY CHANGES DURING WETTING

Corresponding to each of the wetting processes previously described, there is a total energy change. The symbols used for the total energy changes for 1 sq cm of surface wet are h_E, h_A, and $h_{L/S}$, which refer to the *energy lost* by the system during immersional, adhesional, and spreading wetting, respectively. The total energy of each surface and accordingly the total energy change during a given wetting process are related to the free surface energies and their temperature coefficients by eq. 1 of this chapter. This relation is not very useful for the calculation of the total energy changes because there are too many unknown quantities.

Heat of Immersion

The direct calorimetric measurement of the total energy change during immersional wetting is possible for finely divided solids of known surface area.

The technique and sources of error have been described by Harkins[18] and coworkers. In the usual procedure, the carefully cleaned and outgassed solid is sealed in an evacuated glass bulb and immersed in the purified liquid contained in the calorimeter. The heat evolved upon breaking the bulb and mixing the powder with the liquid can be used to obtain the heat of immersion or the energy of emersion h_E of the liquid-solid system. Some typical data on heats of immersion as obtained by Harkins[19] and coworkers are given in Table 22.

TABLE 22

ENERGY OF EMERSION (SEPARATION) h_E (ERG CM^{-2}) OF VARIOUS LIQUIDS FROM CRYSTALLINE SOLIDS

Liquid	Solid						
	$BaSO_4$	TiO_2	SiO_2	ZrO_2	SnO_2	$ZrSiO_4$	Graphite
Water	490	520	600	600	680	850	175
Ethyl alcohol		500	520				
Ethyl acetate	370	360	460		530		
Butyl alcohol	360	350	420		500		
Nitrobenzene		280		310		430	
Carbon tetrachloride	220	240		270	320	410	
Benzene	140	150	150	190	220	260	
Iso-octane		105		110	120	190	

Energies of Adhesion and Spreading

Direct measurement of the total energy change during adhesional or spreading wetting is impossible. The calculation of these quantities is very simple, however, if the heat of immersion of the solid-liquid system is known. By considering the change in the extent of each of the surfaces or interfaces during each wetting process, it is evident that for 1 sq cm of solid wet, the following relations are true:

$$\text{The energy of emersion } h_E = h_S - h_{SL}$$

$$\text{The energy of adhesion } h_A = h_S - h_{SL} + h_L$$

$$\text{The energy of spreading } h_{L/S} = h_S - h_{SL} - h_L$$

Thus

$$h_A = h_E + h_L$$

and

$$h_{L/S} = h_E - h_L$$

The total energy of the liquid surface h_L can be calculated using eq. 1 of this chapter, $h_L = \gamma_L - T(d\gamma_L/dT)$. Therefore a measurement of the heat of immersion, the surface tension of the liquid, and the temperature coefficient of the surface tension of the liquid are required in order to determine h_A or $h_{L/S}$.

It should be emphasized again that definite values of h_E, h_A, and

$h_{L/S}$, characteristic of the solid and liquid, can be obtained only by the exercise of great care in preparing clean solid surfaces and pure dry liquids.

APPLICATIONS

The applications of adsorption and wetting of solid by liquid are far-reaching and important. The wetting of soils is fundamental to the growth of plants in the soil. On the phenomenon also depend: the lubrication of surfaces; the spreading of paint on wood or metal surfaces, of sprays on the leaves of plants, and of ink on paper; the process of washing with or without soap; and the action of adhesives.

The reverse of wetting is essential in such processes as the waterproofing of fabrics by the application of aluminum stearate or wax which prevents the spreading of water without materially decreasing the porosity of the fabric. As mentioned above (cf., also, p. 75), preferential wetting is at the basis of flotation processes for concentration of minerals. In the petroleum industry, oil penetrates with difficulty a sand impregnated with water, and a producing well is sometimes rendered non-productive by the replacement of oil by water in the sand near the bottom of the well.

A few of the technical applications above mentioned will be considered briefly.[2]

Lubrication. The principle involved in lubrication consists in the maintenance of an adsorbed layer of an easily deformable substance (usually a liquid) on each of two solid surfaces so that they are prevented from coming in contact. A good lubricant for metal bearings is adsorbed so strongly that the film is removed from the surfaces only under the influence of great pressure and speed. It has been suggested by Wilson [20] that certain liquids adhere to metal surfaces so strongly that they exist as plastic solid films.

Adam [21] recognizes two types of lubrication in practice: "complete" or "film" lubrication in which a thick film of oil separates the two faces; and "incomplete" or "boundary" lubrication in which a thin film that may be only a molecule thick separates the faces.

The problems of friction and film lubrication have been studied in detail, especially by Hardy and collaborators.[22] It is believed that symmetrical orientation of molecules with the polar groups attached to the surfaces is desirable for the best lubrication. There is a time lag in attaining the maximum lubrication with compounds having polar groups but not with the paraffin hydrocarbons where both ends are alike. Examination by x-rays of films obtained by rubbing greases between smooth surfaces confirmed Hardy's view that molecular orientation of polar lubricants takes place. In an homologous series, lubrication increases with increasing molecular weight, and there is no break where the lubricant becomes a solid, indicating that a natural plane of cleavage exists in a solid lubricant just as in a fluid lubricant. Each CH_2 group appears to have an added shielding effect that is independent of the solid, but in different series each CH_2 group has a different effect. For a given homologous series the effect of the lubricant is given by the equation:

$$\mu = \mu_0 - d - c(n - 1)$$

in which μ_0 is the friction of the clean unlubricated surface; d, the diminution in friction caused by the end groups CH_3 and X where $X = CH_3$, CH_2OH, $COOH$, or $CH(C_2H_5)OH$; c is the diminution in friction caused by each CH_2 group in the straight chain; and n is the number of C atoms in the straight chain, less those in the end groups.

Fixed oils and greases formerly were used almost exclusively for lubrication, but because of their tendency to become gummy and rancid they have been largely replaced by mineral oils. But fixed oils are adsorbed more strongly than mineral oils and are therefore better lubricants for certain purposes. The advantage of fixed oils is sometimes gained by blending small amounts of them with mineral oils. Apparently the efficacy of the fixed oils is due largely to the presence in them of free fatty acids which are strongly adsorbed. Wells and Southcombe[23] patented the addition of 1 to 2% of such acids to mineral oils.

Adhesives. Adhesives are materials which adhere strongly to two surfaces and harden there into a tenacious mass as a result of cooling, evaporation, oxidation, etc. McBain[24] recognizes two types of joints, mechanical and specific. In the former, porous materials are bound together as a result of the adhesive solidifying *in situ* to give a solid film embedded in the pores. Strong adsorption may not be necessary for a mechanical joint but is essential for a specific joint where the adhesive wets the non-porous or slightly porous surfaces and solidifies *in situ.*

For a given non-porous surface and a given adhesive, the thinner the film of adhesive the stronger the joint. Such joints have been found to be stronger than an equal cross section of the adhesive alone.

Since adhesion is specific, certain adhesives will give stronger joints with certain solids than other adhesives will.

In both lubricants and adhesives for specific joints, strong adsorption is essential; but with the former the film must be flexible, and with the latter the film must be non-flexible and must possess a high tensile strength.

Horticultural sprays and insecticides. Such liquids must have the properties of wetting and spreading over the surfaces to be treated. They should therefore possess both a high adhesion with the surface and a low surface tension.[25] Woodman[26] claims that the maximum amount of a given spray liquid is retained at a critical surface tension; at higher tensions the wetting is imperfect, and at lower values the wetting power is not increased but the spreading power is greatly augmented. Soaps may be used to adjust the surface tension to a suitable value. The amount of liquid retained by the leaves may be increased by the addition of small amounts of gelatin which increases the viscosity of the liquid. Moreover, gelatin in concentrations between 0.2 and 0.5% is an excellent stabilizer for sols of certain insecticides such as lead arsenate.

Detergent action of soaps. Soap solutions are good detergents because of their emulsifying action on oils and greases (Chapter 21) and their very efficient wetting power.[27, 28] Soap penetrates fabrics because it is adsorbed by the solid and because the solution possesses a low surface tension and a low interfacial tension against the solid surface. McBain,[29] the leading contributor to the theory of detergent action, recognizes four factors in the process, all of which may or may not be exhibited by a single soap or other detergent: protective action, solubilization, base exchange (see p. 103), and suspending action.

Protective action and suspending action both imply pre-existing particles or such particles or droplets as may be formed by mechanical action. In protective action they are covered by a film supplied by the colloid. In suspending action no colloid need be present, the particle being charged and its sedimentation under the influence of gravity being retarded by the free ions of opposite sign which are held in its neighborhood by electrostatic attraction. In addition to the penetrating effect of soap referred to above, solutions have a suspending action on solid particles which facilitates their removal from the surface of skin or fabric. The optimum concentration of soap for the suspension or deflocculation of solids is in the neighborhood of 0.2 to 0.4%, whereas oils require only 0.05 to 0.1%. This is illustrated in Fig. 22*a*, which indicates the deflocculating action of sodium oleate on manganese dioxide that was finely dispersed in a colloid mill. The optimum concentration of soap for washing fabrics is usually set between 0.2 and 0.4%,[29, 30] although this will naturally vary with the nature of the soap and "dirt," the temperature, and the procedure employed in determining the detergent action. The addition of alkali to soap increases the suspending power as illustrated in Fig. 22*b*, which shows the effect on the deflocculation of a certain carbon produced by adding alkali to potassium myristate solution.[31] The optimum alkalinity for cleansing action is said to be in the neighborhood of pH = 10.5.[32]

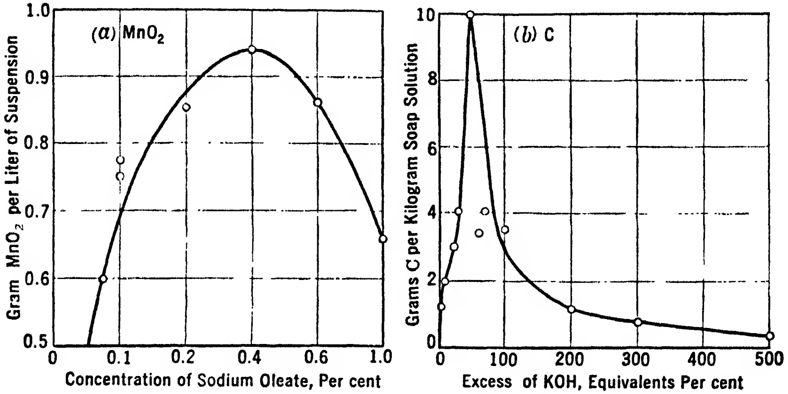

FIG. 22. Deflocculating action of soaps on finely dispersed solids.

Solubilization is the term given to the phenomenon in which colloidal particles adsorb or include otherwise insoluble matter. For example, when an oil insoluble in water is added to a soap solution, it is dissolved or solubilized by the soap solution. The phenomenon must not be confused with emulsification (see Chapter 21). Solubilization is a perfectly reversible process in which single molecules of oil are taken up by solution in the hydrocarbon tails of the detergent ions. This is illustrated in Fig. 23, which is a schematic diagram of the solubilization of benzene in a sodium oleate micelle. X-ray evidence shows that the effective length of the hydrocarbon portion of the micelle is increased when an oil is added as indicated in the diagram.

Oils and other substances soluble in hydrocarbons are solubilized by soap solutions to an extent which varies inversely with their molecular weight. Thus small molecules such as benzene are solubilized to a much greater extent than larger molecules such as cetane ($C_{16}H_{34}$), and the solubilization of the common vegetable and animal oils such as olive oil is too minute to be detected.

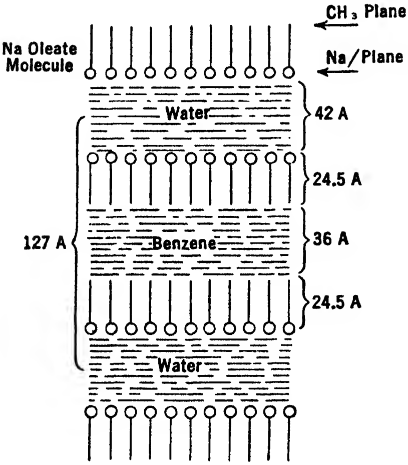

Fig. 23. Schematic diagram of a micelle in 9.12 wt-% sodium oleate solution with 0.791 g benzene per g oleate (McBain).

Sodium silicate is a good deflocculating agent for solids, but it is not a substitute for soap since it does not emulsify or solubilize oils satisfactorily. A mixture of soap and sodium silicate is sometimes used in place of pure soap. In recent years the sodium salts of sulfonated fatty alcohols, known commercially as "gardinols" and "avirols," have come into prominence[33] as soap substitutes. They are colloidal electrolytes which exhibit excellent lathering and detergent properties and possess the distinct advantage over soaps of not being affected by dilute acid solutions or by the presence of alkaline-earth salts.

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CHAPTER 6

Adsorption by Solid IV: Adsorption from Solution of Non-Electrolytes and Weak Electrolytes

In adsorption from solution by solid there are three possibilities: in the first, which is known as *positive adsorption,* relatively more of the solute is adsorbed than of the solvent; in the second, which is termed *negative adsorption,* relatively more of the solvent is taken up than of the solute; and in the third, the solvent and solute are adsorbed in the same ratio as in the solution, and there is no change in concentration. Of these possibilities, positive adsorption is most frequently encountered. This chapter is concerned primarily with the positive adsorption of non-electrolytes and weak electrolytes; the concluding section deals with negative adsorption of such solutes.

POSITIVE ADSORPTION

Typical Examples

The removal of coloring matter from sugar solutions by charcoal has been familiar since 1791 (cf. p. 25). Hydrous stannic oxide may be substituted for charcoal, but this is not done commercially. If a sufficient quantity of infusorial earth is shaken with a solution of any of the aniline dyes and the mixture filtered, the filtrate is colorless. The adsorption of dyes by the hydrous oxides of iron, aluminum, chromium, and tin is the basis of the process of mordant dyeing (cf. Chapter 26).

Lebourdais found in 1848 that digitalin, quinine, strychnine, and other alkaloids can be extracted from aqueous solution by charcoal. In 1912 Lloyd prepared from fuller's earth a hydrous aluminum silicate gel, called Lloyd's reagent, which adsorbs alkaloids strongly from either neutral or acid solutions; the adsorbed alkaloid may then be recovered by a good alkaloid solvent. The adsorption of alkaloids by kaolin is influenced greatly by the *p*H value of the solution: adsorption of quinine takes place strongly at *p*H 6–7, decreases somewhat at lower values, and falls abruptly to zero at pH 8–9.[1] According to Bock, if urine is shaken with Norite charcoal, uric acid is removed completely; creatine largely; urea, total nitrogen, and phosphates considerably; and ammonia, nitrogen, chlorides, and glucose only slightly.

A century ago Bunsen made the important discovery that freshly precipitated hydrous ferric oxide is an antidote for arsenic poisoning. As would be expected, this action was attributed by Bunsen to stoichiometric chemical union of ferric oxide and arsenious acid. Biltz [2] showed, however, that the apparent interaction between the acid and the gel is an adsorption process in which the arsenic content of the hydrous oxide varies continuously with the concentration of arsenious acid in contact with it, giving a typical adsorption isotherm.

The Adsorption Isotherm

The effect of concentration on the amount of adsorption from solution at constant temperature is usually found by adding a definite weight of adsorbent to solutions of varying concentration and determining the equilibrium concentration after adsorption. For such data

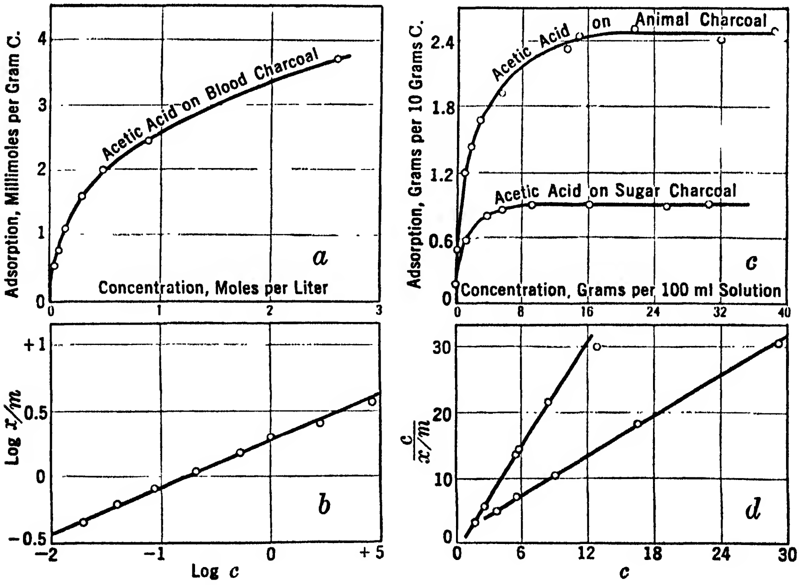

Fig. 24. Typical isotherms for adsorption from solution.

the amount adsorbed per gram of adsorbent (x/m) at each equilibrium concentration c is calculated, and the results are graphed on rectangular coordinate paper. Some typical adsorption isotherms obtained in this way are shown in Fig. 24.[3] Since the curve in part *a* has much the same form as the curves for adsorption of gas by solid at low pressures (Fig. 5), it may be represented by the empirical Freundlich equation $x/m = kc^{1/n}$ or $\log x/m = \log k + 1/n \log c$. This is borne out by the fact that a straight line is obtained when $\log x/m$ is plotted against $\log c$ (Fig. 24*b*). From the straight-line graph the constants are found to be: $k = 2.606$ and $1/n = -0.425$. In Table 23 are given the observed values of x/m and the values calculated by means of the equation: $x/m = 2.606c^{-0.425}$

TABLE 23

ADSORPTION OF ACETIC ACID FROM AQUEOUS SOLUTION BY CHARCOAL

Concentration (moles/l)	x/m		Concentration (moles/l)	x/m	
	Observed	Calculated		Observed	Calculated
0.0181	0.467	0.474	0.2677	1.55	1.49
0.0309	0.624	0.596	0.4711	2.04	1.89
0.0616	0.801	0.798	0.8817	2.48	2.47
0.1259	1.11	1.08	2.7850	3.76	4.01

The curves in Fig. 24*c* show that the adsorption reaches a saturation point at sufficiently high equilibrium concentrations. As we have seen (p. 50), the Freundlich equation cannot represent the flat portion of the curves. Such isotherms are best represented by the Langmuir equation, the linear form of which is $c/(x/m) = 1/ab + c/b$. The applicability of the Langmuir equation to the curves in part *c* is indicated by the linear curves obtained on plotting $c/(x/m)$ against c (Fig. 24*d*).

Reversibility of Equilibrium

To the extent that adsorption is a reversible process, the equilibrium may be approached from either side. For example, in the distribution of acetic acid between charcoal and water, Freundlich[3] obtained a concentration in the water of 0.06078 *M* acid after shaking 1 g of charcoal with 0.0688 *M* acid, whereas the concentration in the water was 0.06064 *M* after shaking 1 g of charcoal with 50 ml of 0.1376 *M* acid and then adding 50 ml of water. Following the same procedure for the distribution of other concentrations of benzoic acid between charcoal and benzene, Freundlich obtained the two final values 0.1177 and 0.1179 *M* acid. Although these data indicate the reversibility of adsorption from solution, it is known that highly activated charcoals adsorb low concentrations of certain solutes irreversibly.

If the adsorbing substance agglomerates, crystallizes, or changes in any other way, its adsorption capacity will change, and the equilibrium will be apparently irreversible. For example, freshly formed mercuric sulfide is submicroscopically crystalline and adsorbs certain dyes strongly; but on standing, it changes spontaneously into larger crystals possessing a much lower adsorption capacity.[4] Sometimes the adsorption is rendered apparently non-reversible by interaction between the adsorbent and adsorbate. For example, arsenious acid is adsorbed in the cold by hydrous zirconia; on standing or boiling, interaction takes place with the formation on the surface of $Zr(HAsO_4)_2$.[5]

Factors Influencing Adsorption

The degree of adsorption at a given temperature and concentration of solution varies with the nature of the adsorbent, the nature of the solute (adsorbate), and the nature of the solvent. The adsorption decreases with rising temperature, but, in general, the effect of temperature change is less marked than in the adsorption of gases by solids.

It is frequently stated that adsorption from solution is greater the lower the solubility of the adsorbate. This rule was based on Lundelius's[6] observation that the ratios of adsorption of iodine by charcoal from solutions in carbon tetrachloride, chloroform, and carbon disulfide are in the order 1:2:4.5, which is close to the inverse ratios of solubility of iodine in these solvents. There are, however, many exceptions to Lundelius's rule, so that, at best, it can be considered only a qualitative statement.[7]

The influence of molecular weight and constitution of compounds on their adsorbability is of importance, especially to organic chemists. A few examples will be given in the following paragraphs.

Traube's rule in adsorption. Traube's rule states that the adsorption of organic compounds from aqueous solution increases strongly and regularly as we ascend the homologous series. This would follow from Gibbs's rule provided that the compounds lower the charcoal-solution interfacial tension in the same order as they lower the air-water interfacial tension (p. 17). Traube's rule applies to the adsorption of a series of fatty acids on purified blood charcoal as shown graphically in Fig. 25*a*[8] and by the data taken from this figure, which are given in Table 24. A similar relationship was observed by Freundlich in the adsorption of urethanes by blood charcoal. To account

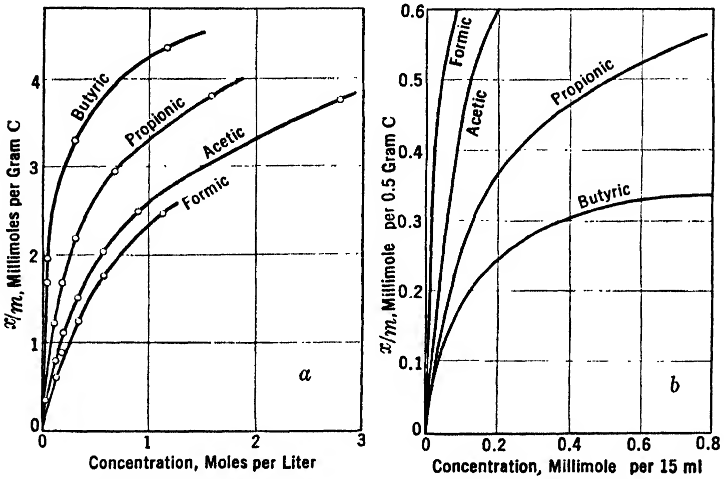

FIG. 25. Isotherms illustrating (*a*) Traube's rule in adsorption and (*b*) reversal of Traube's rule in adsorption.

for the behavior of the fatty acids, it is reasonable to assume that the highly polar carboxyl end of the molecule is oriented toward the water and the non-polar alkyl group toward the non-polar solid adsorbent

TABLE 24

TRAUBE'S RULE FOR THE ADSORPTION OF FATTY ACIDS BY BLOOD CHARCOAL

Adsorbed substance	c for $x/m = 12.6$	$\frac{c_n}{c_{n+1}}$	x/m for $c = 0.1$	$\frac{(x/m)_{n+1}}{x/m}$
Formic acid	0.251	....	0.79	....
Acetic acid	0.169	1.48	1.00	1.26
Propionic acid	0.056	3.01	1.55	1.55
n-Butyric acid	0.016	3.48	2.43	1.56

(cf. Chapter 8). Since the fatty acids of high molecular weight are less polar, they will be less strongly attracted by the water and more strongly adsorbed on the charcoal. From this point of view, the adsorption of fatty acids from solution in a non-polar solvent like toluene by a polar adsorbent like silica should be the reverse of that observed with charcoal. Holmes and McKelvey[9] found this to be true (Fig. 25*b*). On the other hand, this explanation appears to be inadequate to account for a *reversal* of Traube's rule in adsorption on activated sugar charcoals, as observed by Nekrassow.[10] To account for this, Nekrassow assumed that the ash-free charcoal presents a surface that is more polar than water and hence adsorbs the higher homologs less strongly. Dubinin showed that Traube's rule held with sugar charcoals activated in air at 550°; but charcoals activated at 800° gave a reversed series; and those activated between 550 and 800° gave mixed series. Sabalitschka[11] suggested that the reversal of Traube's rule can be explained best on the basis of Herbst's[12] ultraporosity theory, namely, that active charcoal is an assembly of ultrapores such that the available adsorption area of the charcoal decreases for the increasing molecular size of ascending members of an homologous series. At the same time, the activation of the charcoal doubtless renders it more polar as a result of the change from the amorphous to the crystalline state (p. 25).

The adsorption of organic acids and bases is influenced greatly by the *p*H of the solution.[13] For example, the adsorption of propionic acid drops to zero between *p*H 3.5 and 5.5; of succinic acid, between *p*H 4.0 and 7.0; and of caproic acid, between *p*H 4.8 and 7.5. Since these regions cover the ionization ranges for the acids, it is concluded that only the un-ionized acids are adsorbed.

Constitutive influences. Numerous examples of constitutive influences in adsorption have been pointed out by various workers, among whom may be mentioned Freundlich,[14] Miller,[15] Linner and Gortner,[16] and Phelps.[13] Some observations of Miller are given in Table 25. From these data it is apparent that the position of the hydroxyl and amino groups in hydroxy- and aminobenzoic acids has a marked effect on their adsorption. The adsorption values are greatest when these groups are in the ortho position, smallest in the meta position, and intermediate in the para position. This implies that the adsorption depends largely on the nature and arrangement of the atoms or groups in the molecule, certain groups favoring and others opposing the adsorption. Thus, chloro- and dichloroacetic acid are adsorbed much more strongly than acetic acid, and aminoacetic acid is not adsorbed at all. Isobutyric acid is adsorbed less than butyric acid, isovaleric less than valeric, and isocaproic less than caproic. Ammonium hydroxide is not adsorbed at all, but the opposing effect of the hydroxyl group is overcome by substituting methyl or ethyl groups for hydrogen in the base. Thus tetramethylammonium hydroxide is slightly adsorbed, and tetraethylammonium hydroxide is appreciably adsorbed. These facts indicate that molecular orientation is involved in the adsorption process. The statement that those substances which are least soluble are most strongly adsorbed is only a first approximation.[17, 7]

TABLE 25

Adsorption of Organic Acids and Bases by Purified Blood Charcoal
(0.25 g charcoal; 100 ml solution)

Acid	0.01 *M* acid adsorbed (ml)	Acid or base	0.01 *M* acid or base adsorbed (ml)
Benzoic	73.00	Aminoacetic	0.00
o-Hydroxybenzoic	71.78	Butyric	35.39
m-Hydroxybenzoic	61.53	Isobutyric	27.42
p-Hydroxybenzoic	65.36	Valeric	49.39
o-Aminobenzoic	68.53	Isovaleric	44.12
m-Aminobenzoic	57.32	Caproic	62.13
p-Aminobenzoic	65.15	Isocaproic	59.67
Sulfosalicylic	56.10	Ammonium hydroxide	0.00
Acetic	15.68	Tetramethylammonium hydroxide	1.20
Chloroacetic	27.45		
Dichloroacetic	25.54	Tetraethylammonium hydroxide	10.07
Trichloroacetic	17.78		

Linner and Gortner[16] obtained the adsorption isotherms of thirty organic acids which may be arranged in the groups shown in Table 26. The members of the several groups differ only in a single structural unit. Calculations were made of the constants for each acid in both the Freundlich and Langmuir equations. In the table are given these constants together with the average percentage error between the observed and calculated values of the adsorption at comparable concentrations.

Linner and Gortner found that the most reliable point of comparison between the acids was that of maximum adsorption x, where $\beta = x$, on the Langmuir adsorption isotherm. The iso- acids have about the same adsorption maximum as the normal acids, indicating that the branch chain has little effect on the number of molecules adsorbed per unit area. On the other hand, the adsorption is decreased greatly by introducing a keto or hydroxyl group, and the second hydroxyl

TABLE 26

ADSORPTION OF ORGANIC ACIDS BY CHARCOAL

Acid	Freundlich equation			Langmuir equation			Area (A^2)
	α	$1/n$	% error	α	β	% error	
Formic	2.47	0.435	2.6	0.159	1.710	1.0	....
Acetic	2.46	0.351	2.6	0.266	1.736	7.0	21.0
Propionic	2.46	0.236	1.8	0.491	1.885	2.0	21.0
Butyric	2.46	0.177	2.3	0.863	1.957	2.0	....
Valeric	2.84	0.182	2.8	0.872	2.154	5.8	....
Caproic	3.03	0.175	1.8	4.636	1.892	5.4	....
Isobutyric	2.36	0.273	12.3	0.497	1.776	5.5	22.3
Isovaleric	2.51	0.227	2.6	0.902	1.807	5.1	22.0
Glycolic	1.54	0.390	4.1	0.249	0.958	5.1	41.4
Lactic	1.66	0.335	3.6	0.415	1.054	4.0	37.6
Glyceric	1.29	0.267	6.7	0.812	0.823	8.5	48.2
Glyoxylic	3.89	0.455	2.3	0.223	2.275	3.0	17.4
Pyruvic	2.44	0.273	3.5	0.585	1.674	2.8	23.7
Levulinic	1.83	0.183	2.9	2.289	1.307	3.4	30.4
Oxalic	3.62	0.551	4.9	0.332	1.325	3.7	29.9
Malonic	3.88	0.410	3.3	1.540	1.232	5.6	32.2
Succinic	2.83	0.303	4.3	0.467	1.854	6.0	21.4
Glutaric	1.96	0.201	5.1	3.104	1.192	4.8	33.3
Adipic	1.79	0.163	4.5	1.886	1.245	4.5	31.9
Malic	1.28	0.252	2.2	0.574	0.927	2.3	42.8
Tartaric	0.94	0.275	3.3	0.468	0.687	2.5	57.7
Maleic	1.90	0.203	2.9	0.884	1.395	3.6	28.4
Fumaric	2.81	0.248	4.6	5.798	1.224	4.1	32.4
Mesaconic	1.80	0.133	2.4	1.886	1.435	2.9	27.6
Citraconic	1.69	0.167	1.8	1.014	1.337	4.7	29.7
Itaconic	1.54	0.148	1.9	0.904	1.291	4.0	30.7
Methylsuccinic	1.30	0.172	1.6	0.608	1.092	4.2	36.2
Citric	0.73	0.203	3.3	2.757	0.524	11.7	75.7
Bromosuccinic	1.82	0.195	2.0	0.643	1.451	3.0	27.3
Dibromosuccinic	2.58	0.320	2.2	1.119	1.248	3.6	31.7

lowers the adsorption below that of the first. This would be expected in view of the hydrophilic character of the polar hydroxyl and keto groups. Similarly, the adsorption falls off as the number of hydroxyl groups is increased; and double bonds have a decided tendency to decrease adsorption.

An alternation exists, among the values of β in Langmuir's equation, for odd and even acids of the series. Since such alternation is characteristic of the solid state, it is suggested that the lower members of the homologous series of mono- and dicarboxylic acids are adsorbed in the solid state.

Cross-sectional Area of Molecules

Linner and Gortner assumed (1) that the acids listed in Table 26 are adsorbed by charcoal to give a monomolecular layer in which the molecules are close packed at maximum adsorption and (2) that 21 A^2 represents the cross-sectional area of an adsorbed normal fatty acid (p. 133). On the basis of these assumptions, the cross-sectional area occupied by the various acids was calculated. The results are given in the last column of Table 26. It will be noted that the areas occupied by normal fatty acids and their dicarboxylic homologs are in the approximate ratio of 1:1.5; and the ratios of areas of normal acid to monohydroxy acid to dihydroxy acid are, approximately, 1:2:2.5. The interfacial area occupied by the molecules is increased by introducing a halogen or a double bond.

Chromatographic analysis. In 1906 M. Tswett, the botanist, described a method of resolving mixtures of solutes by selective adsorption on porous columns of suitable materials. The general technique is as follows. If a solution is caused to percolate through a closely packed column of powdered adsorbent material, with or without electrophoresis (Chapter 15), one or more components of the solution may be to some degree retained by the adsorbent; and on subsequent percolation through the column, the adsorbates may be further separated and concentrated in discrete bands of the column. The substances thus separated after chemical fixation may, if desired, be examined *in situ* or after removal from the adsorbent by means of elutants.

The ideal chromatographic adsorbent for a given mixture would have the following characteristics, possibly among others: [18]

1. High adsorption capacity for all the solutes yet not so high as to make development or elution difficult.
2. Sufficiently different specific adsorption capacities for the several

solutes to promote their separation by development of the chromatogram.

3. Absence of capacity to cause chemical changes in adsorbate, solvent, or elutant.

4. Non-porous particles of uniform and suitable size.

5. Whiteness or absence of color.

Chromatography has been found useful in (1) qualitative analysis, (2) quantitative analysis, (3) determination of molecular structure, (4) testing substances for molecular homogeneity, (5) establishing the identity or non-identity of substances, (6) purification of substances, (7) concentration of materials from dilute solutions, (8) control of technical products, (9) regeneration of substances from complex addition compounds. Full details and many examples of these nine types of problems for which chromatographic analysis has been found useful will be found in recent monographs on the subject by Zachmeister[19] and by Strain.[20]

NEGATIVE ADSORPTION

Negative adsorption, in which relatively more of the solvent is adsorbed than of the solute, is frequently encountered in non-aqueous binary systems. A typical adsorption curve of this kind is shown in Fig. 26.[21] This phenomenon is always encountered in adsorption from non-aqueous binary systems over the entire concentration range. To illustrate, two typical curves obtained by Bartell and Sloan[22] are shown in Fig. 27 in which ethyl alcohol is taken arbitrarily as the solvent and benzene (curve I) and ethly carbonate (curve II) as the respective solutes. The concentrations are expressed in mole fractions instead of in moles. The adsorption is expressed in terms of change in concentration $H(x_0 - x)/m$ or $H\Delta x/m$, in which H is the total number of millimoles that make up the solution, and x_0 and x are

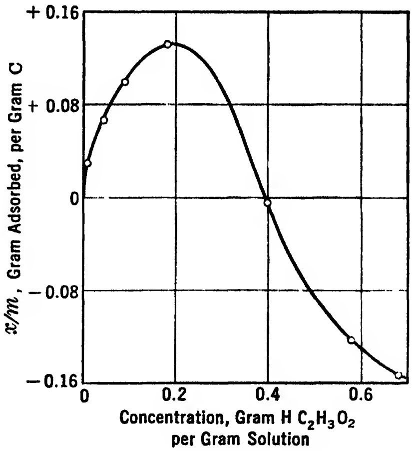

Fig. 26. Isotherm showing negative adsorption of acetic acid from solution in toluene by charcoal.

the mole fractions of solute present before and after adsorption, respectively.

Considering curve II, it is apparent that ethyl carbonate is positively adsorbed up to a value of $x = 0.55$, and negatively adsorbed above this concentration. In other words, ethyl carbonate is preferentially adsorbed from solutions which are relatively dilute in ethyl carbonate, whereas ethyl alcohol is preferentially adsorbed from solutions relatively dilute in the alcohol. At a concentration of 0.55 mole fraction of ethyl carbonate, the solute and solvent are adsorbed equally, and there is no change in concentration.

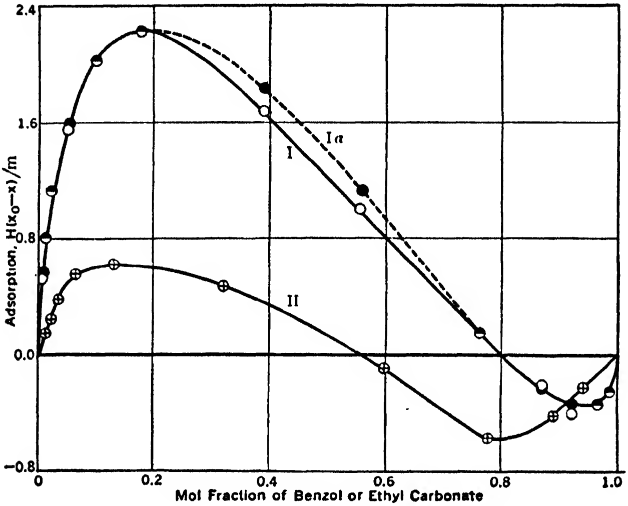

FIG. 27. Adsorption from ethyl alcohol solution of benzene (curve I) and of ethyl carbonate (curve II) throughout the entire concentration range.

When adsorption is measured in terms of change in concentration, the Freundlich adsorption equation takes the form:

$$\frac{H\Delta x}{m} = kx^n(1 - x)$$

Since the apparent adsorption of each component can be represented by this equation, when that component is in low concentration, Bartell and Sloan[22] have attempted to apply it over a greater concentration range. For example, if the change in concentration due to adsorption of benzene (curve I) is represented by the equation:

$$\frac{H\Delta x_1}{m} = \alpha x^n(1 - x)$$

and the change in concentration due to adsorption of ethyl alcohol by a similar equation:

$$\frac{H\Delta x_2}{m} = \beta(1 - x)^d x$$

then, the resultant change in concentration will be equal to the difference between these two terms. The decrease in mole fraction of benzene resulting from the simultaneous adsorption of the two components is thus:[23]

$$\frac{H\Delta x}{m} = \frac{H(x_1 - x_2)}{m} = \alpha x^n(1 - x) - \beta(1 - x)^d x$$

On evaluating the constants by the method of successive approximations, the equation becomes, for the case under consideration:

$$\frac{H\Delta x}{m} = 9.76x^{0.532}(1 - x) - 6.26(1 - x)^{0.662}x$$

The broken curve *Ia* shows how closely the calculated adsorption values approach the observed values for the benzene-alcohol system.

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CHAPTER 7

Adsorption by Solid V: Adsorption from Solution of Strong Electrolytes

EXCHANGE AND HYDROLYTIC ADSORPTION

When non-electrolytes or very weak electrolytes are positively adsorbed, the solute molecule as a whole is necessarily attached to the adsorbent; but when salts are positively adsorbed there are three possibilities. In the first, both ions of the electrolyte are adsorbed in equal amounts, or the adsorption is *molecular.* In the second, one ion is adsorbed but little, if at all, while the other enters into ionic exchange with an impurity in the adsorbent; this is termed *exchange* adsorption. In the third, the specific adsorption either of hydroxyl or of hydrogen ion is so marked that the adsorption causes hydrolytic cleavage of the salt; this is known as *hydrolytic* adsorption. The several types of phenomena will be considered in the following sections.

The adsorption of electrolytes from solution by charcoal has been the subject of numerous investigations,[1] the results of which are frequently contradictory and discordant. This is especially true with reference to salt-adsorption studies which were planned to demonstrate whether or not hydrolytic adsorption takes place. In most of the earlier researches along this line, blood charcoal was employed because it possesses a relatively high adsorption capacity. The material commonly used was Merck's blood charcoal, about which little or nothing was known except that it was purified by treatment with acids. In every instance, however, it contained more or less inorganic material which remained as ash on burning off the combustible matter. In view of the marked effect which impurities may have on adsorption processes, it is not surprising that investigators were frequently unable to reproduce their own results, let alone those of other people.

Exchange Adsorption

Freundlich and Losev [2] shook up a solution of the basic dye crystal violet (chloride) with charcoal and found that the organic cation was taken up, but an equivalent amount of chloride remained in solution. Since the solution reacted acid, it was first assumed that the adsorption had hydrolyzed the dye salt. Later it was found [3] that the acid remaining in solution accounted for only a small fraction of the total chloride, the latter being present chiefly as salt. The explanation of this phenomenon is that the dye cation enters into ionic exchange with some cation, probably calcium, which is present as impurity in the charcoal.

TABLE 27

ADSORPTION OF ALIZARATE BY ALUMINA

Substances mixed		NaCl in 50 ml weighed as		NaCl		Na_2SO_4	
Sol (ml)	Sodium alizarate (M/100, ml)	NaCl	Na_2SO_4	Calculated	Observed	Calculated	Observed
90	25	0.0122	0.0153	0.0293	0.0281	0.0355	0.0352
		NaCl in 75 ml					
80	28	0.0224	0.0291	0.0328	0.0322	0.0398	0.0419

In Table 27 [4] are given some quantitative data on the exchange adsorption of alizarate anion from sodium alizarate solution by alumina containing adsorbed chloride. The alumina in the sol state was treated with a suitable amount of dye solution. The color lake (cf. Chapter 26) precipitated; an aliquot part of the colorless supernatant solution was analyzed for sodium as chloride and as sulfate. As the data indicate, all the alizarate but none of the sodium is adsorbed. The sodium in the solution after formation of the color lake is associated with an equivalent amount of chloride displaced from the alumina gel by the more strongly adsorbed alizarate and hydroxyl ions in the original dye bath. Michaelis and Rona [8] believe that the taking up of electrolytes by charcoal always involves an exchange and that hydrolytic cleavage of a salt does not occur as a result of adsorption, but these investigators were not working with ash-free charcoals.

Applications of ion exchange. Gazzari[5] in 1819 made the interesting and important observation that clay decolorizes liquid manure and retains soluble substances which are given up subsequently to growing plants. This was perhaps the first work on base exchange or exchange adsorption (p. 115); but it remained for Way[6] in 1850 to elucidate the significance of Gazzari's observation. Way originated the instructive experiment of allowing potassium chloride to percolate through a column of soil, which was found to take up potassium but not chlorine and to liberate another element, chiefly calcium, in place of the adsorbed potassium. Similarly, Way found that ammonium was taken up by the soil in exchange with calcium. Thus the ingredients, potassium and ammonium, which are indispensable for plant growth are retained in the soil and prevented from leaching, at the expense of the common element calcium.

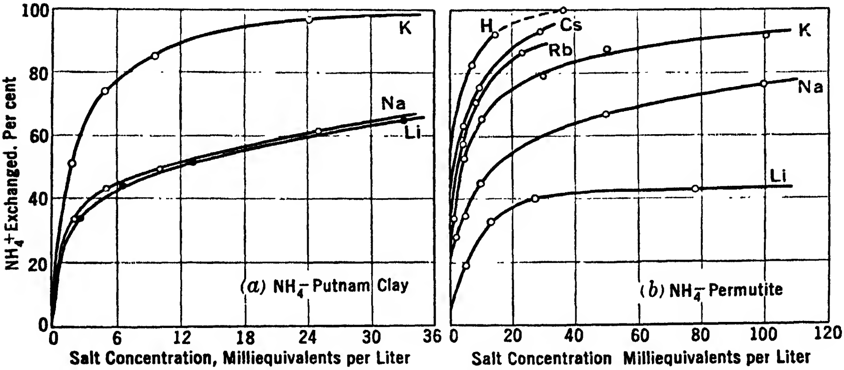


FIG. 28. Isotherms for base exchange (*a*) with ammonium-Putnam clay and (*b*) with ammonium permutite.

Some isotherms illustrating the course of the base-exchange process in a pure ammonium-Putnam clay are given in Fig. 28*a*.[7] Similar types of curves are obtained with both the natural zeolites and the artificial zeolites (permutites) used in water softening (Fig. 28*b*). The bulk of the evidence[8] indicates that the base-exchange process in both soils and permutites should be considered an exchange-adsorption phenomenon rather than a solid-solution phenomenon governed by the mass law.

The nature of the exchangeable cations is of great importance in determining the properties of soils. The undesirable acid soils of the humid regions possess a low "degree of saturation with bases,"[8] and the poor alkali soils of the arid regions possess a high content of exchangeable sodium. Between these two extremes are found the most desirable soils, those which are comparatively rich in exchangeable calcium and usually contain a reserve of calcium carbonate so that they remain largely saturated with calcium.

The saturation capacity of a soil is defined as the sum of the exchangeable bases and exchangeable hydrogen. The acid soils of the humid region have resulted from the gradual displacement of more or less of the desirable calcium by hydrogen, and the alkali soils of the arid regions from the displacement of calcium by sodium. The low productivity of the so-called alkali soils of the western United States is undoubtedly connected with the high proportion of exchangeable sodium in the colloid fraction, which renders the clay more highly dispersed, more slowly permeable, and, in extreme cases, almost impermeable to water and air. As Bradfield [8] points out, the removal of soluble salts by leaching with water is not sufficient to restore such soils to productivity; on the contrary, if the soil contains no calcium or magnesium carbonate, such leaching may make conditions worse. To regain the normal physical conditions of such soils, the essential thing is to restore the normal calcium-sodium ratio. If the soil contains a large reserve of calcium carbonate, irrigation with adequate drainage will eventually bring about normal conditions.[8] If calcium must be added, time will be saved by using the more soluble gypsum in place of calcium carbonate. In a soil containing some calcium carbonate, the most economical way to restore the normal calcium-sodium ratio consists in adding sulfur, which is oxidized to sulfate by soil organisms. Acid soils must be treated with lime or calcium carbonate.

The best-known application of an exchange outside the soil is the use of zeolites in water softening, that is, removing the hardness-producing ions (calcium and magnesium) and substituting the harmless sodium ion. Recently, resinous ion exchangers have been successfully used and show the following points of superiority: [9] (1) they have higher capacity, (2) they have higher exchange velocity, (3) their capacity does not vary with the influent concentration, (4) they are free from iron and silica and thus can impart neither to the effluent, and (5) the products function over a wide *p*H range. The production of water comparable in degree of purity to distilled water has become economically feasible. The process consists of treatment of the water by a hydrogen-cation-exchange resin followed by treatment with a resinous acid adsorbent.

Hydrolytic Adsorption

Bartell and Miller[10] prepared ash-free adsorbent charcoal by carbonizing pure recrystallized cane sugar and activating at high temperatures with a limited supply of air. The adsorption from salt solutions with this charcoal is hydrolytic, the charcoal taking up acids preferentially and setting free an equivalent amount of alkali to the solutions.

TABLE 28

HYDROLYTIC ADSORPTION OF SALTS BY PURE CHARCOAL

Salt	0.01 *N* alkali set free (ml)	0.01 *N* acid extracted from C (ml)	Salt	0.01 *N* alkali set free (ml)	0.01 *N* acid extracted from C (ml)
Na benzoate	9.40	9.50	NaCl	11.36	11.33 *
	29.00	28.16		27.42	27.03 *
Na salicylate	7.84	7.90	KNO_3	40.54	40.22
	13.50	13.54		25.18	24.67
$K_2C_2O_4$	3.90	3.66	K_2SO_4	30.58	20.76 †
	25.36	25.02		24.06	23.99 †
				26.60	26.91 †
$NaC_2H_3O_2$	3.20	2.80			
	1.64	1.78			

* AgCl equivalent to 0.01 *N* HCl = 11.13 and 27.33 ml, respectively.

† $BaSO_4$ equivalent to 0.01 *N* H_2SO_4 = 30.99, 24.37, and 27.14 ml, respectively.

Some typical results, given in Table 28, leave no doubt that hydrolytic adsorption of the several salts has taken place. Moreover, since the chloride and sulfate extracted from the charcoal in the experiments with these salts are equivalent to the acid adsorbed, it follows that the adsorption in these instances is exclusively hydrolytic. This was confirmed with a number of potassium salts of inorganic acids and of less strongly adsorbed organic acids; but with salts of the more strongly adsorbed organic acids, such as benzoic and salicylic, the adsorption is partly hydrolytic and partly molecular. The concentration of potassium in solution after adsorption from its inorganic salts is greater than before the adsorption, indicating that the base is negatively adsorbed by the charcoal.

Two theories of the mechanism of hydrolytic adsorption have been proposed: the gas electrode theory of Frumkin and the oxide theory of Kruyt and Schilow.

Frumkin's gas electrode theory. According to Frumkin and his co-workers,[11] the observed adsorption of acids and not of bases by Miller's charcoal results from the taking up of oxygen during the activation process. If the air-activated preparation is heated in a stream of hydrogen and then brought in contact with a solution of alkali, it adsorbs the alkali positively. Acids are not adsorbed by the oxygen-free charcoal, and base is adsorbed and acid set free when the adsorbent is placed in a potassium chloride solution. A sugar charcoal prepared as nearly gas-free as possible adsorbs neither acid nor base appreciably. Data illustrating these facts are given in Table 29. In the first three series of experiments, 10 ml of solution was brought in contact with 0.5 g of charcoal; and in the fourth and fifth series, 14 ml

TABLE 29

EFFECT OF GAS ENVIRONMENT ON ADSORPTION BY CARBON

Solution	Adsorption by	
	C saturated with H_2	C in the presence of air
I. *N* KCl	0.0215 KOH 0.0210 KOH 0.0205 KOH	0.025 HCl 0.025 HCl
II. 0.01 *N* HCl	0.0 HCl 0.0 HCl	0.140 HCl 0.139 HCl
III. 0.01 *N* KOH	0.0660 KOH 0.0655 KOH	0.0 KOH 0.0 KOH
	C in vacuum	C in the presence of air
IV. 0.01 *N* HCl	0.0 HCl 0.0 HCl	0.140 HCl 0.140 HCl
V. 0.01 *N* NaOH	0.0 NaOH 0.0 NaOH	0.0 NaOH 0.0 NaOH

of solution was treated with 1 g of charcoal. The adsorption values are in millimole per gram of charcoal.

A platinum sponge electrode behaves similarly to ash-free charcoal in the presence of electrolytes. Thus a gas-free electrode causes no hydrolytic adsorption of sodium sulfate, but, if the electrode is saturated with hydrogen in contact with a neutral salt solution, the solution becomes distinctly acid; and if the electrode is washed acid- and hydrogen-free in a current of air, a neutral salt solution in contact with it becomes distinctly alkaline. Frumkin considers that, analogous to the behavior of platinum, activated charcoal acts as a gas electrode in accord with the following scheme. In the presence of oxygen, hydroxyl ions are formed at the expense of the adsorbed oxygen thus:

$$C_xO + H_2O \rightarrow C_x + 2\oplus + 2OH^-$$

the ions going into solution, and the positive charge remaining on the surface of the charcoal. On the other hand, in the presence of hydrogen, hydrogen ions are sent into solution at the expense of the adsorbed gas:

$$C_x + H_2 \rightarrow C_x + 2\ominus + 2H^+$$

and the negative charge remains on the surface of the charcoal which will now adsorb cations from solution. In support of the proposed mechanism, Frumkin showed that the hydrochloric acid adsorbed by an oxygen-holding charcoal is equivalent to the oxygen adsorbed. For example, samples of charcoal containing 0.012, 0.033, 0.044, and 0.052 milliequivalent of O_2/g, adsorb 0.012, 0.035, 0.043, and 0.051 milliequivalent of HCl/g.

Schilow's oxide theory. Schilow and coworkers[12] point out that, contrary to Frumkin's theory, a completely degassed charcoal will adsorb small amounts of hydrochloric acid from dilute solutions. Moreover, Kruyt and de Kadt[13] found that ash-free charcoals which are not heated too highly are negatively charged and adsorb bases, whereas those activated at 1000° are positively charged and do not adsorb bases. To account for the observed facts, Schilow assumed that the adsorption of acids, bases, and salts by ash-free charcoal takes place through interaction with acidic or basic oxides of carbon on its surface.

In Fig. 29 are given the carbon oxides postulated by Schilow. Oxide *A* is assumed to give a slightly basic carbon hydroxide with water; oxide *B*, a strongly basic hydroxide; and oxide *C*, an acidic oxide; *D* represents an inner salt of oxides *B* and *C*. To account for the results, it is assumed that: (1) oxide *A* is stable at all temperatures and at oxygen pressures up to 2 mm, (2) oxide *B* is formed from *A* at 2 mm pressure, and (3) oxide *C* is formed from *B* by heating in oxygen at 300–700°.

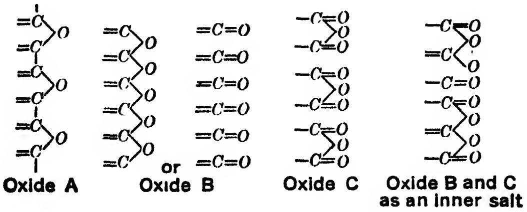
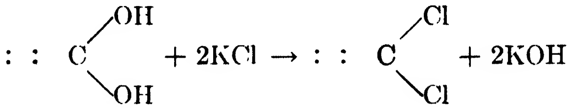
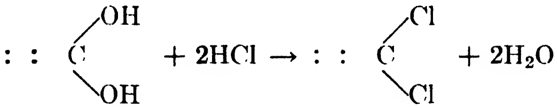


FIG. 29. Schilow's oxides of carbon.

Schilow's explanation of the mechanism of hydrolytic adsorption of potassium chloride by oxide *B* can be represented by the following scheme:



The adsorption of HCl by oxide *B* can be considered a reaction:



Potassium hydroxide would not react at all with oxide *B* but it would with *C*.

Limitations of Frumkin's and Schilow's theories. In a critical survey of the evidence for and against the two theories of adsorption of electrolytes by charcoal, Miller[14] points out that the field to which they apply is quite limited. Apparently, only those substances which are least adsorbed or not adsorbed at all in the presence of air are influenced by the nature of the gas adsorbed on the charcoal, and these only in lower concentrations. Moreover, there are a number of facts which cannot be explained at present by either theory. For example, there is no apparent reason why sodium and potassium hydroxides are not adsorbed in the presence of air, whereas the equally strongly dissociated organic base, tetraethylammonium hydroxide, is adsorbed; and, on the other hand, the weak base ammonium hydroxide is not adsorbed. It is also impossible to say why the adsorption of potassium chloride, which is exclusively hydrolytic, is affected by the gaseous atmosphere, whereas the greater hydrolytic adsorption of potassium benzoate is not affected. The effect of the introduction of polar groups on the adsorption (see p. 93) is not explainable by either theory, nor is the negative adsorption of sodium and potassium hydroxides and its decrease with length of time of contact of solution and adsorbent.

Since a part of the oxygen adsorbed on charcoal is recoverable only as carbon dioxide at elevated temperatures, it seems certain that acidic oxide does exist on charcoal surfaces. The concept of basic oxides of carbon cannot be accepted without reservations, and, as Miller points out, it is difficult to understand why such a basic oxide as Schilow's hypothetical *B* should react with hydrochloric acid but not with benzoic or succinic acids when the fact is that the organic acids are much more strongly adsorbed by charcoal than hydrochloric acid is.

ADSORPTION ON CRYSTAL LATTICES

The principles involved in adsorption from solution so far considered have been derived largely from investigations with charcoal as adsorbent. But it is well known that precipitated oxides and salts may adsorb strongly the ions of inorganic electrolytes and dyes. The contamination of precipitates by adsorption is one of the major problems of analytical chemistry. For example, when an alkali sulfate is precipitated with barium chloride in slight excess, the most usual analytical procedure, the determinations are too low, since some sulfate is weighed as alkali sulfate and calculated as if it were pure barium sulfate. Opposed to this is the adsorption of chloride as barium chloride which tends to make the analytical results too high. The latter effect manifests itself especially in the precipitation of sulfuric acid by barium chloride and the reverse. Hulett and Duschak [15] found it possible to obtain more precise results in such determinations by estimating the chlorine content of the precipitate and deducting the barium chloride equivalent from the weight of the crude barium sulfate. Although the adsorption of chloride ion by barium sulfate is appreciable, Mendelejeff [16] long ago showed it to be small compared to that of nitrate. Mendelejeff's observation was confirmed by Weiser and Sherrick [17] in the course of an investigation of adsorption of various ions by precipitated barium sulfate. The amount of adsorption was determined by direct analysis of the washed precipitate. In Table

30 the ions are arranged in the order of equivalent adsorption, beginning with the most strongly adsorbed ferrocyanide. The adsorption in moles and the solubility of the several barium salts are also included in the table.

TABLE 30

ADSORPTION OF ANIONS BY BARIUM SULFATE

Anion	Ion in excess	Adsorption by 100 moles $BaSO_4$		Solubility of varium salts (millimoles/g water at 25°)
		Gram equivalents	Gram moles	
Ferrocyanide	Ba^{++}	13.20	3.30	0.07
Nitrate	Ba^{++}	8.48	8.48	0.40
Nitrite	Ba^{++}	7.47	7.47	3.10
Chlorate	Ba^{++}	5.84	5.84	1.25
Permanganate	Ba^{++}	2.85	2.85	1.93
Ferricyanide	Ba^{++}	2.70	0.90	Soluble
Chloride	Ba^{++}	1.76	1.76	1.78
Bromide	Ba^{++}	0.83	0.83	3.57
Cyanide	Ba^{++}	0.31	0.31	4.25
Sulfocyanate	Ba^{++}	0.22	0.22	6.13
Iodide	Ba^{++}	0.06	0.06	5.43
Chloride	$SO_4^{=}$	0.125	0.125	1.78
Chlorate	$SO_4^{=}$	0.227	0.227	1.25
Permanganate	$SO_4^{=}$	0.137	0.137	1.93

A systematic study of cation adsorption by barium sulfate was made by Johnston and Adams.[18] In Table 31 are given the amounts of the several cations (expressed as sulfate) adsorbed by 1 g of $BaSO_4$ thrown down in the hot with a slight excess of barium chloride, from solution 0.003 N in HCl and containing the metallic chlorides in the initial concentration $a = 0$ and $b = 0.1\ N$.

Observations similar to the above have been made on barium sulfate and other analytical precipitates by numerous investigators, showing that the adsorption phenomenon is general.

Factors Influencing the Adsorption Process

Valence; the Schulze-Hardy rule. Schulze[19] was the first to point out that the power of active ions to coagulate sols tends to be a function of the valence or the number of electrical charges which they carry. This was confirmed by Hardy and is called the Schulze-Hardy rule. Since the precipitating power of the ions for sols (Chapter 26) depends on the extent of their adsorption, Bancroft[20] restates the Schulze-Hardy rule in the form: a trivalent ion will be adsorbed more strongly than a bivalent ion, and a bivalent ion more strongly than a univalent one. Bancroft emphasized that the rule was merely a first approximation in the coagulation of sols, and the same is true of the rule when applied to adsorption data obtained directly. For example, there is little to suggest the Schulze-Hardy rule in the data given in Table 30, for, although a quadrivalent ion appears to be adsorbed most strongly, four univalent ions are adsorbed more strongly than trivalent ferricyanide. Furthermore, contrary to what is implied in the Schulze-Hardy rule, there is a wide variation in the amount of univalent ions adsorbed, nitrate being carried down 150 times more strongly than iodide. Referring to Table 31, the tendency for cations of high valence to be more strongly adsorbed by barium sulfate is indicated when the adsorption values are expressed in equivalents; but this tendency is less marked when they are expressed in moles. On the other hand, barium sulfate adsorbs trivalent lanthanum much more

TABLE 31

ADSORPTION OF CATIONS BY BARIUM SULFATE

Metal	Sulfate adsorbed by 1 g of $BaSO_4$			
	a Milliequivalent	*a* Millimole	*b* Milliequivalent	*b* Millimole
Mg	0.048	0.024		
Li	0.033	0.033	0.040	0.040
Na	0.029	0.029	0.043	0.043
K	0.033	0.033	0.035	0.035
Al	0.051	0.017	0.060	0.020
Fe (ous)	0.074	0.037	0.120	0.060
Ni	0.062	0.031	0.100	0.050
Cu	0.082	0.041	0.100	0.050
Zn	0.080	0.040	0.100	0.050
Mn	0.128	0.064	0.160	0.080
Cd	0.160	0.080	0.180	0.090

strongly than bivalent magnesium,[21] and trivalent actinium more strongly than bivalent lead.[22]

Although chemically dissimilar ions of the same valence may show a wide variation in adsorbability, indicating that adsorption is a specific property of the ions, the effect of valence may be emphasized by choosing a series of ions of much the same general character. For example, the order of adsorption of the cyanogen compounds by barium sulfate is: $Fe(CN)_6^{iv} > Fe(CN)_6^{iii} > CN > CNS$, in accord with the Schulze-Hardy rule. This rule may be useful therefore in predicting the relative adsorbability of ions, but its limitations must be clearly recognized.

Solubility; the Paneth-Fajans-Hahn rules. Paneth [23] and Horovitz [24] observed that radium is strongly adsorbed by barium sulfate and chromate, whereas it is not adsorbed at all by chromic oxide and silver chloride. Since radium sulfate and chromate are insoluble and radium oxide and chloride are soluble, Paneth formulated the adsorption rule for radio elements: ions will be relatively strongly adsorbed if the compound with the oppositely charged ions of the crystal lattice is slightly soluble. This rule was confirmed and extended by Fajans and his coworkers [24] to include elements other than radio elements. The original Paneth-Fajans rule may be stated as follows: ions will be strongly adsorbed on an ion lattice which forms a difficultly soluble or weakly dissociated compound with the oppositely charged ion of the lattice. An important example of this rule is the usual strong adsorption of common ions by an ion lattice. Thus barium and sulfate ions are both strongly adsorbed by barium sulfate, and silver and halide ions by the silver halides. In further accord with the rule, Fajans and Beckerath [24] found that both thorium B and lead ions are quite strongly adsorbed by silver halide made negative by preferential adsorption of halide ion, and the halides of thorium B and lead are not easily soluble. Moreover, thorium B and lead ions are not adsorbed by a silver halide rendered positive by preferential adsorption of silver ion because thorium B, in the concentrations used, was not attracted to the surface sufficiently strongly to displace the more strongly adsorbed, common silver ion.

The solubility rule, like the valency rule, is useful but, again, only as a first approximation. Referring once more to the data in Table 30, it will be seen that there is a tendency for the ions of the less soluble salts to be the more strongly adsorbed, but the relationship is not quantitative. The parallelism between solubility and adsorbability of ions by barium sulfate is less marked when 50% ethyl alcohol is used as solvent in place of water.[25] Similarly, in the adsorption of anions by silver iodide Beekley and Taylor[26] found that a quantitative relationship between solubility and adsorbability was not approached. The most that can be said is that ions which form the less soluble silver salts tend to be more strongly adsorbed and those which form the more soluble salts tend to be less strongly adsorbed.

Hahn and Imre[27] observed instances in which ions were not adsorbed even when they formed difficultly soluble compounds with the oppositely charged ion of the lattice. To account for this apparent discrepancy, Hahn assumed that, for adsorption of an ion to take place, the sign of the surface charge on the solid had to be opposite to that of the ion. But this is not essential, since Fajans[28] showed that certain dye anions are adsorbed on negatively charged silver halide, and certain dye cations on positively charged silver halide. At the same time, Fajans and Erdey-Grúz[24] found that the presence in the solution of strongly adsorbed anions increases the adsorption of thorium B cation, whereas strongly adsorbed cations decrease the adsorption of thorium B.

In the light of these and similar observations, Fajans formulated what may be termed the Paneth-Fajans-Hahn rules of adsorption of ions on crystal lattices:

1. An ion is strongly adsorbed on an equivalent compound of the salt type only when it forms a difficultly soluble or weakly ionized compound with the oppositely charged ion of the lattice.
2. The adsorption of a cation is raised by adsorbed anions, that is, by charging the surface negatively, and is lowered by adsorbed cations, that is, by charging the surface positively.
3. The converse of (2): The adsorption of anions is raised by adsorbed cations and is lowered by adsorbed anions. The effect on the adsorption of a given ion in both (2) and (3) increases with increasing adsorption of the foreign ion.

Mechanism of the Adsorption

Direct adsorption. Fajans considers adsorption of ions by a crystal lattice to take place through the agency of the residual valences of the ions on the surface of the lattice. Thus, when iodide ion is adsorbed on silver iodide, it becomes attached to the silver ion and so becomes an integral part of the silver iodide lattice. Four factors determine the adsorbability of an ion, as follows:

1. The solubility of the compound formed with the opposite ion of the lattice (see Paneth-Fajans-Hahn rule 1).

2. The hydration of the ion. On adsorption, an ion loses its hydration shell,[28] the dehydration being accompanied by a loss of the heat of hydration. Accordingly, the lower the amount of hydration and heat of hydration of an ion, the greater the relative adsorption.[29]

3. The relative sizes of the adsorbed and the lattice ions, irrespective of whether the ions are adsorbed directly or enter into kinetic interchange with an ion on the surface (see below). An ion whose diameter is larger than that of the lattice ion will be adsorbed less strongly than one whose diameter is smaller.

4. The deformation of the adsorbed ion in a field of force. In general, the more readily deformable an ion, the better it will be adsorbed to the oppositely charged ion of the lattice.

In connection with adsorption by crystals, attention should be called to the interesting fact that the form of the crystals may be modified greatly by the adsorption of foreign substances. For example, sodium chloride crystallizes in cubes from neutral or acid solution and in octahedra from alkaline solution or in the presence of urea; conversely, alum crystallizes in octahedra from neutral solution and in cubes from alkaline solution.[30] This changed development of crystal faces in the presence of a third component is due to adsorption. Saylor [31] gives evidence to support the view that stronger adsorption on one crystal face, relatively to that on a second face, slows down or prevents the growth of the first and favors the more rapid growth of the second. In a comprehensive investigation of the influence of adsorption on crystal growth and habit, France and coworkers [32] carried out a remarkable series of experiments showing the effect of gelatin, dyes, and other organic compounds on growing crystals of copper and potassium sulfates; ammonium, cesium, and potassium alums; and barium, lead, and sodium nitrates. It was found that the adsorption is highly specific. In most instances, the taking up of foreign substances produces a habit modification, but this may be on faces other than those upon which the substance is adsorbed. Adsorption by growing crystals was found to depend on: (1) the residual valency fields of force of the crystal faces, (2) the interionic distances within the faces, (3) the concentration of solution of the foreign substance, and (4) the presence and distribution of polar groups in the foreign substance.

An x-ray diffraction examination of certain dyed and undyed crystals showed no difference in lattice constant. This indicates that the dyes are adsorbed interstitially rather than as individual planes or by replacement of the ions of the unit cell (exchange adsorption).

Exchange adsorption. Kolthoff[33] is of the opinion that, when an ionic precipitate is brought in contact with a solution containing a strongly adsorbable ion, the adsorption is not direct, but instead, an exchange adsorption takes place between the lattice ion and the foreign ion. For example, in the adsorption of lead ion on barium sulfate, the distribution, when kinetic exchange equilibrium is established, may be represented by the following equation:

$$\frac{\text{Pb (surface)}}{\text{Pb (solution)}} = K \frac{\text{Ba (surface)}}{\text{Ba (solution)}}$$

in which K is the distribution coefficient.

Kolthoff recognized that the following factors, in addition to exchange adsorption at the surface, may enter into the adsorption process: (1) direct adsorption only, at active spots or centers on very imperfect crystals; (2) direct adsorption followed by secondary precipitation of a displaced lattice ion; (3) exchange with a third kind of ion already adsorbed on the precipitate; (4) molecular adsorption; (5) activated adsorption in which the adsorbed substance may be ionized on the surface.

An important investigation of the nature of the contamination of barium sulfate by the univalent cations NH_4^+, K^+, Na^+ (see p. 111) and by water has been made by Walter and Walden [*J. Am. Chem. Soc.*, **68,** 1742 (1946)]. The pure sulfate was digested for several hours in solutions of the univalent cations, washed, dried in vacuum at 110°, and examined by x-rays. The results of the observations disclosed that the crystal lattice of pure barium sulfate was distorted by the presence of the contaminating cation, indicating that the univalent cation is in solid solution in the barium sulfate. It appears that an exchange adsorption between barium in the original lattice and univalent cation takes place, giving precipitates that may be formally described "as substitutional solid solutions of barium sulfate plus ammonium, potassium, or sodium sulfate plus water."

Adsorption from Mixtures

In the adsorption by charcoal from mixtures of two non-electrolytes or weak electrolytes, one might expect the adsorption of each to be less than if the other were not present. This was found to be true for the simultaneous adsorption of iodine and acetic acid[34] from solutions in both water and ethyl acetate, and for the adsorption of pairs of organic acids[35] from aqueous solution. Moreover, it was found that the acid which was taken up most readily was displaced the least in the simultaneous adsorption. On the other hand, inorganic salts increase the adsorption of acetic, propionic, and butyric acids, ethyl alcohol, and acetone.[36] Sodium chloride does not change appreciably the adsorption of dextrose by charcoal, whereas the capillary-active urethanes decrease it.

If the adsorption is from an electrolyte solution with no common ion, the most strongly adsorbed cation and anion are taken up most readily and the other pair to a smaller extent. The so-called Paneth-Fajans-Hahn rules (2) and (3) formulate the effect of the presence of one ion on the adsorption of a second; but these rules were not discovered by these men. The facts on which they are based were first recognized by Lachs and Michaelis[37] and by Estrup[38] and have been worked out in detail for the process of dyeing on fibers by Pelet-Jolivet,[39] by Bancroft,[40] and by Briggs and Bull,[41] and for the mordanting process on hydrous oxide mordants by Weiser and Porter[42] (see Chapter 26).

As already pointed out, certain dyes are adsorbed on both positively and negatively charged bodies. For example, erythrosin anion is adsorbed by silver bromide appreciably both in the presence of an excess of silver ion (positive AgBr) and of bromide ion (negative AgBr); on silver iodide, however, the dye anion is adsorbed only when silver ion is in excess.[24] The effects of silver and bromide ion in excess on the adsorption by silver bromide of the acid dye eosin and the basic dye phenosafranine are given graphically in Fig. 30. It is apparent that the adsorption of eosin is very small at the equivalence point but rises sharply with increasing concentration of silver ion; on the other hand, the adsorption of the basic dye increases greatly in the presence of bromide ion and is cut down, but not to zero, in the presence of an appreciable excess of silver ion. The behavior of the basic dye methyl violet is similar to that of phenosafranine.

Because of the strong adsorption of hydrogen and hydroxyl ion, the adsorption of other ions is influenced by the pH value of the solution. This is illustrated in Fig. 31, which shows the influence of pH on the simultaneous adsorption by chromic oxide of oxalate and sulfate ions from a mixture which is 0.01 N with respect to both ions.[42] The adsorption of oxalate is so much stronger than that of sulfate that but little of the latter ion is adsorbed at the neutral point. When the solution is faintly acid, however, oxalate is displaced appreciably by sulfate, and in the strongly acid solutions, the adsorptions approach equivalence. This behavior is probably not due to a shift in the relative adsorbability of the bivalent oxalate and sulfate ions but to relatively greater conversion of bivalent oxalate to less strongly adsorbed bioxalate ion than of bivalent sulfate to bisulfate ion, in the acid solution. Hydroxyl ion is adsorbed more strongly than either oxalate or sulfate, as evidenced by the fact that their combined adsorption is almost zero at a *p*H value of 9.

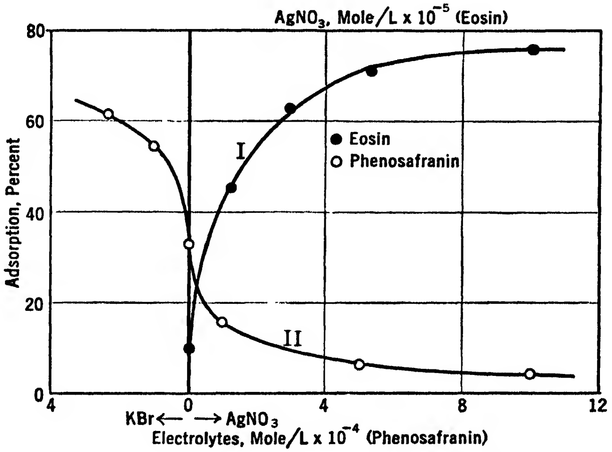


FIG. 30. Effect of excess silver and bromide ions on the adsorption of dyes by silver bromide, (I) 50 ml eosin containing 10^{-5} mole/l with 1 g AgBr, (II) 15 ml phenosafranine containing 1.6×10^{-5} mole/l with 0.2 g AgBr.

Adsorption Indicators

Since silver halides, when positively charged by adsorption of silver ions, adsorb and deform certain dye anions strongly, and, when negatively charged by adsorption of halide ions, adsorb certain dye cations strongly, the dyes even in low concentration give rise to an intensely colored adsorption layer. Fajans[43] and his coworkers have shown that dyes may be employed under suitable conditions as indicators in argentometry. Since the color change at the end point is due to adsorption, Kolthoff[44] called the dyes *adsorption indicators.* The following experiment demonstrates the principle on which the functioning of an adsorption indicator is based.[45] About 3 mg of the sodium salt of eosin is added to a liter of distilled water. The salt is dissociated and partly hydrolyzed, imparting to the solution a greenish fluorescence and a yellowish red color in transmitted light. The addition of 2 ml of 0.1 N $AgNO_3$ causes no appreciable color change since the solubility product of silver eosinate is not exceeded. On adding

0.5 ml of 0.1 N alkali bromide, an intense color change to red or red-violet occurs, and the fluorescence disappears. The highly dispersed silver bromide adsorbs silver ions and, simultaneously, an equivalent amount of eosin ions which are deformed, the process causing a marked change in color. On further addition of bromide, more silver bromide results and the color deepens until the equivalence point is passed, whereupon the excess bromide ions displace the adsorbed eosin ions which return to the solution. The silver bromide particles are decolorized thereby, and the solution takes on its original color and fluorescence. The color change is completely reversible. If a basic dye such as rhodamine 6 G is substituted for eosin, the process is the reverse of the above.

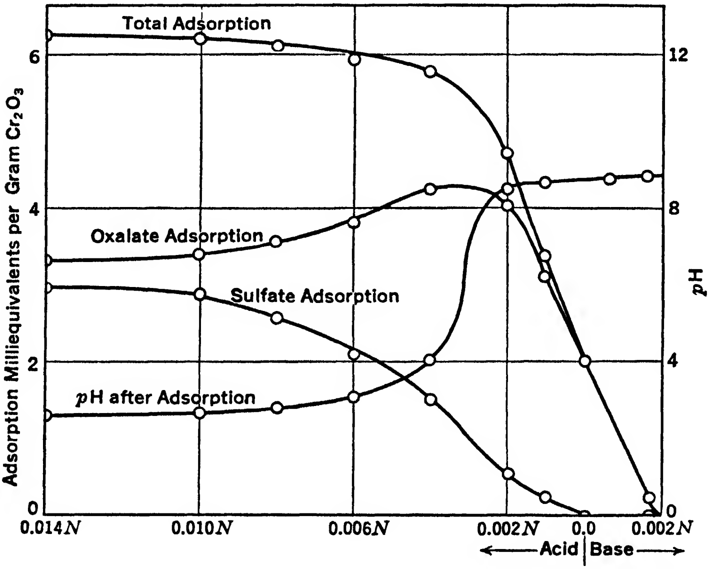


FIG. 31. Simultaneous adsorption of oxalate and sulfate by hydrous chromic oxide at varying pH values.

As already pointed out, Fajans considers the adsorption on ionic lattices to be a direct process, whereas Kolthoff considers it to be wholly or in part an exchange adsorption. According to Fajans's mechanism, a dye anion is adsorbed as a secondary process following the primary adsorption of silver ion, and a dye cation is adsorbed as a secondary process following the primary adsorption of halide ion on the silver halide surface. If this were strictly true, a dye anion should not be adsorbed in the presence of excess halide ion, and a dye cation should not be adsorbed in the presence of excess silver ion. As a matter of fact, acid dyes are frequently adsorbed to some extent even in the presence of excess halide, and basic dyes in the presence of excess silver. Eosin, for example, is useless as an adsorption indicator in the titration of chloride since the dye ion is adsorbed by silver chloride from the beginning of the titration, in spite of the presence of excess chloride ions; hence the end point is not sharp in titrating chloride. On the other hand, eosin is entirely satisfactory in titrating bromide and iodide. Similarly, erythrosin cannot be used as an indicator in titrating silver, chloride, or bromide, but is satisfactory in titrating iodide. The adsorption of phenosafranine and methyl violet in the presence of both excess silver and excess bromide has been considered above (p. 117). In spite of this behavior, phenosafranine is a good adsorption indicator in titrating silver with bromide, and methyl violet may be used in titrating silver with chloride. The essential point is that the dye anion should not be adsorbed very strongly in the presence of ions of the same sign but should be highly adsorbed in the presence of a slight excess of ions of opposite sign, in order that a marked color change may result at or near the equivalence point.

The application of adsorption indicators in quantitative analysis is confined chiefly to the titration of halides with silver or mercurous mercury, or the reverse. In qualitative analysis the adsorption-indicator principle is used in the colorimetric detection of several metals, for example: magnesium with titan yellow; beryllium with curcumin and 1,2,5,8-oxyanthraquinone; and aluminum, with the latter reagent and with alizarin, purpurin, and aurintricarboxylic acid.

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CHAPTER 8

Adsorption of Liquid by Liquid; Spreading of Liquid on Liquid; Molecular Orientation

If a drop of organic liquid (e.g., oil) is placed on the surface of water, the edge of the drop at the air-water interface is subjected to three pulls as indicated in Fig. 32. These are: (1) γ_3, the surface tension of water, (2) γ_2, the surface tension of the organic liquid, and (3) γ_{23}, the interfacial tension of water-organic liquid (cf. p. 81). The effect of (1) is to pull out the edge and flatten out the drop; and the effect of (2) and (3) is to pull in the edge and make the drop more nearly spherical. Accordingly, if $\gamma_3 \geqq \gamma_2 + \gamma_{23}$ the organic liquid will tend to spread over the surface of the water; whereas, if $\gamma_3 < \gamma_2 + \gamma_{23}$, the organic liquid will tend to draw up into a globule.

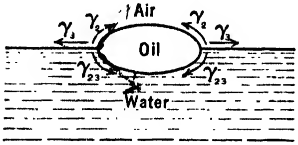

Fig. 32. Drop of oil on water.

Although the above formulation is correct, it is so general that it is limited in its usefulness. The theories of spreading based on the facts of molecular orientation at interfaces and on the work of adhesion and cohesion of liquids are more specific and generally helpful in explaining the phenomena.

MOLECULAR ORIENTATION AND THE SPREADING PROCESS

The systematic study of oil films on the surface of water was made possible by the work of Pockels,[1] who showed that a film on water could be removed completely, or concentrated at any desired portion of the surface, by raking the surface with a suitable paper or metal strip. Using barriers working on the surface of a trough filled to the brim with water, it was possible to vary the surface available for a given amount of oil. The important observation was made that there was no decrease in surface tension when the available area exceeded a certain amount, but a rapid drop in surface tension set in when the area was decreased below the critical value. This was confirmed by Rayleigh,[2] who suggested that the first drop in surface tension marked the point where the molecules were crowded as closely as possible to give a film one molecule thick. The next step in our knowledge of surface films was the concept of Hardy[3] that certain molecules are oriented in the films. Upon this series of facts and ideas were developed the comprehensive theories of Langmuir[4] and Harkins[5] which will be summarized briefly in the following paragraphs.

Spreading of Polar Compounds

Polar compounds. Liquids may be classified as: (1) symmetrical (e.g., pentane, $CH_3CH_2CH_2CH_2CH_3$), in which the two ends of the molecule are alike; and (2) unsymmetrical (e.g., oleic acid, $C_{17}H_{33}COOH$), in which the two ends of the molecule are dissimilar. The $—COOH$ portion of an organic acid is called a *polar group* or radical, to distinguish it from the hydrocarbon portion of the molecule. The term *polar group* is applied to such radicals as $—OH$, $—COOH$, $—CHO$, $—CN$, $—CONH_2$, $—NH_2$, $—NHCN_3$, $—SH$, $—NCS$, $—COR$, $—COOM$, $—COOR$, $—NO_2$, $—CH$, ${=}CH_2$, $—C{\equiv}CH$, and to other groups containing oxygen, nitrogen, sulfur, the halogens, and double or triple bonds. Compounds containing such groups are termed *polar compounds.*

Orientation of polar compounds in films. When a drop of stearic acid is placed on water, it spreads over the surface to give a film one molecule deep. Since the carboxyl groups of the acid dissolve in water, the molecules of acid orient themselves with the carboxyl groups in the water and the hydrocarbon tails packed in side by side vertically above the carboxyl layer. Since the upper surface of the oil film is thus made up of CH_3 groups, there is no particular tendency for a second drop of acid placed on the film to spread out and give a second layer.[6]

The reason stearic acid is practically insoluble in water is that the affinity of the long hydrocarbon chains for water is less than their affinity for each other. If such long hydrocarbon chains happen to get inside the water, they effect a separation of the water molecules; but, since the attraction of water molecules for each other is higher than for the hydrocarbon chains, when the water molecules get together by kinetic motion, they tend to stay together and thus to force out the hydrocarbon chains. Such long chains are carried into aqueous solution only when they are combined with very powerful polar groups. On the other hand, organic acids with relatively short chains, such as acetic, propionic, and butyric, are quite soluble in water.

The principle governing the solubility of one liquid in another is that like attracts like. In accord with this, highly polar liquids are in general mutually soluble, and slightly polar liquids, such as hexane and octane, are soluble in other slightly polar liquids but are insoluble in highly polar liquids. Hydrocarbons are rendered soluble in water by the introduction of polar groups provided that the hydrocarbon chains are short; but, as pointed out above, the solubility decreases with increasing length of the hydrocarbon chains.

As we have seen (p. 16), the solution of polar liquids in water lowers the surface tension, and the concentration of the molecules is higher in the surface film than in the body of the solution. In this film, also, the hydrocarbon portion of the acid is oriented toward the vapor phase, and the carboxyl group toward the liquid. Similar relationships obtain with other types of polar compounds.

Stability of films. Surface films are most stable when the molecules contain groups that attract the water strongly (dissolve in the water), thereby providing a firm anchorage for the lower end of the molecules. The partial obstruction of such groups diminishes or destroys the stability of the films. Table 32 gives a rough classification of the groups and their effect on film stability.

TABLE 32

EFFECT OF GROUPS ON THE STABILITY OF MONOMOLECULAR FLIMS ON WATER[7]

Groups	Attraction for water, W_a	Attraction for like molecules, W_c	Stability of film
Hydrocarbons	Weak	Weak	No film
$—CH_2I$, $—CH_2Br$, $—CH_2Cl$	Strong	Strong	No film
$—CH_2OCH_3$, $—C_6H_5OCH_3$, $—COOCH_3$	Strong	Weak	Collapses at low pressure
$—CH_2OH$, $—COOH$, $—CN$, $—CONH_2$, $—CH{:}NOH$, $—C_6H_4OH$, $—CH_2COCH_3$, $—NHCONH_2$, $—NHCOCH_3$	Very strong	Moderately weak	Stable (with 16 C chains, solubility very low)
$—C_6H_4SO_3H$, $—SO_3H$	Extremely strong	Moderately weak	Dissolve with 16 C chains, but form micelles

THE SPREADING COEFFICIENT AS A MEASURE OF SPREADING TENDENCY

Harkins[5] has demonstrated that spreading of liquids is not limited to polar compounds; hence one is not justified in classifying liquids into two groups: non-spreading liquids which are non-polar, and spreading liquids which are polar. Harkins's method of predicting the spreading tendency of liquids is based on their respective works of *adhesion* and *cohesion.*

If a liquid b spreads over a liquid a without dissolving in it, the surface of a disappears, and two new surfaces are formed: the interface ab and the free top surface b. The amount of free energy used in this operation is the difference between the free energy of the initial surface γ_a and the free energy of the two final surfaces, γ_{ab} and γ_b. Harkins calls this the *spreading coefficient* S, which may be formulated:

$$S = \gamma_a - \gamma_b - \gamma_{ab} \qquad (1)$$

If a bar of spreading liquid a of unit cross section (Fig. 33, I) is pulled apart along the plane p, it will require the *work of cohesion* W_c, which is the work required to form the two new unit surfaces $2\gamma_b$; that is:

$$W_c = 2\gamma_b \text{ ergs/cm}^2 \qquad (2)$$

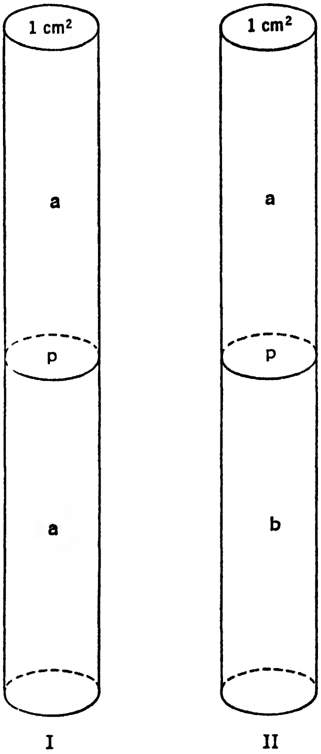

Fig. 33. Liquid bars of unit cross section.

If a bar consisting of the two liquids a and b of unit cross section (Fig. 33, II) is pulled apart at p, the interface ab vanishes and two new surfaces appear. The work involved, called the *work of adhesion* W_a, is thus:

$$W_a = \gamma_a + \gamma_b - \gamma_{ab} \qquad (3)$$

subtracting eq. 2 from eq. 3 gives:

$$W_a - W_c = \gamma_a - \gamma_b - \gamma_{ab} \qquad (4)$$

That is:

$$S = W_a - W_c \tag{5}$$

This means that, if the attraction of the surface of *a* for *b* exceeds the power of *b* to hold together, *b* will spread over *a*. For example, W_c for caprylic acid ($C_7H_{15}COOH$) is 57.6 ergs; W_a is 93.7; and $S = +36.1$. Hence caprylic acid spreads readily over water.

The values of the spreading coefficients of a few organic liquids on water chosen from 92 liquids reported by Harkins are given in Table 33. Since such liquids as hexane, benzene, isopentane, and heptine spread on water, it is apparent that the presence of a polar group is not essential

TABLE 33

SPREADING COEFFICIENTS OF ORGANIC LIQUIDS ON WATER AT 20°

Liquid	$S = W_a - W_c$
A. Spreading liquids	
Butyric acid	45.66
Ethyl ether	45.50
Isoamyl chloride	33.88
Heptaldehyde	32.22
Nitromethane	26.32
Mercaptan	24.86
Oleic acid	24.62
Heptine	22.40
Ethyl bromide	17.44
Chloroform	13.04
Anisole	11.76
Phenetole	10.66
p-Cymene	10.10
Isopentane	9.44
Benzene	8.94
Nitrobenzene	3.76
Hexane	3.41
B. Liquids which form lenses	
Ethylene dibromide	−3.19
Carbon disulfide	−6.94
Monoiodobenzene	−8.74
Bromoform	−9.58
Liquid petrolatum	−13.64

for spreading. In general, a liquid will spread if *S* is positive and will not spread if *S* is negative.

The presence of a polar group has the effect of increasing the work of adhesion W_a very much more than it increases the work of cohesion W_c. The reason for this is shown diagrammatically in Fig. 34, after Harkins. Part *a* shows the orientation of octyl alcohol molecules at the surfaces when a bar of the liquid is pulled apart. The circles represent —OH groups; and the rectangles, the hydrocarbon chains. This figure indicates that the final work of separation will be affected chiefly by the attraction between the non-polar ends of the alcohol molecules. But, in the first period of the separation, some of the hydroxyl groups which are to go on the upper side of the plane will have to be separated from others that are to go on the lower side. Accordingly, one would expect the work of separation of the alcohol to be greater, but not much greater, than that of octane. The actual values are: for octane $W_c = 43.5$ ergs/cm^2; and for octyl alcohol $W_c = 55.1$ ergs/cm^2.

If the octyl alcohol is to be pulled away from water (Fig. 34*b*), the final break must come between the polar OH groups of the alcohol and water. One would therefore expect the work of adhesion to be high; it turns out to be 91.8 ergs/cm^2, which is 66% higher than the work of separating the alcohol from itself.

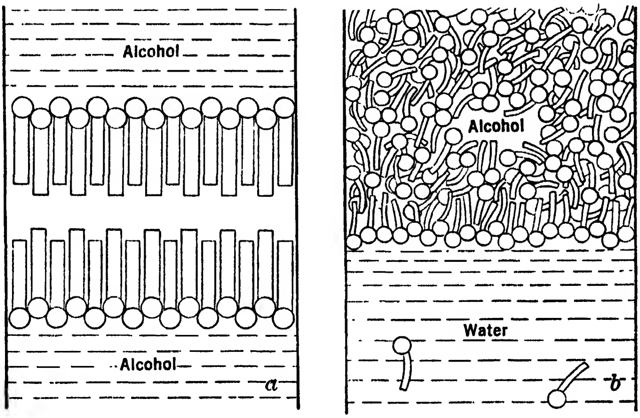

FIG. 34. (*a*) Orientation of octyl alcohol molecules at the surface when a bar of the liquid is pulled apart. (*b*) Octyl alcohol over water showing orientation of alcohol molecules in the interface.

When highly polar groups are present, W_a is usually so large that $W_a - W_c$ is always positive and the liquid spreads. But, even if the work of adhesion toward water is small, spreading may still take place if W_c is small enough. Thus non-polar hexane, for which W_a is only 40.2 ergs, spreads because W_c has the very low value of 36.8 ergs, so that $S = +3.4$. As we have seen, the work of cohesion for polar-non-polar octyl alcohol is 55.1 ergs, almost 20 ergs higher than for hexane; but the alcohol also spreads very readily because it has the very high W_a value of 91.8 ergs, so that $S = +36.7$.

The magnitude of the spreading coefficient S is determined in large measure by the dissymmetry of the molecule, since the coefficient increases as the electrical field of force around the molecule becomes more unsymmetrical. The reason is that W_a toward water is much greater, in comparison with W_c, for unsymmetrical than for symmetrical molecules because the strongest field must be ruptured when the liquid is torn from water, whereas only the weakest field is broken when it is separated from itself.

The non-spreading of a liquid is usually due to a high value of the work of cohesion W_c of the liquid. Such liquids usually accompany the presence of $=S$, $=CS$, or phenyl groups, or the presence of the halogens as substituents in paraffins, benzene, or naphthalene, even though the unsubstituted compound spreads readily. The effect of the halogens as substituents on non-spreading is in the order: $I > Br > Cl$. When only one chlorine is present in a paraffin derivative, it seems to be polar and causes spreading, whereas several chlorine atoms greatly decrease the spreading coefficient and may render the liquid non-spreading.

All non-spreading liquids having a negative S value are practically insoluble in water, and most spreading liquids whose S value is less than $+10$ are insoluble or but slightly soluble in water.

TYPES OF SURFACE FILMS

Film Balances

Investigations of the character of films on the surface of liquids were stimulated greatly by Langmuir's[4] design of a "surface-tension balance" or "film balance" embodying the principles of Pockels's apparatus (p. 122). The Langmuir apparatus consists essentially of a shallow rectangular trough with smooth parallel sides, at the end of which is a balance connected with a movable barrier or "float" on the surface, in such a way that the surface pressure of films can be measured. In using the apparatus, a few drops of a dilute solution of the spreading liquid in a volatile solvent is placed on a clean surface of water in the trough; the solvent evaporates and the liquid spreads over the surface. By means of a paraffined barrier, the film is pushed gently toward the movable float until it is displaced. The force of displacement or film pressure is the force in dynes per centimeter required to return the floats to its original position. The area of film corresponding to a given film pressure is measured. Since the weight of matter added to produce the film can be found, the number of molecules in the film can be calculated. Dividing the area covered by the number of molecules gives the area covered by each molecule, which is equal to the cross section of the molecule. Plotting the film pressure against the area per molecule gives curves which are characteristic for the film-forming substances.

The original Langmuir horizontal type of film balance has been modified and rendered much more sensitive, especially by Adam[8] and by Harkins.[9] Harkins[10] has also adapted Wilhelmy's[11] method of determining surface tension into a film balance of the vertical type with which it is much easier to obtain a certain degree of accuracy than with a balance of the horizontal type.

Monomolecular Films or Monolayers

Langmuir[12] points out that monolayers at interfaces have length and breadth but only monomolecular depth; hence they can move only in two directions. They therefore constitute a different state of matter, since they are two-dimensional gases, liquids, or solids. In the highly expanded form, the films behave as two-dimensional gases; when the molecules are about the same distance apart as in liquids, the films are two-dimensional liquids; and when compressed still further, the films become two-dimensional solids. The equations of state for three-dimensional gases, liquids, and solids have to be modified to account for the kinetic behavior of the molecules in such two-dimensional films.

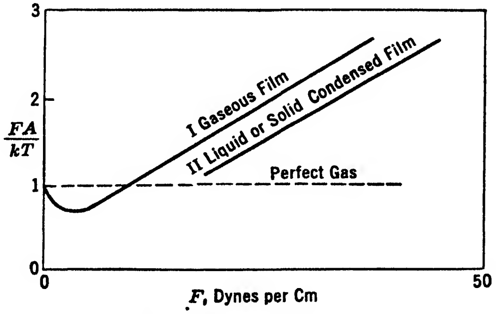

FIG. 35. Curves representing diagrammatically the force-area relationships (FA/kT to F) of films at interfaces.

In a two-dimensional system which acts like a gas, the film pressure F and the area per molecule A correspond to the gas pressure and volume, P and V, respectively, in an ordinary three-dimensional gas. Just as a perfect gas obeys the equation $PV = RT$, so a monomolecular film that behaves like a perfect gas will obey the equation $FA = kT$ or $FA/kT = 1$. Plotting FA/kT against F gives a straight line parallel to the F-axis, if the film behaves like a perfect gas (broken line in Fig. 35). Actually, the curve for a gaseous film has the general form of curve I in Fig. 35. At low pressures FA/kT may approach unity, but at high pressures there is a marked deviation from the behavior of a perfect two-dimensional gas. Unlike a gaseous film, a condensed liquid or solid monolayer gives a curve like II, which extrapolates toward 0,0 at low pressures. From the force-area relationships, six types of films may be distinguished as given in Table 34.[13, 8]

TABLE 34

Types of Monomolecular Films

Name	Characteristics
I. Gaseous	Molecules are separate, moving in the two-dimensional system with the same order of freedom as those in an ordinary gas in three dimensions (curve I, Fig. 35).
II. Vapor expanded	More coherent than ordinary gaseous films but not sufficiently coherent to form islands in equilibrium with gaseous films.
III. Liquid, or coherent expanded	At low pressures, the molecular area is of the order of twice that of a condensed liquid film made up of molecules of the same type. At higher areas, liquid expanded films give islands in a sea of gaseous film. The compressibility is high.
IV. Transitional	Intermediate in characteristics between Types III and V. On compressing an expanded film at a definite temperature, there appears a rather sudden change in state or transition in the film, after which the compressibility becomes great, but not infinite. The compressibility of this intermediate film decreases gradually until it changes into a condensed liquid film.
V. Condensed liquid	The force-area relation, FA/kT to F, is a straight line (curve II, Fig. 35). The compressibility is low but not so low as in Type VI.
VI. Solid	Increasing the pressure on a liquid monolayer gives a condensed film of very low compressibility usually considered as solid. The relation of FA/kT to F is linear, as in Type V (curve II, Fig. 35).

Harkins[7] believes that all true films formed by spreading on water or mercury are never more than a molecule thick. Any excess material condenses into lenses, if liquid, or into little crystals, if solid. As much as 32% of Nujol, a non-polar liquid, was dissolved in an expanded film of myristic acid at low film pressure; all the Nujol was in the monolayer. Increasing the pressure on the film reduced the solubility of the oil in the two-dimensional layer so that molecules of oil jumped out and collected in lenses on top of the monolayer.[14] Non-polar benzene spreads on water to form a film one molecule thick with a film pressure *F* of about 10 dynes/cm at ordinary temperatures. According to Harkins, so-called "liquid" films that are thicker than monomolecular are, in general, very much thicker, and are not true films at all, but are thin layers of a second liquid phase.

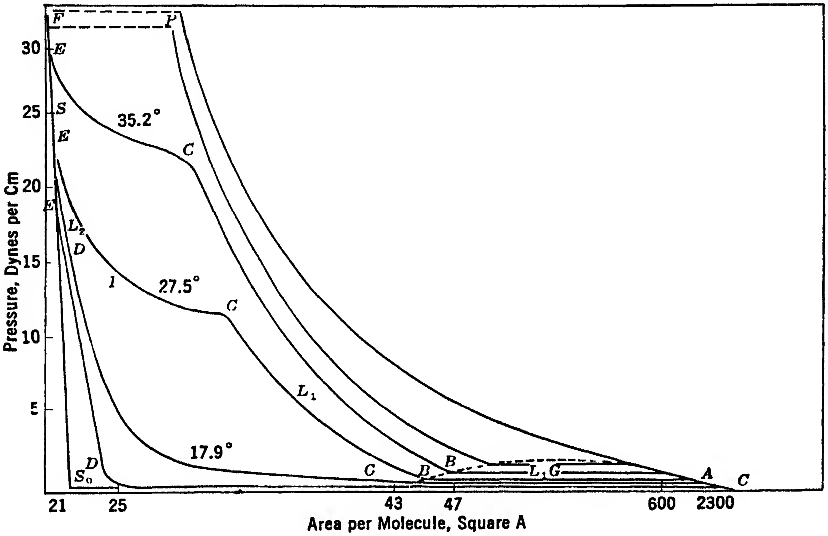

FIG. 36. General phase diagram for monolayers on a liquid subphase (*I*). The lowest temperature of collapse at *P* is below the critical temperature of the L_2 phase.

Figure 36 is Harkins and Jura's[13] more comprehensive phase diagram for monolayers on a liquid subphase in which the film pressure in dynes per centimeter is plotted against the molecular area. The temperatures shown on the curves in Fig. 36 are for pentadecylic acid and should be increased from 8 to 10° for each carbon atom added. The temperatures are much higher with alcohols than with acids.

The surface of water coated with a film gives a different *contact potential*[15] from that of the pure water surface. The difference in contact potential when the film is present and when it is absent is called the *surface potential* of the film. The nature and polarity of the molecules and the manner of their orientation in the monolayers are of primary importance in determining the surface potential.

Molecular dimensions. In the above section on film balances, it was pointed out that the area of a molecule in a monomolecular film is estimated by dividing the film area by the number of molecules in the film. A rough approximation of the "average diameter" of vertically oriented molecules is obtained by taking the square root of the cross section. The length of the molecules in a direction perpendicular to the surface is obtained by dividing the molecular volume (molecular weight/density) by the Avogadro number to get the volume of each molecule, and then dividing the volume by the cross section. Estimations of this kind were made first by Langmuir and later by Adam, Harkins, and others. In Table 35 are given some data by Adam[16] for the cross section of single molecules containing various groups. A number of molecules having nothing in common except a long hydrocarbon chain were found to have the same cross section, about 20.7 A^2. For example, Adam found the cross section of the stearic acid molecule to be 20.7 A^2 and the length to be 26 A; the corresponding values obtained by Harkins[7] were 20.2 A^2 and 25 A, respectively. The experimental values vary with the pressure. For the normal straight-chain alcohol ($R—CH_2OH$), Harkins found the cross section to be 20.2 A^2

TABLE 35

CROSS-SECTIONAL DIMENSIONS OF MOLECULES CONTAINING VARIOUS GROUPS

Group	Cross section (A^2)	Group	Cross section (A^2)
Hydrocarbon chain	20.7	$—CH_2NH_2CONH_2$	25.5
$—CH_2CH_2COOH$	25.1	$—C_6H_4OH$	23.8
$—CH{=}CHCOOH$	28.7	$—C_6H_4NHCOCH_3$	28.2 or 25.8 †
$—CH_2CH_2COOC_2H_5$ *	22	Triglycerides	63
$—CH{=}CHCOOC_2CH_5$	28.7	Glycol dipalmitate	42
$—CH_2OH$	21.7	Cholesterol	39
$—CONH_2$	<21	Hydrolecithin	53
$—CN$	27.5		

* Ethyl, methyl, and allyl esters pack into the same area.

† According to temperature.

at high pressures, and 21.9 A^2 at very low pressures; Adam's value is 21.7 A^2. For the similar acid (R—CH_2CH_2COOH), Harkins obtained 20.2 for the cross section at high pressures. At low pressures the value decreases with the length of the carbon chain. The cross sections at "zero pressure" for the following acids are: margaric (17 C atoms) = 24.6 A^2; stearic (18 C atoms) = 24.4 A^2; nonadecanoic (19 C atoms) = 24.0 A^2; and archidic (20 C atoms) = 23.7 A^2.

Molecules like those of stearic acid stand upright on the surface of water in condensed films but lie flat in gaseous films. Molecules will lie flat even in condensed films if the polar groups are properly distributed along a linear molecule or around an aromatic derivative. The ω-hydroxydecanoic acid polymers illustrate the case of monomolecular films of molecules which lie flat on the surface.[17] The thickness of these films averages 4.5 A, and the distance between molecules in the films is about the same; that is, the molecules are about 4.5 by 4.5 A in vertical cross section. The lengths, that is, the distance along the molecules in the surface, vary from 60 to 1970 A; hence these long molecules lie flat. The differences in the properties of films with different molecular orientations are summarized in Table 36.

TABLE 36

PROPERTIES OF CONDENSED FILMS WITH DIFFERENT ORIENTATIONS OF MOLECULES [17]

Long axis vertical	Long axis horizontal
Molecular area independent of length	Molecular area increases with the length
Withstand high pressures (of the order of 50 dynes/cm)	Collapse at low pressures (2 to 10 dynes/cm)
Surface potential increases with length of molecules up to 18 C atoms	Surface potentials of the same order for both long and short molecules
Compressibility decreases with increasing length of molecules	Compressibility high and independent of length of molecules

Built-up Films or Multilayers

Blodgett[18] in Langmuir's laboratory developed a technique for building up multilayer films up to 200 molecules thick, by spreading monolayer films on top of one another. To do this, the calcium, barium, or lead salt of palmitic or another long-chain fatty acid is allowed to spread on the surface of water in a trough. This film is then compressed on the water surface by spreading a surface-tension depressant such as castor oil, the two films being kept apart by a waxed silk thread. The pressure produced by the so-called "piston oil" (castor oil) is not sufficient to crumple a rigid film of calcium palmitate, say, but will cause it to move upon another suitable surface. If a clean glass slide is raised through the calcium palmitate film, the area decreases by exactly the surface area of the slide, and a monomolecular film deposits on the slide with the —COO groups oriented toward the slide and the hydrocarbon tails above. If now the slide is lowered through the film, a second layer of calcium palmitate is deposited with the hydrocarbon chains oriented toward the hydrocarbon surfaces already on the slide and the —COO groups above, constituting a new surface. Thus, by successive raising and lowering of the slide, films may be built up one at a time. The 1, 3, 5, 7, etc., films are hydrophobic and are wetted by oil but not by water, whereas the 2, 4, 6, 8, etc., films are hydrophilic and are wetted by water but not by oil. When sufficiently thick, the films show beautiful interference colors. The film structure is not destroyed by drying even in a hot-air oven.

Two classes of built-up films are recognized: (1) *Y*-films in which one layer of alkaline-earth soap, say, is deposited on a down trip of the slide and another on the up trip; and (2) *X*-films in which the monolayers are deposited on the down trips only. The contact potential between two metal strips is changed by depositing films on one of them. If the *Y*-films are deposited at a *p*H of 7, they may show a film potential of about 225 millivolts (mv) for the first few layers, after which there is no increase in potential. On the other hand, the film potential of *X*-layers may rise as rapidly as 100 mv per layer if the film is deposited at a *p*H of 9.4, as is usually done; but if the layers are deposited at $pH = 6.3$, the resulting *X*-films are like the *Y*-films in showing no increase in potential after the first few layers.[19] The maximum potential obtained with *X*-films is not often much above 8 volts.

Similar monolayers and built-up films of proteins have been prepared and their properties studied by Langmuir and coworkers.[18] By using the interference colors which such films show and knowing the number of layers in a film, the thickness of protein molecules has been estimated. Protein monolayers deposited under low pressure show thicknesses ranging from 6 to 18 A.

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PART II. SOLS

CHAPTER 9

Formation of Sols I: Condensation Methods

Substances are obtained in the sol state either by gathering smaller particles, molecules, or atoms into particles of colloidal dimensions or by subdividing material in mass into particles of colloidal dimensions. The first process is called *condensation* or *precipitation*, and the second process, *dispersion* or *peptization*. The condensation or precipitation methods for the preparation of sols will be considered in this chapter.

CONDENSATION FROM SOLUTION

Two problems present themselves in the synthesis of stable sols: (1) preparing the material in the colloidal state; (2) maintaining the material in the colloidal state. The factors which determine the form of a precipitate thrown down from solution have been formulated by von Weimarn and by Haber, whose theories will be considered in order.

Von Weimarn's Theory

The velocity equations. Von Weimarn[1] recognized two stages in the process of precipitation from solution: the first, in which the molecules in solution condense to invisible or ultramicroscopic nuclei; and the second, which is concerned with growth on the nuclei as a result of diffusion. The velocity W at the important first moment of the first stage of the process is given by:

$$W = K\frac{\text{precipitation pressure}}{\text{precipitation resistance}} = K\frac{Q - L}{L} = K\frac{P}{L} = KU \qquad (1)$$

in which Q is the total concentration of substance that is to precipitate, L the solubility of coarse crystals, and K a constant. P is the absolute supersaturation, and $P/L = U$ is the percentage supersaturation at the beginning of the precipitation. To take care of factors other than solubility of the precipitating substance and concentration at which precipitation begins, von Weimarn introduces a variable multiplier J, and the equation becomes:

$$W = KJ\frac{Q - L}{P} \tag{2}$$

The Nernst-Noyes equation gives the velocity V of growth on nuclei:

$$V = \frac{D}{S} \cdot O \cdot (Q - L) \tag{3}$$

in which D is the diffusion coefficient, S the thickness of the adhering film (length of the path of diffusion), O the extent of surface, and $(Q - L)$ has the same significance as above.

Examples. Several facts may be interpreted qualitatively by means of the above equations. It will be seen that the velocity of the precipitation depends not on the supersaturation P, but on the percentage supersaturation P/L. Thus, with a given value of P (say, a few grams per 100 ml), a very soluble substance, such as sodium chloride, will deposit nothing at first and finally a few crystals may form; but with the same value of P, an almost insoluble substance, such as aluminum hydroxide or silver chloride, will give an immediate gelatinous or curdy precipitate. The difference is that the velocity of precipitation is much smaller in the first case than in the second. On the other hand, if sodium chloride is formed by the interaction of sodium ethylate or thiocyanate and hydrochloric acid in a mixture of ether and amyl alcohol, in which sodium chloride is practically insoluble, the precipitate is curdy like that of silver chloride.

Although the value of P is not in itself of primary importance in determining the form of the precipitate, its value is not without influence, since quite different results are obtained, depending on whether a given value of P/L is obtained by a large P or by a small L. In the first instance, a large amount of the dispersed phase will be produced, and in the second, very little. Hence a large value of P/L resulting from a large value of P will, in general, give a gelatinous precipitate or a jelly; whereas a large value of P/L resulting from a very small L value will give a large number of highly dispersed particles—a sol. It would appear, therefore, that the dispersed phase can be made to separate in any form desired by suitable alteration of P or L or of both.

Von Weimarn's comprehensive studies on barium sulfate, Table 37, will serve to illustrate the very great influence of concentration of reacting solutions on the form of a precipitate.

It is apparent from Table 37 that barium sulfate is too soluble (L too large) to give a hydrosol, since the $Q - L$ value necessary to give particles of colloidal dimensions is so large that a gel and not a

TABLE 37

EFFECT OF CONCENTRATION OF REACTANTS ON THE PHYSICAL CHARACTER OF BARIUM SULFATE (L = 0.002 g/l)

Normality of $Ba(CNS)_2$ and $MnSO_4$	P	$U = \frac{P}{L}$	Nature of precipitate
0.00005 to 0.00014	0.000 to 0.006	0 to 3	No precipitate in a year. Microcrystals would be expected in a few years, and macrocrystals from large amounts of solution.
0.00014 to 0.0017	0.006 to 0.096	3 to 48	Slow precipitation at U = 8. Momentary sol stage at U = 25. Complete separation in months to hours.
0.0017 to 0.75	0.096 to 43.8	48 to 21,900	Crystal skeletons and needles precipitate in a few seconds at U = 48; beyond this, instantaneous precipitation. Crystals barely recognizable at U = 21,900.
0.75 to 3.0	43.8 to 175.1	21,900 to 87,500	Precipitates, which appear amorphous, form immediately.
3.0 to 7.0	175.1 to 409.0	87,500 to 204,500	Clear cellular jellies.

sol results. To obtain a sol, therefore, L must be diminished. Actually Kato[2] made a sol with aqueous alcohol in which barium sulfate is much less soluble than in water alone.

Precipitation rules. Von Weimarn[3] formulated the following precipitation rules as a result of observations on the precipitation of various salts such as the sulfates of barium, strontium, calcium, and silver from aqueous and aqueous-alcoholic solutions:

1. With increasing concentrations of reacting solutions, the average size of the precipitated individual crystals (not their aggregates) passes through a maximum during the process of direct crystallization.
2. With increasing concentrations of reacting solutions, the size of the crystals decreases continuously after the completion of the process of direct crystallization.
3. For the same absolute concentrations ($Q - L$) of reacting solutions, other conditions being equal, the average size of the precipitated crystals decreases with decreasing solubility of a substance.

4. With increasing viscosity of the dispersion medium, the average size of the particles decreases.

Law of corresponding states. Von Weimarn recognized that the velocity of precipitation W (eq. 1) cannot be measured in actual practice, and in many cases, especially interesting in the synthesis of sols, the velocity of the growth of particles (eq. 3) cannot be determined. In due time, therefore, he introduced a "specific form coefficient" or dispersity coefficient N which is related to the mean magnitude of the single crystals in gram molecules Gm by the expression:

$$Gm \times N = \text{constant}$$

N may be represented qualitatively and in some cases approximately quantitatively by the expression:

$$N = \frac{P}{L} \tag{4}$$

or, taking into account all factors in addition to P/L:

$$N = J\frac{P}{L} \tag{5}$$

in which J has the same significance as in eq. 2.

Now if N is taken as approximately equal to P/L, then, for the different substances x, y, and z,

$$N_x = \frac{P_x}{L_x}; \quad N_y = \frac{P_y}{L_y}; \quad \text{and} \quad N_z = \frac{P_z}{L_z} \tag{6}$$

If the character of the precipitate is to be the same irrespective of the chemical nature of the salt, in other words, if

$$N_x = N_y = N_z$$

then

$$\frac{P_x}{L_x} = \frac{P_y}{L_y} = \frac{P_z}{L_z} \tag{7}$$

This is the simplest expression of von Weimarn's *law of corresponding states for the precipitation process,* which says that, under corresponding conditions of precipitation, the mean magnitude (expressed in gram molecules) of the crystals of precipitated substances is the same.

As might be expected, in the form given in eq. 7, the so-called law is at best only a first approximation. The reason is that so many factors other than P/L may enter into the precipitation process. Among these are the following: the effect of the viscosity of the reacting medium, the variation in solubility with the size of the primary particles (p. 10), polymerization of the reactant molecules, molecular complexity of the reactants, adsorption, the presence of dust particles, the extent of agitation on mixing, the specific tendency to form nuclei, and the specific tendency to grow on nuclei. As we have seen, von Weimarn takes care of these several factors by means of the "multiplier" J so that his generalized equation is:

$$J_x \frac{P_x}{L_x} = J_y \frac{P_y}{L_y} = J_z \frac{P_z}{L_z} \tag{8}$$

in which J_x, J_y, and J_z are specific variable multipliers, "the product of all other factors in addition to P/L which influence the crystallization process. These factors must be expressed in abstract numbers equivalent to P/L." This means that von Weimarn's equation is made quantitative and generally applicable by introducing "variable multipliers," in which are collected together all the several factors known or unknown that have not been evaluated.

Although it is possible to express facts fairly accurately by means of such flexible formulas, it is doubtful whether anything is gained scientifically by regarding equations of this kind as quantitative representations of natural laws.[4] Nevertheless, it should be emphasized that certain statements of von Weimarn have quite general validity. Thus, when the reacting solutions are very dilute, the resulting solid precipitates in a definitely crystalline form. At low concentrations, the velocity of formation of nuclei is small, and the few nuclei which do form grow so slowly at the cost of the solute present in weakly supersaturated solution that large crystals result. Conversely, when the reacting solutions are very concentrated, jellies are formed consisting of drops of the liquid surrounded by the solid. The rate of formation of nuclei is extremely high at the high concentration, so that at any point where the two solutions touch there is formed immediately a network of nuclei which do not have time to crystallize further and so yield a solid film. Subsequently, the nuclei grow into crystals as the interacting substances diffuse through the film.[5]

Haber's Theory

In contradistinction to von Weimarn's views, Haber[6] is of the opinion that the form of precipitates is influenced primarily by the following two factors: aggregation velocity and orientation velocity. When the limit of solubility is exceeded for a given substance, the molecules or molecular aggregates tend to group together into larger aggregates. The velocity of this process is a function of the supersaturation; hence, the higher the supersaturation, the less regular will be the aggregates. The absolute concentration of the reacting ions will also be of importance. By mixing the molecules in a more or less arbitrary manner, instable aggregates are formed which lose energy and become oriented in a regular way in the crystal lattice. The speed of this process is termed the orientation velocity. From Haber's point of view, the form of a given precipitate depends upon its relative velocity of orientation and of aggregation: if the supersaturation is very high, the aggregation velocity predominates and the resulting precipitate is amorphous to x-rays; whereas, if the supersaturation is sufficiently low, the orientation velocity predominates and the precipitate is crystalline. A precipitate amorphous to x-rays becomes crystalline during the aging process. Since the orientation velocity varies with different substances, it follows that, at the same degree of supersaturation, the form of a precipitate will vary with different substances.

Preparation of Sols

In the preceding section were outlined the conditions of precipitation most favorable for the formation of finely divided particles. To prepare stable sols, it is necessary to prevent the agglomeration of the individual or primary particles into aggregates sufficiently large to settle out under the influence of gravity. Since sols are agglomerated by a sufficient concentration of electrolyte, the methods actually employed to prevent agglomeration involve: (1) the keeping down of the concentration of coagulating electrolyte either by a suitable choice of reaction or by dilution, and (2) the addition to the solution of strongly adsorbed protecting agents such as *protecting colloids* which form a water-soluble film around the primary particles and prevent their coalescence into aggregates.[7] The following general procedures are employed in the preparation of sols by precipitation from solution. For detailed description of the methods for preparing specific sols and for the original references, the reader is referred to the books of Svedberg[8] and Weiser.[9]

Reduction without protecting colloids. Reduction with or without the use of protecting colloids is by far the most important chemical reaction for preparing elements in the sol state. Noteworthy examples are the preparation of gold sol by reduction with hydrogen peroxide and with formaldehyde (Zsigmondy's[10] method) and the reduction of silver oxide with hydrogen (Kohlschütter's[11] method). The respective reactions may be represented as follows:

$$2HAuCl_4 + 3H_2O_2 \rightarrow 2Au + 8HCl + 3O_2$$

$$2HAuCl_4 + 3HCHO + 11KOH \rightarrow 2Au + 3HCOOK + 8KCl + 8H_2O$$

$$Ag_2O + H_2 \rightarrow 2Ag + H_2O$$

These reactions have received extended study and throw much light on the following factors as they influence sol formation: concentration of reactants, presence of nuclei, purity of solutions, and the nature of the containing vessel.[12] Among other reducing agents which may be employed are: phosphorus, formaldehyde, hydrazine, phenylhydrazine, carbon dioxide, and acetylene.

To form sols of uniform particle size Zsigmondy devised the process of adding a small amount of sol, containing very fine particles of gold, to the gold chloride solution before adding the reducing agent. Under these conditions the nuclei of gold serve as centers around which the gold is precipitated. A suitable *nuclear solution* results when an ether solution of phosphorus[13] is added to an alkaline solution of gold salt; the particles in the resulting sol are too small to be seen with the ultramicroscope (Chapter 12).

Elements that have been prepared in the sol state by reduction processes include: gold, silver, platinum, palladium, iridium, rhodium, ruthenium, osmium, mercury, bismuth, copper, selenium, and tellurium.

Metal or oxide sols may result during electrolysis of highly dilute solutions of salts. Thus, gold, silver, and mercury sols may be obtained in this way, whereas the less-noble metals give oxide sols. The preparations are impure, and the particle size varies over a wide range.

Reduction with protecting colloids. The stability of hydrosols may be greatly increased by precipitating the finely divided particles in the presence of hydrophilic or "water-soluble" colloids such as gelatin, tannin, gum arabic, casein, glue, starch, biological fluids, plant extracts, albumin, and the sodium salts of protalbinic and lysalbinic acids which are formed by the saponification of albumin. The stabilizing action of these so-called *protecting colloids* results from their adsorption on the surface of the colloidally dispersed solid. In many instances, the protecting colloid may play the combined rôle of reducing and stabilizing agent. For example, highly stable gold and silver sols are obtained by reduction of solutions of salts of the respective metals with tannin or sodium protalbinate.

Oxidation. The oxidation process which is most important in sol formation is the oxidation of hydrogen sulfide by sulfur dioxide. Since most of the sulfur is precipitated in the colloidal state, the reaction which takes place is usually represented by the equation: $2H_2S + SO_2 \rightarrow 3S + 2H_2O$. The actual reaction, however, is much more complicated, a number of thionic acids as well as colloidal sulfur being formed. It is now known that the presence of small amounts of one or more of the thionic acids is essential to the formation of a stable sulfur hydrosol.[9]

LaMer and Barnes[14] prepared monodispersed sols of very uniform particle size by adding 1 ml of 1.5 N $Na_2S_2O_3$ to 1 liter of 0.0015 N H_2SO_4 at 25°. The particles are very small at first but continue to grow until, after 24–30 hours, they are large enough to settle rapidly. The sol can be stabilized at any time so as to stop further change in particle size by titrating the unchanged $Na_2S_2O_3$ with iodine, leaving a slight excess of $Na_2S_2O_3$ to stabilize the dispersion (Chapter 14).

Sols of the halides of silver, lead, and mercury are obtained by oxidation of the corresponding metal sols with chlorine, bromine, or iodine until the characteristic color of the metal sol is destroyed. The stability of the resulting halide sols is greatly increased by the presence of gelatin or other strongly adsorbed material such as ammonium citrate.

Dissociation. Dissociation processes are seldom encountered in the preparation of sols in liquid media. An example is the thermal dissociation of nickel carbonyl in benzene or toluene with the formation of brown to black benzosol or toluosol:[9] $Ni(CO)_4 \rightarrow Ni + 4CO$. The sols are instable except in the presence of a protecting colloid such as rubber. For some unknown reason, the most stable preparation results with a mixture of toluene and benzene in the presence of rubber.

Hydrolysis. Hydrolysis is the reaction most frequently employed in preparing the common hydrous oxide sols. This method was first used more than a century and a quarter ago by Gay-Lussac,[8, 9] who prepared what we now know to be colloidal alumina by hydrolysis of aluminum acetate. Later, Crum[8, 9] prepared an alumina sol, and Péan de St. Gilles[8, 9] a ferric oxide sol, by hydrolysis of the respective acetates in the hot, followed by boiling which removed the excess acetic acid. In general, the hydrolysis of a salt proceeds further at the boiling point than at room temperature because of the increased ionization of water at the higher temperature. Moreover, the degree of hydrolysis is greater if the resulting oxide is highly insoluble and the acid is weak. On this account acetates are better than halides and nitrates; but the latter salts may be used in certain cases. For example, ferric oxide sol is readily prepared by adding a concentrated solution of ferric chloride[8, 9] slowly to boiling water in accord with the following equation: $2FeCl_3 + (x + 3)H_2O \rightarrow Fe_2O_3 \cdot xH_2O + 6HCl$. The hydrolysis of dilute solutions is practically complete at the boiling temperature, but the process is partly reversed in the cold and the acid must be removed by dialysis. Ferric nitrate[8, 9] may be substituted for ferric chloride, but, in general, the percentage hydrolysis of the metallic halides and nitrates is so low, except in highly dilute solutions, that, before dialysis, it is necessary to add a base short of precipitation to the salt under consideration (see below). Sulfates cannot be substituted for acetates, nitrates, and halides since the multivalent anions coagulate the sol much more readily than the univalent anions. Sols may be obtained in certain cases by hydrolysis of non-electrolytes such as silicon sulfide,[9] ferric ethylate,[8, 9] and copper succinimide.[8, 9]

Hydrolysis methods have been used in the preparation of hydrous oxide sols of iron, chromium, aluminum, copper, lead, tin, zirconium, thorium, cerium, bismuth, and silicon.

Double decomposition in which the second product is a non-electrolyte. Since sols are coagulated by electrolytes above a certain concentration, it follows that the preparation of stable sols by double decomposition depends to a large extent on the second product of the reaction. If the reaction is chosen so that the second product is a non-electrolyte or a weakly dissociated electrolyte, the conditions will be favorable to sol formation. The classical example under this heading is the reaction between hydrogen sulfide and a solution of arsenious acid: $2H_3AsO_3 + 3H_2S \rightarrow As_2S_3 + 6H_2O$.[8, 9] The electrolyte concentration is quite low throughout the process, and the sulfide remains dispersed as negatively charged particles stabilized by the preferential adsorption of $S^=$ and HS^- ions. In this case, the conditions for the formation are so favorable that the sol can be made as concentrated as 3 g of As_2S_3 per 5 g of water.[8, 9] Similarly, a stable sol of mercuric sulfide is formed by the interaction of a saturated solution of mercuric cyanide and hydrogen sulfide since hydrocyanic acid, the second product of the reaction, is very weakly dissociated; copper glycocoll treated in a similar way yields a stable cupric sulfide sol.[8, 9]

Organosols of mercuric sulfide are obtained by conducting dry hydrogen sulfide into solutions of mercuric cyanide in methyl, ethyl, and *n*-propyl alcohol and in acetone.[15] Similarly, arsenic trisulfide sols in nitrobenzene and in acetoacetic ester [16] are formed by the action of dry hydrogen sulfide on solutions of arsenic trichloride in the organic solvents. The stability of these sols is probably due both to adsorption of the solvent and to low ionization of the second product of the reaction.

Double decomposition in which the second product is an electrolyte. Because of the coagulating action of electrolytes, a stable sol results when the second product of the double decomposition is an electrolyte, under one of the following conditions: (1) very high dilution or (2) presence in one of the electrolytes of an ion which is adsorbed very strongly by the dispersed particles. As an example of the first, sols of most of the metallic sulfides are obtained by the interaction of very dilute solutions of the respective chlorides and hydrogen sulfide.[17] The classical example of the second is the observation of Lottermoser [18] that, at sufficiently low concentrations, silver halide sols result from the interaction of silver nitrate and alkali halide provided that one or the other of the reactants is in slight excess. With the silver salt in excess, the particles are positively charged by reason of preferential adsorption of silver ion; with the halide in excess, the particles are negatively charged because of preferential adsorption of halide ion. This stabilizing effect of the adsorbed ions is greater than the coagulating action of alkali nitrate, the second product of the metathetical reaction.

Because of the relatively low precipitating power of salts of univalent ions such as ammonium chloride, it is possible to prepare most of the hydrous oxide sols by double decomposition reactions involving the use of hydrochloric acid or ammonium hydroxide. Thus colloidal silica, stannic oxide, and tungstic oxide may be formed by adding a suitable amount of hydrochloric acid to solutions of sodium silicate, stannate, and tungstate, respectively; and colloidal ferric oxide, chromic oxide, alumina, and stannic oxide may be prepared by adding suitable amounts of ammonium hydroxide to solutions of the respective chlorides. If sulfates are used instead of the halides, the amount of alkali which can be added before precipitation is much less because of the flocculating action of sulfate ions. Under favorable conditions, it is possible to add 50 to 75% of the theoretical amount of base to the chlorides before a permanent precipitate is formed. In making sols, it is common practice to mix the reacting solutions short of precipitation and to remove the salt impurities by dialysis either in the hot or the cold (p. 164).

Double decomposition in the presence of strongly adsorbed nonelectrolytes. The precipitation of oxides and salts is frequently prevented from going beyond the colloidal range and the dispersed phase is kept in the sol state by the addition of substances which are strongly adsorbed such as protecting colloids and sugar or glycerol. Thus concentrated stable sols of silver halides and Prussian blue are obtained by precipitation in the presence of gelatin.[19] Silver chromate, hydrous cupric oxide, and hydrous ferric oxide form stable sols in the presence of sugar.[20] Invert sugar holds up about seven times as much ferric oxide as cane sugar. Glycerol is effective in stabilizing ferric oxide sol and calcium phosphate sol, and most insoluble oxides and salts are held in the sol state by sodium protalbinate and lysalbinate.

As we have seen, barium sulfate thrown down from aqueous alcohol gives a gel which forms a sol on shaking with a larger quantity of water. Strong adsorption of alcohol doubtless prevents both coalescence and growth of the dispersed particles since a jelly precipitated from aqueous solution does not give a stable sol on shaking with water. Sodium chloride resulting from the interaction of sodium malonic ester and chloroacetic ester in dry benzene is stabilized in the sol state by strong adsorption of one or more of the organic reagents.[21]

The sols in concentrated electrolyte solutions constitute a special case under this heading. For example, colloidal sulfides and silver halides may be prepared by double decomposition in concentrated sulfuric acid or phosphoric acid.[22] The particles in such sols are without charge; the stability results from strong adsorption of the dispersion medium. It thus appears that a hydrophobic sol of a given charge has two stable zones and two unstable zones, depending on the electrolyte concentration. With little or no electrolyte such sols are unstable; with a small electrolyte concentration, they are stable; somewhat larger concentrations cause flocculation; and finally, very high concentrations again exert a stabilizing influence.

Replacement of solvent. In this general method of sol synthesis, a solution of the substance under consideration is poured into a liquid in which the solute is so insoluble that it appears as a highly dispersed phase. For example, sulfur and phosphorus hydrosols result on pouring alcoholic solutions of the respective elements into water. Similarly, a silver iodide sol is obtained by pouring into water a solution of the salt in potassium iodide. Inorganic sols prepared in this way are relatively instable; on the other hand, if an alcoholic solution of gum mastic is poured into water, a fairly stable sol is obtained.

Cooling of solution. If a solution of water in ether, chloroform, or xylene is cooled rapidly by liquid air or by carbon dioxide snow, the water crystallizes out as highly dispersed ice in an organic medium. The low temperature reduces the solubility of ice in water and thereby increases the percentage supersaturation, $(Q - L)/L$. It also reduces the diffusion coefficient (D, eq. 3), and increases the viscosity, which has the same effect as increasing the length of the diffusion path (S, eq. 3). Since this results in a greater number of nuclei and a slower rate of crystal growth, such ice organosols are quite stable at low temperatures.

CONDENSATION FROM VAPOR

Condensation in Vacuum

If the vapors of a metal are allowed to come in contact with the same metal in mass, the colliding molecules always adhere to it. On the other hand, if the surface with which the metal molecules collide is different, there is a critical temperature above which little or no condensation takes place. Thus, mercury vapor adheres to or is adsorbed by a glass surface without reflection if the glass surface is colder than −135°.

On account of the complete reflection of metallic vapors by a glass wall above the critical point, it is possible to obtain a high degree of supersaturation of metal vapors. Thus Wood[23] and Hamburger[24] heated a cadmium wire electrically in vacuum and obtained vapors of the metal which did not condense on a glass wall at ordinary temperatures. The wall was then touched with a plug of cotton, previously dipped in liquid air, with the result that rapid condensation of very small crystals took place at the point of cooling and continued on the surface film of the metal after the cooling stopped.

The condensation of vapors on a cold surface in vacuum has been applied by Roginsky and Schalnikov[25] to the preparation of several sols. The method consists essentially in the simultaneous condensation, in a special apparatus at the temperature of liquid air, of the vapors of an element and a medium which is liquid at ordinary temperatures. The resulting solid dispersion is then melted and mixed with excess liquid containing a small amount of protecting colloid. By suitable regulation of conditions, hydrosols were prepared of mercury, cadmium, sulfur, selenium, and phosphorus; and organosols of mercury, cadmium, sodium, potassium, rubidium, and cesium. The following organic liquids were used: benzene, hexane, xylene, toluene, ether, and ethyl alcohol. The method should be especially useful for the preparation or organosols in liquids which are decomposed by the electric arc, when the arc serves to vaporize the metals (see below).

Condensation in Gases

Vaporization without an electric arc. If the vapors of a boiling element are conducted into a liquid, condensation takes place sometimes with the formation of a stable sol. Thus mercury sols result on conducting a stream of vapors from the boiling element into cold water containing suitable stabilizing electrolytes such as ammonium salts or citrates.[26] The sols are richer in the more highly dispersed particles the colder the water into which the vapor is carried. Sulfur and selenium sols may be prepared by a similar procedure.

The vaporization and sol formation may be accomplished by passing a current of high density through a metal wire submerged in a liquid. The solid is vaporized in part by the Joule heat but largely by an arcing between portions of the wire as it melts and breaks apart. This procedure should therefore be classified as an arc-vaporization method.

Vaporization in the direct-current arc: Bredig's method. The formation of a sol by passing an arc between electrodes under water is usually classified as a dispersion rather than a condensation process of sol formation. Svedberg[8] points out, however, that the action of the arc consists essentially in the formation of metal gas which subsequently condenses into particles of colloidal dimensions. From this point of view, the electrical disintegration method is essentially a condensation process. It should be emphasized, however, that the phenomenon is probably not always just a simple vaporization and condensation. Thus, with a strong oscillatory discharge, Benedicks[27] observed small craters in the electrodes which he attributed to the action of the liquid on the molten metal, the vaporization of the liquid hurling the metal out of the crater in the form of minute granules. The arcing process in certain cases is admittedly complex, yet it seems probable, as Svedberg contends, that the most important function of the arc, in the actual procedures employed, is to vaporize the metal which subsequently condenses to a sol.

Bredig[28] was the first to use the direct-current arc under water for the preparation of metal hydrosols, and the process is frequently referred to as the Bredig method. Two thick wires of the metal under consideration are placed in cold water or preferably in very dilute alkali or acid, and an electric arc is struck between them. A current of 5–10 amperes at 30–110 volts is satisfactory. The arrangement for preparing sols by this method is shown diagrammatically in Fig. 37. Bredig obtained hydrosols of silver, gold, platinum, palladium, and iridium. Mercury hydrosols can be obtained in this way also, by using as one electrode a jet of mercury and as the other a pool of the element into which the jet falls through the water.[28] Beans and Young [29] have devised a very satisfactory arcing device which provides for stirring, cooling, and semi-automatic arcing in one adjustable compact apparatus.

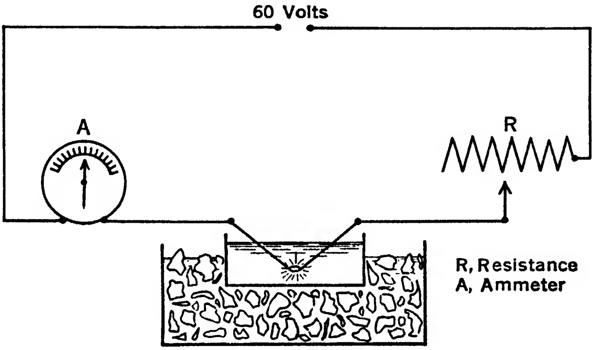

FIG. 37. Bredig's arrangement for preparing sols by electrical pulverization.

The Bredig method is unsatisfactory for the preparation of sols in organic media [30] because of the decomposition of the liquid by the arc. This is best avoided by the use of an oscillating arc.

Vaporization in the oscillating arc: Svedberg's method.[8] The most satisfactory procedure for the vaporization of metals in the preparation of sols was worked out by Svedberg. He employed an alternating-current arc of high frequency, a so-called oscillatory current with a period of 10^{-7} to 10^{-4} second. Two forms of arc were used: the damped oscillatory arc produced by a Leyden jar circuit (Fig. 38) and an undamped oscillatory arc (wave current) obtained by connecting the oscillatory arc to a direct-current potential of 400–500 volts (Fig. 39).

Using a damped oscillatory arc, Svedberg prepared sols of almost all the metals, including the alkali metals, in a variety of dispersion media such as water; methyl, ethyl, propyl, butyl, and amyl alcohols; ethyl ether; acetone; chloroform; and liquid methane. In marked contrast to the action of the direct-current arc, sol formation in the oscillatory arc was accompanied by little or no decomposition of the medium. It was found that the conditions for sol formation were most favorable and the decomposition of the organic medium least when the capacity was chosen as high as possible and the length of spark, the self-induction, and the resistance as small as possible.

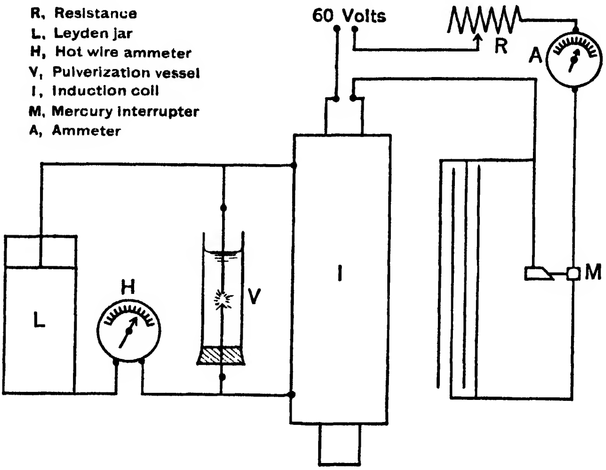

FIG. 38. Svedberg's arrangement for the electrical pulverization of metals with a damped oscillating arc.

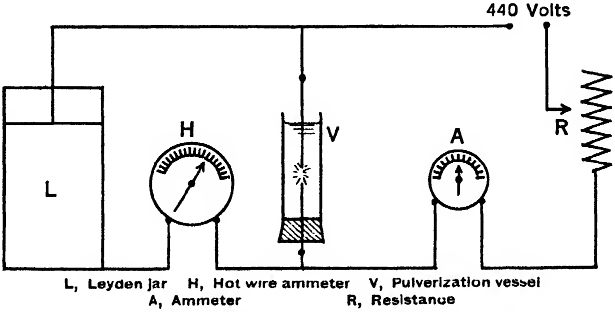

FIG. 39. Svedberg's arrangement for the electrical pulverization of metals with an undamped oscillating arc.

As already indicated, two different processes apparently are taking place in the oscillating arc: vaporization and subsequent condensation of metal, and a real dispersion of molten metal. The particles formed by dispersion of molten metal are much larger than those formed by condensation of vapor. Thus Börjeson, in Svedberg's laboratory, showed that the radius of cadmium particles formed by real dispersion in ethyl alcohol ranged from 0.5 to 25 μ, whereas the mean value of the radius of the condensation product was about 5 $m\mu$; the larger particles of the former settled out on standing.

The damped oscillatory arc has the advantage over the undamped arc in giving more colloidal metal per unit of current and less decomposition of the dispersion medium per unit of dispersed metal.

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CHAPTER 10

Formation of Sols II: Dispersion Methods

Dispersion methods of sol formation consist of the disintegration of materials in mass into particles of colloidal dimensions. This was called peptonization by Graham[1] from analogy with the action of pepsin on proteids in the digestive process; but in colloid chemistry the disintegration process of sol formation is now termed *peptization*. The following general procedures will be taken up in order: addition of peptizing agent, removal of an agglomerating agent, mechanical disintegration, electrochemical disintegration, and partial solution.

Addition of Peptizing Agent

Theory of peptization. A theory of peptization has been outlined by Bancroft.[2] The peptizing action of a solution on a solid material is due to adsorption. If the adsorbed film has a low surface tension on the liquid (water) side and a high value on the opposite side, the film will scrunch up and tend to peptize the solid as the internal phase; if the reverse is true, the solid tends to become the external phase; and if the surface tensions on both sides of the film are the same, neither effect predominates. If Freundlich's view is accepted that adsorption always lowers the surface tension, it follows that an adsorbed substance will tend to peptize the adsorbent. Actual peptization by adsorption will result only when the work required to disintegrate the adsorbent is accomplished by lowering of the surface tension. In practice, solid bodies that are disintegrated by an adsorbed peptizing agent consist for the most part of agglomerates of primary particles of colloidal dimensions. To the extent that this is true, peptization involves the disintegration of colloidal aggregates. This may be accomplished by a liquid, by a non-electrolyte or salt, by an adsorbed ion, or by a peptized colloid.

Peptization by single solvents. Water is adsorbed by such substances as tannin, agar, and gelatin, and these substances are peptized readily in water (cf. Chapter 18). Similarly, cellulose nitrate (pyroxylin) is peptized by amyl acetate, and glycogen and zein by liquid ammonia.[3] The peptizing action is, in general, increased by rising temperature, so that, at higher temperatures, some glasses are peptized by water, and vulcanized rubber is peptized by organic liquids. On the other hand, alcohol peptizes pyroxylin at low temperatures but not at room temperature; and liquid ammonia peptizes glycogen and zein at −33.5° but not at room temperatures. In these cases Bancroft[4] suggests that the polymerized form of the liquids is the peptizing agent. In the event that the amount of a pure substance peptized under a given set of conditions is fairly constant, it might look as though true solution were taking place. This accounts for existing tables of "solubility" data for such systems as tannin in water.

Whitby[5] points out that cellulose nitrate and acetate are polar compounds which swell in and are peptized by polar organic substances such as the lower ketones, esters, fatty acids, and aldehydes; diesters of dicarboxylic acids; aromatic nitro compounds; and primary aromatic amines. Increasing the length of the hydrocarbon chains diminishes the polarity of the molecules and therefore cuts down their swelling power and peptizing action on the cellulose esters.

In contrast to the behavior of polar solvents toward cellulose nitrate, Whitby[5] points out that rubber, a hydrocarbon, is non-polar and, in general, is peptized best by non-polar liquids. Increasing the length of a hydrocarbon chain cuts down the polarity of a solvent and increases its peptizing power for rubber. To illustrate, the following solvents are good peptizing agents for rubber but not for the cellulose esters: aliphatic, aromatic, and terpenic hydrocarbons; higher fatty acids and esters; secondary and tertiary amines.

Peptization by mixed solvents. Mixed solvents sometimes peptize a solid much better than either solvent taken separately. The classical example is the peptization of cellulose nitrates and acetates by a mixture of ether and ethyl alcohol at ordinary temperature where neither solvent is effective by itself; the taking up of casein in pyridine and water, and of cinchonine in chloroform and alcohol, illustrates the same phenomenon. Bancroft accounts for the behavior of mixed solvents by assuming that the presence of one liquid displaces the degree of polymerization of the other, thereby furnishing an effective peptizing agent. In this connection, Centnerszwer[6] showed that ether causes marked polymerization of methyl alcohol. If ether polymerizes ethyl alcohol also, and if the polymerized form is a good peptizing agent for pyroxylin, the action of the mixed solvents is accounted for.

Highfield[7] uses Whitby's concept to explain the superior peptizing action on pyroxylin of a mixture of ether and ethyl alcohol. According to Highfield, the best peptizing agent for cellulose nitrate contains both polar and non-polar groups, the effectiveness of the polar radicals resulting from their similarity to the OH and ONO groups in the ester, and the effectiveness of the non-polar groups following from their similarity to the hydrocarbon group in the ester. From this point of view, a suitable mixture of ether and ethyl alcohol is a better peptizing agent for pyroxylin than either solvent alone, since the mixture gives a satisfactory balance between the two classes of groups. Highfield's hypothesis is suggestive, but it will not account for the peptization of pyroxylin by ethyl alcohol alone at low temperatures or for the failure of a mixture of benzene and ethyl alcohol to peptize pyroxylin.[4]

Peptization by non-electrolytes. Direct peptization by a dissolved non-electrolyte is seldom encountered, but non-electrolytes may prevent the agglomeration of a precipitate. Examples have already been given of the effect of sugars and glycerol on the stability of certain sols (p. 146).

Undissociated electrolytes may exert a peptizing action similar to that of non-electrolytes. For example, the degree of peptization of clay by ammonia appears to be out of all proportion to the concentration of hydroxyl ion, and the peptization of alumina[5] and casein by acetic acid appears to be due in part to the undissociated acid.

Peptization by ions. Peptization by adsorbed ions constitutes one of the commonest methods for preparing sols of the hydrous oxides and salts. In actual practice, the method consists essentially of the following steps: (1) throwing down the precipitate under such conditions that it is an agglomerate of colloidally dispersed particles; (2) washing, preferably by the aid of the centrifuge, until peptization starts; (3) adding an electrolyte which peptizes the mass, giving a sol in which the particles are positively or negatively charged as a result of stronger adsorption of one ion than of the other; and (4) dialyzing to remove excess electrolyte.

Most hydrous oxide sols are peptized by their chlorides, nitrates, and acetates or by the corresponding acids, to give positively charged sols as a result of preferential adsorption of the common cation or of hydrogen ion. Peptization is accomplished less readily by sulfates and other salts with multivalent anions, since the coagulating action of strongly adsorbed anions opposes the peptizing effect of the adsorbed cations. The basic oxides are usually positively charged in the sol state, but negative sols may result in the presence of a suitable excess of alkali, as a result of preferential adsorption of hydroxyl ion. For example, hydrous chromic oxide is peptized by a suitable excess of caustic soda, and little or no chromite is present in the resulting negative sol.[9] The more acidic oxides, like silica or stannic oxide, are peptized by low concentrations of hydroxyl ion.

Precipitated sulfides are peptized by hydrogen sulfide as a result of strong adsorption of SH^- and $S^=$ anions. The particles in silver halide sols may be positively charged by preferential adsorption of the common silver ion from silver nitrate, or negatively charged by preferential adsorption of iodide, bromide, or chloride (cf. p. 145).

Peptization by peptized colloid. The protecting colloids such as gelatin, gum arabic, soap, and saponin not only will prevent agglomeration of sols formed by precipitation methods (p. 146) but also are quite effective peptizing agents in disintegrating agglomerated gels. Inorganic sols may likewise act as peptizing agents. For example, hydrous chromic oxide peptized by sodium hydroxide will prevent the precipitation of considerable ferric oxide; but, if too much ferric oxide is present relative to the chromic oxide, complete precipitation of both oxides takes place.[9] Aniline dyes insoluble in benzene may be peptized by the so-called magnesium and zinc resinates which are peptized by benzene.

Removal of Agglomerating Agent

If the conditions of precipitation are favorable for the formation of particles of colloidal dimensions (p. 136), the system passes through the sol state as an intermediate stage in the precipitation process. The agglomeration of the colloidal particles is due to the presence of electrolytes in the solution. Thorough washing of the precipitated mass to remove the excess of agglomerating electrolyte will result in peptization provided that coalescence and growth of the primary particles have not gone too far. For example, a sol of hydrous ferric oxide is obtained by treating ferric chloride solution with sufficient ammonia to cause precipitation, followed by washing the freshly formed gel by decantation preferably with the aid of the centrifuge. Quite pure, stable sols result by continuing the washing with a supercentrifuge (Chapter 13); in this way Bradfield[10] prepared a cherry-red ferric oxide sol containing 1 equivalent of chlorine to 400 of ferric iron. Peptization by washing is more readily accomplished if the gel is thrown down from chloride than from sulfate solution, since the more strongly adsorbed sulfate is more difficult to wash out. Most freshly precipitated hydrous oxide gels are peptized to a certain extent by washing.

The analytical chemist frequently encounters precipitates that run through the filter paper on washing. Thus zinc sulfide thrown down from chloride solution with ammonium sulfide is peptized in part by washing out the ammonium salt. It is common practice in analytical chemistry to wash certain precipitates with ammonium chloride solution to prevent peptization. Copper ferrocyanide gel thrown down from alkali ferrocyanide solution with a small excess of copper salt is peptized if the adsorbed copper salt is removed by washing.[11] By using hydroferrocyanic acid and cupric acetate to form the gel and washing by the aid of the centrifuge, a sol of almost any desired purity may be prepared.[12] Silver halides, precipitated rapidly in the cold and washed at once by decantation, undergo partial repeptization to the sol state.

Mechanical Disintegration

The formation of sols by mechanical grinding can be accomplished in certain instances. Thus Wegelin[13] prepared sols of silicon and antimony and of the oxides of tungsten, titanium, molybdenum, and vanadium by grinding in an agate mortar; but he had no success with such substances as copper, graphite, sulfur, calcium fluoride, and ferric oxide. The Greeks made metallic inks by grinding with honey, and carbon inks by grinding with gum. Graphite sol is obtained by masticating with tannin and water followed by dilution with water containing a small amount of ammonia.[14] The resulting sol is called "aquadag," the "dag" portion of the word being composed from the first letters of "deflocculated Acheson graphite." The lubricant "oildag" is prepared from aquadag by mixing the moist, well-masticated paste of graphite, tannin, and water with a light mineral oil, agitating the mixture thoroughly, and finally evaporating off the water.

When sols cannot be made simply by grinding, it is usually assumed that this process alone will not yield sufficiently small particles. This is not necessarily true since very minute primary particles may coalesce at certain points, giving aggregates that have the outward appearance of single coarse particles. As an aid to the mechanical dispersion and to prevent coalescence, von Weimarn[15] suggested grinding the dry solid to be dispersed with an indifferent solid which will dissolve on mixing with the dispersion medium. This principle was first applied by Pihlblad,[16] who obtained aniline blue and sulfur hydrosols of varying degrees of dispersity by grinding varying ratios of the solids to be dispersed with urea, and shaking the resulting mixture with water. In a similar way sols of indigo, sepia, sulfur, silver, mercury, gold, etc., have been obtained with glucose or lactose[17] as the neutral diluting agent.

So-called "colloid mills" have been devised for grinding materials on an industrial scale. The original apparatus designed by Plauson[18] consisted of lugs on a beater drum revolving at high speed, which passed through grooves in a stationary baffle where the suspended material was broken up mechanically. This type of mill has been superseded by equipment which employs smooth grinding surfaces with or without grooves.[19] A smooth cylinder may revolve in a slightly tapered stator; a truncated cone, smooth or grooved, may move close to a smooth or grooved conical stator; or smooth disks, a small distance apart, may revolve in opposite directions. The term "colloid mill" as applied to this equipment is a misnomer since, as a rule, the apparatus does not disintegrate hard material into particles of colloidal dimensions. But, since the disintegration by such mills is greater than is usually obtained by other grinding methods, the mills are useful commercially for the peptization of soft solids and, especially, for the breaking up of secondary aggregates and for the formation of emulsions (Chapter 21). To illustrate,[20] the pigment zinc oxide consists of agglomerates of very fine particles which the paint manufacturer must break up thoroughly and suspend uniformly in the vehicle. This is accomplished to advantage in a colloid mill which disintegrates the aggregates and brings the vehicle into intimate contact with the individual particles, from which the adsorbed air film is removed as a result of strong adsorption of the vehicle.

Since the solubility increases with decreasing particle size (p. 10), sufficient grinding of a solid may cause it to dissolve and precipitate in another form. Thus quartz is converted into colloidal hydrous silica by suspending the very finely ground substance in water and boiling.[21]

Electrochemical Disintegration

If a caustic soda solution is electrolyzed with a lead cathode, the metal disintegrates when the current density exceeds a critical value, and the solution is colored black by minute particles of metallic lead. Similar results can be obtained with cathodes of arsenic, antimony, bismuth, thallium, and tin.[20] The disintegration of the cathode is due to the formation of an alloy of the metal and sodium which is promptly destroyed in contact with water. It is probable that the disintegration of electrodes with an alternating current of high current density results from the formation of a hydrogen or metallic alloy which subsequently breaks down, leaving the electrode material in a highly dispersed state.[20]

Partial Solution

Berzelius[20] obtained tellurium in what is now recognized as a hydrosol by passing oxygen through a solution of potassium telluride. The first stage in the process consists in the precipitation of relatively coarse particles of tellurium in accord with the reaction: $2K_2Te + O_2 + 2H_2O \rightarrow 2Te + 4KOH$. In the second stage, the tellurium particles are partly dissolved with the formation of K_2TeO_3, thus: $Te + 2KOH + O_2 \rightarrow K_2TeO_3 + H_2O$; the particles are thereby reduced to colloidal dimensions, and a hydrosol results.[20]

A similar behavior was observed by von Weimarn[21] with the element sulfur. An alcoholic solution of the element was cooled in liquid air with the formation of a clear, very highly dispersed alcosol. On warming slowly, the dispersity decreased, owing partly to agglomeration of the primary particles and partly to solution of smaller particles and reprecipitation on larger ones. This manifested itself in a slight blue opalescence which gradually became stronger and more whitish. As the temperature rose still more, the dispersity increased, owing to re-solution of the particles, and the blue opalescence characteristic of the highly dispersed sol appeared once more. Ultimately the opalescence vanished as the particles dissolved completely.

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CHAPTER 11

Purification of Sols: Permeability of Membranes; Dialysis; Ultrafiltration

The methods of procedure employed in the formation of most sols give preparations which contain more or less electrolyte. Since membranes such as parchment paper, Cellophane, nitrocellulose, cellulose acetate, animal gut, and fish bladder are more permeable to ions in solution than to colloidally dispersed particles, it is possible to purify sols from soluble impurities by preferential diffusion through membranes. This process was termed *dialysis* by Thomas Graham in 1860 (p. 1). Although the process was known earlier by Dutrochet, Liebig, L'Hermite, Fick, Nägeli, and others, the classical application of the experimental technique of dialysis by Graham marks the beginning of colloid chemistry.

The use of a dialyzing membrane for the filtration of colloidal dispersions was called ultrafiltration by Bechhold. Before the experimental techniques of dialysis and ultrafiltration are taken up, brief consideration will be given to the general problem of the permeability of membranes.

PERMEABILITY OF MEMBRANES

Semipermeable Membrane

A membrane is said to be semipermeable when it permits one constituent of a solution—usually water—to pass through and does not allow diffusion of the other constituents or one or more of the other constituents. The plasma membranes of cells are natural membranes of this kind. Traube[1] was the first to recognize a similar permeability in certain gelatinous precipitates, the so-called precipitation membranes of which copper ferrocyanide is the most familiar example. Such a membrane is obtained by holding a solution of copper sulfate in a glass tube which is subsequently immersed in a solution of potassium ferrocyanide. The film of copper ferrocyanide formed at the junction of the two solutions will allow water to pass through but not dissolved substances such as sugar and certain salts. Supported membranes of this kind precipitated in a porous cup have been used in osmotic-pressure studies with sugar solutions. They have withstood pressures as high as 130 atmospheres and have proved to be nearly ideal as regards semipermeability.

Membranes such as parchment and collodion are, as a rule, not semipermeable, since dissolved molecules will pass through them more or less readily.

Theories of Semipermeability [2]

The sieve theory. To account for the action of semipermeable membranes, Traube conceived of them as atomic or molecular sieves through which progressively larger molecules diffused with increasing difficulty. Thus copper ferrocyanide membrane was believed to have pores large enough to allow the small molecules of water to go through, but too small to allow the larger molecules of sugar to pass. From this point of view, the only difference between a copper ferrocyanide membrane and a parchment membrane which stops colloidal particles but not dissolved molecules is in the size of the pores. Comparative tests on a number of semipermeable membranes with various diffusing substances showed, however, that the sieve theory is inadequate.[3] Thus, a membrane quite impermeable to most substances was found to be more permeable to some than another membrane which, in general, possesses high permeability. Moreover, the impermeability of a membrane such as rubber to water and its permeability to the much larger molecules of benzene and pyridine cannot be accounted for on the sieve theory.

The solution theory. This theory of semipermeability postulates that a membrane is permeable to substances that dissolve in it and impermeable to those that do not. This view was anticipated by Liebig[4] in 1848 and given experimental foundation by L'Hermite[5] in 1855. The latter covered a layer of water with a thin layer of castor oil on which was placed a layer of alcohol; the alcohol passed through the oil to the water. Observations with a number of similar combinations led L'Hermite to conclude that substances which pass through membranes first dissolve in them. This mechanism explains the behavior of many systems. For example, Kahlenberg[6] found that benzene, toluene, and pyridine, which are soluble in rubber, diffuse through rubber; whereas water, which is insoluble in rubber, does not pass through. Moreover, trichloroacetic acid passes through a rubber membrane when dissolved in benzene but only very slowly when dissolved in water.

Although solution in the membrane may be a necessary and sufficient criterion for semipermeability in certain systems, Bigelow[7] and Bartell[7] demonstrated conclusively that osmotic effects can be obtained with inert materials where neither solution nor chemical reaction can take place. Thus porous cups served as semipermeable membranes when the pores were sufficiently fine or when they were clogged to a certain extent with such substances as barium sulfate, lead chromate, or lead sulfate. Moreover, finely divided materials such as silica, carbon, and metallic copper, silver, and gold acted as semipermeable membranes when compressed into disks containing very fine pores. The limits of the pore diameters between which osmosis can take place are not definitely known, but they undoubtedly vary from substance to substance. Bartell found the upper limit to be around 0.9 μ with unglazed porcelain clogged with various materials. This is, of course, much too large to represent the dimensions of molecular interstices which Traube believed to be essential for semipermeability in membranes.

The adsorption theory. The osmotic phenomena observed with a distinctly porous, inert membrane, such as a clogged porous plate, are doubtless the result of negative adsorption as suggested by Mathieu[8] and Nathansohn[9] and emphasized by Tinker[10] and Bancroft.[11] If a solid adsorbent takes up relatively more of a solvent than of the dissolved substance, we have negative adsorption, and the solution becomes more concentrated (p. 97). Mathieu observed this phenomenon with a number of solutions, using porous plates, membranes, or capillary tubes as adsorbents. With normal solutions, the concentration in certain capillary tubes was found to be as low as one-tenth normal. The difference in concentration increases with decreasing radius of the capillary tubes, and Mathieu concluded that, with sufficiently fine capillaries, water alone would be adsorbed. The importance of this for the theory of semipermeable membranes was recognized especially by Bancroft and by Tinker, who gave experimental support to the theory by showing that sugar was negatively adsorbed by copper ferrocyanide. Copper ferricyanide, which is impermeable to sugar, likewise adsorbs sugar negatively.[12]

Distinction between an ultrafilter and a semipermeable membrane.[11] From the above considerations, it would appear that a semipermeable membrane is a continuous film in which the solvent will dissolve but not the solute, or a finely porous septum which exhibits such marked negative adsorption that the pore walls are covered with a film of pure solvent that fills the pores. Accordingly, a true semipermeable membrane acts like a solvent and not like a sieve, irrespective of whether it is a more or less continuous septum like rubber or castor oil or a porous one like a clogged porous plate or copper ferrocyanide.

An ultrafilter membrane is a sieve or filter with fine pores. The essential difference between a true ultrafilter membrane and a porous semipermeable membrane is that the former shows no negative adsorption at all or so little negative adsorption that it acts like a sieve and not like a solvent.

In distinguishing between a semipermeable membrane and an ultrafilter membrane, it should be emphasized that pore size is quite as important for a porous semipermeable membrane which functions by an adsorption mechanism as it is for the true ultrafilter membrane which functions as a sieve without the intervention of adsorption phenomena. For example, when a solute fails to pass a membrane because of negative adsorption, the pores must be sufficiently small so that the adsorbed film of solvent fills them; otherwise the solute may pass through the center of the pores. In other words, a membrane of a given composition may be impermeable to a solute because of negative adsorption if the pores are small enough, and may be permeable to the same solute, in spite of negative adsorption, if the pores are too large.

DIALYSIS

Dialysis without Electrolysis

Dialyzing membranes are porous diaphragms which act like a sieve, allowing the passage of substances in molecular solution but holding back colloidally dispersed particles. For example, glucose, sucrose, urea, and sodium chloride pass through the capillaries of parchment paper by a simple diffusion process; on the other hand, with acids and bases, the process is complicated by adsorption or other forces arising within the membrane.[13] Since most membranes are lyophilic, the sieve action may be modified to a certain extent by adsorption of solvent within the pores.

The dialyzing apparatus described by Graham consists essentially of a wide cylindrical tube closed with parchment paper, which is filled with the sol to be dialyzed and immersed in a larger vessel containing the *dialysate,* distilled water in the case of hydrosols. The diffusible material in the sol passes through the membrane into the water which is changed at intervals.

Graham employed parchment as a dialyzing septum, but animal membranes, nitrocellulose, and Cellophane may be employed to greater advantage under certain conditions. The dialysis is more rapid and thorough when the surface of the diaphragm is as large as possible compared to the volume of the sol. This has led to the use of tubing of parchment paper or regenerated cellulose ("Visking" sausage casings). The sol is placed in the tubing and submerged in water, or the sol is placed in a beaker or flask and water is run through the tubing. This procedure enables the sol to be stirred regularly, but it has the disadvantage that the sol may be diluted by a high rate of osmosis from water into the impure sol. To minimize the dilution, the sol may be placed in a bag of Cellophane or collodion tied to a tube; dilution of the sol by osmosis is opposed by hydrostatic pressure as the liquid rises in the tube—*pressure dialysis*.

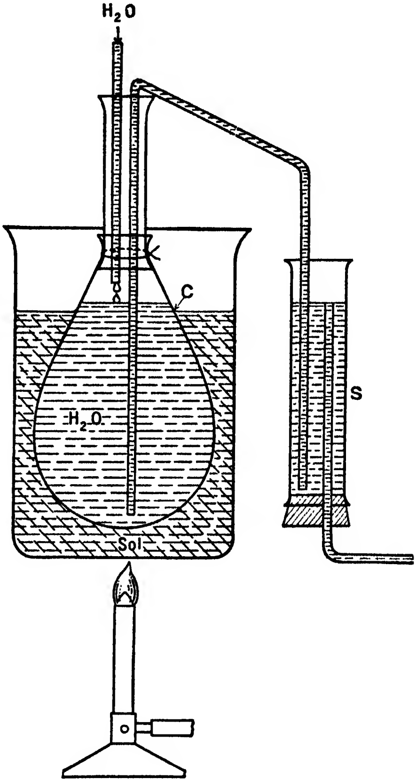


Fig. 40. Neidle's dialyzing apparatus for continuous change of the dialysate.

Nitrocellulose bags or thimbles are prepared by flowing a film of collodion on the inside of glass vessels, allowing most of the solvent to evaporate, and adding water to the flask. After standing a few minutes, the bag may be released from the empty mold by flowing water between the membrane and the glass.[14] Cellophane containers are made by folding a circular sheet in the form of a bag which is tied securely to the end of a glass tube (see Fig. 40). The pores in present-day Cellophane are so fine that it is unsuitable for a dialyzing membrane. This may be remedied by swelling the commercial product in 63–65% zinc chloride solution as described by McBain and Stuewer.[15]

Since the speed of dialysis is greater the larger the difference in concentration of the diffusible material on the two sides of the septum, it is advantageous to change the dialysate continuously. A convenient apparatus described by Neidle[16] is shown diagrammatically in Fig. 40. It is essentially a bag of parchment paper or Cellophane *C* partly filled with water and suspended in a flask or beaker containing the sol to be dialyzed. Distilled water is run at a fairly constant rate into the bag which is maintained a little more than half full by means of an automatic syphon *S*. It is sometimes advantageous to place the sol in the bag with water on the outside. If the sol is stable when heated, the rate of dialysis may be increased enormously by raising the temperature. Thus a purer chromic oxide sol was obtained by 10 hours' dialysis in a Neidle apparatus at the boiling temperature than resulted from 73 days' dialysis at room temperature.

Unfortunately, many sols cannot be dialyzed in the hot, but the rate of dialysis may be augmented by moving the liquids, the membrane, or both. Thus Thoms[17] placed the liquid to be dialyzed and the external liquid in hemispherical glass vessels clamped together at ground edges between which the membrane was held; stirring was accomplished in a rotating machine. A more complicated device, which appears to be quite efficient, is described by Gutbier, Huber, and Schieber.[18] In this apparatus the dialysate is changed continuously while the sol is stirred by a mechanical stirrer, and the membrane is rotated.

Electrodialysis

The rate of removal of soluble impurities from sols is accelerated by the aid of an electric current. The process is called *electrodialysis* and the apparatus an *electrodialyzer*. The diagram of an apparatus used extensively by Bradfield[19] in the purification of clay sols is shown in Fig. 41. Simpler modifications are described by Bartell[20] and by Holmes.[21] The sol is contained in the inner compartment of a three-compartment vessel enclosed between diaphragm walls *D* which prevent the passage of colloidal particles. Electrodes are placed in the water contained in the two outer compartments, and sufficient potential is applied so that not more than 0.5 ampere of current flows. Non-electrolytes are forced through the membrane by electro-osmosis and ions by electrolysis. If necessary, water is allowed to flow at the proper rate into the sol and also the electrode compartments.

This general technique is widely used for the rapid purification of simple inorganic and clay sols and is almost universally employed in the purification of lyophilic colloids such as the proteins, agar, and mastic.

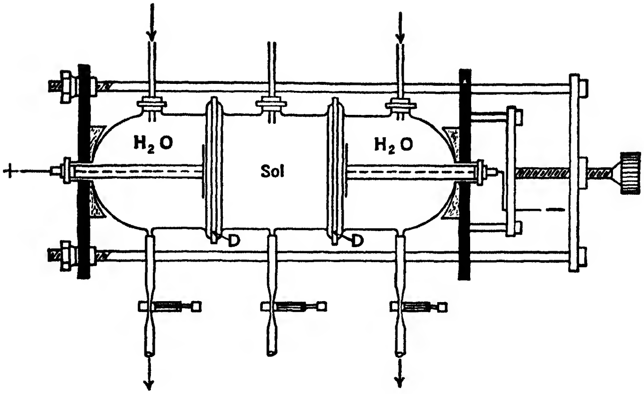


FIG. 41. Bradfield's apparatus for electrodialysis.

Electrodecantation

A simplified vertical type of electrodialyzer with membranes at M_1 and M_2 is shown diagrammatically in Fig. 42.[22] If a negative sol such as arsenic trisulfide or silver iodide is electrodialyzed in such an apparatus with the anode at the bottom, the negatively charged particles concentrate in the region of the anode membrane, and the clear solution collects around the cathode membrane. The solution may be removed by decantation and replaced with pure water. This process was named *electrodecantation* by Pauli.[23] By repeating the process a number of times, concentrated sols of a high degree of purity may be prepared.

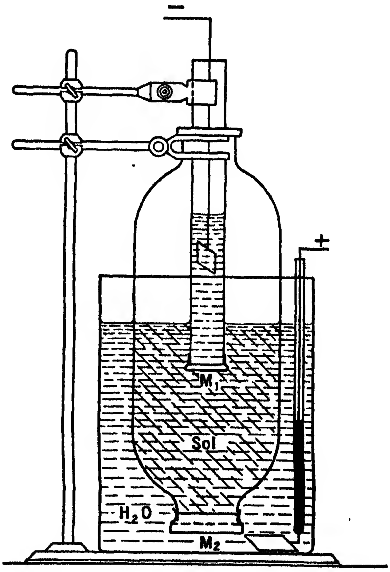


FIG. 42. Apparatus for purification of sols by electrodecantation.

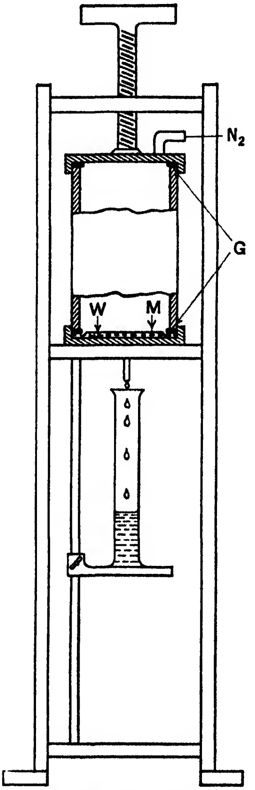
ULTRAFILTRATION

Various devices have been used [24] for filtration through ultrafilter membranes. In the sack ultrafilter, the sol is placed in a dialyzing membrane which is allowed to hang free, the solvent and permeable solute running through slowly. In the suction ultrafilter,[25] the membrane is held in a modified type of Büchner funnel through which the solution is drawn into a suction flask. In the pressure ultrafilter, originated by Bechhold,[26] the solution is forced through the filtration membrane by pressure that may be as high as 10–20 atmospheres.

In practice, pressure ultrafilters are the most important. A simple type manufactured by the Baroid Company is illustrated in Fig. 43. Pressure is applied by connecting with a cylinder of compressed nitrogen. A small apparatus for the ultrafiltration of biological fluids has been described by Nicholas.[27]

The membranes used by Bechhold consisted of filter paper or cloth impregnated with nitrocellulose or with gelatin hardened by formaldehyde. Membranes of graded pore size are usually made of nitrocellulose. The permeability of such membranes has been found to depend on: (1) the nature and concentration of the nitrocellulose; (2) the nature of the peptizing agent; (3) for mixed peptizing agent such as alcohol and ether, the relative proportions of each component; (4) the presence of non-solvent agents such as glycerol and ethylene glycol; (5) the time of drying; and (6) the amount of swelling of the film.

Bechhold obtained a graded series of membranes by impregnating filter paper with glacial acetic acid collodions of varying strengths. Details have been worked out for preparing films of graded porosity by varying the ratio of alcohol to ether.[28] The most impermeable membranes are made from collodions containing the smallest proportion of alcohol.



M, membrane; W, wire gauze; G, rubber gaskets

FIG. 43. Pressure ultrafilter.

Collodion exhibits such little negative adsorption, relatively, that as a rule it does not show the properties of a semipermeable membrane. On the other hand, dried collodion membranes with very small pores may not be true molecular sieve membranes or ultrafilters, as is generally assumed. Thus Grollman [29] found that the sievelike action of collodion is influenced by a layer of adsorbed liquid on the pore walls.

The sign of the charge on a membrane will modify its properties. Thus, positively charged dyes will not pass negatively charged Berkefield and Chamberlain porcelain filters, whereas negatively charged dyes will go through.[30] The reason is that the positively charged dyes coagulate on the negatively charged wall of the siliceous filtering material, clogging the pores. For reference to Donnan equilibrium effects in the ultrafiltration of sols, see Chapter 15.

Ultrafiltration membranes have been prepared by electroplating a film of nickel or phosphor bronze on nickel gauze[31] until very fine pores remain. Such membranes may be used at high temperatures and with solvents that will attack the usual membranes.

Electroultrafiltration. Electrodialysis may be employed as an aid to ultrafiltration. The design shown diagrammatically in Fig. 44 was used by Bechhold and Rosenberg.[32] The anions of the contaminating electrolytes migrate into the collodion bag containing the anode, and the cations go through the ultrafilter membrane, under which is the cathode, and are washed away by the water passing through the membrane. The process is hastened by electro-osmosis (p. 242) which forces water through the negatively charged membrane.

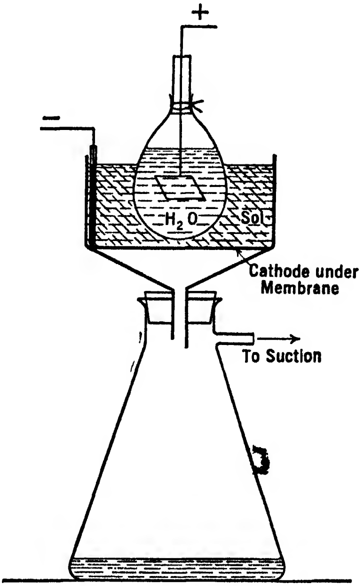


FIG. 44. Electroultrafilter.

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CHAPTER 12

The Optical Properties of Sols

THE TYNDALL PHENOMENON

The presence of small particles suspended in a transparent medium may be shown by projecting a beam of light through the system, provided that the index of refraction of the particles differs from that of the transparent medium. Particles that are large compared with the wave length of light reflect and refract the incident light in the regular way, whereas particles of colloidal dimensions scatter and polarize the incident light to a certain extent. A familiar example of this behavior is observed when a beam of sunlight is admitted through a small hole into a darkened room; the presence of minute particles of dust suspended in the air is revealed as bright, flashing points or motes. Similarly, a strong beam of light passing through a sol appears as a clearly defined cone of illuminated particles. The scattering and polarizing of light by small suspended particles were investigated extensively by Tyndall;[1] hence the behavior has come to be called the *Tyndall phenomenon,* and the path of the illuminated suspended particles as the *Tyndall cone* or *Tyndall beam.*

The phenomenon of light scattering by colloidal dispersions was recognized by Faraday[2] in 1857. He projected a beam of sunlight through a gold sol by means of a lens and reported that "the illumination of the particles within the cone shows their presence as undissolved bodies." Faraday's method of determining whether the particles in a system are molecularly or colloidally dispersed was used almost exclusively for about 50 years until the ultramicroscope and ultrafilter were invented, and it is still employed for making qualitative observations.

Colloidal systems show wide variations in the intensity of the Tyndall cone which they give. In general, the cone is more intense the greater the difference between the index of refraction of the dispersed and dispersing phases. If the index of refraction of the two phases is almost the same, the Tyndall cone will be very faint or entirely absent. For this reason lyophobic sols, especially those of the elements and salts, give much clearer cones than lyophilic systems. In the latter, the similarity in refractive index between the two phases is accentuated by the fact that the solid phase is highly solvated, that is, a part of the liquid medium is closely associated with the solid phase (Chapter 18).

APPLICATIONS OF THE TYNDALL PHENOMENON

The Ultramicroscope

Limit of resolution of objectives. The limit of resolution ϵ of a microscope objective is given by the equation:

$$\epsilon = \frac{\lambda}{2n \sin \alpha} = \frac{\lambda}{2\,\text{N.A.}}$$

in which ϵ is the distance apart which two points must be in order to be distinguished as two points; λ, the wave length of the light employed; n, the refractive index of the medium between the object and the lens of the objective; α, one-half the angle of aperture of the lens; and N.A., the numerical aperture of the lens. From this equation it follows that the resolving power of a microscope may be increased by decreasing λ, by increasing N.A. ($n \sin \alpha$), or by both. Taking (1) $\lambda = 5607$ A, a mean value for white light, (2) α-monobromonaphthalene, a liquid with the maximum n value of 1.66, and (3) $\alpha = 90°$ ($\sin \alpha = 1$), the limit value of ϵ for white light is 0.17×10^{-4} ($0.17\ \mu$). This value has not been obtained experimentally with white light, but the limit of resolution was found to be 0.19–0.20×10^{-4} with an immersion objective of N.A. = 1.35, an immersion condenser of N.A. = 1.30, and with light of λ = about 4500 A. When ultraviolet light is used with quartz lenses, a resolving power of $0.075\ \mu$ has been reported. It appears therefore that the limit of microscopic visibility is about 0.1–$0.2\ \mu$. The invention of the ultramicroscope has made possible investigations on particles of much smaller size.

The slit ultramicroscope. In the slit ultramicroscope invented by Siedentopf and Zsigmondy,[3] an intense beam of light, preferably from the sun or a direct-current arc, is passed through an adjustable slit and is focused by means of a lens and a microscope objective in the center of a small cell containing the sol to be examined. This cell with quartz windows is attached by an adjustable mechanism to the objective of an ordinary microscope which is focused to give a sharp image of a part of the Tyndall cone in the cell. Figure 45 shows diagrammatically the path of light rays which impinge on an ultramicroscopic particle, the diffracted rays being focused at point *E* at right angles to the illuminating rays. The ultramicroscope is thus an apparatus for magnifying the individual bright specks resulting from the diffraction of the light by colloidally dispersed particles. Although the particles themselves are too small to be seen by the magnification employed, the light diffracted by the particles reveals their number, position, and Brownian motion.

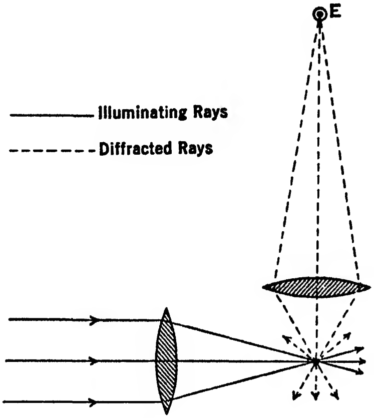

FIG. 45. Diagram of the path of light rays which impinge on a particle in the slit ultramicroscope.

Particles of gold as small as 8 mμ in diameter can be counted in the slit ultramicroscope with arc-light illumination, and as small as 5 mμ in diameter with sunlight illumination. In the immersion ultramicroscope, where the objectives of the horizontal illuminating system and of the microscope system are so close together that a drop of sol can be suspended between them, Zsigmondy,[3, 4] counted particles as small as 3 mμ in diameter and differentiated particles as small as 1.7 mμ from the water in which they were dispersed.

Particle size. The average size of the particles in a sol may be determined by counting the number in a given volume by means of the slit ultramicroscope and analyzing for the concentration of dispersed phase. If n is the number of particles per milliliter of sol, m the total amount of dispersed phase per milliliter, and d the density of the dispersed phase, then the volume v of a single particle is: $v = m/nd$. Assuming that the particles are cubes, the length of one side l is: $l = \sqrt{m/nd}$.

The procedure for counting the number of particles in a given volume of sol with the slit ultramicroscope has been described in detail by Zsigmondy,[3] Burton,[5] and others, and detailed directions are supplied with the apparatus by the manufacturer. The accuracy of the determinations depends on the correctness of the following assumptions: (1) all the colloidal particles appear as spots of light, that is, no *amicrons* are present which are too small to be detected; (2) the density of the colloidally dispersed particles is the same as for the substance in mass; (3) the particles are cubical in shape; (4) the particles are primary units and not agglomerates which may be dispersed by the dilution necessary to make a rapid count.

Other ultramicroscopes. In the slit ultramicroscope, the axis of the illuminating system forms a right angle with the axis of the observation microscope (orthogonal illumination). Other ultramicroscopes have been devised in which both systems lie in the same axis (coaxial illumination). In the latter, it is necessary to have an arrangement which prevents the illuminating rays from reaching the eye of the observer. Two such devices which have proved useful are the paraboloid condenser and the cardioid condenser designed to fit directly in the frame of a good microscope, taking the place of the ordinary substage condenser.

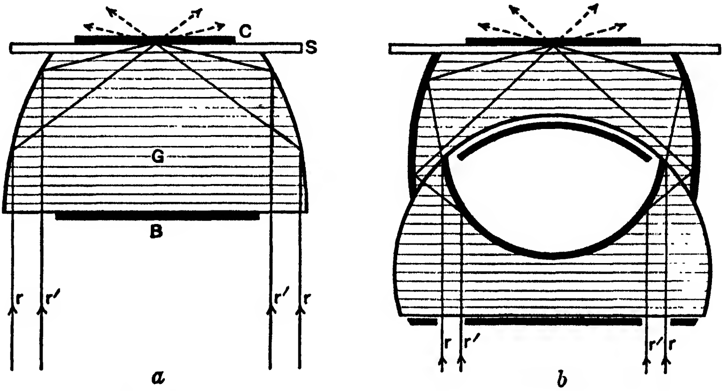

FIG. 46. Path of light rays: (*a*) through the paraboloid condenser; (*b*) through the cardioid condenser.

Figure 46*a* is a diagram showing the path of the light rays through a paraboloid condenser. The glass block *G* has curved faces which are silvered so as to act as a parabolic mirror. The black glass disk *B* prevents the direct illuminating rays from entering the objective of the microscope. The reflected light rays *r* and *r′* are focused at a point slightly below the plane of contact of the glass slide *S* with the cover glass *C*. The slide *S* contains a small depression in which the colloidal system is placed. The microscope is focused at the point where the light rays converge within the sample.

Figure 46*b* shows the way in which the cardioid condenser brings light to a focus in the axis of the microscope without allowing the incident ray to reach the eye. This arrangement is more nearly optically perfect than the paraboloid condenser, but it cannot be used to advantage unless the glass slide, the cover glass, and the depth of the specimen meet rigid requirements.

Figure 47 is a diagram of a useful and convenient ultramicroscope system which occupies an intermediate position between those using orthogonal and those employing coaxial illumination. In this arrangement, first used by Cotton and Mouton,[6] the incident rays are reflected from the inclined face of a rectangular glass prism and strike the sample at an angle. The rays do not enter the microscope because they are wholly reflected by the cover glass *C* which is placed over the sample on the slide *S*.

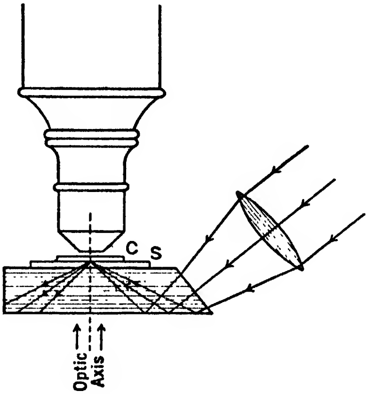

FIG. 47. Diagram of Cotton and Mouton's ultramicroscope.

Another system which has been found useful for the ultramicroscopic examination of certain substances is the Spicerer [7] lens. This arrangement is characterized by the presence of a tiny gold mirror on one of the lenses of the microscope. Light from the microscope mirror passes through a tiny core of optical glass in the center of a dark-field condenser and focuses on the gold mirror which reflects it at an angle to the surface of the material under observation on the microscope slide. The light is again refracted from the specimen back into the microscope lens to the eye of the observer. At the same time, the core of optical glass in the condenser acts like the paraboloid condenser and transmits light which strikes the specimen from below at an angle, giving an ultramicroscopic field. Seifriz [8] found this lens system useful in the ultramicroscopy of protoplasm, and Thiessen [9] applied it to investigations of the cell-wall structure of coal and woods.

Limitations of the ultramicroscope. Although the ultramicroscope in its various forms has proved to be a useful laboratory tool,[10] its limitations must be clearly recognized. Since molecules of gases and liquids will scatter light, the ultramicroscope cannot be used as a means of proving the heterogeneity of a colloidal dispersion. Moreover, as we have seen, the index of refraction of the dispersed and dispersing phases may be so nearly alike that a colloidal system may appear homogeneous in the ultramicroscope. Finally, it must be remembered that the observer does not see the actual particles of a solid phase in the ultramicroscope, but only the light that is reflected, refracted, and scattered by the solid phase. Accordingly, the size or form of a body cannot be determined accurately by direct ultramicroscopic observation. It was claimed for a time that the ultramicroscope revealed a sponge structure rather than a honeycomb structure in jellies such as gelatin (Chapter 20). Although jellies appear to have a sponge structure, it is now known that one cannot distinguish between the two types of structure by an ultramicroscope.[11]

The Tyndallmeter

The Tyndallmeter is an apparatus devised by Tolman and Vliet[12] to measure the intensity of the Tyndall beam. The apparatus was developed during World War I for the purpose of determining the concentration of toxic and obscuring smokes and investigating their change in concentration with time. It may also be used for measuring the intensity of the beam in a sol or solution. The apparatus consists essentially of an electric-light bulb as a source of light which passes through a condensing lens, giving a beam of parallel light. This illuminates the suspended particles, giving a Tyndall beam, the intensity of which is measured by a Macbeth illuminator.

Tolman found that the intensity of a Tyndall beam produced by passing a light of given strength through smoke is directly proportional to the concentration of the dispersed phase provided that (1) the degree of dispersion does not change with the concentration, and (2) the concentration is not so high that the opacity of the cloud modifies the result.

The intensity I_T of scattered light may be expressed by the equation $I_T = knd^6$, where d is the diameter and n the number of particles. Since the concentration c is proportional to nd^3, the above equation becomes: $I_T = kcd^3$. This equation holds only for small particles. With large particles which reflect the incident light, $I_T = k_1nd^2$; that is, I_T is proportional to the area of the reflecting surface. Expressed in terms of concentrations, $I_T = k_1c/d$, which states that, for particles larger than, say, 10^{-4} cm, the intensity of the scattered light is inversely proportional to their diameter.

The Nephelometer

The nephelometer is an apparatus involving the principle of the Tyndall phenomenon, which is used in analytical chemistry to determine the amount of a suspended colorless precipitate that is too small for accurate gravimetric determination.[13] The apparatus was developed by Richards and Wells[14] for comparing the opalescence of dilute suspensions of silver chloride, in connection with certain atomic-weight determinations. In the colorimeter and turbidimeter, the light enters the glass bottom of the sample tube and passes up through it, whereas in the nephelometer an intense light is supplied at right angles to the glass container and the suspension is rendered opalescent by reflection and scattering. The opalescence of a suspension of unknown composition is compared with that of a standard containing a known amount of the same suspended material. Johnson[15] has investigated in detail the various factors that influence the so-called equal opalescence end point in the estimation of small amounts of silver or chloride. Among other things, it was found that the particles in the suspensions compared must be of the same size and of the same index of refraction.

In addition to the application of nephelometry to atomic-weight determinations, it has been employed in such varied analytical determinations as (1) phosphorus in cast iron; (2) acetone, by the addition of a silver mercury cyanide to produce opalescence: (3) hemoglobin in blood; (4) lecithin in blood, by oxidation which yields phosphoric acid that is precipitated as a silver phosphate suspension.

The Electron Microscope

As noted on p. 172, ordinary light as a means of observation has limitations directly related to its wave length, so that two points separated by a distance less than one-half the wave length of light cannot be resolved but appear as a single blur. The use of ultraviolet light, with shorter wave length than ordinary light, increased the resolving power as far as was possible until the light source was replaced by a beam of electrons having a much shorter wave length than even ultraviolet light. An ordinary light microscope employs glass lenses; an ultraviolet light microscope employs silica lenses; and the electron microscope uses electrostatic or electromagnetic lenses. In Fig. 48*a* is represented a diagram of an electromagnetic lens such as is employed in the R.C.A. electron microscope. In Fig. 48*b* and *c* is shown diagrammatically the similarity between the action of optical lenses in the light microscope (*b*) and of electromagnetic lenses in the electron microscope (c). With the latter apparatus magnification of 25,000–100,000 diameters is readily obtained, thereby making it possible to study the particle size and structure of a wide variety of inorganic and biological material. To illustrate its use in biological studies, Fig. 49 shows an electron micrograph of *Staphylococcus aureus* (*a*) before (×17,500) and (*b*) after (×16,000) (note disintegration) the addition of penicillin.

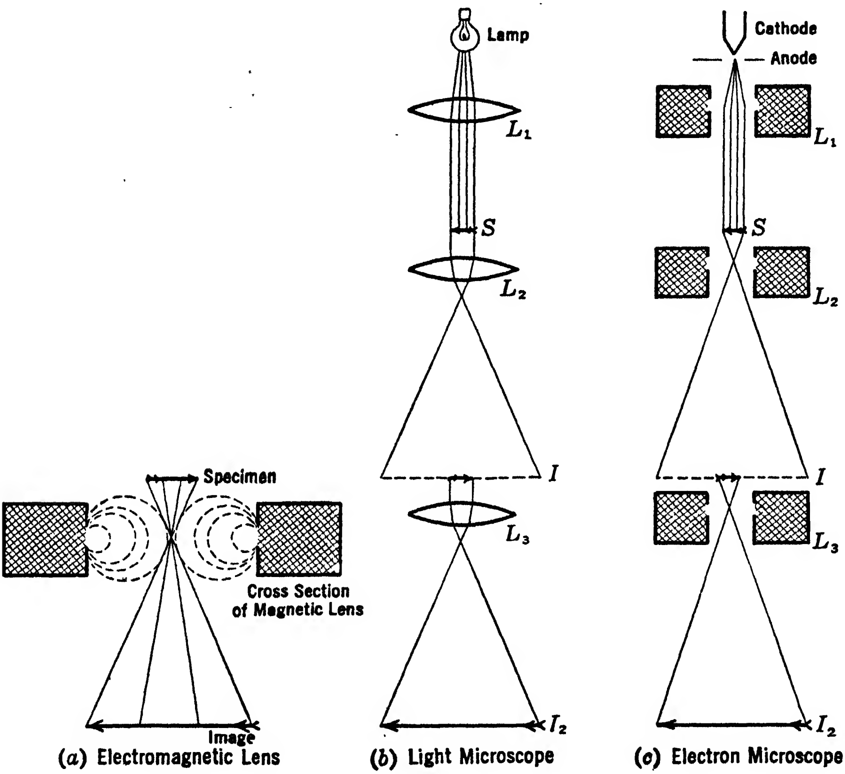

FIG. 48. (*a*) Diagram of the action of an electromagnetic lens. (*b* and *c*) Comparison of the action of the optical lenses in the light microscope with the electromagnetic lenses in the electron microscope. (Courtesy of the Radio Corporation of America)

DOUBLE REFRACTION

In general, the shape of colloidal particles is not exactly spherical, and, therefore, they may exhibit double refraction when the Tyndall

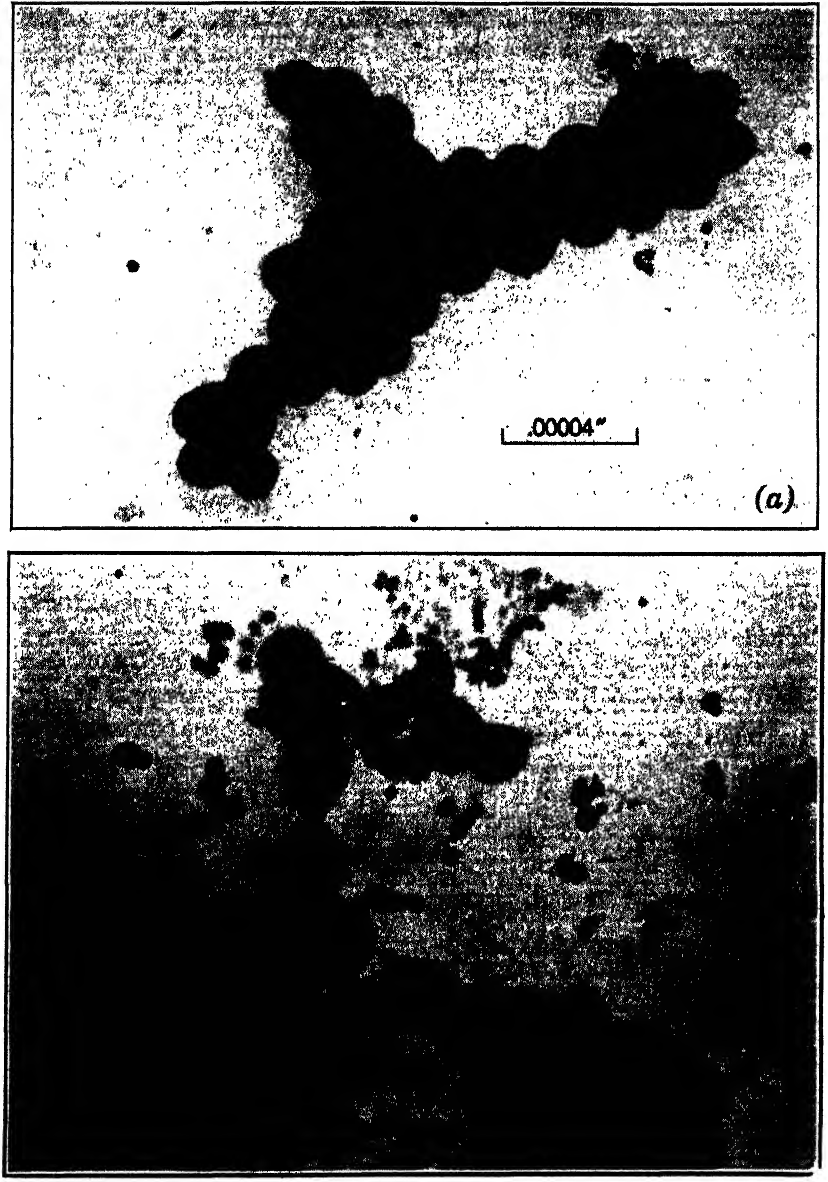

FIG. 49. Electron micrograph of *Staphylococcus aureus* (*a*) before (×17,500) and (*b*) after (×16,000) the addition of penicillin. (Courtesy of the Radio Corporation of America)

beam is viewed between crossed nicols in a magnetic or electric field, or simply by flowing. Majorana[16] first observed magnetic and electric double refraction in an aged ferric oxide sol, and the effect has come to be known as the *Majorana phenomenon.* The property is due to orientation of the particles of the sol since the orientation and concomitant double refraction were observed directly by working with a sol containing particles large enough to see in the microscope. Moreover, a ferric oxide gel, formed by coagulation of the aged sol in an electric field, exhibited permanent double refraction, whereas coagulation under ordinary conditions gave an optically inactive gel. Large particles caused a greater effect than small ultramicrons since the Brownian movement of the ultramicrons prevented sufficient orientation to cause pronounced double refraction.

Certain sols exhibit marked double refraction on stirring or on allowing the sols to flow. This phenomenon is known as *streaming double refraction.* It has been studied extensively by Freundlich and coworkers,[17] who have observed it in sols of ferric oxide, vanadium pentoxide, silver cyanate, tungsten trioxide, soap solutions, clay suspensions, and in solutions of a number of dyes such as benzopurpurin, alizarin, and aniline blue. In most of these, the double refraction appears to be due in large measure to the anisotropic nature of the particles themselves rather than to the latticelike arrangement of rod- or disk-shaped isotropic particles. With tungsten trioxide sol, however, the form and size of the particles are the important factors in changing the nature of the Tyndall light, since the anisotropy of the particles is negligible.

X-RAY AND ELECTRON DIFFRACTION

X-ray diffraction. Crystals diffract x-rays analogously to the diffraction of light by an optical grating. This behavior was suggested in 1912 by Laue, who first proposed the use of a crystal as a diffraction grating. When a narrow beam of x-rays was passed through a crystal and fell upon a photographic plate, a series of spots appeared on the plate. Using first a section of zinc blende, a crystal with cubic symmetry, Laue showed that the positions of the spots corresponded with diffraction of very short waves by a cubic arrangement of scattering atoms or molecules in the crystal. The theory and experimental methods of crystal analysis by x-rays are described in detail by Bragg and Bragg.[18]

The Laue method is useful only for the analysis by x-rays of a single relatively large crystal. A powder method developed independently by Debye and Scherrer in Germany and by Hull in America uses very small, even colloidal, crystals in random orientation in a bulk mass of the material or dispersed as a sol. The principle is essentially as follows: a narrow beam of x-rays falls upon an aggregate containing a large number of small crystals, such that there will always be some so oriented that a given reflection is possible; the sum of the reflected or diffracted beams from a large number of the small fragments will lie on a circular curve. If recorded on a photographic plate perpendicular to the incident beam, each type of diffraction from the crystal fragments appears as a ring surrounding the central spot *I*, as represented by Fig. 50*b*, taken from Bragg and Bragg for a crystalline aggregate *P* typical of a face-centered cubic crystal lattice. Sometimes it is more convenient to employ a cylindrical camera with the sample at the center of the camera and the film around the circumference. Then beams, which are diffracted through all angles up to nearly 180°, are recorded on the film. The principle is shown in Fig. 51. When the exposed film is unrolled and developed it has the appearance shown in Fig. 51*b*, after Bragg and Bragg.[18] The rays diffracted through an angle make arcs like the inner rings in Fig. 50*b*. When diffracted through 90°, the arc becomes a straight line; when

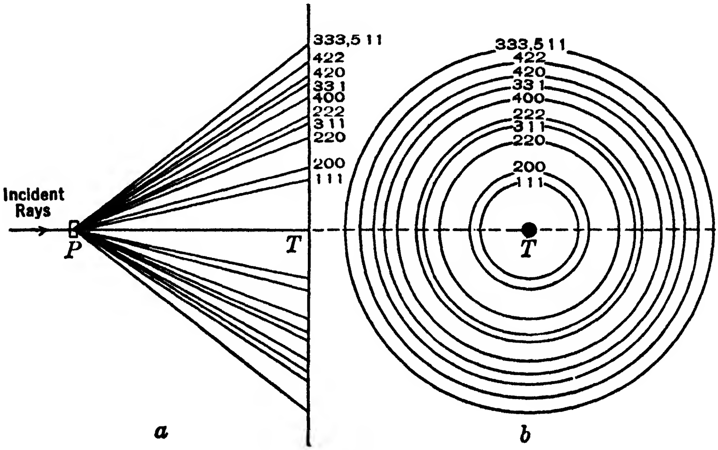

FIG. 50. The rings of a powder photograph on a flat plate. The positions of the rings are those typical of a face-centered cubic lattice. (From Bragg and Bragg: *The Crystalline State*)

diffracted through an angle larger than 90°, the curvature is the reverse of that for the smaller angles of diffraction.

Electron diffraction. The discovery that an electron beam is diffracted by matter as if it were a train of waves was made independently by Davisson and Germer in America and by G. P. Thompson in England. By passing electrons at a potential between 10,000 and 60,000 volts through thin films, G. P. Thompson found diffraction effects similar to those represented in Fig. 50*b* for x-rays. Electron rays may be used in place of x-rays when a very thin sample is available, when the crystal size is so small that well-defined x-ray diffraction rings are not obtained, and when the amount of crystalline material is very small.

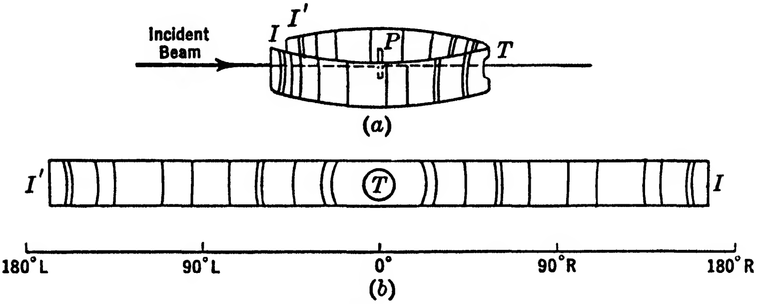

Fig. 51. Diagram of a powder photograph on a cylindrical film. (From Bragg and Bragg: *The Crystalline State*)

COLOR

Colloidal systems, especially the lyophobic sols, exhibit a wide variety of colors. For example, gold sols are usually red, violet or blue but may be yellowish brown or brown; and silver sols have been obtained in all shades of yellow to brown, in different shades of clear red, vermilion, dark red, and violet, and in a variety of tones of green and blue, blue-gray, and black. The various factors which may influence the color of substances have been discussed at length by Bancroft.[19] Some of these will be considered briefly.

When light falls on a substance, a part is absorbed, and the remainder is reflected if the material is opaque or transmitted if it is translucent or transparent. Two kinds of colors are distinguished: pigment and structural. Pigment colors result with transmitted light when the light absorbed depends on the molecular structure of the substance observed. The colors of solutions of permanganate, copper sulfate, and dyes are examples of pigment colors. Structural colors are caused or modified by the physical structure of the body observed. The rainbow and the color of snow and of chopped ice are typical examples of structural colors.

An opaque substance appears white if it does not absorb selectively any of the wave lengths of the light falling on it and provided the surface is rough so that the reflected light is diffused or scattered. Powdered glass, snow, paper, enamel, foam, etc., appear white because of the light scattered by the surface. White is therefore a structural color.

If the surface absorbs light selectively as metallic surfaces do, the color will be that of the reflected light. A distinction must be made between (1) the color reflected from the surface, (2) the surface color, and (3) that which is reflected from just beneath the surface, the body color. For example, the surface color of indigo is red, whereas the body color is blue. Similarly, the surface color of magenta is green, and the body color is red. The surface color is apparently due to resonance, the substance emitting the wave lengths that it absorbs very strongly.

The color of a transparent or translucent material depends on whether the color reaches the eye by transmission through the solid or by surface reflection. For example, a thin sheet of gold foil has the usual yellow color of gold by reflected light, but the color of the transmitted light is green. If we start with yellow gold and make it more porous, it becomes first brown and then black. The sensation known as black results from complete absorption of light, plus contrast.

In sols, the nature of the dispersing medium will cause the dispersed phase to have a different color from the color it has in air. This is due in part to the difference in the index of refraction of the dispersing medium and air and in part to the reflecting and absorbing properties of the medium. As an illustration, crystallized copper sulfate which is blue by transmitted light is white when powdered, as a result of scattering by the irregular surface. If this white powder is suspended in an organic liquid which has the same index of refraction, the particles will appear blue.

Tyndall blue. If very fine particles of a weakly absorbing material are suspended in a transparent solid, liquid, or gas, the particles scatter blue light more than red light; hence such a system appears red by transmitted light and blue by reflected light. This blue of turbid media, known as Tyndall blue, is observed with sols of mastic and sulfur, skimmed milk, and tobacco smoke. The blue of the sky is a Tyndall blue which results from the scattering of the light by drops of liquid and particles of dust suspended in the air, or by the oxygen or nitrogen molecules themselves. There is no pigment in blue eyes; the color is a Tyndall blue which is more intense the finer the particles that give rise to the blue color; sufficiently coarse particles give gray eyes. A combination of structural blue with a yellowish brown pigment in front of the iris accounts for green, hazel, brown, and black eyes in different individuals.[19]

The theory of the Tyndall blue has been worked out by Lord Rayleigh,[20] who deduced that the intensity of the scattered light is directly proportional to the square of the size of the particles and inversely proportional to the fourth power of the wave length. For a sol the intensity of the scattered light I in the direction at right angles to the path of the incident light is given by the equation:

$$I = N = \frac{9\pi^2 V^2 A^2}{\lambda^4 x^2} \cdot \left(\frac{n_1^2 - n^2}{n_1^2 + 2n^2}\right)^2$$

where N is the number of particles in unit volume, V is the volume of the particles, A^2 is the amount of energy falling on the particles, λ is the wave length, x is the distance between the source of light and the particles, and n_1 and n are the refractive index of water and of the particle, respectively. The inverse proportion of the fourth power of the wave length to the intensity of scattering explains why the scattered light is much bluer than the incident light.

This equation for weakly absorbing, insulating particles does not apply for metallic conducting particles, as is evidenced by the variety and brilliance of the coloring in sols of the metals.

Effect of particle size. To explain the color of metallic sols, Mie[21] has modified Lord Rayleigh's formula by introducing into it the complex indices of refraction[22] for the ordinary indices of refraction of the metals. Mie is thus led to conclude that red gold sols must consist of spherical particles under 40 mμ in radius that scatter but little light, whereas blue gold sols have larger particles that radiate more strongly. As a matter of fact, however, blue gold sols have been prepared in which the particles are much smaller than 40 mμ. This is explained by assuming either that the particles are not spherical or that they consist of loose aggregates of smaller units.

Ostwald[23] has formulated the rule that the variation in color of sols with particle size is due to a shifting of the absorption maximum toward the regions of longer wave length with decreasing degree of dispersion. If this rule applies, the color of a given sol would change through yellow → red → blue → purple → green → brown with increasing particle size. This appears to take place with sols of sulfur and selenium, but the rule is not generally applicable to metallic sols.

Barnes and LaMer[24] showed that sulfur sols of very small particle size polarize light at 90° to the direction of the incident beam. Sols with the larger particles disperse scattered light to form bands of different colors whose intensity, polarization, and angular distribution depend on the particle size. The form of the transmittance curve observed for light passing through monodispersed sulfur sols agrees with the prediction of the Mie theory. The diameter and number of particles per unit volume can be calculated from the transmittance as a function of the wave length.

One must conclude, therefore, that the color of sols is a complex, resultant light effect that depends on the nature of the dispersed phase and of the dispersion medium. For a given sol system, the color depends on the size and shape of the primary particles and on the form and closeness of packing of primary particles in agglomerates.

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CHAPTER 13

The Kinetic Properties of Sols

BROWNIAN MOVEMENT OF COLLOIDAL PARTICLES

In 1827 the English botanist Robert Brown[1] observed that pollen grains suspended in a liquid on a microscope stage were in continuous motion in the liquid. Later experiments disclosed that the motion was not that of living material but was common to all finely divided solids and liquids. The zigzag motion of suspended particles is called *Brownian movement.*

The Brownian movement is not caused by external influences such as vibration, convection currents, or the effect of light, nor does it originate from gravitational, magnetic, electrical, or surface-tension forces. The motion is caused by bombardment of the suspended particles by the molecules of the liquid in which they are dispersed.[2] In accord with this, the rapidity of the motion is greater the smaller the particles. Particles larger than 4 μ in diameter do not exhibit Brownian movement, but they become quite lively at diameters of 0.1 μ and give apparent trajectories up to 20 μ when the diameter is reduced to 10 mμ.[3] Svedberg[4] observed a velocity of 200–400 mμ per second for particles 10–50 mμ in diameter in a platinum sol.

Since it has been established conclusively that the Brownian movement results from bombardment of the dispersed particles by the molecules of the dispersion medium, Einstein[5, 6] assumed that suspended particles should behave like dissolved molecules, exerting an osmotic pressure and diffusing through the dispersion liquid; in other words, that the gas laws should apply in the same way for suspended particles as for dissolved molecules. Since molecules are in general invisible, it is of special interest and importance to know the behavior of ultramicroscopically visible colloidal particles which apparently behave like molecules.

The velocity of Brownian movement cannot be measured with any degree of accuracy, but an expression was derived almost simultaneously by Einstein[5] and Smoluchowski[6] for calculating the rectilinear displacement of colloidal particles in unit time. Einstein's[7] simplified derivation will be given.

Einstein's Equation: Derivation

Consider a cylindrical vessel (Fig. 52*a*) filled with a dilute solution in which the molecules of solute are large compared to those of the solvent. The vessel is divided into two parts *A* and *B* by means of the semipermeable piston *S*. If the concentration is greater in *A* than in *B*, the piston will move from left to right. The force causing the piston to move is the difference in osmotic pressure, *K*, between *A* and *B*; *K* becomes zero when the concentrations in the two compartments are equal. It follows from this that the force of osmotic pressure is responsible for the equalization of concentration caused by diffusion, since the diffusion may be prevented by applying an external force equal to *K*, the osmotic force.

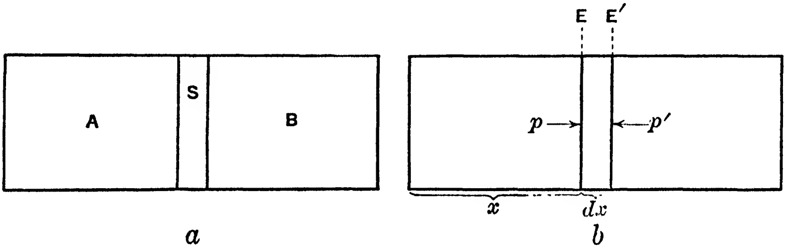

FIG. 52. Diagram of cylindrical vessel filled with dilute solutions separated by semipermeable membrane.

Consider next a cylinder of solution (Fig. 52*b*) of unit cross section without a piston, but with a higher concentration in the left-hand than in the right-hand portion. The osmotic pressure p acts on the plane *E* from the left, and the osmotic pressure p' acts on the plane *E′* from the right. The difference in osmotic pressure is thus $p - p'$. Designating the distance from the end of the vessel to *E* by x and to *E′* by $x + dx$, the volume of the solution under consideration is dx. The osmotic pressure per unit volume of solution is thus:

$$K = \frac{p - p'}{dx} = -\frac{p' - p}{dx} = -\frac{dp}{dx}$$

For dilute solutions, the osmotic pressure is $p = nRT$, where n is the number of gram molecules of solute per unit volume. Hence the effective osmotic force *K* acting on the dissolved substance per unit volume is:

$$K = -RT\frac{dn}{dx} \tag{1}$$

The velocity v of the motion of a molecule under the influence of a force k is:

$$v = \frac{k}{f} \tag{2}$$

where f is the frictional resistance of the molecules. For molecules that are spherical and large compared to the molecules of the solvent, Stokes's law applies:

$$f = 6\pi\eta r \tag{3}$$

in which η is the viscosity of the solvent, and r the radius of the sphere.

In the unit volume under consideration, there are n gram molecules of solute or nN actual molecules, where N is the Avogadro number. Since the force K is distributed among these nN molecules, it will impart to each a velocity that is $1/nN$ of the velocity it would impart to a single molecule. Hence, from eqs. 1 and 2, the velocity of the molecules resulting from K is:

$$v = \frac{1}{nN} \cdot \frac{K}{6\pi\eta r} \tag{4}$$

Since K is the osmotic force, it follows from eq. 1 that:

$$vn = -\frac{RT}{N} \cdot \frac{1}{6\pi\eta r}\frac{dn}{dx} \tag{5}$$

or

$$-\frac{vn}{dn/dx} = \frac{RT}{N} \cdot \frac{1}{6\pi\eta r} \tag{6}$$

The amount of solute which will diffuse across unit area at constant rate in unit time under unit concentration gradient is the specific diffusion rate or diffusion constant D. This, according to Fick's law, is:

$$-D\frac{dn}{dx} = vn \tag{7}$$

the minus sign signifying that the solute diffuses in the direction of decreasing concentration. On combining eqs. 6 and 7 one obtains:

$$D = \frac{RT}{N} \cdot \frac{1}{6\pi\eta r} \tag{8}$$

which expresses the diffusion constant in terms of the viscosity of the medium and the radius of the particles which are large compared to those of the medium.

The next point to be taken up is the relationship between diffusion and the irregular, random motion of the molecules resulting from thermal energy which tends to eliminate any original inequality in concentration.

Consider the diffusion of a dilute solution of spherical molecules, large compared to those of the solvent, along the x-axis of the cylindrical vessel of unit cross section represented in Fig. 53. Suppose that the position of all molecules along the x-axis is known at time t and at time $t + \tau$, where τ is such a small interval that the changes in the distribution of the solute molecules are very slight. Because of the random motion of the molecules, during the time τ the x coordinate of a given molecule will have shifted a distance Δ_1, of a second Δ_2, of a third Δ_3, etc. Moreover, the displacements, Δ_1, Δ_2, Δ_3, etc., will be in part negative (to the left) and in part positive (to the right), and their magnitudes will differ. Since the solution is dilute, the displacements result from the solvent molecules alone, the solute molecules being too far apart to influence one another appreciably. Accordingly, the mean displacement Δ will be the same in various parts of the solution where the concentrations may vary slightly, and the $+\Delta$ values will equal the $-\Delta$ values. Substituting from the individual displacements the mean value Δ, the mean diffusion may be determined along the x-axis of the dissolved molecules through unit cross section of the cylinder (Fig. 53) in time τ. During this interval, there will pass through the plane E from left to right only those molecules which are less than the distance Δ to the left of E. In the diagram, these molecules all lie between the planes E_1 and E. But, since only one-half of the molecules have positive displacements, only one-half of them will pass through plane E. One-half of the dissolved molecules between E_1 and E, in gram molecules, is $\frac{1}{2}n_1\Delta$, where n_1 is the mean concentration in the volume E_1E or the concentration in the mean plane M_1. Since the cross section is unity, $n_1\Delta$ represents the total number of gram molecules between E_1 and E.

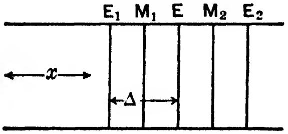

FIG. 53. Diagram representing diffusion of dilute solution of spherical particles.

Similarly, the amount of solute that passes through E from right to left in the time τ is $\frac{1}{2}n_2\Delta$, where n_2 is the concentration in the mean plane M_2. The difference between the two concentrations is:

$$\tfrac{1}{2}\Delta(n_1 - n_2) \qquad (9)$$

which is the net quantity of solute that diffuses across plane E in time τ. Since the coordinate of E is x, eq. 6 may be expressed in terms of a differential quotient as follows:

$$\frac{n_2 - n_1}{\Delta} = \frac{dn}{dx} \quad \text{or} \quad n_1 - n_2 = -\Delta\frac{dn}{dx} \tag{10}$$

Hence, from eqs. 9 and 10, the amount in gram molecules of solute which diffuses through E in time τ is:

$$-\frac{1}{2}\Delta^2\frac{dn}{dx} \tag{11}$$

and the amount that diffuses in unit time (second) is:

$$-\frac{1}{2}\frac{\Delta^2}{\tau}\frac{dn}{dx} \tag{12}$$

Dividing 12 by dn/dx gives $-\Delta^2/2\tau$, the quantity that will diffuse under unit potential gradient. This is the diffusion coefficient D again; that is,

$$D = \frac{\Delta^2}{2\tau} \tag{13}$$

Combining eq. 13 with 8 gives:

$$\Delta^2 = \frac{RT}{N}\frac{\tau}{3\pi\eta r} \tag{14}$$

or

$$\Delta = \sqrt{\tau}\sqrt{\frac{RT}{N}\frac{1}{3\pi\eta r}} \tag{15}$$

Since suspended particles are assumed to behave like dissolved molecules, eq. 15 is the general formula for the Brownian movement in which Δ is the average displacement along the x-axis in time τ of a spherical particle of radius r.

The Einstein Equation: Tests of Validity

The displacement of colloidal particles has been arrived at in different ways. Perrin[1, 8, 9] traced the motion of a particle of gamboge by marking its position in the field of the microscope, on cross-section paper, at 30-second intervals. Intermittent photographs of rubber latex particles were taken by Henri[10] and of vermilion particles by Seddig.[11] Svedberg[4] photographed the position of the particles as a sol was allowed to flow slowly through the cell of the slit ultramicroscope. Wavy lines were obtained, a diagram of which is shown in Fig. 54. If the velocity of flow of the sol carries the particle the distance $x = 4$ times the amplitude A, in time t, the mean average velocity is $4A/t$. By means of such experimental techniques, the validity of Einstein's equation has been tested as explained in the following paragraphs.

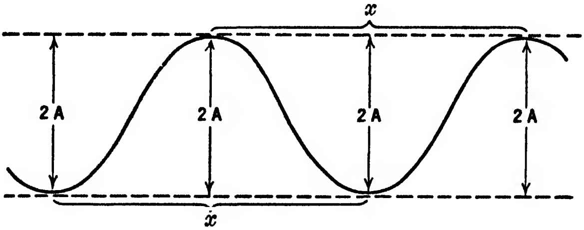

FIG. 54. Diagram showing position of a sol particle when sol is flowed slowly through the ultramicroscope cell.

The time law in Brownian movement. For a given particle size and at constant temperature, the value of $\sqrt{RT/N \cdot \frac{1}{3}\pi\eta r}$ in eq. 15 is constant; hence

$$\Delta = k\sqrt{\tau} \tag{16}$$

This relation, known as the *time law* in Brownian movement, was established independently of the theoretical considerations of Einstein, from observations on gamboge by Chaudesaigues [9] and on gold sols by Svedberg.[12] Svedberg's results are given in Table 38.

TABLE 38

TIME LAW IN BROWNIAN MOVEMENT

Time (units of 1.48 sec)	Δ (μ) (r = 27 mμ)		Δ (μ) (r = 52 mμ)	
	Observed	Calculated	Observed	Calculated
1	3.1	3.2	1.4	1.7
2	4.5	4.4	2.3	2.4
3	5.3	5.4	2.9	2.9
4	6.4	6.2	3.6	3.4
5	7.0	6.9	4.0	3.8
6	7.8	7.6	4.5	4.2

Displacement in Brownian movement. Svedberg made absolute measurements of displacement which were found to be in good agreement with the values calculated from Einstein's equation, taking $N = 6.0 \times 10^{23}$. Some values for gold particles of 22-mμ radius are given in Table 39. With large gold particles, the observed displacements are always smaller than the calculated values, probably because the particles are not spheres as the Einstein equation assumes.

TABLE 39

ABSOLUTE MEASUREMENTS OF DISPLACEMENT IN BROWNIAN MOVEMENT

Time (sec)	1	2	3	4
Δ, calculated	4.3	5.8	6.6	8.3
Δ, observed	4.1	5.8	7.6	8.2

At constant temperature and with particles of a given size, the Einstein equation may be written:

$$\Delta = k\sqrt{\frac{\tau}{\eta}} \tag{17}$$

Svedberg[13] in 1906 found this relationship to apply empirically with platinum sols. His data are given in Table 40. From these results, it was concluded that $2A/\tau =$ constant, and $2A\eta =$ constant. Since in the experiments $2A$ and η were interdependent, the two equations cannot be used independently. This fact is expressed by combining them into $2A/\tau \times 2A\eta =$ constant or

TABLE 40

BROWNIAN MOVEMENT OF PLATINUM PARTICLES

Dispersion medium	$\eta \cdot 10^3$	$2A$ (μ)	τ (sec)	$2A/\tau \cdot 10^{-2}$	$2A\eta \cdot 10^2$
Acetone	3.2	6.2	0.016	3.9	2.0
Ethyl acetate	4.6	3.9	0.014	2.8	1.8
Amyl acetate	5.9	2.9	0.013	2.2	1.7
Water	10.2	2.1	0.0065	3.2	2.1
n-Propyl alcohol	22.6	1.3	0.0045	2.9	2.9

$$2A = k\sqrt{\frac{T}{\eta}} \tag{18}$$

which is the same as eq. 17, since $\Delta = 2A$.

Svedberg and Chaudesaigues [9] found also that the following relationships, which follow from Einstein's equation, hold experimentally:

$$\Delta = k\frac{1}{\sqrt{r}} \tag{19}$$

and

$$\Delta = k\frac{1}{\sqrt{\eta}} \tag{20}$$

The Avogadro number. The applicability of Einstein's equation is further shown from determinations of the Avogadro number N, from the observed values of Δ, r, and η for a sol. With a gold sol containing highly dispersed particles, Svedberg and Inouye [14] obtained for N the value 6.2×10^{23}. Perrin,[15] working with relatively large gamboge and mastic particles varying in size from 0.212 to 5.5 μ, obtained values of N varying from 6.6 to 7.8×10^{23}. This means that, within the limits of experimental error, the value of N is independent of the size of the particles. In other words, the kinetic theory of gases holds irrespective of the particle size, the mean kinetic energy of all particles being the same at the same temperature.

OSMOTIC PRESSURE

From the kinetic point of view, the Brownian movement of suspended particles will give an osmotic pressure. The van't Hoff expression for the osmotic pressure p in solution is:

$$p = cRT$$

where c is the number of molecules per unit volume. For a colloidal solution, the expression for the osmotic pressure is:

$$p = \frac{n}{N}RT \tag{21}$$

where n is the number of suspended particles in unit volume, and N is the Avogadro number. Because of the relatively small number of particles in a sol of known dispersity, the observed value of the osmotic pressure is too low to verify the assumption that an equivalence exists between a suspended particle and a molecule. A number of observations of osmotic pressure of hydrophobic sols have been reported, but most of them are vitiated either by faulty technique or by the presence of electrolytes in the sol (cf., however, Bjerrum's work on Cr_2O_3 sol, p. 248). In general, hydrophobic sols free from electrolytes show no accurately measurable osmotic pressure, lowering of the freezing point, or elevation of the boiling point.

The osmotic pressure of hydrophilic sols such as proteins is low even when the material is molecularly dispersed. The upper limit for such systems was probably approached by Sörensen,[16] who obtained an osmotic pressure of 86 cm of water for an egg-albumin sol containing 22.66 g/100 ml. The sol appears to be molecularly dispersed, but the individual hydrated molecules with a molecular weight of about 34,000 are of colloidal dimensions (cf. pp. 199 and 205).

DIFFUSION

Brownian movement of suspended particles leads to diffusion that is given by Einstein's equation, eq. 8:

$$D = \frac{RT}{N} \cdot \frac{1}{6\pi\eta r} \tag{8}$$

The validity of this formula has been tested experimentally. Using a specially designed diffusion apparatus to measure the diffusion coefficient D, Svedberg[17] calculated the radius of gold particles in a certain highly dispersed sol to be 1.29 mμ as compared with 1.33 mμ obtained by a procedure not based on the diffusion velocity. Similar results were found by Westgren[18] with selenium sol. Taking the value 1.33 mμ for the radius of the gold particles, Svedberg calculated N with eq. 8 and found it to be 5.8×10^{23}, in fairly good agreement with this constant as found by other methods.

SEDIMENTATION

Sedimentation Velocity: Stokes's Law

Sedimentation by gravity. A particle suspended in a liquid tends to settle out under the influence of gravitational force G in dynes, which is given by the equation:

$$G = \tfrac{4}{3}\pi r^3(\rho_1 - \rho_2)g \tag{22}$$

where r is the radius of spherical particles, g is the acceleration due to gravity; and ρ_1 and ρ_2 are the densities of the particles and the medium, respectively. If the particle is moving in the liquid with the velocity v, the force of liquid friction f is given by Stokes's law:

$$f = 6\pi\eta r v \tag{23}$$

where η is the viscosity of the liquid. Since G is constant and f varies with the velocity of fall of the particle, the velocity attains a constant limiting value when $f = G$. From eqs. 22 and 23 this limiting velocity v_0 is:

$$v_0 = \frac{2}{9}\frac{(\rho_1 - \rho_2)g}{\eta} r^2 \tag{24}$$

Since v_0 varies directly with r^2, the velocity of sedimentation drops off rapidly with decreasing particle size. This is shown by Burton's[19] calculations (Table 41) of the rate of fall of silver spheres in water at 20° ($\eta = 0.01$).

TABLE 41

VELOCITY OF FALL OF SILVER SPHERES IN WATER

Radius (cm)	v_0 (cm/sec)	Time (sec to fall 1 cm)
1.0	200,000.0	0.000005
0.1	2,000.0	0.0005
0.01	20.0	0.05
0.001	0.2	5.0
0.0001	0.002	500.0
0.00001	0.00002	50,000.0 (= 0.58 day)
0.000001	0.0000002	5,000,000.0 (= 58 days)

The value of v_0 can be measured with considerable accuracy if the particles are sufficiently large to settle relatively rapidly. It is possible, therefore, to determine the radius r of fairly coarse particles by means of Stokes's equation for the rate of sedimentation under gravity. To determine the size of clay particles Odén[20] immersed one pan of an analytical balance in the clay suspension. As the particles settled out as a function of time, the weight on the immersed pan increased, from which the rate of settling and the mass of the particles settling in unit time were determined. Another sedimentation device that has proved useful in the estimation of particle size is the sedimentation tube designed by Wiegner[21] and modified for specific purposes by Kelly[22] and Stamm.[23] Such apparatus is standard equipment in the colloid chemistry laboratory.

Sedimentation Velocity: Svedberg's Equation

The ultracentrifuge. With particles of colloidal dimensions, the rate of sedimentation under gravity is negligibly slow because the back diffusion acts in opposition to the gravitational force. If the force of gravity is increased by means of a centrifuge, the rate of settling is increased. So-called supercentrifuges have been constructed which run at 40,000 rpm and generate a force in excess of 42,000 times that of gravity. Such equipment is useful for washing precipitates that settle very slowly and in the preparation of sols (p. 156), but it cannot be employed in the estimation of the size of colloidally dispersed particles because vibration of the apparatus sets up convection currents that modify the effect of the centrifugal force. To overcome this difficulty, Svedberg[24] and coworkers have devised an apparatus called an ultracentrifuge which may be defined as "a centrifuge of low or high power in which convection does not occur and in which it is possible to measure any redistribution of the contents."[25, 26] In Svedberg's apparatus this redistribution is followed by determination of either the light adsorption or the refractive index.

Two kinds of measurements are used in the determination of particle or molecular weights by means of the ultracentrifuge: (1) sedimentation velocity plus diffusion, and (2) sedimentation equilibrium (see p. 202). In the first method, with which we are concerned in this section, the centrifugal field is strong enough to cause the molecules or particles to sediment with measurable velocity. If the sedimentation velocity is referred to unit field and to water at 20° as dispersing medium, it is called the sedimentation constant s:

$$s = \frac{dx/dt}{\omega^2 x} \frac{\eta}{\eta_0} \frac{1 - V\rho_0}{1 - V\rho} \tag{25}$$

in which x is the distance from the center of rotation, dx/dt is the velocity of settling, ω is the angular velocity, V is the partial specific volume of the dispersed phase, η and ρ are the viscosity and density of the sol, and η_0 and ρ_0 are the corresponding quantities for water at 20°.

By combining sedimentation and diffusion data, the particle or molecular weights M are calculated by means of the equation:

$$M = \frac{RTs}{D(1 - V\rho)} \tag{26}$$

where R is the gas constant; T, the absolute temperature; and D, the diffusion constant (eq. 8).

When the above equation is employed in molecular-weight determinations, an accurate independent measurement of the diffusion constant D must sometimes be made on the small amount of material. For this purpose Lamm[31] has designed a microapparatus in which a diffusion cell is employed that requires only about 1 cc of solution.

The initial cost of the Svedberg ultracentrifuges is so great that their use is greatly restricted. In recent years, however, small, relatively inexpensive, quantitative ultracentrifuges have been devised on the principle of a rotor driven by compressed air and spinning on a thin cushion of air—the spinning top of Henriot and Huguenard.[28] Different designs have been worked out by Beams[29] and McBain.[25, 30] Beams[29] has also developed "suspended rotor" types of ultracentrifuges driven by air, steam, and electricity, which have been adapted and improved by various workers to suit their special problems. With such instruments, centrifugal forces up to 4,000,000 times gravity have been obtained, the maximum value being limited only by the tensile strength of the material from which the rotor is fabricated. With the progress that is being made in the design and operation of small, inexpensive ultracentrifuges, their general use may be realized in the near future.

Applications of the ultracentrifuge: 1. Molecular weights. Svedberg's ultracentrifuge has been used extensively to determine what are called the "molecular weights" of proteins, celluloses, other biochemical compounds, dyes, soaps, etc. For reasons to be discussed subsequently (p. 205) it seems advisable, in many instances, to designate the apparent molecular weights of such colloidally dispersed materials as "particle weights."[27] In this connection Svedberg writes: "A very striking but rather unexpected property of protein solutions discovered by ultracentrifugal analysis is the perfect molecular homogeneity. This means that the solution of a certain protein is either uniform with regard to molecular weight or contains a limited number of different molecular species, as a rule in equilibrium with each other."

In Table 42 are given the particle or molecular weights of a number of typical proteins and high polymers as obtained by Svedberg and coworkers from sedimentation velocity and diffusion data.

TABLE 42

MOLECULAR OR PARTICLE WEIGHTS (*M*) OF VARIOUS PROTEINS AND OTHER HIGH POLYMERS DETERMINED BY SVEDBERG[24] AND OTHERS

Protein	*M*	Protein	*M*
Lactalbumin	17,500	Edestin	309,000
Gliadin	26,000	Amandin	329,000
Zein	35,000	Excelsin	294,000
Lactoglobulin	41,800	Erythrocruorin from different sources	17,100 1,636,000 3,140,000
Pepsin	35,500		
Insulin	40,900		
Egg albumin	43,800	Hemocyanin from different sources	446,000 503,000 820,000 2,785,000 3,316,000
CO-hemoglobin (horse)	69,000		
CO-hemoglobin (man)	63,000		
Serum albumin	70,200	Tobacco virus mosaic	15–20,000,000
Serum globulin	167,000		
Thyroglobulin	628,000		

High polymer	*M*	High polymer	*M*
Cotton cellulose	200,000–400,000	Polystyrene	30,000–270,000
Regenerated cellulose	90,000–110,000	Rubber	64,000
Cellulose acetate	50,000–250,000	Ovalbumin	34,500
Cellulose nitrate	100,000–160,000	Cellulose acetate	10,000–50,000
Ethyl cellulose	125,000	Cellulose nitrate	75,000
Methyl cellulose	14,000–38,000	Ovalbumin	29,000
Poly-ω-hydroxydecanoic acid	27,000	Hemoglobin	65,000–68,000

Application of the ultracentrifuge: 2. Distribution of particle sizes of proteins. Two different properties of the solute may be utilized for determining the concentration distribution in the rotating solution: light absorption and refraction. In both cases it is necessary to use long-focus lenses in order to avoid parallactic errors with the relatively thick layers studied. When using the absorption method, photographic exposures of the sedimenting column are made from time to time with light of a wave length absorbed by the solute. Measurement of these pictures by means of a microphotometer give the relation between the concentration *c* and the distance *x* from the center of rotation. Each molecular species or particle size is brought out as a step on the *c-x* curve. The most precise procedure for obtaining the real concentration distribution in the sample under con-

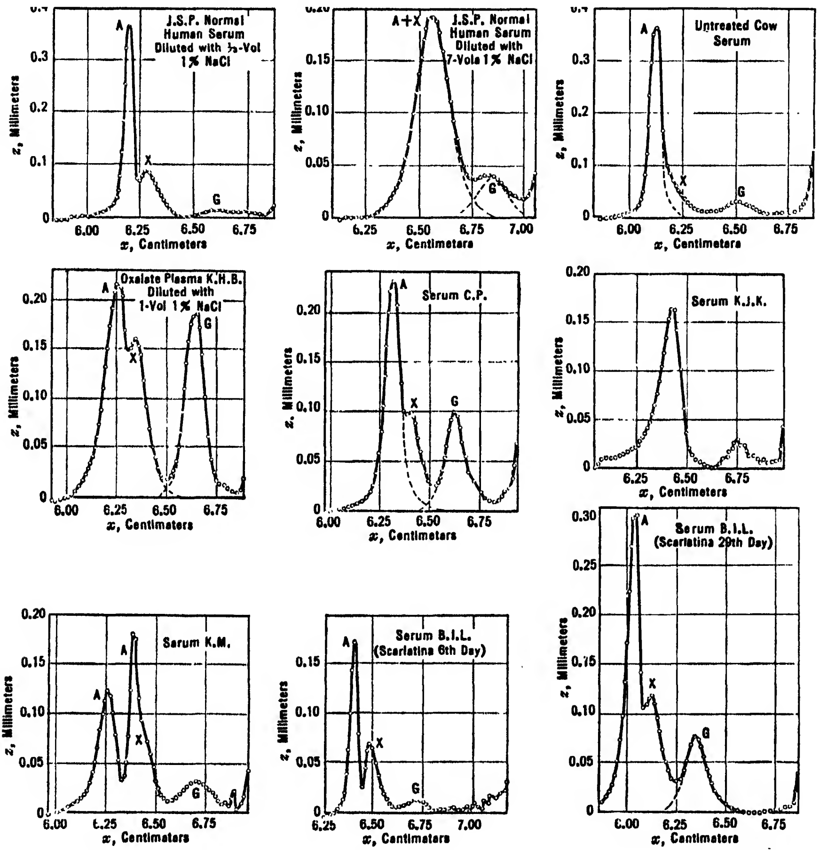

Fig. 55. Sedimentation diagrams of normal human and cow sera and of pathological human sera (McFarlane). K.H.B., pulmonary tuberculosis; C.P., ulcerative condition in rectum; K.J.K., nephritis; K.M., tumor of bile duct; B.I.L., scarlatina.

sideration is to take pictures of a finely ruled scale through the sedimenting column of solution, using light of a wave length that is not absorbed. From a measurement of the displacement of the lines *z*, the concentration gradient *dc/dx* is obtained as a function of the distance from the center of rotation. Each molecular species or particle size is therefore shown as a maximum on the *z-x* curve.

To illustrate z-x curves and their applicability for diagnostic purposes some sedimentation diagrams obtained by McFarlane[31] at the Lister Institute, London, are reproduced in Fig. 55.

Referring to Fig. 55, it will be noted that both human and cow serum show maxima corresponding to albumin and globulin. In the first diagram of the figure the globulin maximum is very much depressed, and there appears another maximum (the "x component"), probably corresponding to half or fourth molecules of globulin. In the cow serum, this dissociation product is completely hidden in the albumin maximum. Comparison of normal human serum with pathological sera reveals a number of differences. In the first place, the globulin content as well as the "x component" is usually very much increased in pathological sera. Sometimes new components appear, as in malignant tumor of the bile duct. The albumin fraction may be unsymmetrical, as in nephritis, indicating the presence of molecules of lower molecular weight than serum albumin (possibly dissociation products). The globulin content often increases during a disease, probably as a result of immunization, e.g., in scarlatina.

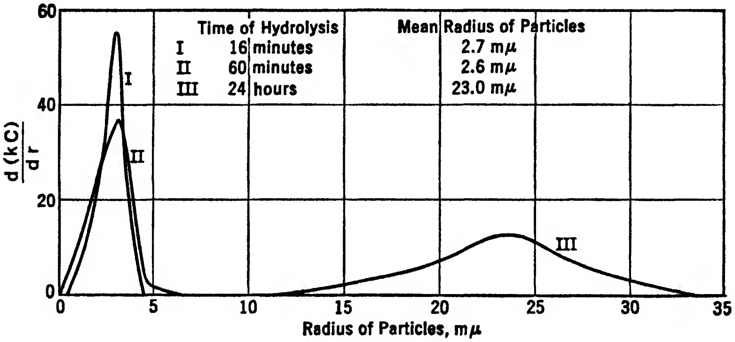

FIG. 56. Effect of time of hydrolysis of boiling 0.005 N $FeCl_3$ on the weight-optical distribution curves of colloidal Fe_2O_3 (weight-optical signifies that an apparent concentration is determined which is the product of the concentration C of particles of radius r and the absorption constant k of such particles).

Application of the ultracentrifuge: 3. Distribution of particle sizes in hydrosols. By means of the ultracentrifuge the particle size and distribution of particle sizes in sols may be determined. Nichols, Kraemer, and Bailey[32] have investigated, in this way, ferric oxide sols formed by hydrolysis of ferric chloride at 100° for varying lengths of time. Some typical results, given graphically in Fig. 56, show that the particles in such sols are not uniform in size and that the mean radius of the particles increases with the duration of heating the sol.

Sedimentation Equilibrium: Equations of Perrin and Svedberg

In a gravitational field. The settling of colloidal dispersions under the influence of gravity is opposed by the osmotic pressure and diffusion occasioned by the Brownian movement. After a time, these two opposing forces come to an equilibrium state, the so-called *sedimentation equilibrium.* In Fig. 57 is given Perrin's diagrammatic representation of the distribution of uniformly sized particles in a gamboge sol when sedimentation equilibrium is established. Smoluchowski[6] pointed out that this distribution may be represented by Laplace's hypsometric formula by means of which atmospheric pressure at a given height is calculated. Perrin[15] has derived the equation for the distribution of particles in sols.

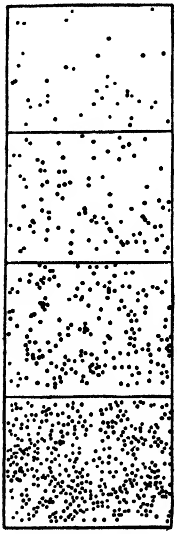

FIG. 57. Diagrammatic representation of the distribution of uniformly sized particles in a gamboge sol (Perrin).

Start with a system in equilibrium in a cylindrical vessel 1 cm^2 in cross section. At height x_1 above the bottom of the container, there are n particles, and at height x_2, the small distance dx above x_1, there are $n + dn$ particles. Now the tendency of the particles to diffuse upward is determined by the osmotic pressure which, from eq. 21, is $n/N\ RT$ at height x and $(n + dn)/N\ RT$ at height x_2. The difference in diffusion tendency in these two layers is thus:

$$-dn\frac{RT}{N} \tag{27}$$

This change in osmotic pressure is balanced by the gravitational force of the particles between the planes at x_1 and at x_2. Since the cross section of the vessel is 1 cm^2 and the distance between the planes is dx, the volume is dx. If n is the number of particles in unit volume, then ndx is the number of particles between the planes, and, from eq. 22, the force of gravity is:

$$ndx\tfrac{4}{3}\pi r^3(\rho_p - \rho_{H_2O})g \tag{28}$$

where ρ_p and ρ_{H_2O} are the densities of the particles and of water, respectively. Equating 27 and 28 gives:

$$-\frac{RT}{N}dn = ndx\frac{4}{3}\pi r^3(\rho_p - \rho_{H_2O})g$$

or

$$-\frac{dn}{n}\frac{RT}{N} = \frac{4}{3}\pi r^3(\rho_p - \rho_{H_2O})gdx \tag{29}$$

Integrating this expression between n_1 and n_2 at the heights x_1 and x_2 gives Perrin's equation:

$$\frac{RT}{N}\ln\frac{n_2}{n_1} = \frac{4}{3}\pi r^3(\rho_p - \rho_{H_2O})g(x_1 - x_2) \tag{30}$$

In a centrifugal field. Equilibrium is established in a centrifugal field when, during the time dt, the quantity ds of the dispersed phase that is driven by centrifugal force through unit surface toward the periphery is the same as that which diffuses toward the center of rotation. The sedimentation velocity is:

$$\frac{ds}{dt} = c\omega^2 xM(1 - V\rho)\frac{1}{f} \tag{31}$$

and the diffusion velocity is:

$$\frac{ds}{dt} = -RT\frac{dc}{dx}\cdot\frac{1}{f} \tag{32}$$

where c is the concentration of sol, f the frictional coefficient (eq. 23), and ω, x, M, V, ρ, R, and T are the same as the corresponding symbols in eqs. 25 and 26. Equating eqs. 31 and 32 and eliminating give:

$$\frac{dc}{c} = \frac{M(1 - V\rho\omega^2 xdx)}{RT} \tag{33}$$

Integrating eq. 33 between the points x_1 and x_2 corresponding to concentrations c_1 and c_2, and solving for M, give Svedberg's equation for calculating particle or molecular weight:

$$M = \frac{2RT\ln(c_1/c_2)}{(1 - V\rho)\omega^2(x_1^2 - x_2^2)} \tag{34}$$

Validity of equations. Perrin tested eq. 30 by measuring the number and size of the particles in sols of mastic and gamboge after sedimentation equilibrium was established. His counts were made with a microscope, using a dark-field condenser, so that the distance between the layers x_1 and x_2 was of microscopic dimensions. Within this narrow range, the agreement between observed and calculated values of n was fairly good. Conversely, the average value of a large number of determinations of N, using this technique, was 6.8×10^{23}.

Similar measurements on gold sols were made by Westgren[18, 33] over a wider range, as shown in Table 43. With particles 21 mμ in radius, the equation applied from 0 to 1100 μ, that is, over a range of 1.1 mm. Similar results were found with particles 20.5, 25.5, 31.5, and 50 mμ in radius. The equilibrium was obtained with smaller particles by allowing them to diffuse up from a concentrated layer of sol at the bottom of the observation cell. With the 50-mμ sol, the same equilibrium was obtained by both diffusion and settling. The mean value of N for a number of determinations on gold sols was found to be 6.05×10^{23} in agreement with the generally accepted value of 6.06×10^{23}.

TABLE 43

SEDIMENTATION EQUILIBRIUM IN GOLD SOLS

Height x (μ)	Number of particles		Height x (μ)	Number of particles	
	Observed	Calculated		Observed	Calculated
0	889	886	600	217	239
100	692	712	700	185	192
200	572	572	800	152	154
300	428	460	900	125	124
400	357	369	1000	108	100
500	253	297	1100	78	80

Burton and Currie[34] and Porter and Hedges[35] failed to confirm the observations of Perrin and Westgren, probably because they did not work under conditions necessary for the attainment of equilibrium.[36]

From sedimentation equilibrium data on protein sols obtained with the ultracentrifuge, Svedberg calculated the molecular weights by means of eq. 34. The resulting values agreed well with those found from sedimentation velocity data (Table 42).

MOLECULAR WEIGHT *VS.* PARTICLE WEIGHT OF COLLOIDALLY DISPERSED PARTICLES

Since a colloidal particle suspended in a liquid behaves like a dissolved molecule, measurements of osmotic pressure, diffusion, and sedimentation in colloidal systems have given the necessary data for calculating the so-called "molecular weight" of the dispersed particles. For example, 6.06×10^{23} particles of Perrin's gamboge will weigh 30,000,000,000 g or approximately 33,000 tons. Perrin points out that the largest granules of mastic which follow the laws of perfect gases are visible in sunlight under a strong lens, the particles behaving as would the particles of a perfect gas with a gram-molecular weight of 200,000 tons. Obviously, these are not the ordinary molecular weights of the chemist. Moreover, since the particles of a suspened substance may vary widely in size, it is apparent that the substance can have any number of so-called molecular weights, depending on the size of the dispersed particles. And finally, different substances may have the same molecular weight because a suspended particle of gold, for example, may weigh the same as a suspended particle of alumina. In other words, the so-called molecular weights of suspended substances are not specific and vary continuously with the degree of subdivision.

This point of view seems to contradict the usual concept of molecular weights as used by the chemist. The gram-molecular weights determined from vapor density or change in vapor pressure are fixed values, specific for each substance. The absolute molecular weight, that is, the weight of a single molecule, is the gram-molecular weight divided by the Avogadro number; but, as Bancroft[37] points out, the two concepts of molecular weight are not so divergent as they seem. The molecular weight of a suspended particle is the weight, or a function of the weight, of the individual particle. It varies continuously, therefore, with the particle size and is non-specific. On the other hand, the molecular weight of a gaseous or dissolved substance is the weight of a single molecule of that substance. Hence the weight of a single molecule is the lower limiting value which the weight of a suspended particle approaches continuously, as the particle is continuously subdivided. The specificity comes in only at the limiting values, the weights of the single molecules.

Under the circumstances, it would seem highly desirable to speak of the particle weight of suspended particles, using the term molecular weight in its time-honored sense to refer to the weight of a single molecule. The gram-particle weight and the gram-molecular weight would be the particle weight and molecular weight, respectively, multiplied by the Avogadro number. In some instances it appears that the molecular weights of large single molecules of proteins have been determined. Only when this is known definitely should the term molecular weight be substituted for the term particle weight of a dispersed protein.

VISCOSITY AND PLASTICITY

Viscosity

Viscosity is a property of liquid systems which depends largely on the relation between kinetic motion and free or specific surface. It may be defined as the internal friction of a liquid or its resistance to flow or shear. It is measured by: (1) the time of flow through an orifice under a fixed head or pressure (Ostwald or Engler viscosimeters); (2) the force needed to shear layers of liquid past each other (Couette or MacMichael viscosimeters); (3) the rate of fall of a sphere through a tube of liquid (falling-ball viscosimeters). The standard of viscosity, the *poise,* is the tangential force required to maintain a velocity of 1 cm/sec between two planes 1 cm^2 in area and 1 cm apart. The *centipoise* is 0.01 of a poise. The fluidity ϕ of a liquid is the reciprocal of the viscosity η: that is, $\phi = 1/\eta$.

The equation of Poiseuille (after whom the *poise* is named) for the rate of flow of a liquid through a capillary tube is:

$$V = \frac{\pi r^4 P}{8 l \eta} \tag{35}$$

where V is the volume of liquid of viscosity η that flows through a capillary tube of length l and radius r, under a pressure P in unit time. The equation is known as *Poiseuille's law.* It represents the facts for pure liquids, solutions, and hydrophobic sols when the pressure is not too high. Hydrophilic sols, on the other hand, frequently fail to obey Poiseuille's law, the observed viscosities varying with the rate of capillary flow. This is especially true if the sols tend to form jellies or if the particles deviate markedly from a spherical shape. Such sols possess not only a liquid viscosity but also a certain amount of elasticity[38] such as is found in solids.

Since viscous flow is proportional to the driving pressure, the simplest form of the velocity equation is:

$$\frac{V}{P} = K \qquad (36)$$

in which V is the volume of liquid passing through the capillary in 1 sec; P, the pressure in g/cm^2 producing the flow; and K, a constant.

Viscosity of sols. The viscosity of dilute hydrophobic sols is, in general, about the same as that for water and increases regularly but slightly with the concentration. The viscosity of hydrophilic sols, on the other hand, increases rapidly with increasing concentration. The form of the viscosity-concentration curves of the two types of sols is shown diagrammatically in Fig. 58.

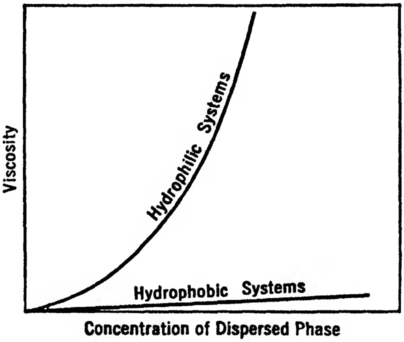

Fig. 58. Viscosity-concentration curves for hydrophobic and hydrophilic systems.

Einstein[39] has deduced an equation for the viscosity of a suspension of rigid spheres in any liquid:

$$\eta_s = \eta_m(1 + k\varphi) \qquad (37)$$

in which η_s is the viscosity of the suspension; η_m, that of the medium; φ, the volume of the dispersed phase; and k, a constant which Einstein first made 1 and later 2.5. This equation applies equally well to dilute suspensions and hydrophobic sols. Hatschek[40] derived a similar formula in which $k = 4.5$, for cases in which the dispersed material is less than 40% of the total volume.

According to the Einstein equation, the viscosity of a sol depends only on the volume of the dispersed phase and not at all on the degree of dispersity. Odén[41] found, however, that the viscosity of a sulfur sol increases with the degree of dispersion. To account for this behavior, Hatschek[42] assumed a film of adsorbed water around the sulfur particles, a factor which was not taken into account when the equation was derived. For sulfur particles having a diameter of 10 mμ, Hatschek calculated that the thickness of the adsorbed film is 0.87 mμ, corresponding to an increase in volume of 62%.

Other empirical viscosity equations that have been proposed are:

$$\eta_s = \eta_m \frac{1}{1 - \sqrt[3]{\varphi}} \quad \text{(Hatschek}^{43}\text{)} \tag{38}$$

$$\eta_s = \eta_m \frac{1 + 0.5\varphi}{(1 - \varphi)^4} \quad \text{(Kunitz}^{44}\text{)} \tag{39}$$

$$\eta_s = K_m M c \quad \text{(Staudinger)} \tag{40}$$

In the Staudinger equation, K_m is a constant for each homologous polymeric system, c is the concentration in base moles per liter, and M is the average molecular weight.

Kunitz maintains that eq. 39 applies not only to solutions of sugars but also to high polymeric materials such as glycogen, starch, casein, and rubber for concentrations up to 50%. Mark[45] has summarized in tabular form other useful expressions for the specific viscosity of high polymeric systems. He[45] has also discussed in detail the limitations and applicability of the Staudinger equation for determining molecular weight from viscosity measurements and proposed modifications of the Staudinger equation to make it more applicable for the polymers of low molecular weight in an homologous series.

Smoluchowski[46] pointed out that the viscosity of a suspension of charged particles should be different from one containing uncharged particles since the motion of charged particles in a liquid sets up an opposing electromotive force which causes an apparent rise in the viscosity. He therefore combined Einstein's eq. 37 with the electrokinetic equation (eq. 11), obtaining the following:

$$\eta_s = \eta_m \left\{1 + 2.5\varphi \left[1 + \frac{1}{\lambda \eta_m r^2}\left(\frac{D\zeta}{2\pi}\right)^2\right]\right\} \tag{41}$$

in which λ is the specific conductivity; r, the radius of the particles; D, the dielectric constant; and ζ, the electrokinetic potential. This equation applies to hydrophilic as well as to hydrophobic sols. Its importance in connection with the theory of the stability of hydrophilic sols will be considered in Chapter 18.

Many factors affect the viscosity of hydrophilic sols: concentration, temperature, degree of dispersion, solvation, electrical charge, previous thermal treatment, previous mechanical treatment, presence or absence of other hydrophilic colloids as impurities, presence of both electrolytes and non-electrolytes, rate of flow, and rate of shear.

Plasticity

Viscous flow is proportional to the driving pressure (eq. 36). Fluids start to flow and continue to flow by the driving force of their own weight. Certain substances, on the other hand, start to flow only after the application of external pressure. Such substances are said to be *plastic,* and their flow is designated as *plastic flow.* The force necessary to deform the system so that plastic flow can begin is called the *yield value.* The relationship between viscosity and plasticity [47] is shown diagrammatically in Fig. 59. For a truly viscous system, the increase in rate of flow with increase in the applied force is a linear function, as represented by the line *AB* which passes through the origin. The line *CD* which represents plastic flow intersects the force axis at the right of the origin. The force *AE* is called the *yield value.* In investigating plastic substances, it is necessary to determine not only the rate of flow per unit of applied force but also the yield value.

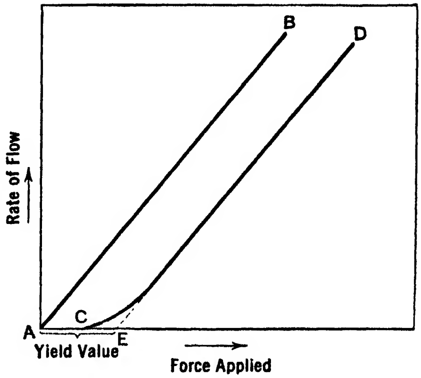

FIG. 59. Diagrammatic representation of the relationship between viscosity and plasticity.

As we have seen, the simplest equation for viscosity is: $V/P = K$. In terms of plasticity this becomes:

$$\frac{V}{P - p} = K \tag{42}$$

in which p is the yield value pressure in g/cm^2.

An equation for plastic flow proposed by Bingham and White [48] is:

$$\text{Consistency} = \frac{\pi r^4 g(P - p)t}{8lV} \tag{43}$$

in which r is the radius and l the length of the capillary in centimeters; g, the acceleration due to gravity; t, the time in seconds; V, the volume of flow; and $(P - p)$ has the same significance as in eq. 42. As a rule plasticity is expressed in terms of *mobility* μ which is the reciprocal of *consistency.*

Staudinger's Viscosity Law and the Molecular Weight of High Polymers [49]

The viscosity of solutions of high polymers, measured at the same weight concentration, increases with increasing length of the polymer chain. Staudinger's equation which gives the increase in relative viscosity in terms of the molecular weight of the high polymer is:

$$\frac{\eta}{\eta_0} - 1 = KMc = \eta_{sp} \tag{44}$$

in which η is the viscosity of solution, and η_0 is the viscosity of the pure solvent; (η/η_0), the relative viscosity which is measured directly in a capillary viscosimeter; $(\eta/\eta_0) - 1$, the specific viscosity η_{sp}. The specific viscosity changes with concentration, and Staudinger's law most nearly represents the facts if the measurements are extrapolated to zero concentration. η_{sp}/c, with decreasing concentration c, approaches as a limit the intrinsic viscosity $[\eta]$. In terms of intrinsic viscosity, Staudinger's law becomes:

$$[\eta] = KM \tag{45}$$

The coefficient K depends only slightly on the molecular weight, M. Therefore, if the viscosity is known for one sample of known molecular weight, it is possible by the use of Staudinger's equation to make a fair estimate of the molecular weight of other samples (see p. 199).

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CHAPTER 14

The Constitution of Sols: The Electrical Double Layer

CONSTITUTION OF HYDROPHOBIC SOLS

Sols of the hydrophobic type, which include most of the sols of the elements, their oxides, and salts, can be prepared fairly free from electrolytes; but it was demonstrated first by Graham and confirmed repeatedly thereafter that, in the absence of protecting colloids, some electrolyte must be present in the sols to ensure their stability. Thus, silver halide sols are peptized in a stable form by a small excess of silver nitrate or of alkali halide; metallic sulfide sols are kept in the sol state by a small excess of hydrogen sulfide; and hydrous oxide sols, formed by hydrolysis of metallic chlorides, are stabilized by a little metallic chloride or hydrochloric acid. The constitution of the colloidal particles and the rôle of the stabilizing electrolyte in several typical sols will be considered in the following sections.

Salt Sols

Sols of the silver halides are typical of salt sols. The particles in these sols possess a definite crystal lattice on the surface of which is adsorbed either silver ions or halide ions, depending on which is present in excess. To illustrate, the constitution of a portion of a particle in (*a*) negatively charged silver iodide sol and (*b*) positively charged silver iodide sol is represented diagrammatically in Fig. 60. Consider first the negatively charged particle which exists in the presence of a slight excess of hydriodic acid. The roman letters Ag and I represent the respective ions in the silver iodide lattice, whereas the letters I^- (in italics) and H^+ represent the respective ions of the stabilizing electrolyte. At some active edge or spot, iodide ions are adsorbed by the silver ions of the lattice, thereby setting up a double layer. The attached iodide ions constitute the inner portion of the layer, and hydrogen ions, the outer portion. The outer portion consists of a diffuse layer of ions, a few of which are held by the electrostatic attraction of the negative inner layer but most of which, because of relatively higher kinetic energy, exert sufficient osmotic repulsive force against the attraction of the inner layer to influence a hydrogen electrode and so may be detected potentiometrically. The latter ions are represented in the diagram to the right of the broken line. The particle is negatively charged because the inner negative portion of the double layer is attached and the outer positive portion is diffuse. Hence all that portion of the particle to the left of the broken line will move to the anode under electrical stress, and the hydrogen ions in the outermost portion of the outer layer to the right of the broken line will move to the cathode. Although the attached inner layer is represented as uniform, it is probably somewhat diffuse also.

Following the usual terminology, the electrolyte to which a sol owes its stability is called the *stabilizing electrolyte* (hydriodic acid in the case under consideration); the adsorbed ions which constitute the inner portion of the double layer are called the *stabilizing ions* or *potential-determining ions* (I^- in Fig. 60*a*); the ions which constitute the outer diffuse portion of the double layer are termed the *counter ions* (H^+ in Fig. 60*a*). Sols in which hydrogen ions are the counter ions are sometimes called *acidoid sols.* The dispersed particle plus the entire double layer is called the *colloidal particle* or *micelle;* the dispersed particle plus that portion of the double layer which migrates with it under electrical stress is called the *charged particle* or *charged micelle.*

In the positively charged silver iodide particle represented in Fig. 60*b*, silver nitrate is the stabilizing electrolyte, silver ions (in italics) are the stabilizing ions, and nitrate ions are the counter ions.

Arsenic trisulfide sol typifies the large group of metallic sulfide sols. Linder and Picton[1] recognized the necessity for the presence of a slight excess of hydrogen sulfide for the stability of such sols and concluded therefore that they are polymerized hydrosulfides such as $16As_2S_3 \cdot H_2S$. Pauli and Semler[2] considered $H_2As_2S_4$ to be the stabilizing electrolyte in arsenic trisulfide sol and believed the sol to be a strongly dissociated complex acid to which they assigned the formula $[xAs_2S_3 \cdot As_2S_4H_2 \cdot As_2S_4H]^- + H^+$. This formula was made to fit the specific case where but one of four hydrogens is displaced on coagulating the sol with barium chloride, the remaining three appearing in the supernatant solution after coagulation. But, as a matter of fact, it is now quite generally recognized that the composition of the sol particles varies with the method of preparation, the excess of peptizing electrolyte, the age, and the treatment to which the sol is subjected. There appears no good reason for attempting to assign a definite formula to a mixture of such variable composition. Precipitated in the presence of hydrogen sulfide, the resulting hydrous particles adsorb H_2S and also adsorb the stabilizing HS^- ions which constitute the inner portion of the double layer on the particles; the counter H^+ ions form the diffuse outer portion of the double layer. The constitution may be represented as shown diagrammatically in Fig. 61*a*.[3] The particles of an aged sol contain more or less H_3AsO_3, and thioarsenate in minute amounts is neither excluded nor established.[4]

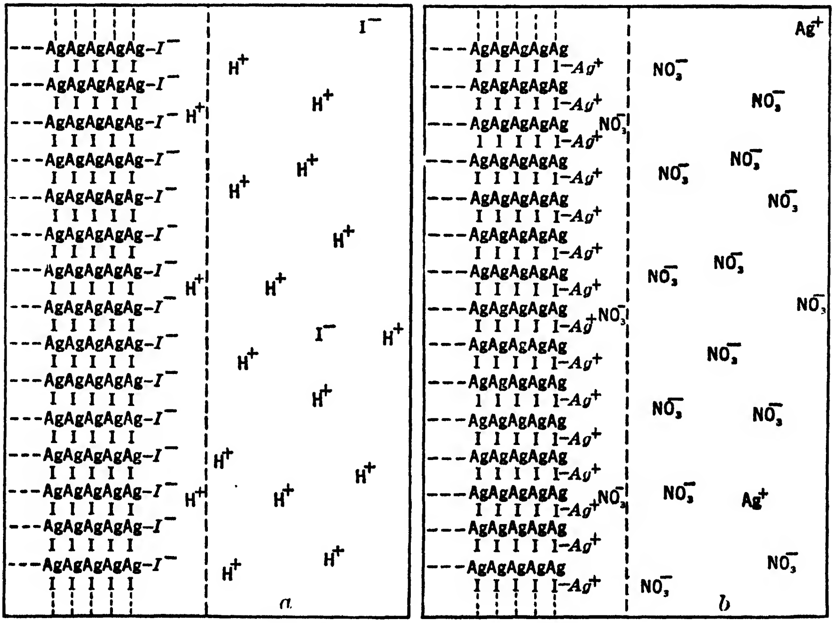

FIG. 60. Diagrammatic representation of the constitution of a portion of a particle of (*a*) negatively charged silver iodide sol, (*b*) positively charged silver iodide sol.

Copper ferrocyanide gives a highly stable sol with potassium ferrocyanide or hydroferrocyanic acid as the stabilizing electrolyte. A diagram of the constitution of the particles in such a sol is given in Fig. 61*b*, in which $R^{\equiv}$ represents the stabilizing $[HFe(CN)_6]^{\equiv}$ ion.

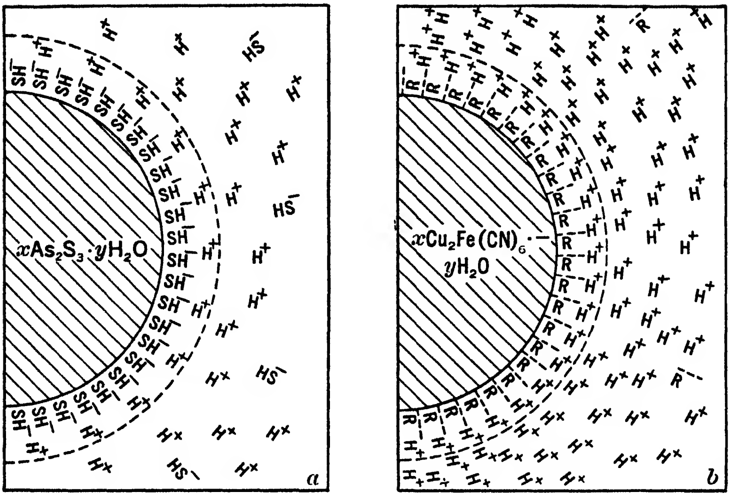

FIG. 61. Diagrammatic representation of the constitution of the particles in (a) arsenic trisulfide sol, (b) copper ferrocyanide sol.

Hydrous Oxide Sols

Hydrous oxide sols have played an important rôle in colloid chemistry, both theoretical and applied.[5] The constitution of the particles in such colloidal systems has been the subject of many inquiries.

As has been pointed out, a sol of hydrous ferric oxide formed by hydrolysis of ferric chloride, or by peptization of the hydrous oxide gel with ferric chloride, always contains more or less chloride, however carefully it may have been purified by dialysis. The presence of chloride in the dialyzed sol led Wyrouboff and Verneuil[6] to suggest that the various preparations contain basic salts or chlorides of condensed hydroxides. This idea was further extended and developed by a number of people, including Duclaux,[7] Malfitano,[8] Hantzsch and Desch,[9] and Linder and Picton.[10] Thus the constitution of ferric oxide sols was represented by such formulas as $[20Fe(OH)_3 \cdot FeCl_3]$ and $[45Fe(OH)_3 \cdot FeCl_3]$.

The view that the oxide sols are oxysalts or basic salts meets with serious objection at the outset, since definite oxychlorides or basic chlorides are obtained, if at all, only under special conditions. No oxychloride of aluminum has been established with certainty, and but one ferric oxychloride has been identified: FeOCl prepared by heating ferric chloride in a bomb tube between 270 and 410°. As a matter of fact, the ratios of Fe to Cl in ferric oxide sols have been found to vary all the way from 6 to 2700, depending on the method of formation and purification.

Pauli[11] considers the colloidal particles in hydrous oxide sols to be complex ions resulting from the ionization of complex electrolytes allied to the Werner compounds. Since the composition of a given sol varies with the conditions of preparation, Pauli represents it by a general formula. This is: $[x\mathrm{Fe(OH)_3}\cdot y\mathrm{FeOCl}\cdot\mathrm{FeO}]^+$, (Cl^-) for hydrous ferric oxide, and herein $x = 32$ to 350 and $y = 4$ to 5.7. Although this formulation may be satisfactory in a general way, it is difficult to justify the details of the formula, since no one has established the existence of $\mathrm{Fe(OH)_3}$, and FeOCl is obtained only under special conditions in a bomb tube at elevated temperatures.

Thomas[12] suggests that the dispersed phase in hydrous oxide sols, such as alumina sol formed by peptizing the alumina gel from amalgamated aluminum in dilute hydrochloric acid, consists of olated and possibly oxolated aluminum oxychloride complexes of the Werner type resembling the polyol basic chromic salts formulated by Bjerrum.[13] It has been found by x-ray diffraction analysis that the gel formed by the action of amalgamated aluminum on water at 100° is $\gamma\text{-}\mathrm{Al_2O_3}\cdot\mathrm{H_2O}$ [or $\gamma\text{-}\mathrm{AlO(OH)}$], and, later in this chapter (p. 221), evidence will be given to show the dispersed phase in a sol prepared by Thomas's procedure is $\gamma\text{-}\mathrm{Al_2O_3}\cdot\mathrm{H_2O}$. The exact crystal structure of $\gamma\text{-}\mathrm{Al_2O_3}\cdot\mathrm{H_2O}$ is not known, but when this is worked out, the structure of the dispersed phase in Thomas's sol will be known.

The constitution of positively charged hydrous alumina sol particles may be represented diagrammatically as shown in Fig. 62*a*.[14] Although the particles consist largely of the hydrous oxide, they usually contain some chloride that is difficult to displace. Moreover, the actual composition is determined by the method of formation and the subsequent history. Accordingly, the particle, exclusive of the double layer, has a composition represented by some point in the three-component diagram $\mathrm{Al_2O_3}$—HCl—$\mathrm{H_2O}$ which may be represented $x(\gamma\text{-}\mathrm{Al_2O_3}\cdot\mathrm{H_2O})y\mathrm{HCl}\cdot z\mathrm{H_2O}$. The stabilizing ions of the fixed inner portion of the double layer are Al^{+++} and H^+, and the counter ions of the diffuse outer layer are Cl^-. The chloride ions of the diffuse layer which influence the calomel electrode, and so may be detected potentiometrically, are represented in the diagram to the right of the broken line.

Hydrous stannic oxide gives a typical, negatively charged oxide sol. The gel formed by hydrolysis of stannic chloride is readily peptized by a small amount of ammonia.[15] The sol particles are crystalline, giving the same x-ray diffraction pattern as the mineral cassiterite. It is probable that hydroxyl ions are the chief stabilizing ions, although some stannate ions, formed by solution of the gel in ammonia, may be present in the inner fixed portion of the double layer, the outer diffuse portion of which is ammonium ions. The constitution of a particle is represented diagrammatically in Fig. 62*b*.

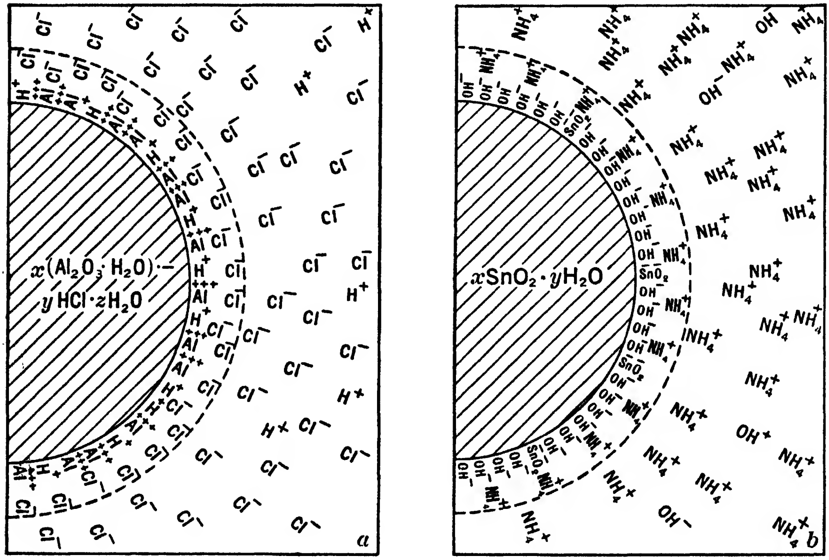

FIG. 62. Diagrammatic representation of the constitution of the particles in (*a*) hydrous alumina sol, (*b*) hydrous stannic oxide sol.

Since hydrous oxide sols formed in the presence of chloride, say, always contain more or less chloride, Thomas believes that such preparations should be designated metallic oxychloride sols rather than hydrous oxide sols. He recognized that the term ferric oxychloride hydrosol, for example, is objectionable since it connotes a definite chemical compound when no such meaning is intended. Nevertheless, he prefers to refer to hydrous oxide sols as oxysalt sols since the colloidal particles are not pure hydrous oxides or hydroxides. To be consistent, the metal sols and salt sols should be renamed, since the dispersed phase in such systems is not pure metal and salt, respectively. It is difficult to see what would be gained by introducing such a change in our terminology. As we have seen, the ratios of iron to chlorine in ferric oxide sols have been variously reported between 6 and 2700. To designate a sol with a low chloride content as an oxychloride sol is like calling precipitated barium sulfate a chlorosulfate because it contains some adsorbed barium chloride.

Element Sols

Sols of the elements are highly dispersed particles of metal or nonmetal stabilized by preferential adsorption of one of the ions of a stabilizing electrolyte. The stabilizing electrolyte in gold sol prepared by reduction of chloroauric acid, or by arcing gold electrodes in dilute hydrochloric acid solution, is $HAuCl_2$, according to Pauli.[16] $AuCl_2^-$ ion forms the inner portion of the double layer, so that the particles are negatively charged. Silver sols may be prepared by the arcing method in pure water,[17] the stabilizing electrolyte being AgOH, which results from oxidation of the silver. The stabilizing ions are OH^- ions adsorbed either directly on the surface of the silver lattice or, more likely, on a film of oxide on the particle surface. Platinum sols may likewise be prepared by the arcing process in pure water.[18] The particles have a film of PtO_2 around them, and the stabilizing electrolyte is $H_2Pt(OH)_6$. Sulfur sol formed by oxidation of hydrogen sulfide by sulfur dioxide (p. 143) is stabilized as a negative sol by preferential adsorption of pentathionate ion from pentathionic acid formed

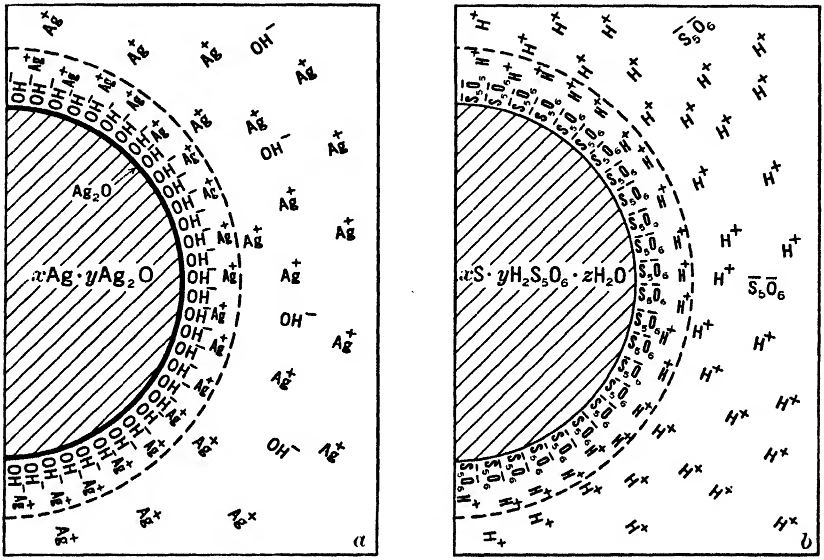

FIG. 63. Diagrammatic representation of the constitution of the particles in (a) silver sol, (b) sulfur sol.

in the process. This list could be extended to include most of the metals and solid non-metals. The constitution of the negatively charged colloidal particles in silver sol and sulfur sol is shown diagrammatically in Fig. 63*a* and *b*.

Formulation of the Constitution of Sols

Diagrams like those in Figs. 60, 61, 62, and 63 are useful for representing the constitution of sols; but, to conserve space, it is suggested that the constitution of hydrosols such as those mentioned in the preceding paragraphs be represented symbolically as shown in Table 44.

TABLE 44

SYMBOLIC REPRESENTATION OF THE CONSTITUTION OF SOME TYPICAL HYDROSOLS

Sol	Solid phase	Inner ionic layer	Diffuse outer ionic layer
Silver iodide (−)	$[x\mathrm{AgI}]$	I_n^-	$(n - q)\mathrm{H}^+, q\mathrm{H}^+$
Silver iodide (+)	$[x\mathrm{AgI}]$	Ag_n^+	$(n - q)\mathrm{Ag}^+, q\mathrm{Ag}^+$
Arsenic trisulfide	$[x\mathrm{As_2S_3} \cdot y\mathrm{H_2O}]$	$(\mathrm{HS}^-)_n$	$(n - q)\mathrm{H}^+, q\mathrm{H}^+$
Copper ferrocyanide	$[x\mathrm{Cu_2Fe(CN)_6} \cdot y\mathrm{H_2O}]$	$[\mathrm{HFe(CN)_6}^{\equiv}]_n$	$(3n - q)\mathrm{H}^+, q\mathrm{H}^+$
Ferric oxide	$[x\mathrm{Fe_2O_3} \cdot y\mathrm{HCl} \cdot z\mathrm{H_2O}]$	$\mathrm{Fe}_m^{+++}, \mathrm{H}_n^+$	$(3m + n - q)\mathrm{Cl}^-, q\mathrm{Cl}^-$
Alumina	$[x(\mathrm{Al_2O_3} \cdot \mathrm{H_2O}) \cdot y\mathrm{HCl} \cdot z\mathrm{H_2O}]$	$\mathrm{Al}_m^{+++}, \mathrm{H}_n^+$	$(3m + n - q)\mathrm{Cl}^-, q\mathrm{Cl}^-$
Stannic oxide	$[x\mathrm{SnO_2} \cdot y\mathrm{H_2O}]$	$(\mathrm{OH}^-)_n$	$(n - q)\mathrm{NH_4}^+, q\mathrm{NH_4}^+$
Gold	$[x\mathrm{Au}]$	$(\mathrm{AuCl_2}^-)_n$	$(n - q)\mathrm{H}^+, q\mathrm{H}^+$
Platinum	$[x\mathrm{Pt} \cdot y\mathrm{PtO}]$	$[\mathrm{Pt(OH)_6}^{=}]_n$	$(2n - q)\mathrm{H}^+, q\mathrm{H}^+$
Silver	$[x\mathrm{Ag} \cdot y\mathrm{Ag_2O}]$	$(\mathrm{OH}^-)_n$	$(n - q)\mathrm{Ag}^+, q\mathrm{Ag}^+$
Sulfur	$[x\mathrm{S} \cdot y\mathrm{H_2O}]$	$(\mathrm{S_5O_6}^{=})_n$	$(2n - q)\mathrm{H}^+, q\mathrm{H}^+$

Examination of Sols by X-ray Diffraction Methods

Many materials that appear amorphous when examined by the microscope have been found to be crystalline on applying the technique of x-ray diffraction. By this procedure it has been found possible to determine the constitution of many highly gelatinous substances (p. 181). The composition of the colloidal particles in sols has also been determined by examining the gel resulting from evaporation, ultrafiltration, or coagulation of the sol. For example, it was found[19] that the moist gels obtained by ultrafiltration of alumina, stannic oxide, and indium hydroxide sols gave the respective x-ray diffraction patterns of $\gamma\text{-Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$, SnO_2 (cassiterite), and $\text{In}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ or In(OH)_3. Although it is often assumed that sol particles have the same constitution in the sol state as in the gel from the sol, the accuracy of the assumption can be established only by direct x-ray examination of the sols themselves.

The chief difficulties in the direct examination of sols by x-rays are: (*a*) the relatively low concentration of the solid phase; (*b*) the scattering of the x-rays by the water in the samples; and (*c*) the possibility of coagulating the sol by x-rays. Weiser and Milligan[20] minimized

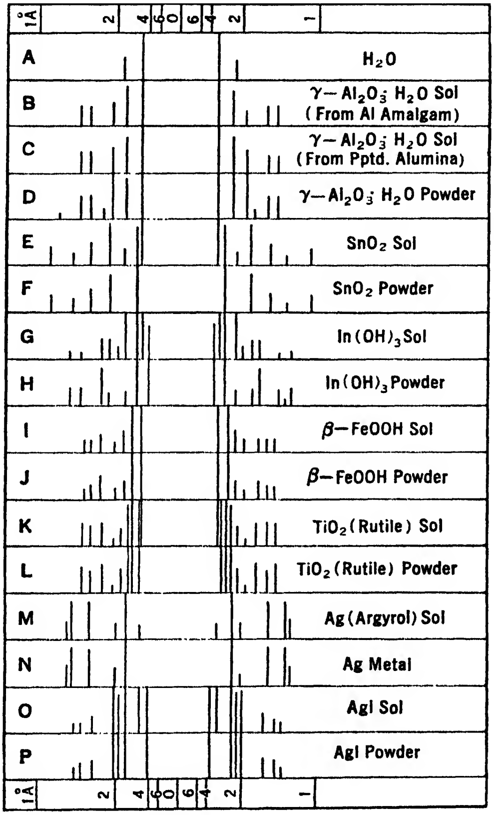

FIG. 64. Diagrams of the x-ray diffraction patterns of sols and of the powdered solids precipitated from the sols.

the first two difficulties by working with sols that were not too dilute and avoided the third by means of a special camera through which a continuous stream of sol was flowed in the path of the x-ray beam. Quite satisfactory diffraction patterns of the sols were obtained which were compared with the patterns from the corresponding powders. The results are shown in diagrammatic form in Fig. 64. These results are conclusive. In every instance, the x-ray diffraction pattern from the sol is a composite of the pattern of pure water and of simple oxide, salt, or element. If the sol is weak or the primary crystals very minute, the water bands predominate in the pattern; whereas, with stronger sols or larger primary crystals, the water bands appear less pronounced. Like the precipitated gels of elements, salts, and hydrous oxides, the particles in the hydrosols are not polymerized bodies or condensation products but consist essentially of aggregates of minute crystals of element, in the elementary sols; of simple salt, in the salt sols; and of simple oxide or of simple hydrate or hydroxide, in the oxide sols.

THE CONSTITUTION OF HYDROPHILIC SOLS

Hydrophilic sols of proteins, agar, etc., differ from the above-mentioned hydrophobic sols in that the stabilizing action of the solvent is more important than the charge on the particles. For example, a gelatin sol is stable when the particles have a positive charge, when they have a negative charge, and when they have no charge at all. The *p*H value at which the particles have neither a positive nor a negative charge is called the *isoelectric point* (p. 241); for gelatin, this is at *p*H = 4.7. Although one may have a stable hydrophilic sol without the particles having a charge, we shall see in Chapter 18 that the charge influences the stability to a certain extent in all cases and is quite important in some. To cite one example, casein forms a sol in either dilute acid or dilute basic solution, but is not peptized by water alone.

The isoelectric point of an amino acid in molecular solution lies at a certain *p*H value which is independent of the concentration. This is not true for protein sols; hence it is concluded that the colloidal particles of a protein consist of a number of molecules, only a part of which are on the outside in a position to react with the surrounding medium. If the medium is acidified with HCl, reaction takes place with the amino groups at the surface, forming RNH_3Cl, which ionizes to give RNH_3^+ ions that remain attached to the particle and Cl^- ions which form the outer portion of a diffuse layer; thus, the particle is positively charged. On the other hand, if the medium is rendered basic with sodium hydroxide, this reacts with carboxyl groups at the surface to give RCOONa which ionizes to give $RCOO^-$ ions that are attached to the surface and Na^+ ions that constitute the diffuse outer layer; thus negatively charged particles result. At the isoelectric *p*H value, there are as many —COONa groups as there are $—NH_3Cl$ groups, so that the charge on the particle is zero.

The constitution of the particles in hydrophilic sols may be represented by diagrams similar to those for hydrophobic sols stabilized by the preferential adsorption of ions. For example, in Fig. 65 are given diagrammatic representations of (*a*) a positively charged and (*b*) a negatively charged protein particle. The constitution of positive, negative, and neutral protein particles may be represented symbolically as follows:

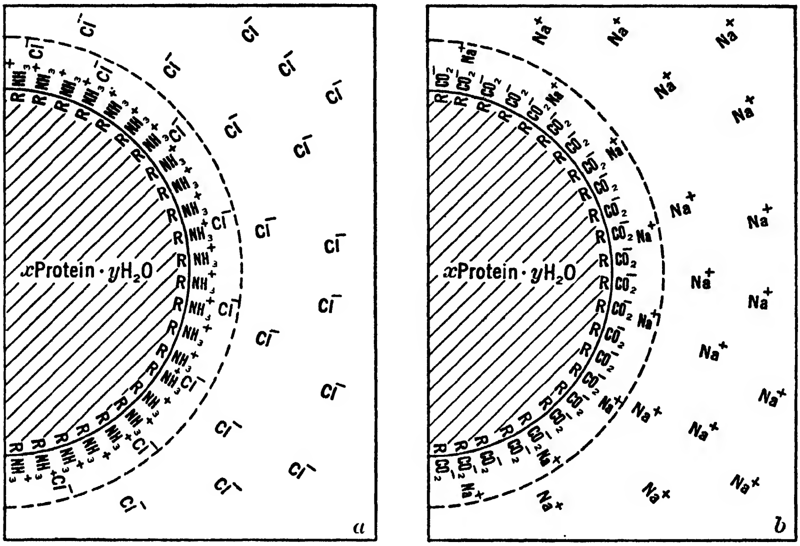

FIG. 65. Diagrammatic representation of the constitution of protein particles in (*a*) positively charged sol, (*b*) negatively charged sol.

Positively charged particle: $[x\text{protein},\ y\text{H}_2\text{O}]\cdot(\text{RNH}_3^{+})_n(n-q)\text{Cl} \vdots q\text{Cl}$

Negatively charged particle: $[x\text{protein},\ y\text{H}_2\text{O}]\cdot(\text{RCOO}^{-})_n(n-q)\text{Na} \vdots q\text{Na}$

Neutral particle: $[x\text{protein},\ y\text{H}_2\text{O}]$

Colloidal Electrolytes

The term *colloidal electrolytes* was suggested by McBain[21] for salts in which an ion has been replaced by a highly hydrous multivalent micelle that carries an equivalent sum-total of electrical charges and conducts electricity as well as or better than the simple ions it replaces (p. 247). The charged colloidal particles in such systems are termed *ionic micelles*.

Soap solutions furnish good examples of colloidal electrolytes.

These have been investigated extensively by McBain [22] during the past 40 years. As a result of an exhaustive study of the electrical and osmotic behavior of soap solutions such as sodium palmitate NaP ($P = C_{15}H_{31}COO^-$), he concludes that at certain concentrations the salt dissociates to give P^- anions which agglomerate to form highly hydrous colloidal particles that have the formula $(P^-)_n \cdot mH_2O$, in which n may be of the order 10–20. In other concentration ranges, neutral colloidal soap particles, $(NaP)_x \cdot mH_2O$, may exist, and at still others, there may be no colloidal particles but only: $NaP \rightleftarrows Na^+$ and P^-. In Fig. 66 are shown the relative proportions of the various constituents of pure sodium palmitate in different concentrations at 90°, as found by McBain. Thus, the nature of a soap solution varies with its concentration and also with its temperature.

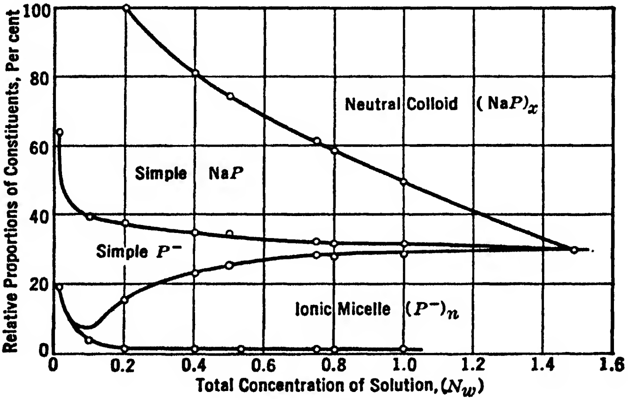

FIG. 66. Relative proportions of the constituents in different concentrations of sodium palmitate solution at 90°. (The field below the bottom curve is the proportion $(NaP)_2 \cdot HP$ present.)

McBain and Bowden [23] point out that the ionic micelle must contain a certain amount of neutral colloid and therefore should be formulated $(NaP)_x \cdot (P^-)_n \cdot (H_2O)_m$; but the amount of $(NaP)_x$ is small compared to $(P^-)_n$, most of the $(NaP)_x$ existing independently as neutral micelles.

Many substances, in addition to soaps, belong to the group of colloidal electrolytes. Among these may be mentioned certain dyes, indicators, the higher sulfonic acids and hydrochlorides, silicates, tellurates; in fact, most substances with high molecular weight or with long carbon chains which are capable of splitting off ordinary ions that agglomerate to give ionic micelles. To cite another illustration, Congo red, which may be formulated Na_2R, dissociates to give Na^+ ions and $R^=$ (or

NaR^-) ions which agglomerate to form a hydrous ionic micelle that may be formulated $(R^=)_n \cdot mH_2O$. But, since the colloidal particle doubtless contains some undissociated dye, the constitution of the ionic micelle is best represented by the formula $(Na_2R)_x \cdot (R^=)_n \cdot (H_2O)_m$ or $(Na_2R)x \cdot (NaR^-)_n \cdot (H_2O)_m$, analogous to the formulas of the soap micelle.

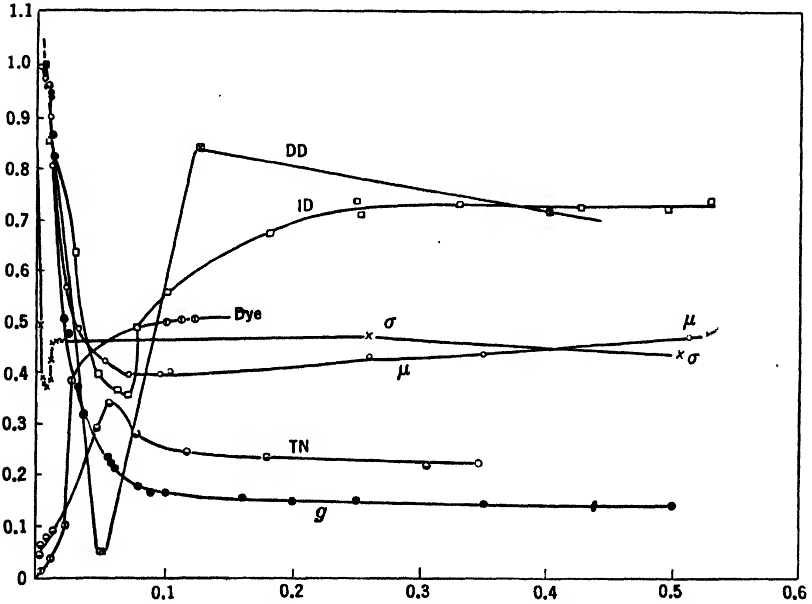

FIG. 67. Quantitative data for solutions of a typical colloidal electrolyte, lauryl sulfonic acid, including conductivity (μ), transport number (TN), osmotic coefficient (*g*), integral diffusion coefficient (1D), differential diffusion coefficient (DD), dye solubilization, dye, surface tension (σ), to show the shape of each curve and the actual concentrations at which maxima and minima occur for different properties.

Some prefer to regard such hydrophobic sols as ferric oxide, arsenic trisulfide, and gold as electrolytes with colloidal ions. It must be emphasized, however, that there is a fundamental difference between sols, on the one hand, and non-colloidal, complex electrolytes such as potassium ferrocyanide, the cobalt amines, and the complex platinic salts, formulated by Werner, on the other. There is also a distinct difference between colloidal ferric oxide and such colloidal electrolytes as the soaps and Congo red, in that the latter contain ionic micelles which are made up of groups of ions having a definite composition and which carry one charge for each equivalent of the ion, whereas the micelles of ferric oxide sol have no definite composition and may carry hundreds or thousands of equivalents for each free charge.

In addition to the soaps and the dyes, most of the biocolloids, for example, the bile salts, and the gums belong to this class of compounds, the colloidal electrolytes. A few inorganic salts such as silicates and clays belong in this group, but the vast number are synthetic organic compounds and derivatives, including the soap substitutes to which reference has already been made (p. 224).

Some quantitative data obtained in McBain's laboratory and shown in Fig. 67 illustrate the behavior of a typical colloidal electrolyte, lauryl sulfonic acid, a highly soluble, non-hydrolyzable free acid, based upon a paraffin chain of 12 carbon atoms. These quantitative data are explained by McBain by assuming the presence of many sizes and kinds of colloidal particles, shifting according to the concentration. Lottermoser and Puschel first demonstrated the existence of a critical zone in which appears a maximum concentration of colloidal micelles.

THE ELECTRICAL DOUBLE LAYER

Nature

The older concept of the double layer at the interface solid-solution assumed it to consist of two "monoionic" layers of opposite charge touching each other at the boundary plane.[24] The modern theory due to Gouy [25] assumes that the total potential drop caused by the double layer occurs in the outer liquid portion which consists of a diffuse layer of ions. Stern [26] assumes that part of the ions remain attached to the surface (within the broken lines in Figs. 60–63), and part are free to move. He thus takes into account the size and physical properties of the ions constituting the outer layer. The attached ions are held by electrostatic and physical forces which differ for each ion; that is, each ion possesses a specific adsorption potential. The curve in Fig. 68 represents diagrammatically the drop in potential ψ in the liquid

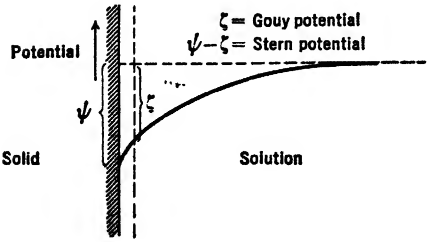

Fig. 68. Schematic curve for the drop in potential in the liquid phase in contact with a colloidal particle.

phase in contact with a colloidal particle. This is made up of two parts: (1) the potential in the diffuse mobile part of the double layer—the Gouy, electrokinetic, or ζ-potential; and (2) the potential in the attached portion of the double layer—the Stern potential, $\psi - \zeta$. The potential curve may be more complicated, sometimes containing a maximum or a minimum (for a discussion of other types of potential curves, see Chapter 19). But, even if one disregards these complications, it is usually difficult to find a relation between the different parts of the total potential drop. Moreover, there exists a discrepancy between the total double layer potential (150–200 mv for AgI sol) and the potential drop in the outer layer (80 mv for AgI sol). Verwey[27] first accounted for the discrepancy by assuming that a part of the double layer potential occurs within the solid phase. He[28] has now given up this explanation and suggests that the discrepancy arises from the fact that ζ-potentials calculated from mobility measurements are too low because the equation used in the calculations is inadequate.[29]

Formation

As we have seen, a double layer at the surface of colloidal particles may be formed by (1) preferential adsorption of one ion of an electrolyte in which the particle is suspended or (2) by direct ionization of some of the surface molecules. In the absence of one or the other of these phenomena, a double layer may result from selective adsorption of H^+ or OH^- ions from water.

If one takes the relatively simple case of silver iodide suspended in dilute hydriodic acid (Fig. 60), a double layer is set up as a result of (*a*) adsorption of iodide ion on the surface (inner layer) and (*b*) orientation of hydrogen ions in the immediate vicinity (diffuse outer layer). For electrostatic reasons, the negative charge on the surface, as well as the equal positive charge in the solution, is localized in the immediate neighborhood of the boundary layer, and the potential drop caused by the double layer is in the same region. The potential difference between silver iodide and the solution is thus determined by a distribution of the common iodide ions over both phases. Ions which both phases have in common and which are subjected to a distribution equilibrium to give the double layer are called ***potential-determining ions***, after Lange.[30] For a silver iodide electrode at equilibrium, the potential E is given in accord with the classical work of Nernst and van Laar[31] by the equation:

$$E = E_0 - \frac{RT}{nF} \ln \alpha_{\text{I}^-} \tag{1}$$

where R is the gas constant; T, the absolute temperature; F, the faraday; α_{I^-}, the activity of I^- ions; and n, the valence of the ion $= 1$. Furthermore, if E_0 is the potential drop silver iodide-solution and α_0 is the equilibrium activity of iodide ions at the point of zero charge, then:

$$E - E_0 = \frac{RT}{nF} \ln \frac{\alpha_0}{\alpha_{\text{I}^-}} \tag{2}$$

Since $E - E_0 = \epsilon$, the total potential drop due to free charges is:

$$\epsilon = \frac{RT}{nF} \ln \frac{\alpha_0}{\alpha_{\text{I}^-}} \tag{3}$$

which at 20° is:

$$\epsilon = 0.058 \log \frac{\alpha_0}{\alpha_{\text{I}^-}} \tag{4}$$

For a constant capacity of the double layer, the amount of iodide adsorbed per gram of AgI, x/m, is proportional to ϵ; hence

$$\frac{x}{m} = k_1 + k_2 \log \alpha_{\text{I}^-} \tag{5}$$

in which k_1 and k_2 are constants, fixed by the location of the zero point of charge and by the adsorption capacity. According to Verwey, the adsorption x/m at the equilibrium concentration of iodide ion c_{I^-} is given by the equation:

$$\frac{x}{m} = \log k + \frac{1}{n} \log c_{\text{I}^-} \tag{6}$$

It is apparent that Verwey's equation for the adsorption of the potential-determining iodide ion on silver iodide differs from the Freundlich equation, which, for the case at hand, would be: $\log x/m = \log k + 1/n \log c_{\text{I}^-}$. Verwey[32] refers to this taking up of potential-determining electrolytes with the formation of a double layer as a process of assimilation rather than as one of adsorption. From Gibbs's equation (p. 19) it follows that an electrolyte which lowers the surface tension of a solution is positively adsorbed and one which raises the surface tension of a solution is negatively adsorbed. Since the taking up of potential-determining electrolytes does not follow Gibbs's criterion, Verwey contends that it is not an adsorption phenomenon. The difference is that one ion of the potential-determining electrolyte goes from the solution onto the solid phase, causing a surface charge which theoretically could be effected from within this phase by the application of an external electric current. The surface tension is, therefore, not connected directly with the accumulation of electrolyte in the boundary layer but only indirectly as a result of the charge of the double layer thus formed; hence the process is not called adsorption. Similarly, it is argued that the exchange of lattice and counter ions (p. 115) should not be called adsorption. True adsorption of an electrolyte, according to Verwey, consists in the accumulation, as a whole, of an electrolyte in that part of the solution which is nearest the surface; it is, therefore, not accompanied by a change of the total boundary potential drop.

The author of this book prefers to be not so logical as Verwey and will continue to refer to the concentration of potential-determining ions at surfaces, and to the exchange of lattice and counter ions, as adsorption phenomena. In the sense of Verwey, true adsorption of indifferent electrolytes at ion lattices is encountered rarely if at all.[33] The taking up of ions from indifferent electrolytes is represented better by Freundlich's equation than by the equation which Verwey found to hold for the adsorption of potential-determining ions.

The essential difference between the building up of a double layer by adsorption of potential-determining ions and the formation of a double layer by adsorption from solutions of indifferent electrolytes would, therefore, appear to be that, in the first instance, the adsorption is represented by the equation $x/m = \log k + 1/n \log c$; and in the second instance, by the equation $\log x/m = \log k + 1/n \log c$. It is assumed by Verwey that the building up of the primary double layer by assimilation of potential-determining electrolyte is required for the primary stability of hydrophobic sols. It follows from this that the adsorption of potential-determining ions, only, will peptize a substance; the adsorption of indifferent ions will merely serve to influence the stability of a sol once formed.

In accord with this view, it has been found that positively charged silver iodide sols are obtained only in the presence of the common silver ion, whereas negatively charged sols[34] are formed in the presence of a suitable excess of the following alkali compounds: iodide, bromide, chloride, cyanide, thiocyanate, phosphate, ferricyanide, and ferrocyanide; but not in the presence of fluoride, nitrate, chlorate, permanganate, formate, carbonate, sulfate, chromate, dichromate, and hydroxide. Since many of the anions in the second list form insoluble silver salts and so should be adsorbed (see p. 112), Kruyt concluded that adsorption of an anion is not sufficient in itself to form a negative silver iodide sol; he considers the essential factor to be that the adsorbed anion should give an isomorphous silver salt. It appears, however, that the ion need not be exactly isomorphous to effect peptization; for example, alkali chloride and bromide, which give cubic silver halides, peptize silver iodide, which is hexagonal when negative. The important thing is that the adsorbed ion should fit the lattice sufficiently well that it will be taken up by the lattice to a certain extent and so will be distributed in both phases, in other words, will be a potential-determining ion. Whenever ions fit the lattice to a certain extent, it is probable that an exchange of lattice ions takes place between the adsorbed ion and iodide ion. This liberates iodide ion from the lattice which may become the predominating potential-determining ion even in the presence of other isomorphous ions.

Distinction between Electrochemical (ϵ) and Electrokinetic (ζ) Potentials

The thermodynamic or electrochemical potential ϵ at the interface of two solutions of activity α_1 and α_2 is given by the Nernst equation (cf. eq. 3):

$$\epsilon = -\frac{RT}{nF}\ln\frac{\alpha_1}{\alpha_2} \tag{7}$$

The ϵ-potential of a half-cell with respect to some arbitrary reference state ϵ_0 is:

$$\epsilon = \epsilon_0 - \frac{RT}{nF}\ln\alpha_{M^+} \tag{8}$$

where α_{M_+} is the activity of the ion in equilibrium with the surface M. The ϵ-potential is the potential difference between two points, each of which is located well within the body of the two phases in contact. It is therefore the potential across the entire ionic double layer at the interface solid-solution.

The electrokinetic or ζ-potential is the difference in potential between the immovable liquid layer attached to the surface of the solid phase and the movable liquid layer in the body of the liquid. The difference between the ϵ- and ζ-potentials may be illustrated diagrammatically, as shown in Fig. 69.

Diagram *A* in the figure represents a classical Helmholtz double layer at the surface of a particle. The broken line *xy* represents the boundary between the movabel and immovable layers. Plotting distance from the solid wall as abscissa and potential as ordinate, the total drop in potential is represented by the line *ab*. This is the ϵ-potential. Since the potential is wholly within the immobile double layer, the ζ-potential is zero.

In Fig. 69*B*, the outer layer is diffuse, so that a part of the plus charges are in the mobile layer. The total drop in potential (ϵ-potential), as represented by the curve *abc*, is the same as in *A* but is made up of two parts: (1) the part within the immovable layer *ab*, and (2) the part outside the immovable layer *bc*. The latter is the electrokinetic potential. The thickness of the immovable part of the double layer is greater, and the charge density within the double layer is less, than in *A*.

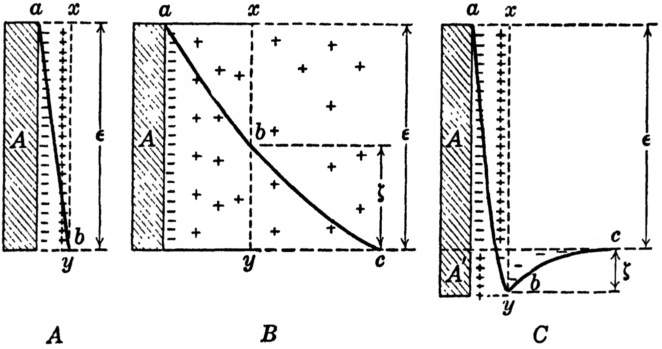

FIG. 69. Diagrams showing the relationship between the electrochemical (ϵ) potential and the electrokinetic (ζ) potential at constant charge density but with varying thickness of the double layer.

In Fig. 69*C* is given another form of the potential curve which cuts below the point of zero charge—the isoelectric point. In this instance, the ϵ-potential is still the same, but the ζ-potential is smaller than in *B* and opposite in sign. This means that the sign of the charge on the particle has been reversed.

The difference between ϵ- and ζ-potentials was demonstrated in a striking way by Freundlich and Ettisch,[35] who measured both potentials independently, using identical samples of glass in contact with identical solutions of salts. Their data are shown graphically in Fig. 70, in which potentials are plotted against electrolyte concentrations. In the case of ϵ-potentials, the curves approximate straight lines, as would be expected, since this potential is related directly to concentration changes. On the other hand, the form of the ζ-potential curves varies widely in an unpredictable way that is independent of the ε-potential.

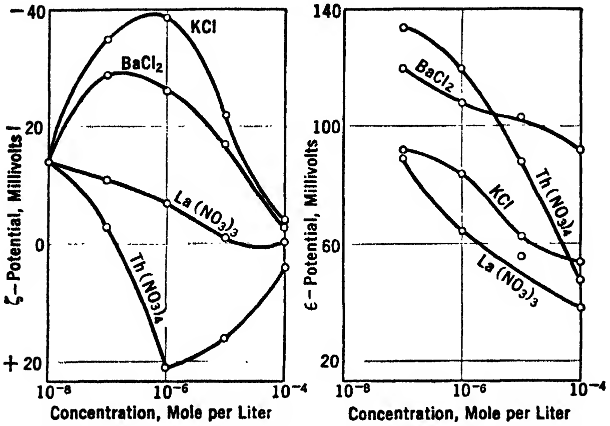

FIG. 70. Electrokinetic and electrochemical potentials at glass-solution interfaces.

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25. Gouy: *J. phys.* (4), **9**, 457 (1910); *Ann. phys.* (9), **7**, 129 (1917); Chapman: *Phil. Mag.* (6), **25**, 475 (1913); Herzfeld: *Physik. Z.*, **21**, 28, 61 (1920); Debye and Hückel: **24**, 185, 305 (1923).
26. Stern: *Z. Elektrochem.*, **30**, 508 (1924); cf. also Janssen: *Physik. Z. Sowjetunion*, **4**, 322 (1933).
27. Verwey: *Rec. trav. chim.*, **53**, 933 (1934); *cf.* Smoluchowski: Graetz's *Handbuch der Elektrizitat und des Magnetismus,* Vol. 2, p. 366 (1914).
28. Verwey: *Symposium on Lyophobic Colloids,* Utrecht, **57**, 81 (1937).
29. Cf. McBain: *J. Indian Chem. Soc.* (Ray Commemoration Vol.), 67 (1933).
30. Lange and Berger: *Z. Elektrochem.*, **36**, 171 (1930).
31. van Laar: *Lehrbuch der theoretischen Elektrochemie,* Leipzig (1907).
32. Verwey: *Chem. Rev.*, **16**, 363 (1935); *Wis-Natuurk. Tijdschrt.*, **7**, 89 (1934).
33. Cf. Weiser: *Inorganic Colloid Chemistry,* Vol. III, New York (1938).
34. Kruyt and van der Willigen: *Z. physik. Chem.*, **A139**, 53 (1928); Kruyt and Cysouw: **A172**, 49 (1935); Basinski: *Kolloid-Beihefte,* **36**, 258 (1932).
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CHAPTER 15

Electrokinetic and Electrochemical Properties of Sols

In the concluding section of the last chapter, it was shown that a distinction can be made between electrokinetic (ζ) potential and electrochemical (ϵ) potential. It seems advisable therefore to consider separately the electrokinetic and electrochemical phenomena in colloidal systems.

ELECTROKINETIC PHENOMENA[1]

The electrokinetic phenomena encountered in colloid chemistry are summarized in Table 45.

TABLE 45

ELECTROKINETIC PHENOMENA

Name	Phenomenon	Produced by
Electrophoresis	Movement of sol particles with respect to the liquid	Applied EMF
Electro-osmosis	Movement of liquid with respect to particles fixed in a porous diaphragm; movement in a single capillary tube	Applied EMF
Sedimentation potential (reverse of electrophoresis)	EMF produced	Movement of particles with respect to liquid
Streaming potential (reverse of electro-osmosis)	EMF produced	Movement of liquid with respect to particles fixed in a porous diaphragm; movement in a capillary tube

Equations for Electrokinetic Phenomena

The electrokinetic formulas commonly used in colloid chemistry may be derived as follows: [2, 3]

Electro-osmosis. Figure 71 is a cylindrical capillary of radius r with an electrode at each end, a distance l apart. Under a potential difference E, water flows through the tube at the rate of volume V per second. The wall of the capillary is negatively charged, and, at a distance δ, an equal number of positive charges are present in the liquid. The motion of the liquid under E results from this double layer of charges: the negative charges adhere to the wall, and the positively charged layer of liquid moves along the tube toward the cathode. If the liquid particles move at a mean velocity, u per second, then:

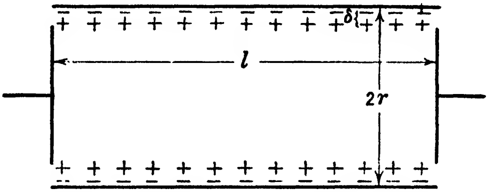

Fig. 71. Diagram of cylindrical capillary.

$$V = \pi r^2 u \tag{1}$$

The velocity u results because E overcomes the force of friction which is proportional to the viscosity η of the liquid and to the velocity gradient du/dx, where dx denotes the distance of the particle from the wall. Within the double layer, $du/dx = u/\delta$; hence the force of friction is $\eta \cdot u/\delta$. Combining this with eq. 1, the frictional resistance per unit area becomes: $\eta V/\pi r^2 \delta$.

For a potential E and electrodes a distance l apart, the potential gradient H per centimeter is: $H = E/l$. If the quantity of electricity per square centimeter of the surface—the charge density—is q, then Hq is the electrical force. When this equals the frictional resistance,

$$Hq = \frac{\eta V}{\pi r^2 \delta} \tag{2}$$

If the double layer is considered to be a condenser with the potential ζ between the plates, then:

$$\zeta = \frac{4\pi \delta q}{D} \tag{3}$$

where D is the dielectric constant. Combining eqs. 2 and 3,

$$V = \frac{r^2\zeta HD}{4\eta} \tag{4}$$

or, since $Hl = E$:

$$V = \frac{r^2\zeta ED}{4\eta l} \tag{5}$$

For a bundle of capillaries or a diaphragm of cross section Q, eq. 5 becomes:

$$V = \frac{Q\zeta ED}{4\pi\eta l} \tag{6}$$

If I denotes the current strength and κ the specific conductivity of the liquid system in the capillaries,[2] then the resistance R is given by $l/Q\kappa$; and, from Ohm's law, $E = IR$, it follows that $E = Il/Q\kappa$. Substituting this value of E in eq. 6:

$$V = \frac{\zeta ID}{4\pi\eta\kappa} \tag{7}$$

which states that the volume of liquid transported through a diaphragm in a given time is directly proportional to the current and is independent of the length of the capillaries and the cross section of the diaphragm. This generalization was found empirically in experimental studies by Wiedemann[4] and is sometimes called *Wiedemann's first law.*

Poiseuille's law (p. 206) is: $V = \pi Pr^4/8\eta l$, where P is the pressure applied in forcing a liquid through a capillary. Combining this with eq. 5 gives:

$$P = \frac{2\zeta ED}{\pi r^2} \tag{8}$$

which states that, for a given diaphragm material, the difference in hydrostatic pressure maintained between the two sides of a porous diaphragm is proportional to the applied EMF and is independent of the dimensions of the diaphragm. This generalization was likewise found empirically by Wiedemann[4] and is known as *Wiedemann's second law.*

Streaming potential. If a volume V of liquid under a hydrostatic pressure P is forced through a diaphragm, the mechanical work is PV. This is balanced by the electrical work EI, so that $PV = EI$ or $V/I = E/P$. Writing eq. 7 in the form:

$$\zeta = \frac{4\pi\eta\kappa}{D} \cdot \frac{V}{I} \tag{9}$$

substituting E/P for V/I, and solving for E give:

$$E = \frac{\zeta PD}{4\pi\eta\kappa} \tag{10}$$

This is an equation for the streaming potential which results when a liquid is forced through a capillary.

Electrophoresis. Turning from the flow of liquid in a diaphragm consisting of stationary capillary spaces to the case where the diaphragm material is broken into fine pieces and suspended in a liquid, we find that the application of an electrical potential causes the particles with their layers of charges to move through the liquid. In electro-osmosis of water, we have seen from eq. 1 that $u = V/\pi r^2$. Combining this with eq. 4 gives:

$$u = \frac{\zeta HD}{4\pi\eta} \tag{11}$$

This is the equation for the electrophoretic velocity of a cylindrical particle moving in a liquid. Debye and Hückel[5] claim that, for spherical particles, 6 should replace 4 in the denominator of eq. 11; but this is questioned by Henry.[6]

Sedimentation potential. The sedimentation potential or *Dorn*[7] *effect* is given by the same equation that applies for streaming potentials, viz.:

$$E = \frac{\zeta PD}{4\pi\eta\kappa} = \frac{\zeta PDR}{4\pi\eta} \tag{12}$$

where the electromotive force E is proportional to the hydrostatic pressure difference P produced by particles falling through a liquid.

Electrophoresis

The phenomenon of electrophoresis may be easily observed by means of the apparatus shown in Fig. 72. A colored sol is placed in the funnel tube, and potassium chloride solution of the same conductivity as the sol is added to a depth of a few centimeters in the U-tube. The sol is then run in slowly until the electrodes are immersed, as shown in *A*. On connecting with a source of constant voltage, the boundary of the sol migrates to the anode or cathode, depending on the sign of the particle charge (see *B* of Fig. 72). This procedure is useful for determining the sign of the charge on colloidal particles. In this way it may be demonstrated that the following hydrosols, for example, are positively charged: the hydrous oxides of iron, chromium, aluminum, thorium, etc.; the silver halides in the presence of a slight excess of Ag^+ ion; proteins on the acid side of the isoelectric point; and basic dyes such as methylene blue. On the other hand, the following typical hydrosols are negatively charged: the hydrous oxides of tin, silicon, and vanadium; most metals; sulfur and selenium; silver halides in the presence of a slight excess of halide; sulfides; ferrocyanides; soaps; acid dyes, such as Congo red; gum arabic, rosin, mastic; and proteins on the alkaline side of the isoelectric point.

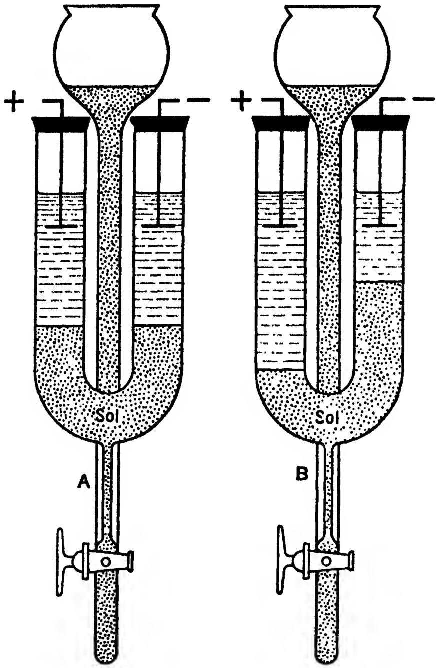

Fig. 72. Diagram of apparatus for demonstrating electrophoresis.

The moving-boundary procedure may be used also to measure the electrophoretic mobility, if the necessary precautions are taken. These include the use of non-polarizable electrodes and of a suitable overlying liquid such as the ultrafiltrate from the sol; suitable buffer solutions may be used when working with protein sols. Tiselius [8] has designed a special apparatus for the electrophoretic separation of mixtures of proteins. A diagram of the Tiselius apparatus is given in Fig. 73. A detailed account of the operation of the apparatus and its applications is given by Tiselius [8] and by Abramson.[1]

The mobility of a single particle may be followed in a microcell by means of a microscope or an ultramicroscope. In addition to the electrophoretic mobility of the particle in one direction, there is an electro-osmotic flow along the walls of the cell in the opposite direction. Accordingly, the true electrophoretic velocity can be observed at only two levels: in a cell of rectangular cross section, these levels are at 21% of the distance from the top or from the bottom of the cell; and in a cylindrical cell, the levels are at 14% of the diameter of the capillary.[9] Microcells of rectangular cross section are more satisfactory than cylindrical cells since complications in locating the desired level in the latter may lead to serious errors in the measurement of electrophoretic velocity.[10]

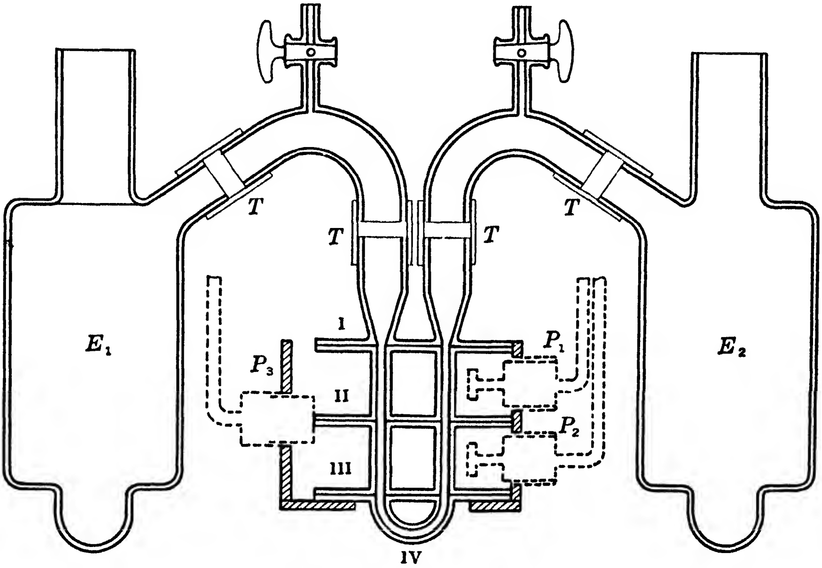

FIG. 73. Electrophoresis cell (Tiselius). E_1 and E_2 represent the electrode tubes; T, rubber tubings; I, II, III, IV, the four U-tube sections, of which II and III can be moved with the pneumatic arrangement P_1, P_2, P_3.

The order of magnitude of the mobilities of colloidal particles is similar to that of most ions other than hydrogen and hydroxyl which move with greater velocities. In Fig. 74 is shown the influence of electrolytes with cations of varying valence on the mobility of the particles in a silver iodide sol, as found by Kruyt and van Gils.[11] The mobility in microns per second at 1 v/cm is plotted against the negative logarithm of the electrolyte concentration. For multivalent cations, the mobility decreases with increasing concentration until an unstable state is reached at about 1 μ/sec, and the sol coagulates. For univalent ions, the critical mobility is much higher. The zone of instability is indicated by the broken lines in the figure. It will be noted that, above a certain concentration of thorium nitrate and hexol (a hexavalent cobalt amine) nitrate, the direction of the motion changes. The importance of this behavior in connection with the action of electrolytes on sols will be considered in the next chapter.

The electrophoretic mobility u being known, the ζ-potential may be calculated from eq. 11: $\zeta = 4\pi\eta u/HD$. The ζ-potential curves are identical in form with those in Fig. 74.

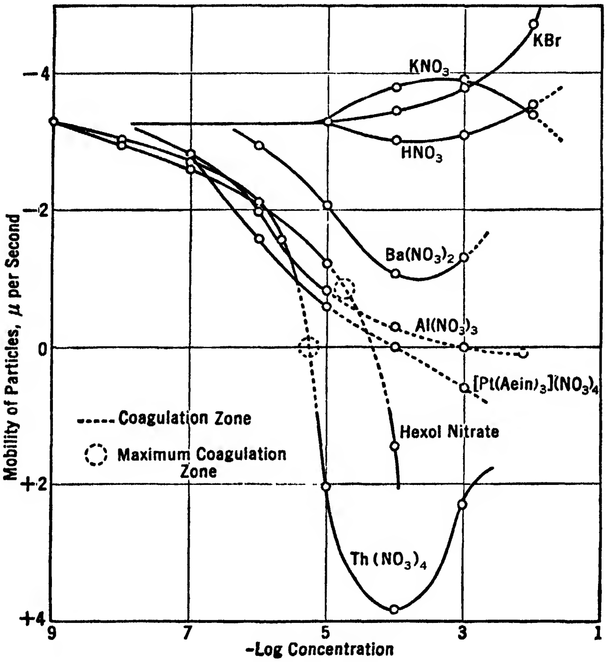

FIG. 74. Effect of varying concentrations of electrolytes on the mobility of the particles in a silver iodide sol.

Isoelectric point. Both the moving-boundary technique[12] and the microscopic electrophoresis method[13] have been used to determine the isoelectric point of amphoteric colloids such as the proteins. The *isoelectric point* of a colloidally dispersed material is the pH value or hydrogen-ion activity of the dispersion medium at which the dispersed phase does not migrate in an electric field. Table 46 gives the range of isoelectric points reported by different investigators, for a few proteins and other amphoteric substances.[14] The isoelectric point of a definite protein in a given medium is quite sharp. The range of values reported for a supposedly definite protein results from one or both of the following causes: (1) the isoelectric point varies somewhat with the nature and concentration of ions other than hydrogen, which may be present in the solution; and (2) many proteins are in reality not well defined, and the nature of the procedures involved in isolation and purification may modify them appreciably.

TABLE 46

Isoelectric Points of Amphoteric Bodies

Substance	Isoelectric point (pH)	Substance	Isoelectric point (pH)
Albumin (cows' milk)	4.6	Hide powder	4.8–5.5
Albumin (hens' eggs)	4.6–5.0	Histone	8.5
Albumins (serum)	4.7–5.2	Insulins	5.0–5.7
Casein (cows' milk)	4.6–4.9	Lecithin (hens' eggs)	2.6–2.7
Fibrins	4.7–7.2	Levetin (hens' eggs)	3.8–5.0
Fibrinogens	4.9–5.5	Pepsins	2.5–3.3
Gelatins	4.4–5.6	Protamines	10.0–12.4
Globulins (serum)	5.1–5.5	Silk fibroins	2.5–5.1
Glutenin	5.3–5.4	Trypsin	7.0–8.0
Hemoglobins	6.8	Wools	3.4–4.8

Technical applications. An important technical application of electrophoresis is the electrodeposition of rubber. Not only may the negatively charged latex particles be coagulated by electrical means, but also, under suitable large-scale operations, they may be electroplated on the surfaces of metal, cloth, and wood.[15] The electrodeposited rubber may be vulcanized readily, giving a product of exceptionally high tensile strength. Moreover, hygroscopic bodies and salts may be washed out after the electrodeposition, giving a material of high insulating properties.

The electrophoresis process is also used in obtaining clay with properties that are especially suitable for the manufacture of porcelain. A stable suspension of the clay is prepared by peptization with water glass, and the finer particles are separated by electrophoresis either in a modified filter press or in a machine designed to precipitate the particles on a rotating anode from which they are scraped continuously.[16]

Electroplating and electrorefining of certain metals, such as lead, are accomplished satisfactorily only in the presence of small amounts of hydrophilic colloids which migrate toward the cathode and are deposited simultaneously, giving a product of small crystal size.

Electro-osmosis

Electro-osmotic flow may be observed qualitatively in the following way. Copper electrodes dipping into a slightly acidified copper sulfate solution are separated by a porous cup which is filled with solution and fitted with a rubber stopper containing a glass tube 3 or 4 ft in length. Since the cup is negatively charged under these conditions, the electrode on the inside of the cup is made the cathode. On applying a potential, the electro-osmotic flow is into the porous cup, the level of liquid rising in the glass tube until it overflows.

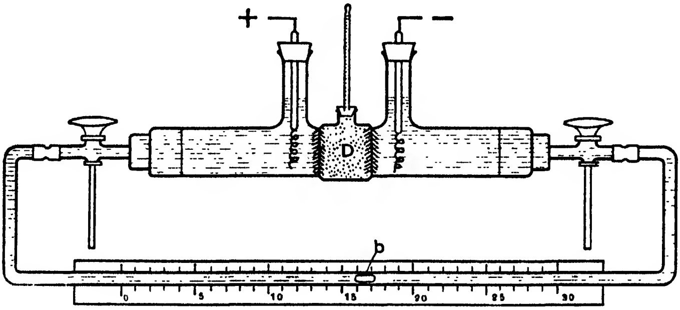

Fig. 75. Diagram of apparatus for measurement of electro-osmosis or of streaming potential.

In Fig. 75 is shown a diagram of Briggs's[17] electro-osmotic apparatus for accurate measurements. The diaphragm *D* separates the platinum electrodes. The volume of liquid which flows through the diaphragm in a given time is measured by the motion of an air bubble *b* in a capillary tube.

The direction of flow of liquid is toward the cathode if the diaphragm is charged negatively, and toward the anode if it is charged positively. The sign of the charge on a diaphragm is determined by the nature of the ion adsorbed preferentially; hence the direction in which an aqueous solution will flow through a diaphragm will depend on the nature of the dissolved substance.[2, 18] A diaphragm will tend to become positively charged in acid solution and negatively charged in basic solution. Perrin[2] observed this with diaphragms of the oxides of aluminum, zinc, copper, cobalt, and nickel; zinc carbonate, zinc sulfide, barium sulfate, chromic chloride, silver chloride, boric acid, sulfur, graphite, naphthalene, Carborundum, and gelatin. At the isoelectric point of the diaphragm, which is different for each substance, there is no motion of the water.

The effect of ions other than hydrogen and hydroxyl in changing the magnitude of the charge on the membrane tends to be more marked the higher the valence, in accord with the Schulze-Hardy rule (p. 110). For example, in dilute acid solution, the flow of solution to the anode through a chromic chloride diaphragm increases in the presence of anions in the order $Fe(CN)_6^{iv} > SO_4 > Cl$, because the adsorption of these anions decreases in the same order and hence the positive charge increases in this order. Conversely, in dilute alkaline solution the flow to the cathode through a Carborundum diaphragm increases as the cation changes in the order: $La > Ba > Na$. As noted above, the flow is to the cathode with a porous cup in slightly acid copper sulfate solution; but in slightly acid copper nitrate solution the flow is toward the anode. In the first case, the adsorption of sulfate is greater than that of the combined adsorption of copper and hydrogen, whereas, in the second case, the adsorption of cations is greater than that of univalent nitrate.

Negative osmosis. A phenomenon closely connected with electro-osmosis is the so-called negative osmosis in which the solution in an osmometer, permeable to both solvent and solute, moves to the water instead of the solution. For example, in a porous cup osmometer, Graham[19] observed a flow of water into a 1% K_2CO_3 solution, causing a rise of 21–38 cm in 5 hours, whereas with a 1% $H_2C_2O_4$ solution the flow was the opposite way, causing a lowering of 14 cm in 5 hours. Both the rise and depression are temporary, since, at equilibrium, the levels inside and outside the osmometer must be the same. These results have been confirmed and extended by Girard[20] and by Bartell and coworkers.[21] As we have seen, water tends to flow toward the anode by electro-osmosis through a positively charged diaphragm. If the diaphragm separates two concentrations of acid, the current will tend to flow from the more concentrated to the more dilute solution; but, on open circuit, the dilute solution will be positively charged, and hence the rate of flow through the diaphragm to the concentrated solution will be retarded. Conversely, if the diaphragm is negatively charged, the rate of flow through the diaphragm to the more concentrated solution will be increased. There can, of course, be no negative osmosis with a semipermeable membrane (p. 161).

Technical applications. Electro-osmosis has not proved very successful technically,[22] but the phenomenon has been applied to a certain extent in the removal of water from peat, in dewatering moist clay, and in drying dye pastes. A novel application is in cutting clay into bricks by means of wire. Ordinarily a lubricant must be used on the cutting wires to prevent the clay from adhering to them. But, if the wires are made the cathode and an anode is inserted in the clay block, the clay no longer sticks to the wire, and the power consumption is reduced 25–30%. The effect is due to the formation, by electro-osmosis, of a lubricating film of water on the cutting wire. Similarly, Crowther and Haines[23] showed that, by lubricating the plowshare with a film of water, the energy required to plow clay is reduced by the process of electro-osmosis; but unfortunately the saving in mechanical energy is not great enough to compensate for the electrical energy required.

The use of electro-osmosis to force tanning liquor into hides has been suggested, but the process has not proved successful, partly because of oxidation of the tannin at the anode.

Streaming Potential

The earlier work on streaming potential was carried out by flowing liquids through single capillary tubes, but porous diaphragms may be used in an apparatus such as Briggs's electro-osmotic cell shown in Fig. 75. This apparatus becomes a streaming-potential cell by forcing a liquid under a definite pressure through the diaphragm and measuring the potential set up. From the observations, the ζ-potential may be calculated from eq. 10, which becomes, on rearranging,

$$\zeta = \frac{4\pi\eta\kappa E}{PD}$$

where κ is the specific conductivity of the liquid as it appears in the pores of the diaphragm.

Using the streaming-potential technique in a special apparatus, Bull and Gortner[24] determined the influence of increasing concentrations of various electrolytes on the ζ-potential, the thickness δ of the Helmholtz double layer, and the charge density q in the double layer, at a cellulose-water interface. The results with potassium, calcium, and thorium chlorides are shown graphically in Fig. 76. It is apparent from these data that the distance δ which separates the charge in the double layer is responsible for the lowering of the ζ-potential with increasing salt concentration. On the other hand, q, the charge density per square centimeter, increases while the double layer is diminishing in thickness. At a large value of q and a very small value of δ, the layer may collapse and then reverse. This behavior is manifested especially in the thorium chloride curves. The importance of these observations in interpreting the action of electrolytes on sols will be considered in the next chapter.

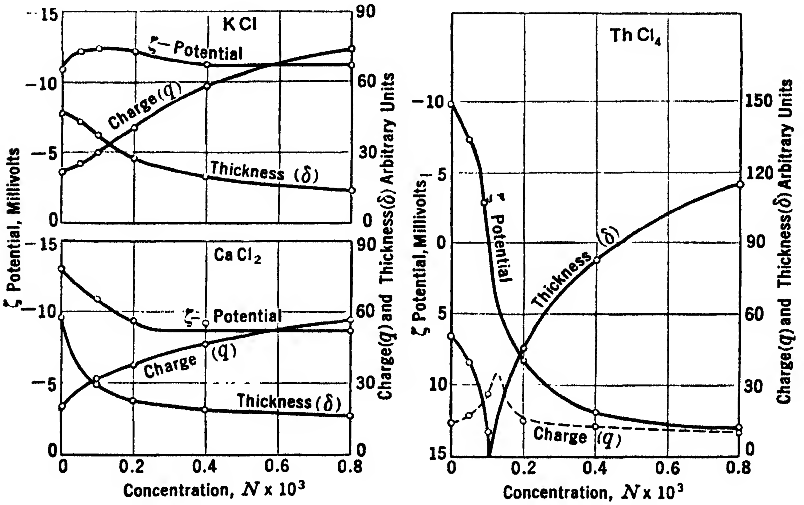

FIG. 76. Effect of concentration of various electrolytes on the ζ-potential, thickness δ of the double layer, and the charge density q in the double layer at a cellulose-water interface.

ELECTROCHEMICAL PROPERTIES

Conductivity

Since the particles migrate under electrical stress, it is obvious that a sol should possess a certain conductivity independent of the presence of electrolytes. The conductivity κ in a pure sol can be calculated from Smoluchowski's equation:

$$\kappa = \frac{n}{N}\,\frac{4\pi r\eta(r + \delta)u^2}{\delta} \tag{13}$$

in which n is the number of particles per unit volume, N the Avogadro number, u the mobility, η the viscosity, r the radius of the particles, and δ the thickness of the double layer. For a gold sol containing particles of 10-mμ radius, a mobility of 5.2 μ/sec, and a distance between charges δ = 5 mμ, κ is found to be 1.2×10^{-7}. Since the value due to the migration of the particles is so low, it is obvious that most of the conductivity in metallic sols results from impurities in the dispersion medium.[25] In general, the conductivity of sols decreases with increasing purity of sol. In some cases the conductivity is even less than that of the dispersion medium. Thus, if mercury is dispersed in conductivity water by means of the oscillating arc, the conductivity of the resulting sol is less than that of the water,[26] probably because of adsorption of residual electrolyte impurities by the particles.

Wintgen[27] determined the amount of colloidal material deposited by 1 faraday of current and designated this the "electrochemical equivalent" or "equivalent aggregate" (p. 249) of the sol. The necessary data were obtained from electrical conductivity and electrophoresis measurements in a U-tube on the sols themselves and on the ultrafiltrate from the sols. From such observations on a ferric oxide sol containing 1.601 g Fe_2O_3 and 0.06014 g Cl in 100 g of sol, the following composition of the colloidal particles was deduced: $(\boxed{75.35Fe_2O_3 \cdot 7.86HCl \cdot xH_2O}FeO)^{+}_{10,230}$, $10,230Cl^{-}$.

McBain[28] points out that Wintgen's estimate of the charge on colloidal particles is much too high because of methodical errors in the experiments. Among these may be mentioned: (1) failure to divide the observed mobilities by a factor m[29] (the number of units to one electrical charge) in finding the conductivity; (2) neglect of Donnan equilibrium effects during ultrafiltration. McBain and McClatchie[30] found that the ultrafiltrate from a sol varies manyfold with the rate of ultrafiltration, and that it is only with very slow ultrafiltration that the filtrate approaches the Donnan membrane distribution (p. 247), owing to the presence of charged particles. For example, the *p*H of the filtrate obtained by rapid ultrafiltration of a ferric oxide sol was less than that of the sol, whereas the *p*H of the filtrate from very slow ultrafiltration was much greater than that of the sol.

McBain's extended investigations on the soaps (cf. p. 224) disclosed that strong solutions of such compounds as sodium palmitate and potassium stearate gave a conductivity equal to that of a salt, whereas the osmotic activity as measured by the freezing-point method, say, was sufficient to account for only the potassium or sodium ions, in other words, only one-half the value for an ordinary salt. The reason for this behavior is that the palmitate or stearate ions form aggregates of ions which conduct the current even better than an equal number of single ions, but which are so large that they exhibit but little osmotic activity. Congo red behaves like the soaps in this respect. As already pointed out (p. 223), such solutions are termed *colloidal electrolytes,* and the colloidal aggregates of ions are called *ionic micelles.*

Electromotive Force: Membrane Equilibrium

Donnan's[31] theory of membrane equilibria deals with the equilibria resulting when a membrane separates two electrolytes, one at least of which contains an ion that cannot diffuse through the membrane. Donnan showed that, if one starts with two completely ionized electrolytes, e.g., NaCl and NaR, separated by a membrane impermeable to the ion R, equilibrium will be established only when the product of the concentration of sodium and chloride ions has the same value on both sides of the membrane, thus:

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

where $[\mathrm{Na}^+]_1$ and $[\mathrm{Cl}^-]_1$ are the molar concentrations of sodium and chloride ions on the one side of the membrane (solution 1), and $[\mathrm{Na}^+]_2$ and $[\mathrm{Cl}^-]_2$ are corresponding concentrations on the opposite side of the membrane (solution 2). When equilibrium is established, in solution 1, let:

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

and in solution 2, let:

$$y = [\mathrm{Cl}^-]$$

$$z = [\mathrm{R}^-]$$

from which

$$y + z = [\mathrm{Na}^+]$$

Since the product $[\mathrm{Na}^+] \times [\mathrm{Cl}^-]$ will be the same in both solutions at equilibrium, it follows that:

$$x_2 = y(y + z)$$

It is obvious that x must be greater than y so long as z has a finite value; hence the concentration of chloride ion in solution 1 must be greater than in solution 2, whereas the concentration of sodium ion must be greater in solution 2 than in solution 1. This gives rise to a potential difference E across the membrane which is represented by the equation:

$$E = \frac{RT}{F} \log \frac{x}{y} \quad \text{or} \quad E = \frac{RT}{F} \log \frac{\alpha_x}{\alpha_y} \qquad (14)$$

in which R is the gas constant, T is the absolute temperature, F is the faraday, and α_x and α_y are the activities of the ions on the two sides of the membrane.

The accuracy of these deductions has been established by investigations on a number of systems, for example: (1) with solutions of potassium chloride and lithium chloride, using a layer of amyl alcohol as a membrane;[32] (2) with solutions of Congo red and sodium chloride, using a parchment membrane;[32] and (3) with solutions of potassium and sodium chlorides and potassium and sodium ferrocyanides, respectively, using a copper ferrocyanide membrane,[33] especially when activities are substituted for concentrations.[34] It is of interest to inquire into the nature of the action of the membrane in each instance. In the first example, the amyl alcohol acts as a non-porous semipermeable membrane (p. 164) in which the lithium chloride dissolves and passes through, and the potassium chloride does not. In the second example, the parchment functions as an ultrafilter or dialyzing membrane (p. 164), the concentration, osmotic, and electrical effects being caused by the inability of the large ionic micelle of the colloidal electrolyte to diffuse through the pores. In the third example, the copper ferrocyanide acts as a semipermeable membrane for ferrocyanide ion, according to a mechanism proposed by Weiser.[35]

TABLE 47

OSMOTIC PRESSURE AND MEMBRANE POTENTIAL OF Cr_2O_3 SOLS

HCl c_2 (moles/liter)	$[Cr_2O_3]$ (moles/liter)	p (cm of water)	E_m (mv)	m = 1000		m = 500		m = 250	
				p_1	E_a	p_1	E_a	p_1	E_a
0.010	0.042	7.6	....	1.0	13	2.1	14	4.1	18
0.010	0.038	6.0	6.4	0.9	13	1.9	15	3.7	20
0.005	0.038	9.7	10.5	0.9	14	1.9	15	3.7	17
0.005	0.027	5.0	....	0.6	14	1.4	16	2.7	20
0.005	0.027	4.8	....	0.6	14	1.4	16	2.6	20
0.005	0.026	4.4	9.1	0.6	15	1.3	16	2.5	21
0.0025	0.026	7.5	16.1	0.6	15	1.3	16	2.5	18
0.001	0.026	17.8	28.2	0.6	14	1.3	14	2.5	15
0.005	0.025	4.2	7.4	0.6	14	1.3	16	2.4	20
0.010	0.025	2.5	5.2	0.6	14	1.3	18	2.4	100

Some observations of Bjerrum[36] on chromic oxide sol will serve to illustrate an application of membrane-potential studies. Bjerrum placed suitable portions of a well-dialyzed chromic oxide sol in collodion bags and surrounded them by solutions of hydrochloric acid of varying concentration. The outside solution was renewed daily until equilibrium was established, and the osmotic pressure and membrane potential were measured in a special apparatus. A few observations are given in Table 47.

The measured osmotic pressure p is the sum of the pressure p_1 of the colloidal particles and the pressure p_2 caused by the difference in the number of dialyzable ions inside and outside the membrane, that is:

$$p = p_1 + p_2 \tag{15}$$

According to Avogadro:

$$p_1 = RT\frac{[Cr_2O_3]}{m} \tag{16}$$

and according to Avogadro and Donnan:

$$p_2 = RT\frac{[Cr_2O_3]^2}{4E_a^{\,2}c_2} \tag{17}$$

where $RT = 24{,}700$ at 18°; m is the number of Cr_2O_3 molecules in a single particle; and E_a is the *equivalent aggregate*, that is, the number of Cr_2O_3 molecules carrying one electrical charge (p. 246). Values of p_1 corresponding to the observed p values were calculated from eq. 16 for various assumed values of m; and, from these p_1 values, p_2 values were obtained from eq. 15, and E_a values from eq. 17. The calculated values of p_1 and E_a for m = 1000, 500, and 250 are included in Table 47. Bjerrum took the smallest value of m which gives a constant E_a as the correct m, and the corresponding average value of E_a as the correct E_a. From the recorded data, it appears that m is greater than 250 and less than 1000; it is probably about 500 with E_a about 15. This means that the colloidal particle contains something like 1000 chromium atoms and carries 30 free positive charges (cf. p. 246).

The above observations illustrate the importance of keeping in mind the possibility of effects due to Donnan phenomena in studies of osmotic pressure, diffusion, and sedimentation on colloidal systems (Chapter 13).

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CHAPTER 16

The Stability of Hydrophobic Sols I: Coagulation by Electrolytes

The stability of hydrophobic sols depends on the electrokinetic or ζ-potential of the colloidal particles. The addition of electrolytes to the sols usually lowers the ζ-potential, which is calculated, from the migration velocity u of the particles moving under a potential H in a medium of viscosity η and dielectric constant D, by means of the equation: $\zeta = 4\pi\eta u/HD$ (p. 237).

THE CRITICAL ζ-POTENTIAL

The ζ-potential of the particles need not be reduced to zero in order that coagulation may take place. This has led to the concept of a critical ζ-potential, above which the sol is relatively stable and below which it coagulates rapidly. The concept was proposed by Powis[1] as a result of his observations on oil drops and on arsenic trisulfide sol. In Table 48 are given the ζ-potentials at the surface

TABLE 48

CRITICAL ζ-POTENTIALS OF PARTICLES IN SOLS

(1) Arsenic trisulfide sol (−)			(2) Ferric oxide sol (+)		
Electrolyte	Conc. (meq/l)	ζ-potential (mv)	Electrolyte	Conc. (meq/l)	ζ-potential (mv)
KCl	40.0	44	KCl	100.0	33.7
$BaCl_2$	1.0	26	NaOH	7.5	31.5
$AlCl_3$	0.15	25	K_2SO_4	6.6	32.5
$Th(NO_3)_4$	0.20	27	Aniline sulfate	8.0	31.4
$Th(NO_3)_4$	0.28	26	$K_2C_2O_4$	6.5	32.5
$Th(NO_3)_4$	0.40	24	$K_3Fe(CN)_6$	0.65	30.2

of (1) arsenic trisulfide particles[1] and (2) ferric oxide particles[2] when sufficient amounts of the several electrolytes are added to cause rapid coagulation. It will be noted that the critical ζ-potential for the negative arsenic trisulfide sol is about 26 millivolts for all multivalent cations; and for the positive ferric oxide sol it is approximately 32 millivolts for all anions. The critical mobility and ζ-potential of arsenic trisulfide in the presence of potassium chloride are appreciably higher than for the other salts. A similar behavior was observed with salts of the KCl type on silver iodide sol (p. 240). This is not a question of the univalence of potassium ion, since Briggs[3] showed that the critical mobility of univalent new fuchsin and strychnine cations for arsenic trisulfide sol is the same as for bivalent barium. On the other hand, Briggs obtained an S-shaped curve on plotting potassium chloride concentration against the mobility (or ζ-potential) of arsenic trisulfide particles. In some instances with salts of the KCl type, the curve increases from the start to a maximum and then falls off; in others, it decreases from the start;[4] and in still others, it decreases to a minimum and then rises.[5]

Kruyt and coworkers[6, 4] postulate a decrease in dielectric constant to account for the lower critical mobility and the corresponding higher critical ζ-potential for salts of the KCl type. Mukherjee and coworkers[7] and Ghosh[2] believe that a decrease in dielectric constant alone would not account for the observed results and suggest that the anomalous behavior is due in part to the stabilizing action of adsorbed chloride which opposes the precipitating action of potassium ion.

Because of the anomalous effect of certain coagulating electrolytes on the mobility of sol particles, Mukherjee contends that one should not speak of a critical mobility or critical ζ-potential. This point of view seems a bit extreme under the circumstances. In most instances electrolytes effect coagulation at a critical mobility or ζ-potential. The fact that we do not know enough at present to interpret adequately the behavior with certain salts is no reason to abandon the whole concept of critical mobility or ζ-potential. This is especially true when we consider that the anomalous behavior is usually encountered only with salts that precipitate in high concentration, and not always with these. For example, Ghosh observed a normal behavior of potassium chloride with his ferric oxide sol (Table 48). Similarly Jenny and Reitemeier[8] found a normal behavior with clay hydrosols (p. 271), and Bikerman[9] with arsenic trisulfide sol in ethyl acetoacetate.

PRECIPITATION VALUES OF ELECTROLYTES

Typical experimental results. Several methods have been employed from time to time for determining the relative precipitating power of electrolytes. Since the process is transitory, it is necessary to compare the electrolyte concentrations which produce the same velocity of coagulation. The rate of coagulation has been followed by means of viscosity measurements[10] on alumina sol; by colorimetric observations[11] on gold sol and Congo rubin sol; with a spectrophotometer[12] on gold sol and arsenic trisulfide sol; and with a turbidimeter[13] on arsenic trisulfide sol. For the most part, however, a comparison is made of the concentrations which just cause complete precipitation in a definite period of time, not less than 2 hours. Some typical precipitation-value data on two negative sols are given in Tables 49 and 50 and on a positive sol in Table 51.

TABLE 49[14]

PRECIPITATION VALUES (x) OF ELECTROLYTES FOR ARSENIC TRISULFIDE SOL

Electrolyte	x (millimoles/l)	Electrolyte	x (millimole/l)
$KC_2H_3O_2$	110.0	Morphine chloride	0.425
$KCHO_2$	86.0	Crystal violet	0.165
LiCl	58.4	New fuchsin	0.114
NaCl	51.0	$MgCl_2$	0.717
KNO_3	50.0	$MgSO_4$	0.810
KCl	49.5	$CaCl_2$	0.649
$K_2SO_4/2$	65.6	$SrCl_2$	0.635
NH_4Cl	42.3	$BaCl_2$	0.691
HCl	30.8	$Ba(NO_3)_2$	0.687
$H_2SO_4/2$	30.1	$ZnCl_2$	0.685
Guanidine nitrate	16.4	$UO_2(NO_3)_2$	0.642
Strychnine nitrate	8.0	Quinine sulfate	0.240
Aniline chloride	2.52	$AlCl_3$	0.093
		$Al(NO_3)_3$	0.095
		$Al_2(SO_4)_3/2$	0.096
		$Ce(NO_3)_3$	0.080
		$Ce_2(SO_4)_3/2$	0.092

The Schulze-Hardy[17] rule. This rule of coagulation states that: (1) the effective ion in the precipitation of sols by electrolytes is the ion opposite in sign to the charge on the colloidal particles and (2)

TABLE 50 [15]

PRECIPITATION VALUE (x) OF SALTS FOR COPPER FERROCYANIDE SOL

(A) Salts with cations of varying valence		(B) Potassium salts	
Salt	x (millimoles/l)	Salt	x (millimoles/l)
KCl	35.6	KNO_3	28.7
$NaCl$	92.5	KBr	27.5
$Ba(C_2H_3O_2)_2$	0.445	K_2SO_4	47.5
$BaCl_2$	0.458	K_2HPO_4	47.5
$SrCl_2$	0.538	K_2CrO_4	80.0
$MgSO_4$	0.760	$K_2C_4H_4O_6$	95.0
$Al_2(SO_4)_3$	0.058	$K_2C_2O_4$	170.0
$Ce(NO_3)_3$	0.034	$K_3Fe(CN)_6$	205.0
$Th(NO_3)_4$	0.038	$K_4Fe(CN)_6$	260.0

TABLE 51 [16]

PRECIPITATION VALUES (x) OF SALTS FOR FERRIC OXIDE SOL

Salt	x (millimole/l)	Salt	x (millimoles/l)
Ferrocyanide	0.067	Bromate	31.3
Ferricyanide	0.096	Thiocyanate	46.9
Dichromate	0.188	Chloride	103.1
Tartrate	0.200	Chlorate	115.6
Sulfate	0.219	Nitrate	131.2
Oxalate	0.238	Bromide	137.5
Chromate	0.325	Iodide	153.6
Iodate	0.900	Formate	172.5

the precipitating power of the effective ion increases greatly with increasing valence of the ion. The effective ion is sometimes referred to as the *precipitating ion* of an electrolyte, whereas the ion having the same sign of charge as the particles is called the *stabilizing ion*. Referring to the tables, it will be seen that the effect of cations predominates with the negative sols, and of anions, with the positive sol. Moreover, if one disregards the univalent organic ions, the salts with precipitating ions of the same valence fall in fairly well-defined groups, the precipitating power of which is in the order: quadrivalent > trivalent > bivalent > univalent. If the lowering of the ζ-potential results wholly or in part from adsorption of the ion of an electrolyte with the sign of charge opposite to that on the sol, the Schulze-Hardy rule states that the adsorption of precipitating ions is in the order: quadrivalent > trivalent > bivalent > univalent. In actual experiments, it is found that ions of the same valence do not behave alike; this is especially true of the univalent ions. Moreover, the behavior of alkaloid and dye anions follows no rule as to valence. The Schulze-Hardy rule must therefore be regarded merely as a useful first approximation.

Various attempts have been made to explain the valency rule, with but limited success. Whetham[18] applied the theory of probabilities and concluded that the molecular precipitation concentrations will be:

$$\frac{1}{C_1} : \frac{1}{C_2} : \frac{1}{C_3} \cdots = 1 : x : x^2$$

where C_1, C_2, and C_3 are the precipitation values of electrolytes with univalent, bivalent, and trivalent precipitating ions, and x is a constant. Freundlich assumed that, in the precipitation of sols by electrolytes, equivalent amounts of ions of varying valence are adsorbed from equimolar solutions (p. 261). If this were true, the following relationship should hold:[19]

$$\frac{1}{C_1} : \frac{1}{C_2} : \frac{1}{C_3} \cdots = 1 : 2^n : 3^n \cdots$$

where the C's have the same significance as before, and n is a constant. In most cases the above formulas fit the experimental data so roughly that they are of questionable use.

From consideration of a theory of the interaction of the double layers on hydrophobic sol particles, Verwey[20] concludes that, for monovalent, divalent, and trivalent ions, the precipitation concentrations should be in the ratio

$$1:(\tfrac{1}{2})^6:(\tfrac{1}{3})^6 = 100:1.6:0.13$$

This represents only approximately the data reported in the preceding tables.

Ostwald[21] maintains that coagulation of a sol takes place when the activity coefficient of the precipitating ion reaches a certain value which is constant for ions of all valences. This rule is likewise limited in its applicability and usefulness.[22, 26]

Traube's rule in coagulation. With homologous series of organic salts as coagulating electrolytes, Freundlich and coworkers[23] found the precipitating power to increase regularly with the addition of CH_2 groups in accord with Traube's rule which states that the capillary activity, that is, the lowering of the surface tension of water and the adsorption by solid adsorbents, increases regularly with the addition of CH_2 groups in an homologous series (p. 16). This is illustrated in Table 52 with two different sols of arsenic trisulfide. The addition of each successive pair of CH_2 groups causes a marked falling off in precipitation value. Similar observations were made on a hydrous ferric oxide sol with a series of sodium salts of fatty acids. Also, the difficultly soluble sodium fumarate was found to have a much higher coagulating power for ferric oxide sol than the more readily soluble isomeric sodium maleate. This accords with the usual view that the least soluble substance is the most capillary active, that is, the most strongly adsorbed.

TABLE 52

COAGULATION OF ARSENIC TRISULFIDE SOLS BY HOMOLOGOUS AMINE CHLORIDES

Electrolyte	Sol *a*, 0.475 g/l		Sol *b*, 0.465 g/l	
	Pptn. value, x (millimoles/l)	Activity factor, x_n/x_{n+1}	Pptn. value, x (millimoles/l)	Activity factor, x_n/x_{n+1}
NH_4Cl	35.00	...	51.0	...
$C_2H_5NH_3Cl$	18.20	1.9	17.5	3.0
$(C_2H_5)_2NH_2Cl$	9.96	1.8	5.3	3.3
$(C_2H_5)_3NHCl$	2.78	3.5	1.5	3.5
$(C_2H_5)_4NCl$	0.89	3.2	0.85	1.8

Effect of concentration of sol. The precipitation value of electrolytes for sols changes with the concentration of sol, a phenomenon first observed by Mukopadhyaya.[24] Burton and coworkers[25] formulated the rule that, in general, the precipitation value of univalent precipitating ions increases with the dilution; that of bivalent ions is almost constant and independent of the sol concentration; and that of trivalent ions varies with the sol concentration. Weiser and Nicholas[26] showed that Burton's rule is not generally applicable since, with many sols, especially those of the hydrous oxides, the precipitation value of electrolytes decreases with dilution of sol, irrespective of the valence of the precipitating ion. Some results of Weiser and Nicholas are shown graphically in Fig. 77, in which the percentage concentration of sol is plotted against the ratio of each precipitation value for a given electrolyte to that for the strongest sol. Three factors appear to determine the effect of dilution of sol on the precipitation value: (*a*) the smaller number of particles in the weaker sol requires less electrolyte to lower the ζ-potential to the coagulation point; (*b*) the decreased chance of collision requires a lower potential, and hence more electrolyte, to effect coagulation in a given time; and (*c*) the ion having the same sign of charge as the sol has a stabilizing effect. Of these three factors, (*a*) predominates with electrolytes containing strongly adsorbed multivalent precipitating ions that cause precipitation in low concentration, (*b*) can usually be disregarded, and (*c*) may be of primary importance with electrolytes that precipitate only in high concentrations. Rossi and Marescotti[27] attribute the difference in the behavior of arsenic trisulfide sol and ferric oxide sol to the greater increase in the degree of dispersity which the former undergoes on dilution. In this connection Sorum[28] found that the precipitation value of potassium chloride for ferric oxide sol increases with the dilution when the sol is very pure. Weiser and Milligan,[26] in a recent study, found that only a fortuitous combination of circumstances as regards nature of sol, purity of sol, and adsorba-

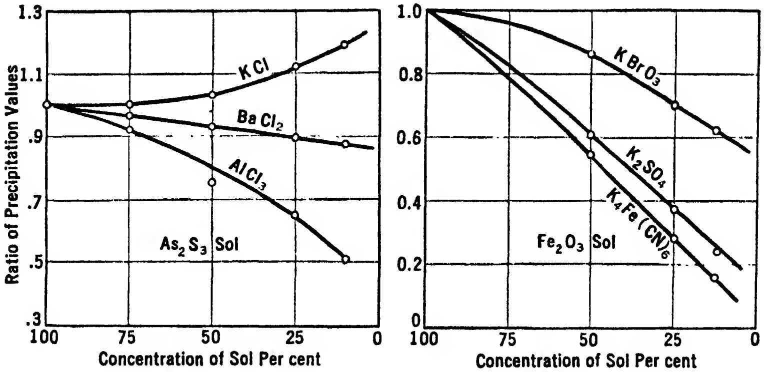


FIG. 77. Effect of concentration of arsenic trisulfide sol and of ferric oxide sol on their stability toward electrolytes.

bility of precipitating ions of a given valence can give precipitation value-sol concentration curves in accord with Burton and Bishop's rule.

Effect of stabilizing ions. Although it is often assumed that one is justified in neglecting the effect of anions in the precipitation of negative sols and of cations in the precipitation of positive sols, this will be true only if the adsorption of the ion having the same sign of charge as the sol—the stabilizing ion—is negligible, either because of its nature or the dilution. In Tables 48 and 49, it will be noted that the precipitation values of potassium salts may vary appreciably with the nature of the anion. The values are brought closer together in some instances by substituting activity coefficients for concentrations of precipitating ions;[21] but it is apparent, in the examples under consideration, that the precipitation values may differ appreciably even when the activity coefficient of potassium ion is not changed.

Reversal of sign of charge: irregular series. In Figs. 70, 74, and 76 it will be noted that the sign of the ζ-potentials of glass, colloidal silver iodide, and cellulose, respectively, are reduced from an appreciable negative value to zero, and finally to a positive value, by adding successively increasing amounts of thorium nitrate. The charge reversal from negative to positive has been accomplished only with salts having multivalent cations, and the reversal from positive to negative only with hydroxyl ion. The phenomenon of charge reversal has resulted in what is called *irregular series* in the coagulation of

TABLE 53[29]

ACTION OF THORIUM NITRATE ON GOLD SOL

$Th(NO_3)_4$ (millimoles/l)	Color after 5 min	Remarks
0–0.00084	Red	Sol negative
0.00086–0.00088	Red to blue	Sol negative
0.00090	Blue	Precipitation value of negative sol
0.00090–0.0028	Blue	
0.0030	Violet blue	End of first precipitation zone
0.0040	Red	Sol positive
0.0040–15.0	Red	Sol positive
17–19	Violet	Sol positive
20	Blue	Precipitation value of positive sol

sols, an example of which is given in Table 53.[29] Thorium nitrate reduces the ζ-potential of the particles in a gold sol to the coagulation point and then reverses it, owing to strong adsorption of thorium ion, of hydrous thorium oxide, or both. The resulting positive sol is coagulated by nitrate ion in relatively high concentration. Ferric, aluminum, lanthanum, or thorium chloride may be substituted for thorium nitrate. Similarly, an irregular series is obtained with arsenic trisulfide sol,[30] using aluminum chloride, ferric chloride, thorium nitrate, or basic dyes; and ferric oxide sol gives an irregular series with sodium hydroxide[31] or with disodium phosphate which hydrolyzes to give hydroxyl ions. In these instances there are two zones of coagulation, one of a negative (positive) sol and the other of a positive (negative) sol. This is shown diagrammatically in Fig. 78. As already noted, the reversal in the sign of charge is brought about by strong adsorption either of an ion or of a hydrous oxide in the case of salts with multivalent cations that may hydrolyze appreciably.

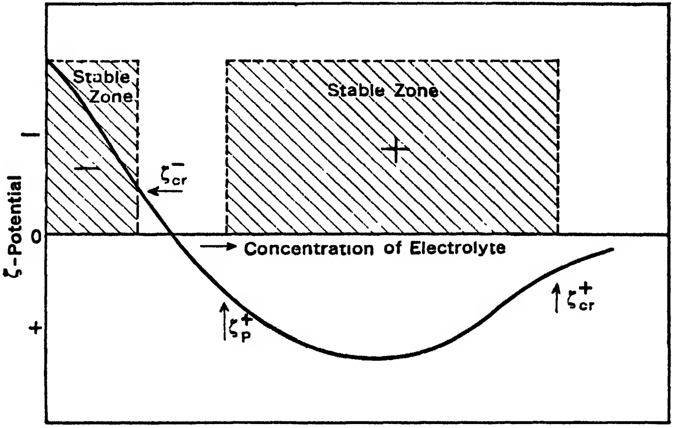


FIG. 78. Diagram showing the existence of two coagulation points with a stable zone between. ζ_{cr}^{-} and ζ_{cr}^{+} are the critical potentials for the negative and positive sol, respectively. ζ_{p}^{+} is the potential at which the particles are peptized as a positive sol.

Action of Non-electrolytes

The addition of non-electrolytes to hydrosols, both positive and negative, usually decreases their stability toward electrolytes. The sensitization has been attributed to a decrease in the dielectric constant[32] of the medium; but this is not the only factor. Sugar stabilizes sulfide sols and alcohol sensitizes them toward electrolytes, but one is not justified in ascribing the difference to the dielectric constant. Kruyt and van Duin[33] observed that the precipitation value of univalent and trivalent ions for arsenic trisulfide sol was lowered in the presence of phenol and of propyl alcohol, whereas that of bivalent ions was raised.

From a study of this behavior, the author[34] concluded that the sensitizing action toward electrolytes is due at least in part to the displacing of a stabilizing ion or the cutting down of the adsorption of a precipitating ion. These two actions are antagonistic, and so the precipitation value may be increased, decreased, or remain unchanged in the presence of a non-electrolyte. It was found, for example, that the adsorption of barium ion is cut down by the presence of phenol, and the precipitation value is increased by the presence of phenol. This means that the sol is sensitized in the sense that less barium must be adsorbed to reduce the potential to the coagulation point; the higher precipitation value in the presence of phenol results from the cutting down of the adsorption of barium by the non-electrolyte.

In general, the influence of foreign non-electrolytes on the stability of lyophobic sols can be accounted for, at least qualitatively, by considering[35] the effect on: (1) the dielectric constant of the medium, (2) the viscosity, (3) the degree of ionization of the electrolytes present, and (4) the selective adsorption of the precipitating and stabilizing ions by the dispersed particles. All these factors are measurable and are known to have more or less influence on the stability. Chaudhury[36] believes that the change in interfacial tension between the dispersed particles and the surrounding medium has an important bearing on the tendency of the particles to coalesce.

Effect of radiations and agitation. Radiations such as x-rays, α-rays from radium, and ultraviolet light have a sensitizing action on most sols. The exposure may not cause coagulation, but it usually lowers the stability toward electrolytes. The direct cause of the sensitization is not always obvious, but in the case of arsenic trisulfide sol, Freundlich and Nathansohn[37] showed that light brings about the photochemical oxidation of the stabilizing electrolyte, hydrogen sulfide, to sulfur and pentathionic acid; the acid then reacts with more hydrogen sulfide until the sol is finally coagulated completely.

Stirring accelerates the velocity of coagulation of sols by electrolytes, particularly when ions of high coagulating power are employed and when the concentration of electrolyte is in the region of the precipitation value. Freundlich and coworkers[38] found that sols of ferric oxide and copper oxide may be coagulated by prolonged stirring without the addition of electrolyte, provided that air is stirred into the sol, thereby increasing the extent of air-liquid interface. The particles are so strongly adsorbed at this interface that agglomeration gradually results (cf. p. 305).

MECHANISM OF THE COAGULATION PROCESS

Adsorption of Precipitating Ions

Linder and Picton[39] first reported the adsorption of cations by negative arsenic trisulfide particles during the coagulation of sol. Later Whitney and Ober[40] investigated the phenomenon and concluded that equivalent amounts of various cations were adsorbed by the same sol. This work was extended by Freundlich,[41] who at first claimed an equivalent adsorption of ions of varying valence even when different sols were employed. A similar relationship was found with hydrous oxide sols, which led Freundlich to conclude that, in general, equivalent amounts of varying precipitating ions are adsorbed at the precipitation value with both positive and negative sols. This general conclusion was found to be untenable by the author,[42] and Freundlich[43] has now abandoned it.

Some typical adsorption data on two different sols are given in Tables 54 and 55. There is no question that adsorption of precipitating ions accompanies the coagulation process, but the adsorption values are not equivalent. The adsorption values of alkaline-earth cations by arsenic trisulfide are similar but not identical and differ widely from sol to sol; and the adsorptions of ions other than the alkaline earths are far from equivalent. With hydrous alumina sol, also, the adsorption values are far from equivalent even for ions of the same valence. In accord with what one might expect, the most strongly adsorbed ion has the highest precipitating power (lowest precipitation value), as shown by the data in the second part of Table 55.

There are at least two reasons why the adsorption values are not equivalent at the precipitation value: (1) less of a strongly adsorbed ion needs to be taken up to reduce the potential to the coagulation point,[44] and (2) adsorption by agglomerating particles takes place in varying amounts, depending on the nature and concentration of the added electrolyte.

TABLE 54

Adsorption of Cations during the Precipitation of Arsenic Trisulfide Sol

Cation	Conc. of sol (g/l)	Adsorption (meq/g)	Observer	Cation	Conc. of sol (g/l)	Adsorption (meq/g)	Observer
Ba	6.4	0.116	Weiser[42]	Aniline	....	0.074	Freundlich[41]
Sr	6.4	0.107	"	New fuchsin	....	0.076	"
Ca	6.4	0.093	"	UO_2	4.14	0.088	"
Ba	11.8	0.060	"	Ce	4.14	0.069	"
Sr	11.8	0.056	"	Ba	1.55	0.21	Freundlich[43]
Ca	11.8	0.043	"	Zn	1.55	1.50	"
Ba	21.5	0.072	"	Ni	1.55	1.22	"
Sr	21.5	0.069	"	In	....	0.56	"
Ca	21.5	0.073	"	Te	....	0.37	"
Ba	10.0	0.110	Whitney and Ober[40]	Th	....	0.27	"
				New fuchsin	....	0.08	"
Sr	10.0	0.082	Whitney and Ober[40]	Methylene blue	....	0.13	"
Ca	10.0	0.100	Whitney and Ober[40]				

TABLE 55

Adsorption during Coagulation of Colloidal Alumina

Ion	Precipitation value (millimoles/l)	Adsorption value		Observer
		(Millimole/g)	(Meq/g)	
Ferrocyanide	0.08	0.073	0.29	Gann[41]
Ferricyanide	0.10	0.09	0.27	"
Oxalate	0.36	0.18	0.36	"
Picrate	4.00	0.18	0.18	"
Salicylate	8.00	0.30	0.30	"
Ferrocyanide	0.094	0.320	1.280	Weiser[42]
Ferricyanide	0.133	0.405	1.214	"
Sulfate	0.269	0.498	0.997	"
Oxalate	0.350	0.571	1.142	"
Chromate	0.650	0.435	0.870	"
Dithionate	0.813	0.328	0.657	"
Dichromate	0.888	0.318	0.629	"

Acclimatization. Since adsorption by colloidal particles during agglomeration is never negligible and may rise to large proportions, it is not surprising that such colloids as hydrous ferric oxide,[45] arsenic trisulfide,[45] and albumin require less electrolyte to cause precipitation when added all at once than when added stepwise through a long interval of time, particularly when the slow addition produces fractional precipitation of the sol. This phenomenon is known as "acclimatization," meaning that the colloid becomes acclimated to its surroundings when the electrolyte is added slowly, and hence more is required to produce a given result. It would appear, however, that the necessity for using more electrolyte to effect complete precipitation on slow addition arises not so much from the adaptability of the colloid to the presence of electrolytes, as from fractional precipitation which not only removes ions owing to adsorption by agglomerating particles but also alters the stability of the sol by decreasing its concentration. From this point of view, the factors which determine the excess required for a given slow rate of addition are: the extent to which the colloid undergoes fractional precipitation, the adsorbing power of the precipitated colloid, the adsorption of the precipitating ions, and the effect of dilution of the sol on the precipitation value of electrolytes[46] (p. 257).

Nature of the Adsorption: Titration of Sols

In the precipitation of hydrophobic sols with electrolytes, the precipitating ions enter into exchange adsorption (p. 101) with the counter ions in the outer diffuse portion of the double layer on the particles. For example, in the precipitation of arsenic trisulfide sol, the precipitating cations are taken up in exchange with hydrogen ions; and in a ferric oxide sol, anions are adsorbed in exchange with chloride ions. If the electrolyte is added stepwise, there is a stepwise exchange adsorption of the precipitating ion. At the same time, counter ions may be displaced from the attached (Stern, p. 226) portion of the outer layer. This simultaneous adsorption and counter ion displacement has been followed quantitatively with several hydrosols. For example, the stepwise displacement of chloride from hydrous oxide sols was determined potentiometrically in the following way.[44] A series of calomel half-cells was made by adding definite amounts of electrolyte to a definite amount of sol in which calomel was suspended, and pouring the mixture on a layer of mercury in a small glass vessel. After standing 24 hours, the potential was determined against a standard calomel electrode, and the chloride concentration calculated. The results of such "titrations" of a ferric oxide sol with potassium sulfate, ferricyanide, oxalate, and chromate are given in Fig. 79; the "titration" data for potassium sulfate are shown in Table 56. In these cases the anions are taken up practically completely by the sol particles in concentrations up to and including the

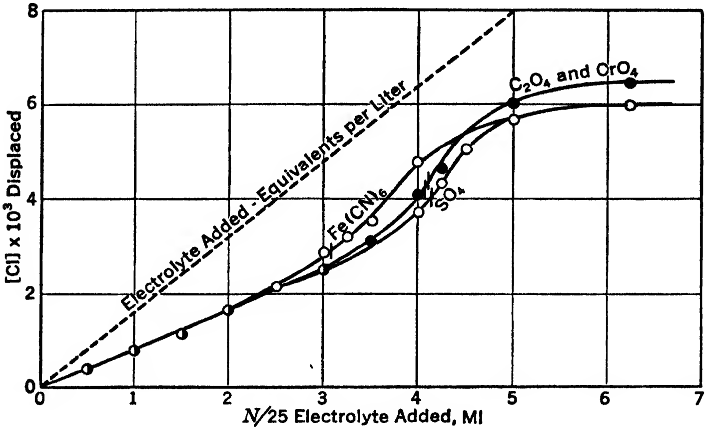


FIG. 79. Titration of ferric oxide sol with solutions of potassium salts.

TABLE 56

TITRATIONS OF Fe_2O_3 SOL WITH K_2SO_4

Ml of K_2SO_4 added to 20 ml of sol Total volume 25 ml	Volt	α Cl⁻ × 10^3	[Cl] × 10^3	[Cl] displaced × 10^3	[Cl] equivalent to [SO_4] added × 10^3
0.0	0.0910	2.29	2.37	0.0	0.0
0.5	0.0880	2.58	2.69	0.32	0.80
1.0	0.0843	2.98	3.11	0.74	1.60
1.5	0.0804	3.48	3.64	1.27	2.40
2.0	0.0778	3.83	4.02	1.65	3.20
2.5	0.0748	4.31	4.54	2.17	4.00
3.0	0.0727	4.67	4.93	2.56	4.80
3.5	0.0700	5.19	5.49	3.12	5.60
4.0	0.0675	5.73	6.07	3.70	6.40
4.25	0.0647	6.38	6.68	4.31	6.80
4.50	0.0626	6.93	7.40	5.03	7.20
5.00	0.0605	7.52	8.04	5.67	8.00
6.25	0.0597	7.76	8.31	5.94	10.00

precipitation values indicated by vertical lines cutting the curves. To cause coagulation, less trivalent ferricyanide needs to be adsorbed than of bivalent sulfate, and less chloride is displaced at the precipitation value of the trivalent ion than at the precipitation value of the bivalent ion.

Some typical observations[47] of the simultaneous adsorption of precipitating ions and displacement of counter ions are shown graphically in Figs. 80 and 81. Figure 80 gives the results of "titrating" two different hydrous oxide sols with potassium sulfate. It will be noted that the coagulating sulfate ion is adsorbed almost completely up to the precipitation value (indicated by an arrow), above which the adsorption curve is similar to that of the usual isotherm. The curve for the displacement of chloride from the innermost (Stern) portion of the outer layer falls well below that of the adsorption curve, since a part of the adsorbed sulfate ions replaces the counter chloride ions which are so far out in the diffuse layer that they are measured potentiometrically in the original sol.

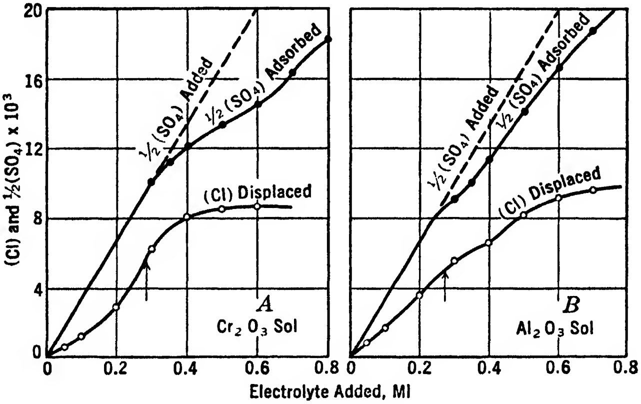


FIG. 80. Simultaneous adsorption of sulfate ion and displacement of chloride ion in (*A*) chromic oxide sol, (*B*) alumina sol.

Figure 81 gives the results of titrating two sols of the so-called *acidoid* type with barium chloride. In these instances, barium ions are adsorbed in exchange with hydrogen ions in the diffuse outer layer. The adsorbed barium ions displace hydrogen ions from the Stern layer. Again, the adsorption of barium is much greater than the displaced hydrogen since a large part of the hydrogen replaced by barium was measurable in the original sol. Unlike the behavior of the hydrous oxide sols, the displacement of counter ions from the innermost portion of the outer layer of the acidoid sols is practically complete at the precipitation concentration.

Lowering the ζ-potential. The older view of Freundlich that coagulation is the result of neutralization of the charge on the particles by equivalent adsorption of ions of opposite charge is no longer tenable. In the first place, coagulation does not result, in general, from equivalent adsorption of precipitating ions; and in the second place, the charge density in the double layer increases on adding electrolytes (p. 245). The important thing for electrolyte coagulation is the lowering of the ζ-potential. This is usually accomplished by contraction of the double layer or, if preferred, by a compression of the outer layer surrounding the dispersed particles. This decreases the distance between the two layers of opposite charge, and a lowering of the ζ-potential follows. For many years, the author has attempted to represent diagrammatically the manner in which the ζ-potential on the particles may be lowered as a consequence of the observed exchange adsorption. To illustrate: in Fig. 82 are given the diagrams of a particle of ferric oxide sol (a) before and (b) after the addition of sulfate ion. In this sol, the potential-determining Fe^{+++} and H^+ ions constitute the attached inner portion of the double layer with Cl^- in the diffuse outer layer. On adding $SO_4^=$ ions, which are more strongly adsorbed than Cl^- ions, the latter are displaced to a

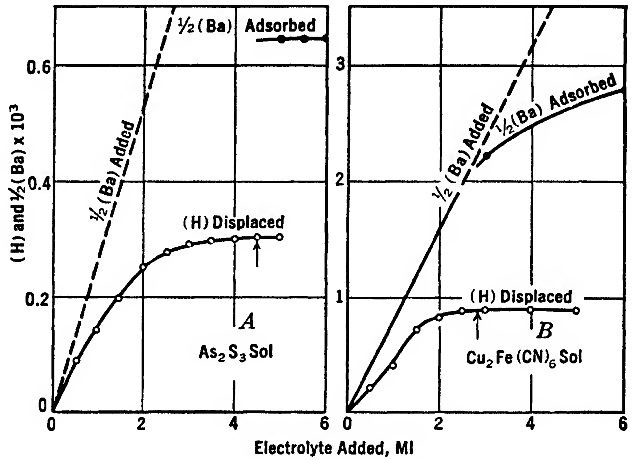
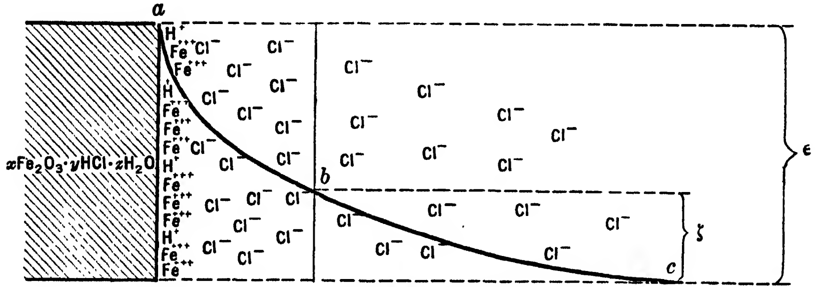
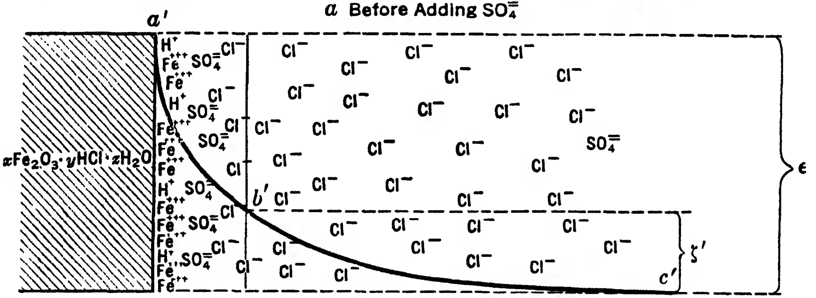


FIG. 81. Simultaneous adsorption of barium ion and displacement of hydrogen ion in (A) arsenic trisulfide sol, (B) copper ferrocyanide sol.

certain extent from the Stern layer, and the sulfate takes up a position closer to the inner layer. The distance between the layers is thereby diminished, and the ζ-potential falls. For an ion that is less strongly adsorbed than sulfate, a higher concentration will be necessary to effect the same lowering of the potential. In general, the thickness of the double layer is reduced by ions of varying valence in the order: trivalent > bivalent > univalent, which is the same as the usual order of adsorption and displacing power of the ions. This means that less of a trivalent ion needs to be adsorbed than of a bivalent or univalent ion to lower the ζ-potential to the coagulating point.



a Before Adding $SO_4^=$



b After Adding $SO_4^=$

FIG. 82. Diagrammatic representation of the constitution of a portion of a particle in a ferric oxide sol (*a*) before and (*b*) after the addition of sulfate ion.

This interpretation of the mechanism of the coagulation process is admittedly a qualitative one. In the first place, no mention is made of a change in the inner layer on adding electrolytes; but, as we have seen (p. 258), the ions of the electrolyte having the same sign of charge as the particles—the stabilizing ions—have an effect that one may not be justified in neglecting. Moreover, it has been pointed out (p. 251) that the ζ-potential is a value calculated from mobility measurements, and the equation is known to be more or less imperfect. Finally, factors other than exchange adsorption may contribute to the reduction of the distance between the charges in the double layer. Indeed Verwey[20] concludes that, in the case of silver iodide sol, exchange even of multivalent ions has nothing to do with the coagulation phenomenon. However this may be, the process of coagulation of sols by electrolytes appears to be quite complicated.

Flocculation of Clays

Clay sols are negatively charged and are usually flocculated by low concentrations of neutral salts. The Schulze-Hardy valency rule may apply fairly well, at least for certain sols. Hall and Mouson,[48] for example, determined the precipitation values of various chlorides, sulfates, and nitrates on a clay sol and found the order to be: H, Al $>$ Ca, Ba, Mg $>$ K $>$ Na; and the stabilizing power of the anions to be: $OH > SO_4 > NO_3 > Cl$.[49] Bradfield[50] showed, however, that the valency rule can have no general validity since the flocculation value may vary widely with slight changes in (1) hydrogen-ion concentration, (2) concentration of sol, and (3) nature of the exchangeable cations. The important findings of Bradfield have been confirmed and extended by Wiegner,[51] Baver,[52] Mattson,[53] and especially by Jenny and Reitemeier,[54] whose work will be considered in some detail. The investigations on clay sols confirm and extend the mechanism of the coagulation process outlined in the preceding section.

ζ-Potential, exchange, and flocculation data for clay sols. The migration velocity u of the particles of various clay sols prepared from natural Putnam clays was measured with an ultramicroscope in an open cataphoresis cell, and the ζ-potential in millivolts calculated from the average of a number of measurements, using the equation: $\zeta = 4\pi\eta u/HD$ (p. 237). The percentage release of the cations from the multivalent clays was determined after treating with potassium chloride, and that of the univalent clays was calculated from exchange values with NH_4-clay. Since potassium and ammonium ions are adsorbed and released equally well, the data are comparable quantitatively. Flocculation values were obtained both for KCl and for MCl, where M is the cation common to the clay. The data are given in Table 57. The amount of electrolyte added to the system is expressed in terms of "symmetry values, S," that is, in multiples of the number of milliequivalents of adsorbed ions in the system. The magnitude of the exchange, expressed in percentage of the symmetry concentration equal to one ($S = 1$), is called the *symmetry value.*

Effect of the charge and size of adsorbed cations on the ζ-potential. The influence of charge and size of the adsorbed cations on the ζ-potential of clay particles is shown graphically in Fig. 83 (Table 57).

TABLE 57

ζ-POTENTIAL, EXCHANGE ADSORPTION, AND FLOCCULATION OF CLAYS

Sol	μ	Temp. (°C)	ζ (mv)	% release (symmetry value)	Flocculation values S-concentrations	
					KCl	MCl
Li-clay	3.45	30.3	58.8	68.0	22.6	26.0
Na-clay	3.41	28.9	57.6	66.5	11.2	14.8
K-clay	....	....	56.4	48.7	7.8	7.8
NH_4-clay	3.48	33.2	56.0	50.0	5.4	4.9
Rb-clay	3.25	30.3	54.9	37.4	.....	.....
Cs-clay	3.02	30.3	51.2	31.2	5.6	4.2
H-clay	2.84	30.3	48.4	14.5	1.5	0.36
Mg-clay	3.18	30.3	53.9	31.32	2.9	0.69
Ca-clay	3.27	32.8	52.6	28.80	3.0	0.55
Sr-clay	3.06	30.3	51.8	25.76	2.6	.....
Ba-clay	3.01	30.3	50.8	26.75	2.3	.....
La-clay	2.74	21.2	45.5	13.96	0.86	.....
Th-clay	3.11	32.2	50.4 47.1	1.85	0.60	.....
M.B.*-clay	2.57	33.7	40.5	.....	0.0	.....

* Methylene blue.

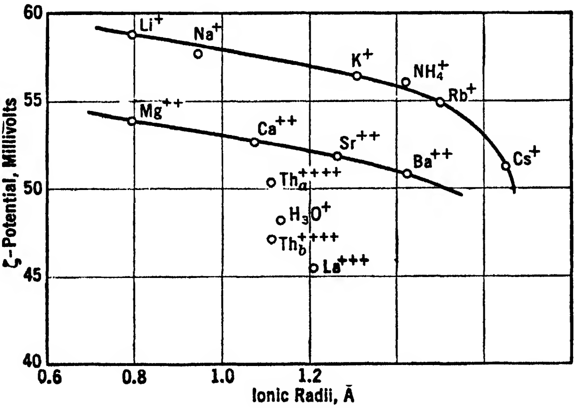


FIG. 83. Effect of charge and size of adsorbed cations on the ζ-potential of colloidal clay particles.

When rare-gas type ions of equal size are compared, the potential tends to be lower as the valence of the ion is higher. The comparison must be restricted to ions of equal size since certain uni-clays (*e.g.*, Cs-clay) have lower potentials than some of the bi-clays (*e.g.*, Mg-clay). Comparing rare-gas type ions of equal valence, the ζ-potential is higher the smaller the adsorbed cation. This agrees with Wiegner's view that the most highly hydrated ions (in general, small ions are strongly hydrated) cause the highest ζ-potential.

Z-potential and ionic exchange. Jenny visualizes clay particles as plate-shaped crystals which hold adsorbed ions on their surfaces. Because of heat motion and Brownian movement, the ions are not at rest but oscillate and, at some times, may be a considerable distance from the wall. The cation of an added electrolyte may slip between the negative wall and the positive oscillating ion, the former becoming adsorbed and the latter remaining in solution as an exchanged ion. From this point of view, the more loosely an ion is held, the greater the average distance of oscillation and the greater the likelihood of replacement; and conversely, the more closely the cation sticks to the surface, the less readily will it be replaced. Since the average distance of oscillation corresponds directly to the average thickness of the double layer, it would follow that clays with high ζ-potentials should have adsorbed ions which are easily exchangeable. A comparison of the ζ-potential with the percentage release of adsorbed ions (columns 4 and 5 of Table 57) supports this deduction. Since thorium is so difficult to replace it is probable that the observed ζ-potential of Th-clay is much too high.

Z-potential and flocculation values. The close relationship between ζ-potential and flocculation value is again illustrated by the data of Table 57 shown graphically in Fig. 84 in which the precipitation values of potassium chloride are plotted against the ζ-potential. Obviously, it takes much more electrolyte to coagulate a clay with a high ζ-potential than one with a low potential. The curve cuts the x-axis well above zero, in accord with Powis's concept of a critical potential for flocculation (p. 221). For the systems under consideration, the critical potential appears to be 42 millivolts. That this value must be approximately correct is evidenced by the behavior of methylene blue-clay which has a potential of 40.5 millivolts and therefore flocculates completely without the addition of electrolyte.

Flocculation values and exchange adsorption. The flocculation values F and exchange adsorption values E of various electrolytes for three different clays are given in Table 58. Both values are ex-

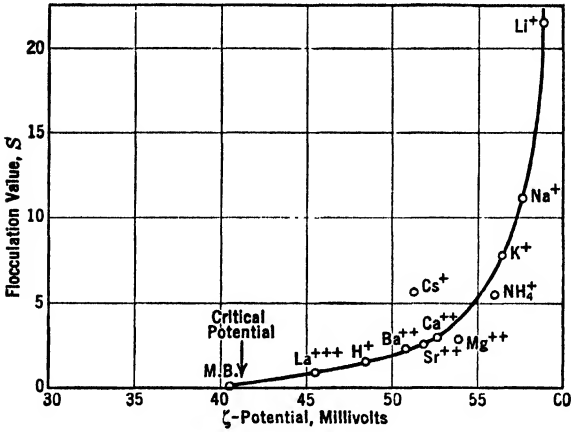


FIG. 84. Flocculation values of potassium chloride for uni- and poly-clays.

TABLE 58 *

RELATION BETWEEN FLOCCULATION VALUES (*F*) OF ELECTROLYTES AND EXCHANGE ADSORPTION (*E*)

Electrolyte	NH4-clay		Ca-clay		H-clay	
	F (*S*)	*E* (*S*)	*F* (*S*)	*E* (*S*)	*F* (*S*)	*E* (*S*)
LiCl	8.0	32.0	4.8	13.08	2.9	6.6
NaCl	8.0	33.5	4.5	12.74	2.7	6.2
KCl	5.4	51.33	3.0	28.80	1.5	14.5
NH_4Cl	4.9	50.0	2.5	29.35	1.3	.....
RbCl	4.7	62.56	1.87	43.85	1.17	28.20
CsCl	2.8	68.78	1.17	50.83	0.73	39.73
HCl	0.98	84.89	0.55	77.80	0.36	50.0
$MgCl_2$	1.22	65.44	0.59	47.53	0.47	15.78
$CaCl_2$	1.27	63.56	0.55	50.0	0.47	26.89
$BaCl_2$	1.16	71.67	0.55	52.96	0.35	23.78
$La(NO_3)_3$	0.90	.....	0.47	.....	0.18	.....
$ThCl_4$	0.75	80.89	0.36	80.24	0.16	.....

* After Jenny and Reitemeier.[54]

pressed in symmetry values S (p. 268). With the exception of H^+ ion, the valency rule applies, but only in the sense that the ion with the highest valence precipitates in the lowest concentration. Ions of the same valence, especially univalent ions, show a wide variation in precipitation value. Whenever the flocculating electrolyte contains a foreign cation, exchange adsorption always takes place. Comparing the flocculation and ionic exchange data of Table 58, it appears that those ions which are weakly adsorbed have high flocculation values, whereas ions which are taken up strongly by exchange precipitate in low concentrations. This may be shown graphically by plotting the flocculating power F_p, which is the reciprocal of the flocculation value, against the exchange adsorbability (Fig. 85). The resulting curves may be represented by the empirical equations:

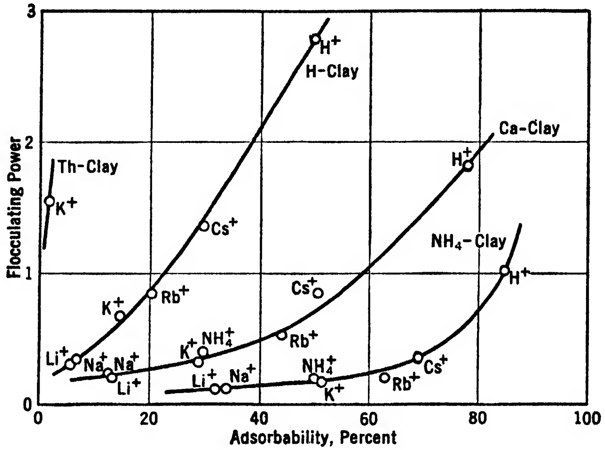


FIG. 85. Relationship between the exchange adsorbability of univalent ions and their coagulating power for clays.

$$F_p = 0.14e^{-0.0332\,E} \text{ (for Ca-clay)} \quad \text{and} \quad F_p = 0.284e^{-0.0431\,E} \text{ (for H-clay)}$$

In other words, the coagulating effect of an ion increases exponentially with its exchange adsorbability. The position of the curves for the different clays emphasizes the fact that the flocculation value of a given cation is determined in large measure by the nature of the exchangeable ion initially present in the clay.

If the clay contains a highly hydrated univalent ion such as Na-clay, the ζ-potential is high since the ions are loosely bound and oscillate through considerable distances. This means that the effective width of the double layer is great or the degree of dissociation is high. The flocculation value of an electrolyte for such a clay varies widely with the properties of the coagulating ion. If it is highly hydrated and univalent, such as Li^+ ion, the extent of the exchange adsorption will be relatively small, and the change in ζ-potential will be altered but little. The necessary lowering of the potential will be produced by a decrease in thickness of the double layer or a decrease in dissociation,[53] which requires large amounts of electrolyte (15–20 *S*). On the other hand, if the precipitating ion is univalent but not hydrated, such as Cs^+ ion, exchange adsorption predominates strongly, giving the particle a new outer layer which is so strongly attracted by the inner layer that the ζ-potential drops sharply. Very little electrolyte is required to repress the new outer layer to the critical distance characteristic of the critical potential; hence the flocculation values are small, of the order of 1 *S*.

Now, if the original clay contains non-hydrated univalent ions such as cesium, or multivalent ions such as thorium, the ζ-potential is low to begin with. The addition of a highly hydrated ion such as lithium will produce a small exchange which will tend to increase the thickness of the double layer and thus raise the ζ-potential.[52] The peptizing action is finally overbalanced by the repressing effect of more electrolyte, and flocculation results with concentrations of medium magnitude (2–10 *S*), but somewhat higher than the common ion values. Finally, if the coagulating ion is similar in nature to the one on the clay originally, ionic exchange again assumes greater proportions without greatly modifying the ζ-potential. Flocculation is occasioned chiefly by the necessary decrease in dissociation at low electrolyte concentrations, often less than 1 *S*.

In the flocculation of acid clay sols with bases, the first step in the process is the neutralization of the acid followed by the coagulation of the resulting clay salt. The precipitation value of a salt-base mixture such as KCl—KOH and $CaCl_2$—$Ca(OH)_2$ involves not only the coagulating action of the cation but also the neutralizing and peptizing influence of the hydroxyl ion.[55]

Verwey's theory of the stability of sols. The views of Verwey[20] and the Dutch school of colloid chemists furnish the most significant contribution to a quantitative theory of the stability of hydrophobic sols that has been advanced since Freundlich's theory which has been confirmed and amplified in the preceding sections. Hamaker[56] proposed a general theory of sol stability in terms of potential curves which give the potential energy of two particles with respect to each other as a function of their mutual distance. He considered different types of potential curves, all of which consisted of an attractive potential due to London-van der Waals forces between the particles, superimposed on a repulsive potential due to the introduction of the double layers surrounding the particles. The view of Hamaker that a system of charged colloidal particles and oppositely charged counter ions will show an attraction between the particles for certain distances was challenged by Langmuir,[57] who argued that a system of charged colloidal particles and oppositely charged counter ions will show an attraction between the particles for certain distances, but was supported by Levine and Dube [58] and Corkill and Rosenhead,[59] who argued that attractive forces always predominate from the double-layer interaction. In the light of the conflicting viewpoints, the theory of the interaction of double layers was reviewed in detail by Verwey [20] in relation to sol stability. He concluded that the interaction must be associated with an increase of the free energy, leading to a repulsion between the particles. The repulsive potential, calculated from a consideration of the free energy for certain special cases, has been combined with the London-van der Waals attractive potential calculated by Hamaker to obtain curves of *potential against distance* which agree well with certain experimental data, including those on the effect of electrolyte concentration and valences of the ions on coagulation. Some curves of potential energy of interaction against distance between particles, showing the effect of electrolyte concentration, are given in Fig. 86. The graphs refer to the case of two spherical particles with radius $a = 10^{-5}$ cm, using the constant proportionality factor $A = 10^{-12}$ for the London-van der Waals potential. $s = R/a$ is the distance between the particle centers measured in a units: $a = 10^{-5}$ cm for a value of the double-layer potential $z = 1$, measured in units of kT/e (for $z = 1$, kT/e is 25.6 millivolts at room temperature; for $z = 2$, $kT/e = 57.2$ millivolts, etc.). The electrolyte concentration n is expressed as κ from Debye's relationship $\kappa = \sqrt{8\pi ne^2/\epsilon^{-kT}}$ ($\kappa = 10^{-7}$ holds approximately for a 0.1 N solution; $\kappa = 10^{-6}$ for 0.001 N, etc.; k is the Boltzman constant: 1.38×10^{-16} ergs/deg/molecule).

Although Verwey's theory appears to agree with various colloid chemical data, we have seen (p. 255) that it does not fit exactly the calculated ratio among the precipitation concentrations of monovalent, divalent, and trivalent ions in certain cases. Verwey points out that his theory needs amplification before it will fit all the complicated phenomena involved in hydrophobic sol stability. One handicap in making comparisons of calculated with experimental data is "that the

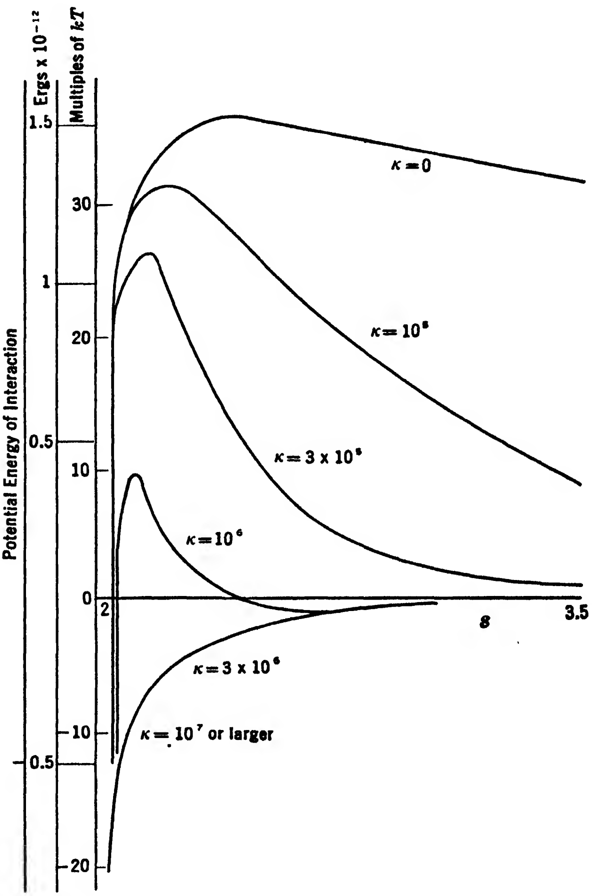


FIG. 86. Potential energy of interaction against distance between centers of two spherical particles (in units of particle radius $a = 10^{-5}$ cm for $z = 1$; see text), showing the influence of electrolyte concentration n expressed by Debye's κ. (After Verwey)

potential drop in the diffuse layer has usually been calculated from electrophoretic data. We know now that the potentials calculated in this way are more or less incorrect because we cannot neglect the relaxation effect in electrophoresis" (cf. reference to McBain's criticism of ζ-potential calculations, p. 252).

COAGULATION BY MIXTURES OF ELECTROLYTES

Linder and Picton,[60] in their early work on the coagulation of sols, observed that the precipitating action of mixtures of two electrolytes for arsenic trisulfide sol is approximately additive provided that the precipitating power of each is of the same order of magnitude, whereas the precipitating action may rise appreciably above an additive relationship if the electrolytes vary widely in precipitating power. Some observations of the author,[61] given in Fig. 87, illustrate the behavior of various mixtures of barium chloride with alkali chlorides on arsenic trisulfide sol. The concentrations of barium chloride are plotted as abscissa, and the concentration of the alkali chlorides as ordinate. In the same figure, the precipitation values of mixtures of potassium and sodium chlorides are given to show the additive relationship which obtains with mixtures of similar precipitating power.

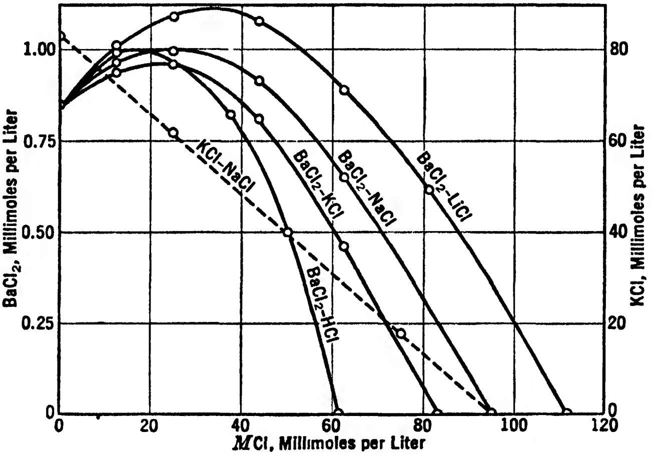


FIG. 87. Coagulation of arsenic trisulfide sol with mixtures of electrolytes.

From similar observations on sulfur sol, which is highly hydrous, Freundlich and Scholz [62] concluded that hydration of the sol and of the precipitating ions is of primary importance in determining whether or not the precipitating action of mixtures will be additive. This is not the only factor since an additive relationship is usually observed in precipitating hydrous oxide sols with mixtures. The precipitating action of mixtures appears to be influenced by two factors in addition to hydration: (1) the antagonistic effect of each precipitating ion on the adsorption of the other, and (2) the stabilizing influence of the ions having the same sign of charge as the sol.

The antagonistic effect of one ion on the adsorption of another is illustrated in Table 59,[63] which gives the precipitation values of barium chloride and the alkali chlorides for arsenic trisulfide sol, together with the exchange adsorption of barium ion during the precipitation of the sol with barium chloride alone and when mixed with a constant amount of the alkali chlorides. It is apparent that the univalent ions cut down the adsorption of barium in the order: Li < Na < K < H. Since, under otherwise constant conditions, one would expect the adsorption of a given cation to be reduced by the presence of a second in proportion to the adsorbability of the latter, it follows that the order of adsorbability of the univalent ions is: H > K > Na > Li. This is the same order one would deduce from the precipitation values of the salts (Table 59), assuming that the salt containing the most readily adsorbed cation precipitates in lowest concentration. In general, the adsorption and the precipitating power of alkali cations follow the order: Li < Na < K < Rb < Cs.[64] This series is the reverse of the order of hydration of the ions. The hydration or lyotropic series will be encountered again in the sections on the stability of hydrophilic sols (p. 295) and the swelling of gels (p. 331).

TABLE 59

ADSORPTION OF BARIUM ION BY ARSENIC TRISULFIDE

Electrolytes added to 100 ml sol Total volume 200 ml	Barium adsorbed (meq/g)	Precipitation values (millimoles/l)	
30 ml 0.02 *N* $BaCl_2$	0.058	$BaCl_2$	1.37
30 ml 0.02 *N* $BaCl_2$ + 30 ml 0.5 *N* LiCl	0.019	LiCl	88.7
30 ml 0.02 *N* $BaCl_2$ + 30 ml 0.5 *N* NaCl	0.014	NaCl	73.5
30 ml 0.02 *N* $BaCl_2$ + 30 ml 0.5 *N* KCl	0.009	KCl	63.7
30 ml 0.02 *N* $BaCl_2$ + 30 ml 0.5 *N* HCl	0.007	HCl	52.5

Associated with this so-called *ion antagonism* in adsorption is the effect of stabilizing ions in raising the precipitation concentration of mixtures above the additive value. Dhar and his collaborators[65] are of the opinion that, in the precipitation of negative sols by mixtures, cation antagonism is much less important than the stabilizing action of anions in bringing about the departure from an additive relationship. Certainly, the stabilizing effect predominates if one of the electrolytes contains a potential-determining ion (p. 227), for example, in the precipitation of negative copper ferrocyanide sol with mixtures of potassium ferrocyanide and barium chloride.

Further reference to the phenomenon of ion antagonism will be made in Chapter 21.

KINETICS OF THE COAGULATION PROCESS

Ultramicroscopic observations on sols to which electrolytes are added disclose that concentrations appreciably below the precipitation value cause no apparent change. On gradually increasing the concentration, a zone of *slow coagulation* is reached where a small addition causes a rather large decrease in coagulation time. With still more electrolyte, the precipitation value is attained above which is the zone of *rapid coagulation.*

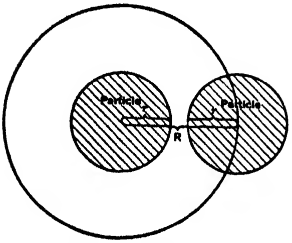


FIG. 88. The sphere of action in the coagulation process.

Smoluchowski [66] assumes that, in rapid coagulation of particles of equal size and of radius r, one particle becomes permanently fixed to another when the two approach within a certain minimum distance defined as the radius R of the sphere of action. If $R > 2r$ as shown in Fig. 88, the sol is more or less stable, whereas agglomeration takes place whenever the centers of the particles are at a distance less than R, that is, when $R < 2r$.

Starting with this assumption, Smoluchowski deduced equations for the decrease in the number of particles with the time for different stages of coagulation, as a function of the radius of action R, the diffusion constant D (p. 189), and the original number of particles per unit volume. The simplest equation which gives the rate of disappearance of simple primary particles when all collisions are effective is:

$$n_1 = \frac{n_0}{(1 + \beta t)^2} \tag{1}$$

where n_0 is the number of primary particles in unit volume at zero time and n_1 is the number of particles at time t; and β is a constant which is equal to $4DRn_0$, where R is the radius of action, and D the diffusion coefficient. This considers only the uniting of primary particles into doublets, whereas multiple particles containing three, four, or more primary units are formed. For the total number of all particles Σ_n present at a given time, the equation is:

$$\Sigma_n = \frac{n_0}{1 + \beta t} \tag{2}$$

The Smoluchowski equation for rapid coagulation has been verified repeatedly.[67] It may be tested readily on gold sol since the primary particles appear green in the ultramicroscope and the aggregates brown. Moreover, by adding a protecting colloid such as gelatin, the coagulation may be stopped after a given time interval and the number of particles counted. Some typical data from Zsigmondy are given in Table 60.

TABLE 60

DECREASE IN NUMBER OF PRIMARY PARTICLES IN GOLD SOL

t seconds	0	2	5	10	20	40
n_1 observed	1.97	1.35	1.19	0.89	0.52	0.29
n_1 calculated	1.97	1.65	1.31	0.93	0.54	0.25

Müller[68] has successfully extended Smoluchowski's theory to take care of the rapid coagulation of sols with particles of varying size, and Smoluchowski[66] has modified his equation to represent the slow coagulation process when only a part of the collisions are effective. Smoluchowski's modified eq. 1 is:

$$n_1 = \frac{n_0}{(1 + \epsilon\beta t)^2} \tag{3}$$

in which ϵ represents the fraction of the collisions that are effective and lead to the formation of agglomerates.

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CHAPTER 17

The Stability of Hydrophobic Sols II: Mutual Coagulation and Protection

MUTUAL COAGULATION OF HYDROPHOBIC SOLS

When suitable amounts of two sols of opposite sign are mixed, complete mutual coagulation takes place. On either side of the zone of mutual coagulation, the direction of the electrophoresis of the particles is determined by the sol which is present in excess. These facts are illustrated by some results of Billitzer[1] (Table 61), on mixing varying amounts of positive ferric oxide sol (3.036 g Fe_2O_3/l) and negative arsenic trisulfide sol (2.07 g As_2S_3/l), in a total volume of 10 ml. Some data of Biltz[2] are shown diagrammatically in Fig. 89 and of Weiser and Chapman[3] in Fig. 90. In obtaining the data for Fig. 90 special precautions were taken to determine sharply the limits of the

TABLE 61

MUTUAL ACTION OF FERRIC OXIDE AND ARSENIC TRISULFIDE SOLS

Milliliters of sol		Observations	Electrophoresis of supernatant sol
Fe_2O_3	As_2S_3		
9	1	No change	To cathode
8	2	A little clouding after some time	To cathode
7	3	Immediate clouding, then precipitation	To cathode
5	5	Immediate precipitation, incomplete	To cathode
3	7	Almost complete precipitation	
2	8	Immediate precipitation, incomplete	To anode
1	9	Immediate precipitation, incomplete	To anode
0.2	9.8	Clouding, no precipitation	To anode

zone of mutual coagulation. The width of this zone varies considerably with different pairs of sols under identical experimental conditions.

FIG. 89. Range of mutual coagulation of oppositely charged sols (Biltz).

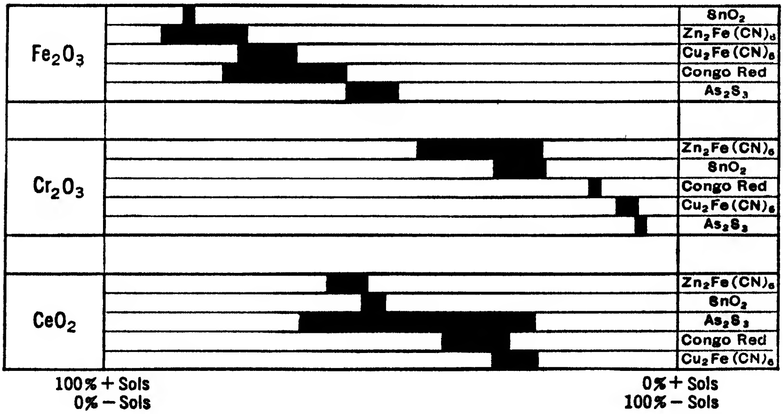

FIG. 90. Range of mutual coagulation of oppositely charged sols (Weiser and Chapman).

Mechanism

The mutual coagulation process is ordinarily attributed to the mutual discharge of the electrically charged particles of opposite sign, with subsequent agglomeration into clumps that settle out. The observations of Biltz (Fig. 89) are commonly cited to show that the action is determined exclusively by the magnitude of the potential of the particles.[4] Thus, a comparison of the precipitating action of a series of sols is said to disclose that, whereas the optimum amount of positive sols required to precipitate negative sols varies, the order is always the same. That this is not true is evidenced by the results given in both Figs. 89 and 90, which show that the order of sols in the right-hand column differs for each of the sols in the left-hand column.

Lottermoser [5] observed that the most nearly complete coagulation of positively charged silver iodide containing a slight excess of silver nitrate, and negatively charged silver iodide containing a slight excess of potassium iodide, was obtained when the excess of silver nitrate in one sol was just equivalent to the excess of potassium iodide in the other. This suggests that interaction between the stabilizing ions is the cause of the mutual coagulation of oppositely charged sols.[6] This cannot be generally true since mutual coagulation takes place very frequently where interaction between stabilizing agents is a remote possibility.[7] At the same time, the purity of sols influences the position and width of the zone of mutual coagulation. To account for the behavior of various combinations, it is concluded that the precipitating power of positive sols for negative sols is not determined exclusively by the magnitude of the ζ-potential of the particles in the respective sols. Other factors which may play a part are: (*a*) mutual adsorption of oppositely charged particles that may be independent of the potential which results from the electrical double layer, (*b*) the presence of precipitating ions as impurities in the sols, (*c*) the interaction between stabilizing ions.

From mobility measurements on mixtures of positively and negatively charged sols with and without the addition of electrolytes, Hazel and McQueen [8] conclude that mutual coagulation is due primarily to mutual adsorption of oppositely charged particles with a consequent unequal redistribution of the total charge around the particles. Using a technique previously described (see p. 263), the author [9] has studied, by potentiometric analysis, the changes in composition of the double layers when two sols of opposite sign of charge are mixed. Some data for mixtures of negative copper ferrocyanide sol and positive ferric oxide sol are shown graphically in Fig. 91. Hydrogen (and ferric) ions are the stabilizing ions of the ferric oxide sol, and chloride ions are the counter ions in the diffuse double layer of this sol. In the cupric ferricyanide sol, the strongly adsorbed ferrocyanide ions are the stabilizing ions, and hydrogen ions are the counter ions. On adding negatively charged cupric ferrocyanide sol to positively charged ferric oxide sol, mutual adsorption lowers the ζ-potential on both kinds of particles. To oppose this lowering of the ζ-potential on the ferric oxide particles, hydrogen ions are adsorbed from solution with a consequent lowering of the hydrogen-ion activity of the sol mixture below the value resulting from dilution with water. This effect predominates through the higher and medium concentrations of ferric oxide sol, the hydrogen-ion activity increasing again only in mixtures relatively rich in cupric ferrocyanide sol.

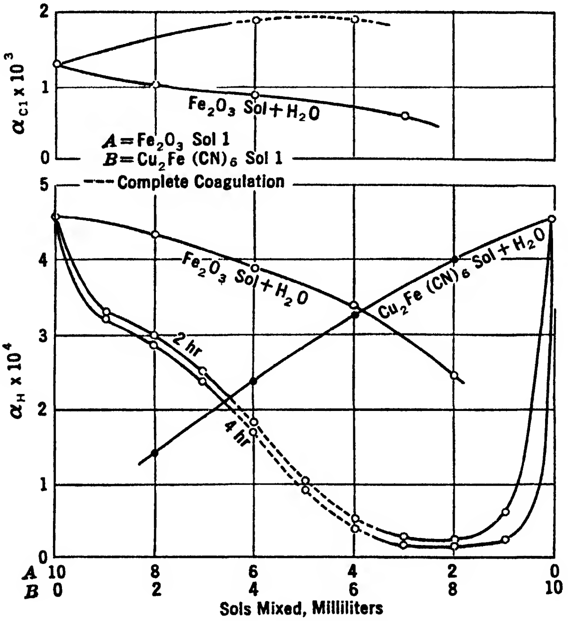

FIG. 91. Potentiometric analysis of sol mixtures.

The mutual adsorption of cupric ferrocyanide and ferric oxide particles results in a displacement of counter chloride ions from the outer portion of the double layer of the ferric oxide sol in much the same way that strongly adsorbed negative ions, such as sulfate, displace chloride ions from the outer portion of the double layer of this sol. Similarly, the mutual adsorption causes a displacement of the counter hydrogen ions from the cupric ferrocyanide sol. But hydrogen ions are strongly adsorbed by ferric oxide particles, whereas chloride ions are very weakly adsorbed by cupric ferrocyanide particles. The net result is an increase in the chloride-ion activity of the mixture at the same time that the hydrogen-ion activity falls off.

Complete mutual coagulation results when the ζ-potential (or mobility) of the mixture of colloidal particles is reduced below a critical value necessary for stability. Since hydrogen ions are the stabilizing ions of ferric oxide sol and the counter ions of cupric ferrocyanide sol, it is theoretically possible for the zone of complete mutual coagulation to come before, at, or after the minimum in the α_{H^+}-composition curve for mixtures of these two sols. When the data are plotted as in Figure 91, the complete mutual coagulation zone comes before the minimum is reached in the hydrogen-ion activity.

The mutual adsorption of oppositely charged particles gives all the suspended particles the same sign of charge on either side of the zone of mutual coagulation. An interesting example of this is the action of negative chromic oxide sol, peptized by excess sodium hydroxide, in preventing the precipitation of oxides that are not peptized by alkalis (cf. p. 156). Northcote and Church[10] observed that complete solution (sol formation) takes place when the chromic oxide is associated with 40% Fe_2O_3, 12.5% MnO, and 20% of either CoO or NiO; and that complete precipitation of both Cr_2O_3 and the other oxide results when the former is associated with 80% Fe_2O_3, 60% MnO, and 50% of either CoO or NiO. This anomalous behavior is readily explained in view of the colloidal nature of alkaline solutions of chromic oxide. The colloidal oxide adsorbs to a limited degree and so carries into colloidal solution the hydrous oxide of iron, manganese, cobalt, nickel, copper, and manganese, thus preventing their precipitation. The latter oxides likewise adsorb chromic oxide and, therefore, tend to take it out of colloidal solution in alkali; accordingly, if they are present in sufficient amount, they will carry down and so decolorize practically completely the green sol of chromic oxide.[11]

MUTUAL COAGULATION OF HYDROPHOBIC AND HYDROPHILIC SOLS

Although gelatin is usually regarded as a protecting colloid for sols, Billitzer showed that gelatin in acid solution (pH < 4.7) is a positive sol and precipitates negative sols like gold or arsenic trisulfide, but not positive sols like hydrous ferric oxide. On the other hand, gelatin in weakly acid, neutral, or ammoniacal solution (pH > 4.7) is a negative sol and precipitates hydrous ferric oxide sol, but not gold sol or arsenic trisulfide sol. No precipitate results if gelatin is first added to colloidal ferric oxide followed by the addition of ammonia. In the latter case, a stable mixture of positive sols is changed simultaneously to a stable mixture of negative sols by the addition of hydroxyl ion. Very highly purified gelatin containing not more than a trace of electrolyte is positive with respect to arsenic trisulfide sol and so sensitizes and coagulates the sol at low concentrations.[12]

Brossa and Freundlich [13] studied the precipitation and repeptization of negatively charged colloidal albumin by means of colloidal ferric oxide in the presence of electrolytes. The amount of albumin thrown down by the ferric oxide sol decreases with decreasing concentration of electrolytes until eventually only a slight turbidity results, which disappears on adding a sufficient amount of ferric oxide sol. Apparently, the colloidal ferric oxide in sufficient amount adsorbs completely the colloidal albumin and prevents its precipitation. The ferric oxide-albumin sol formed in this way is positively charged, but it is much more sensitive than the original ferric oxide sol.

PROTECTIVE ACTION OF HYDROPHILIC SOLS

The Gold Number

Negatively charged hydrophilic or "water-soluble" colloids are good protecting agents for negative sols, and positively charged hydrophilic colloids are good protecting agents for positive sols. The protective action on a given sol varies widely with different substances, and Zsigmondy devised what he called the *gold number* as a means of measuring the relative protective power. The gold number is defined as the number of milligrams of protecting colloid added to 10 ml of Zsigmondy's gold sol (p. 142) which just fails to prevent the change in color from red to blue on the addition of 1 ml of 10% NaCl solution. The gold number varies with the size of the gold particles, and Zsigmondy recommends that the sol be prepared by the nuclear method (p. 142) in such a way that it contains particles approximately 25 mμ in diameter. The gold number is greater the finer the particles, that is, the greater the extent of surface.

The procedure is about as follows: After determining the approximate concentration of protecting colloid required, 0.01-, 0.1-, and 1.0-ml portions are put into the beakers, and 10 ml of gold sol is added to each. After shaking 3 minutes, 1.0 ml of 10% NaCl is added to each. If the color changes in the first beaker and not in the others, the gold number lies between 0.01 and 0.1 ml of the protecting colloid. By repeating with concentrations between these limits, more exact values are obtained. The gold numbers found in this way by Zsigmondy [14] and by Gortner [15] for several hydrophilic colloids are given in Table 62.

TABLE 62

GOLD NUMBERS

Substance	Gold number	
	Zsigmondy	Gortner
Gelatin	0.005–0.01	0.005–0.0125
Casein	0.01	....
Egg albumin	....	0.08–0.10 *
Protalbinic acid	0.03–0.08 (Na salt)	0.15–0.20
Lysalbinic acid	0.02–0.06 (Na salt)	0.10–0.125
Gum arabic	0.15–0.5	0.10–0.125
Dextrin	6.20	....
Dextrin (British gum)	....	125–150
Soluble starch	....	10–15
Potato starch	About 25	....
Sodium oleate	0.4–1.0	2–4

* Highly purified egg albumin has a gold number of about 7 (private communication from Henry B. Bull).

The gold number gives only a rough indication of the protective action, since it is influenced by a number of factors. Mention has been made of the effect of size of particles in the gold sol. The *p*H value must be controlled also. Thus Tartar and Lorah [16] obtained a constant value for gelatin only between *p*H values of 8 and 5; below *p*H = 4.7, the protective action decreased very rapidly with increase in the hydrogen-ion concentration. Moreover, the degree of dispersion of the protecting colloid has a marked effect, as shown by observations on gelatin by Mentz [17] and Elliott and Sheppard; [18] thus it was found that the protective action increased with decreasing concentration on account of the greater dispersity at higher dilution. Also, the protective action of gelatin sols was observed to decrease with age, probably because of an increase in particle size.

Elliott and Sheppard attempted to use the gold number for the purpose of grading gelatins, but the values vary so little with different samples that the method is of slight value. The procedure has been used to give a qualitative measure of the degree of purity of such substances as gum arabic [19] and dextrin,[20] and to distinguish between different proteins such as the globulins, crystalline albumin, and noncrystalline albumin obtained by the fractional precipitation of egg white,[21] and the several albumoses formed by digestion of egg white.

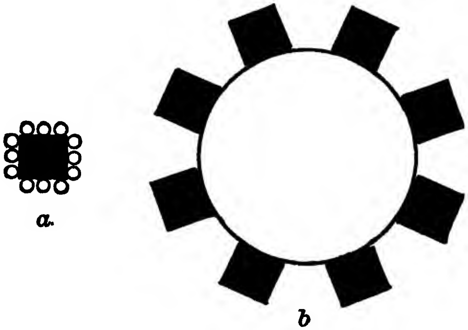

Fig. 92. Diagrammatic representation of colloidal gold particles of a given size (*a*) surrounded by smaller gelatin particles, (*b*) attached to a larger gelatin particle (Zsigmondy).

Unsuccessful attempts have been made to use the gold number to advantage in testing pathologic urine.

Theory of the Protective Action

Since it has been demonstrated conclusively that gold adsorbs gelatin strongly,[22] the protective action of hydrophilic colloids such as gelatin on hydrophobic sols such as gold is due to mutual adsorption of colloids of the same sign of charge. Mutual coagulation takes place in a critical range if the sols are of opposite sign of charge; but if the protecting colloid is added in excess of the mutual coagulation concentration, the charge on the hydrophobic sol is reversed, and it is then protected by mutual adsorption.[23] Three possibilities arise in a typical case such as Zsigmondy's alkaline gold sol and gelatin: (1) assuming a constant gelatin concentration, if the particles of gelatin are smaller and more numerous than the gold particles, the mutual adsorption will result in the formation of a protecting film of gelatin on gold (see Fig. 92*a*), thereby minimizing the coagulating action of electrolytes; (2) if the particles of gelatin and gold are of the same size, an arrangement similar to that in (1) is possible, but in this case there are fewer particles to be distributed over the gold surface and, in consequence, a lower protection prevails; (3) if the gelatin particles are much larger than the gold particles, the latter are adsorbed on the surface of the protecting colloid as shown diagrammatically in Fig. 92*b*.

In case (3), if the number of gold particles is very great relative to the number of gelatin particles, the gold may be crowded so close on the surface of the gelatin that it amounts to an agglomeration, and the sol changes in color from red to blue.

Lange's Gold Sol Reaction

Lange's *gold sol reaction* of the cerebrospinal fluid is an important application of the action of proteins with gold sol, in the diagnosis of certain diseases. In this test, observations are made of the effect of mixing varying amounts of the spinal fluid with a constant amount of gold sol. Lange's method of procedure is as follows. The fluid, which must be free from blood, is diluted in the ratio of 1:10 with 0.4% sterile NaCl solution. A series of 10 test tubes is then prepared, in the first of which is placed 1 ml of the 1:10 fluid; in the next, 1 ml of 1:20; in the third, 1 ml of 1:40; and so on. To each of the tubes is added rapidly 5 ml of bright-red neutral gold sol, the mixtures are shaken thoroughly, and observations are made after 5 minutes, 30 minutes, and 24 hours. A normal spinal fluid does not change a satisfactory sol, except that sometimes the first tube takes on a purplish or reddish-violet color. A pathological fluid, on the other hand, coagulates the sol to different degrees at different concentrations. If the several colors, after 24 hours, are plotted as ordinate against the concentration of the spinal fluid as abscissa, a curve is obtained which is more or less characteristic for certain types of disease. The colors are numbered as follows: cherry red, 0; bluish red, 1; reddish blue, 2; deep blue, 3; pale blue, 4; colorless, indicating complete coagulation, 5.

Three types of curves having clinical significance are recognized (Fig. 93). At the left is the paretic zone where the reaction in the first five or six tubes is of the 5 type, after which the color values fall off rapidly to 0. This type of curve indicates dementia paralytica. The middle zone is known as the luetic zone. Here, the change starts at 0, rises as high as 3 to 4 in the fourth and fifth tubes, and then returns to 0. This type of curve is given by patients suffering from neurosyphilis of the non-parenchymatous type; but it is not an exclusive diagnosis of this disease, since a similar curve is obtained in other conditions. The zone at the right, where the maximum color change occurs in the higher dilutions, is the meningitic zone. Spinal fluids giving this type of curve are obtained from patients with suppurative or tubercular meningitis.

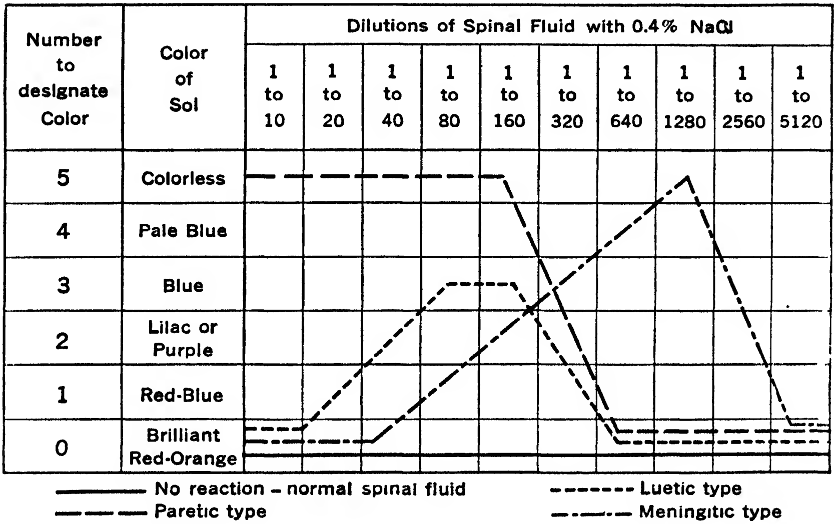

FIG. 93. Reaction types of spinal fluid with gold sol.

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CHAPTER 18

The Stability of Hydrophilic Sols

Certain substances take up liquids strongly, swell in them, and become peptized to form sols. Gelatin swells in water and is peptized by water to give a hydrophilic sol; similarly, rubber swells in benzene and is peptized by benzene to give a benzophilic sol. This chapter is concerned chiefly with hydrophilic sols, but, in many respects, the discussions will apply equally well to organophilic systems. Before considering the factors that affect the stability of hydrophilic sols, it seems advisable to summarize the essential differences between hydrophilic and hydrophobic sols.

DISTINCTIONS BETWEEN HYDROPHOBIC AND HYDROPHILIC SOLS

In hydrophilic sols a closer attraction or affinity exists between the dispersed phase and water than is found in hydrophobic sols, with the result that the particles in hydrophilic sols are surrounded by a hydration shell. This is in part responsible for the differences between the two classes of sol systems that are given in Table 63. It should be emphasized again that no classification of this kind is perfect. Typical hydrophobic and hydrophilic sols show the characteristic differences given in the table, but there are borderline cases such as the sols of molybdenum trioxide, tungsten trioxide, and zirconium dioxide which exhibit properties intermediate between the two types.

COAGULATION OF HYDROPHILIC SOLS BY ELECTROLYTES

Hydrophilic sols may be coagulated by electrolytes, but, as a rule, much larger amounts are necessary than with hydrophobic sols. Because of the high electrolyte concentrations that may be required for coagulation, the process has come to be termed "salting out."

TABLE 63

PROPERTIES OF HYDROPHOBIC AND HYDROPHILIC SOLS

Type of sol	Hydrophobic	Hydrophilic
Examples	Sols of elements, oxides, and salts	Sols of proteins, higher carbohydrates, and soaps
Presence of electrolyte	Small amount essential for stability	Not essential for stability
Stability toward electrolyte	Coagulated by small amounts	Not coagulated by small amounts
Reversibility of coagulation	Irreversible as a rule	Reversible as a rule
Ultramicroscopic image	Bright particles in motion	Diffuse light cone
Electrical charge	Definite sign, not readily changed	Sign changed readily by suitable change in the *p*H value
Electric field	Particles migrate	Particles may or may not migrate
Viscosity	About the same as for water at the same temperature	Viscosity greater than water and rises rapidly with decreasing temperature and increasing concentration

Coagulation of Albumin

Alkali and alkaline-earth salts. The isoelectric point of purified egg albumin is in the neighborhood of $p\text{H} = 4.6$. Accordingly, the pure protein particles suspended in water or dilute alkali are negatively charged, whereas the particles suspended in dilute acid are positively charged. In Table 64 are given some typical data from Hofmeister[1] on the coagulation of negative albumin sol by alkali salts. From these data one would deduce the following order of coagulating power: (*a*) for the anions:

$$\text{citrate} > \text{tartrate} > SO_4 > \text{acetate} > Cl > NO_3 > ClO_3 > I > CNS$$

and (*b*) for the cations:

$$Li > K > Na > NH_4 > Mg$$

Pauli[2] investigated this phenomenon extensively and found the same order of cations as Hofmeister for the negative albumin sol; but the order of anions was:

$$F > SO_4 > PO_4 > \text{citrate} > \text{tartrate} > \text{acetate} > Cl >$$
$$NO_3 > ClO_3 > Br > I > CNS$$

The order for salts of the alkaline earths[3] is: (*a*) for the cations: Ba > Ca; and (*b*) for the anions: acetate < Cl < Br < I < CNS. The anion order is the reverse of that with the alkali salts; and the alkaline-earth salts render a neutral sol acid, probably as a result of hydrolytic adsorption (p. 105).

TABLE 64

COAGULATION VALUES (x) OF SALTS ON NEGATIVE ALBUMIN SOL

Salt	x (moles/l)	Salt	x (moles/l)
Sodium citrate	0.56	Sodium iodide Sodium thiocyanate	Saturated. No pptn.
Sodium tartrate	0.78		
Sodium sulfate	0.80		
Sodium acetate	1.69	Lithium sulfate	0.78
Sodium chloride	3.62	Potassium sulfate	0.79
Sodium nitrate	5.42	Sodium sulfate	0.80
Sodium chlorate	5.52	Ammonium sulfate	1.00
		Magnesium sulfate	1.32

In a negative sol, one would expect the cations to favor coagulation and the anions to oppose it; hence reversal of the sign of charge would be expected to reverse the order of ions. Pauli found this to be true on making the sol 0.01–0.03 N with HCl before coagulation.

So-called electrolyte-free serum albumin gives a stable sol even though it is electrically neutral.[4] The addition of alkali or alkaline-earth chlorides does not give it a charge.

The Hofmeister series. The order of anions and cations as given above is known as the *Hofmeister series* or *lyotropic series* of ions. These series are encountered in other phenomena of both a colloid chemical and a physical chemical nature. Among the colloidal processes, attention has been called to the lyotropic series in the coagulation of sol (p. 277), and reference will be made to the series in connection with the swelling of gelatin (p. 331). Moreover, Gortner and coworkers[5] found the order of the peptizing action of ions on the globulins of wheat flour to be: (*a*) for the anions: I > Br > tartrate > Cl > SO_4 > F; and (*b*) for the cations: Ca > Mg > Sr > Ba > Li > Na. These are the reverse of the orders deduced for the salting out of negative albumin sol. Similarly, Gustavson[6] observed the following orders in the peptization of collagen: (*a*) for the anions: CNS > I > Br > Cl > SO_4 > S_2O_3; and (*b*) for the cations: Ca > Sr > Mg > Na > K. Büchner[7] has shown that the lyotropic effects of the ions can be expressed quantitatively by "lyotropic numbers" which depend in a simple way on the heat of hydration of the respective ions.

Among the physical chemical phenomena in which the lyotropic series manifest themselves may be mentioned the effect of neutral salts on: (1) the surface tension of water; (2) the displacement of the maximum density of water; (3) the rate of inversion of cane sugar; and (4) the solubility in water of non-electrolytes such as the amino acids, urea, quinone, and hydroquinone.[8]

The lyotropic order of ions is, in general, the same as the order of hydration of the ions. Since water associated with the ions is not available as a solvent, the lyotropic influence may be traced in some instances to removal of solvent. This would account, in part at least, for the effect of salts on the solubility of non-electrolytes and on the rate of inversion of cane sugar, but would not explain their effect in displacing the maximum density of water and in changing the surface tension of water. The latter phenomena may be accounted for, tentatively, by assuming with Bancroft[9] that the presence of ions influences the association equilibrium of water: $n\mathrm{H_2O} \rightleftarrows (\mathrm{H_2O})_n$, the ions at one end of the series favoring association, and at the other end, dissociation, of the solvent.

In connection with the coagulation and peptization of hydrophilic colloids, adsorption of ions may supplement the effect which is attributed to taking up water or modifying the water equilibrium, $n\mathrm{H_2O} \rightleftarrows (\mathrm{H_2O})_n$. In coagulating positively charged sols, anions will have a precipitating and cations a stabilizing effect, whereas, in coagulating negatively charged sols, cations will have a precipitating and anions a stabilizing action. The converse of this behavior obtains in the peptization of hydrophilic colloids to form positive or negative sols. It appears, therefore, that the adsorption of ions follows essentially the same order as their hydration or their effect on the water equilibrium.

Heavy-metal salts. Salts of silver, copper, and zinc cause precipitation of negative albumin sol in low concentrations. Moreover, the coagulation is irreversible, whereas the gel thrown down with alkali salts is reversed by removing the excess electrolyte. What appears to be an "irregular series" is obtained with copper and zinc salts (cf. p. 258). For example, a sol containing 1 part of egg albumin in 10 of water is coagulated by copper salt solutions from 0.001 to 1 *N*; no precipitation takes place between 1 and 6 *N*; and precipitation again results above 6 *N*. Similarly, zinc salts give a precipitate between 0.001 and 0.5 *N*, no precipitate between 0.5 and 4 *N*, and a precipitate again above 4 *N*. The zone of non-precipitation is narrowed if the sol contains more albumin.

The precipitates contain the heavy-metal ions, and many people believe that definite chemical compounds are formed. Against this view is the remarkable variation in the composition of the precipitates. Thus albumin-copper precipitates varying in composition from 1.4 to 20% CuO have been obtained. If one explains the so-called "irregular series" on the basis of chemical compound formation, it is necessary to assume a series of compounds some of which are soluble and others insoluble.

In many respects sols of casein behave similarly to those of egg albumin toward hydrogen and hydroxyl ions and the ions of neutral electrolytes. Casein sol differs from egg-albumin sol in being completely coagulated at the isoelectric point.

Coagulation of Gelatin

Gelatin sols are like albumin sols in requiring high concentrations of alkali salts for coagulation, for example, 4 *N* KCl and 0.75 *N* Na_2SO_4. The order of precipitating power of anions is: $SO_4 >$ citrate $>$ tartrate $>$ acetate $>$ Cl; and of cations: Na $>$ K $>$ Rb $>$ Cs $>$ NH_4 $>$ Li. The coagulation values of the metallic chlorides obtained by Büchner[10] do not show a simple relationship to the lyotropic behavior of the cations as represented by their *lyotropic numbers:* Li, 115; Na, 100; K, 75; Rb, 69.5; Cs, 60. Unlike the behavior with albumin sols, the order of ions does not reverse on changing from alkaline to acid gelatin sols. Moreover, albumin takes up (adsorbs) both iodide and chloride ions and is peptized by them, whereas gelatin takes up neither iodide nor chloride to any marked extent but is peptized strongly by alkali iodide and only very weakly by alkali chloride. Bancroft explains the difference in peptizing action of the two salts by postulating a different effect on the solvent. Since alkali iodides lower the temperature of the maximum density of water to a greater degree than the chlorides, and since this is probably due to greater displacement of the equilibrium $n\text{H}_2\text{O} \rightleftarrows (\text{H}_2\text{O})_n$ to the left by iodides than by chlorides, it is suggested that the unpolymerized form of water is a better peptizing agent for gelatin than the polymerized form.

Sols of glycogen, fibrin, agar, gum arabic, and starch are similar to gelatin in their behavior toward neutral electrolytes. None of the sols is coagulated simply by bringing the particles to the isoelectric point.

Mechanism of Electrolyte Coagulation

The differences in the behavior of hydrophobic and hydrophilic sols toward electrolytes are an important reason for classifying sols into the two types. Kruyt and his coworkers, Bungenberg de Jong, Tendeloo, and others,[11] have pointed out, however, that there are unmistakable similarities in the action of electrolytes on the two types. They recognize two factors that determine the stability of hydrophilic sols: (1) the electrical potential on the particles and (2) hydration of the particles. The first factor predominates in hydrophobic sols since coagulation results when the potential on the particles is reduced below a critical value. With hydrophilic sols, on the other hand, the potential may be reduced to zero (the isoelectric point) without coagulation taking place. The predominating stabilizing factor, under these circumstances, is the power of the colloid to adsorb, swell in, and be peptized by, the solvent. This phenomenon is termed *hydration* or, more generally, *solvation*. The two stability factors will be discussed separately.

The potential factor: the electroviscous effect. The effect of electrolytes on the mobility of the particles in hydrophilic sols cannot be followed so readily as in hydrophobic sols. But, as we have seen (p. 208), the ζ-potential of particles influences the viscosity in accord with Smoluchowski's equation:

$$\frac{\eta_s - \eta_m}{\eta_m} = 2.5\varphi\left[1 + \frac{1}{\lambda\eta_m r^2}\left(\frac{D\zeta}{2\pi}\right)^2\right]$$

Accordingly, if the ζ-potential is lowered by the addition of electrolytes, it manifests itself in a decrease in viscosity. This influence of the ζ-potential on the viscosity of hydrophilic sols is termed the *electroviscous effect.*

In Fig. 94*a* and *b* are shown Kruyt and Bungenberg de Jong's[11] observations of the influence of electrolytes on the electroviscous effect with two typical hydrophilic sols, agar and starch, respectively. As ordinates are plotted the concentrations of electrolytes in milliequivalents, and as abscissa, the ratio $\Delta\eta$, of the relative change of viscosity in the sol containing electrolyte $[(\eta_s - \eta_m)/\eta_m]_E$, to that in the electrolyte-free sol $[(\eta_s - \eta_m)/\eta_m]_0$; that is $\Delta\eta = [(\eta_s - \eta_m)/\eta_m]_E : [(\eta_s - \eta_m)/\eta_m]_0$. With every electrolyte, a small addition lowers the relative viscosity decidedly, and further additions have little effect. Since the sol is negatively charged, the effect of the cations predominates; and the lowering of the relative viscosity with various cations is in the order: quadrivalent > trivalent > bivalent > univalent. Moreover, with the sexvalent hexol ion ($[\mathrm{Co}\{(\mathrm{OH})_2\mathrm{Co}(en)_2\}_3]^{++++++}$, in which *en* is ethylene diamine), the viscosity of starch sol decreases at first and then increases as the sign of the charge is reversed.

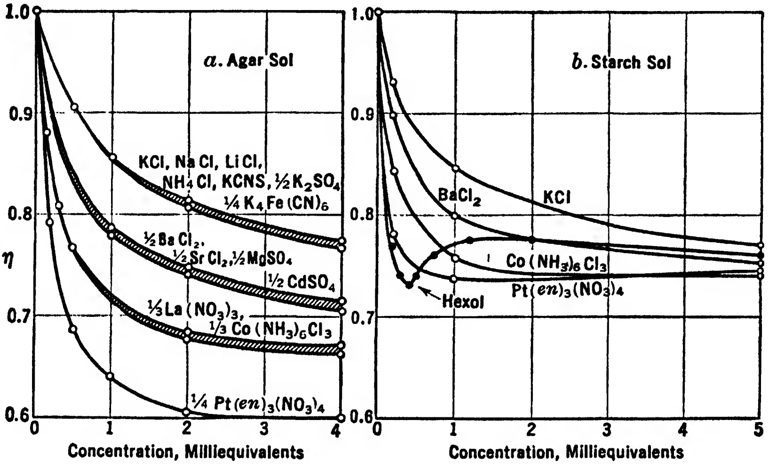

FIG. 94. The influence of electrolytes on the electroviscous effect (*a*) with agar sol, (*b*) with starch sol.

The above results indicate that electrolytes influence the ζ-potential of hydrophilic sols in much the same way as of hydrophobic sols. But, as already noted, lowering of the ζ-potential is insufficient in itself to cause coagulation of hydrophilic sols because of the stabilizing action of the hydration shell around the particles.

The hydration factor. The effect of salts on hydrophilic sols such as agar and starch is first to lower the ζ-potential on the particles and then to render them more hydrophobic by withdrawing water from the hydration shell. The first process requires a small amount of electrolyte only, whereas the second process, in general, requires a considerable amount. The first process takes place roughly in accord with the valency rule, and the second process is related to the power of the ions to take up water in accord with the Hofmeister or lyotropic series. The combined potential lowering and dehydrating action of electrolytes is illustrated in Fig. 95, which shows the effect of magnesium chloride and magnesium sulfate on the relative lowering of the viscosity of agar sol, $\Delta\eta = [(\eta_s - \eta_m)/\eta_m]_E$, in which the index E signifies that η_s is for the sol containing electrolyte and η_m is for the electrolyte solution. Since the sol is negatively charged, the initial lowering of viscosity in low concentrations results from the magnesium ion in both salts; hence the curves coincide approximately. At higher concentrations, the dehydrating action operates, and this is much greater for sulfate than for chloride, in accord with the position of these ions in the lyotropic series. The horizontal portion of the sulfate curve lies below the chloride curve, and the sulfate curve soon drops rapidly as coagulation takes place. The second drop is not observed with magnesium chloride within the concentration range investigated because of the lower dehydrating action of this salt. In line with this difference in behavior, a certain concentration of magnesium sulfate renders the particles visible in the ultramicroscope, whereas a corresponding concentration of magnesium chloride does not dehydrate them sufficiently to render them visible.

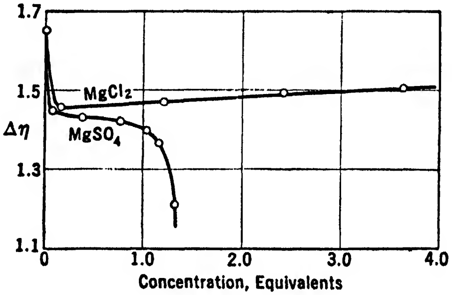

FIG. 95. Effect of salts on the relative lowering of the viscosity of agar sol.

The particles in a hydrophilic sol may be dehydrated by the addition of a relatively high concentration of alcohol or acetone. This manifests itself by a change in the relative viscosity, as shown in Fig. 96, which gives the relative change in the viscosity $\Delta\eta$ of agar sol by alcohol, at a temperature of 45°. $\Delta\eta = [(\eta_s - \eta_m)/\eta_m]_A$, where the index A signifies that η_s is for the sol containing alcohol and η_m for the medium of aqueous alcohol. It is apparent that, when the alcohol concentration reaches approximately 50% by weight, the viscosity falls off rapidly and the sol becomes more hydrophobic. This is indicated not only by the lowered relative viscosity but also by the appearance of the sol in the ultramicroscope. The dehydration of agar sol by alcohol is insufficient in itself to cause coagulation because the particles possess sufficient ζ-potential to keep them dispersed. The resulting hydrophobic sol is quite as sensitive to the action of electrolytes as other hydrophobic sols. This is evidenced by the precipitation values of electrolytes for a system containing 1 volume of sol plus 5 volumes of alcohol. The values in millimoles per liter are: $KCl = 1.25$; $BaCl_2 = 0.047$; $[Co(NH_3)_6]Cl_3 = 0.030$. The precipitation values are low compared to the salting-out values of the alcohol-free sol, and the cation with the highest valence precipitates in the lowest concentration, in accord with the Schulze-Hardy rule (cf. p. 110).

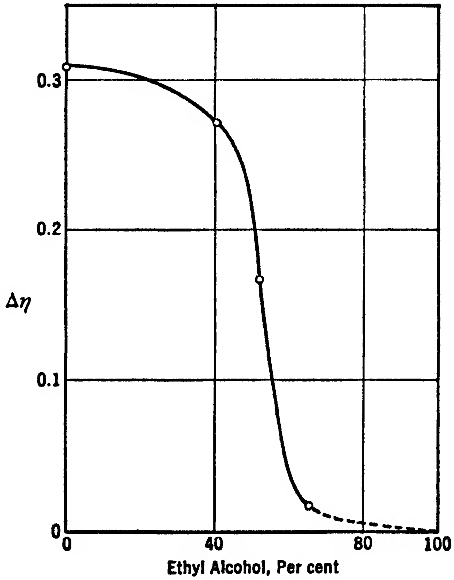

FIG. 96. Effect of alcohol on the relative change of viscosity of agar sol.

From the above considerations, one seems justified in concluding with Kruyt that the salting out of hydrophilic sols by salts consists in (1) the lowering of the potential on the particles and (2) the dehydration of the particles. Freundlich [12] accepts this view with reservations since he believes that what Kruyt terms hydration may involve not only adsorption, swelling, and peptization but true solubility as well. In any event, the coagulation of hydrophilic sols is a complex phenomenon as indicated further by the phenomena to be described in the following sections.

COAGULATION OF HYDROPHILIC SOLS BY OTHER METHODS

Mutual Coagulation; Coacervation

Two hydrophilic sols of opposite sign of charge may mutually coagulate each other. Thus, colloidal basic dyes coagulate negative albumin sol, and colloidal acid dyes coagulate positive albumin sol. The coagulation of the collagen of hide by tannin is the first step in the vegetable tanning process. Tannin also coagulates sols of albumin, gelatin, agar, and starch, under suitable conditions. If the sols are free from electrolyte, however, a mixture of sols with hydrophobic properties will result. For example, if a small amount of tannin sol is added to a pure agar sol, the resulting mixture has a milky appearance, gives a clearly defined ultramicroscopic image, has a viscosity which is about the same as that of water, and is coagulated by low concentrations of electrolytes. Kruyt's [13] explanation of this behavior is that the agar particles adsorb tannin (pentadigallol glucose), the glucose end of the molecules being oriented toward the particles and the phenol groups toward the water. In this way the agar particles lose their hydration shell, and the adsorption complex is hydrophobic since it is surrounded by hydrophobic phenol groups. If a large amount of tannin (35% or more) is added to agar, a stable hydrophilic mixture results. A possible explanation of this is that the molecules of tannin in the relatively thick film surrounding the particles are only partly oriented, and that the outside of the layer is more hydrophilic than hydrophobic.

In the salting out of many hydrophilic sols, the coagulum is liquid rather than solid. Moreover, under certain conditions the dispersed phase comes out in the form of various-sized liquid droplets instead of forming two liquid layers. The sol particles are accumulated or heaped together in the separating droplets; this is termed *coacervation,* which means literally *heaped together,* and the droplets are called *coacervates*. The phenomenon, which has been studied extensively by Bungenberg de Jong and coworkers,[14] is encountered most frequently when two hydrophilic sols of opposite sign of charge are mixed together. Typical systems which form coacervates are: amylophosphoric acid with various protein sols, and gum sols with protein sols below the isoelectric point of the proteins. To illustrate, below $pH = 4.7$, gelatin is positively charged, and gum acacia is negatively charged; coacervates result on mixing the two oppositely charged sols.

The mechanism of the process by which coacervates are formed is represented diagrammatically in Fig. 97. *A* and *B* are the oppositely charged hydrophilic particles surrounded by a water shell. The electrostatic forces tend to pull them together and cause coalescence and agglomeration, but these forces are opposed by the elasticity of the water shells. The net result is that the individual particles retain their identity, but a number of them are held together by electrostatic attraction, forming droplets of liquid which come out as a separate phase—a coacervate. A true coacervate may be caused to redisperse at a constant pH value by adding a salt which will lower the ζ-potential on either component of the system. The most effective dispersing agents are salts with multivalent cations or anions.

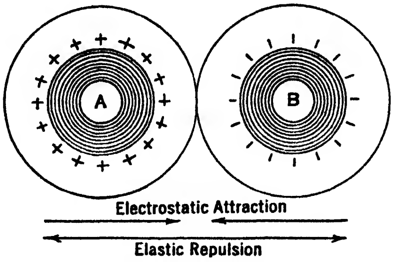

FIG. 97. Diagrammatic representation of the formation of a coacervate (Gortner).

Bungenberg de Jong[15] considers the phenomenon of coacervation to be of special importance because many biological phenomena can be duplicated by model systems of coacervates. For example, protoplasm is an aqueous system of hydrophilic colloids which retains its identity on immersion in water, and systems of coacervates can be prepared which parallel closely the behavior of protoplasm. The aging of complex coacervates may be accompanied by the phenomena of vacuole formation and the extrusion of liquid from the droplets.

Coagulation by Heat

Certain protein sols (albumins, globulins, and globins) coagulate at some definite temperature which is fairly constant for each protein. A familiar example is the heat coagulation of egg white. The phenomenon appears to involve three distinct processes: [16] denaturation, flocculation, and irreversible coagulation.

The first reaction in the series is apparently an intramolecular rearrangement whereby certain chemical groups that are not detectable in the native protein appear in the modified product. This process is called *denaturation,* and the modified protein is called *denatured protein.* Denaturation is a necessary but insufficient reaction in the production of the final coagulated material.

The second process is flocculation of the denatured molecules. This process resembles closely flocculation of sols of the hydrophobic type in which the ζ-potential is the predominating stability factor.

The third and final step consists in the formation of an insoluble coagulum from the flocculated mass. It may be compared to the aging of a hydrous oxide gel which is rendered non-peptizable by standing in contact with the mother liquor or by heating.

The individuality of the three processes may be demonstrated experimentally. An egg-albumin sol in a salt-free medium is shifted from its isoelectric condition by addition of acid or base and is heated. The sol remains perfectly clear, but the thiol groups have become exposed, and there is considerable increase in viscosity of the system. The protein is denatured; this process is generally considered to be non-reversible.[17] The clear sol of heat-denatured protein is next brought to its isoelectric point. This results in flocculation of the denatured molecules, giving a flocculum that is completely peptized by either acid or base. The coagulation process is, therefore, completely reversible and is the only one of the three that is. Finally, the flocculated protein is allowed to stand or is heated further, whereby a coagulum results that is no longer peptized by acid or base. Nothing short of hydrolysis of the protein will render the coagulated product peptizable. Partial peptization of a heat-precipitated protein will result if the final step is not complete.[18]

The velocity of the denaturation process increases 600 times for a rise of 10°. For this reason, a sol of serum albumin or of egg albumin near the isoelectric point flocculates suddenly within a rather narrow range of temperature. If the *p*H value is considerably removed from the isoelectric point of the protein, it may be boiled for a long time without visible evidence of denaturation; but, as we have seen, a change has taken place since the heated sol coagulates, whereas an unheated one does not, on bringing the two to the isoelectric point.

Mechanical Coagulation

Certain hydrophilic sols may be coagulated by shaking or by bubbling gas through them, provided that the colloidal material is sufficiently surface-active to concentrate strongly in the surface film[19] (p. 261). The mechanical coagulation is caused by accumulation of dispersed phase in the surface as a result of the large development of surface by the air bubbles. When the bubbles rise and break, the excess material which they carry to the surface of the sol precipitates out. Albumin is highly surface-active and may be coagulated in this way. The optimum *p*H value at which albumin and hemoglobin will coagulate by shaking is the isoelectric point of the protein.

The mechanical coagulation of albumin sols may be accomplished by shaking them with liquids immiscible with water such as toluene, chloroform, and isoamyl alcohol.

THE ISOELECTRIC POINT OF PROTEINS AND THEIR PROPERTIES

The stability of protein sols, such as gelatin, is at a minimum at the isoelectric point (p. 240). Other properties of such sols which are at a minimum at or very close to the isoelectric point are osmotic pressure, swelling (p. 329), membrane potential (p. 247), precipitation by alcohol, viscosity, and conductivity. Loeb[20] investigated the effect of neutral salts on these properties and concluded that the salts were without appreciable influence, the hydrogen-ion concentration being the only important factor. Loeb's contribution was to emphasize the great importance of the hydrogen-ion concentration in the colloidal behavior of proteins, but the influence of ions other than hydrogen and hydroxyl cannot be disregarded. This may be illustrated by Kruyt and Tendeloo's[21] work on the effect which salts may have on the *p*H-viscosity curve of gelatin. This curve for a salt-free gelatin is shown diagrammatically in Fig. 98. Now, if a positively

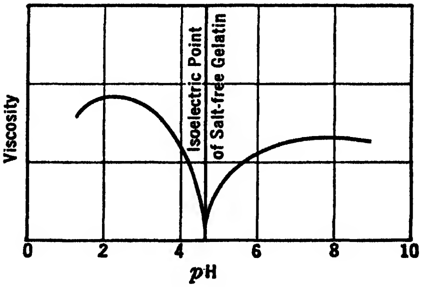

Fig. 98. Diagram of the *p*H-viscosity curve of salt-free gelatin.

charged sol with a $p\text{H} = 4.4$ is treated with $K_3Fe(CN)_6$, the effect of the trivalent ion is to lower the viscosity. A minimum is reached when the salt concentration is 1.25 meq/l, above which the viscosity again increases, the pH value remaining unchanged. This means that the isoelectric point may be established by bringing the sol to $p\text{H} = 4.7$ or by making it $p\text{H} = 4.4$ and adding 1.25 meq/l of $Fe(CN)_6^{\equiv}$. Similarly, the sol may be made $p\text{H} = 4.9$ and the isoelectric point established by adding 0.2 meq/l of $Co(NH_3)_6^{+++}$. It follows, therefore, that the isoelectric point and other properties of a protein are not determined exclusively by the hydrogen-ion concentration.

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PART III. GELS

CHAPTER 19

Gels I: Gelatinous Precipitates and Jellies of Inorganic Substances

Gelatinous precipitates and jellies are the two forms of solid or semi-solid colloids included under the general term *gel.* In Chapter 9, it was pointed out that inorganic substances may be obtained in the gelatinous form by precipitation under such conditions that the percentage supersaturation (P/L) is very high. The rapid precipitation of highly insoluble material usually gives a gelatinous mass with a supernatant liquid—a gelatinous precipitate. It is frequently possible, however, to bring about uniform precipitation throughout the entire solution with the formation of a jelly which differs from a gelatinous precipitate mainly in that at the outset all, or nearly all, the liquid is enclosed by the precipitated phase. Gels of such inorganic substances as chromic oxide, silica, and manganese arsenate, which lose their elasticity on drying, are called rigid or *non-elastic gels* in contradistinction to the *elastic gels* such as gelatin and agar which are characterized by perfect elasticity through certain narrow limits and by retaining their elasticity and coherence on drying. This chapter will deal primarily with the inorganic, inelastic gels, and the following one with the organic, elastic gels.

GELATINOUS PRECIPITATES

Formation and Structure

An insoluble substance which adsorbs water strongly is readily precipitated from solution as a gelatinous precipitate. Typical examples are ferric oxide, chromic oxide, alumina, and arsenic trisulfide. Gelatinous precipitates are viscous, and they may be plastic; in most instances they are not amorphous but consist of myriads of tiny crystals. This raises the question of whether the submicroscopic crystals are themselves gelatinous and so impart the gelatinous property to the mass. Harrison[1] claims that benzopurpurine and chrysophenene form gelatinous, needle crystals which are so thin that they lack rigidity and so flexible that they can be bent and twisted into various shapes. A cluster or network of such needle-shaped, flexible crystals that adsorb water strongly would form the viscous or plastic mass commonly called a gelatinous precipitate. If the crystals are compact and rigid rather than thin and flexible, they would not form a gelatinous precipitate unless they united in some way to form a network structure that possessed the flexibility and elasticity which characterizes a mass of thin needle crystals. Obviously the particles need not be crystalline, and in some instances they probably are not. A gelatinous precipitate is apparently a network resulting from the coalescence of minute particles which adsorb water strongly.[2] If the particles do not adsorb water very strongly and if the tendency to coalesce into a network structure is not great, a high concentration of the dispersed particles is necessary, as with calcium carbonate and barium sulfate. Since neither tendency is very marked in a metal such as gold, gelatinous precipitates of gold are obtained only under special conditions. On the other hand, platinum black adsorbs water rather strongly and gives a gelatinous precipitate when thrown down rapidly by the reduction of a sodium chloroplatinate solution with sodium formate. Indeed, Benton[3] once prepared a platinum jelly in this way. Similarly, Börjeson[4] in Svedberg's laboratory prepared a cadmium jelly by allowing a very dilute sol of cadmium in alcohol to stand for some time in a glass bottle. In this case, the particles were only 5 mμ in radius, and the cadmium concentration but 0.2 to 0.5%.

Conclusive visual evidence of the structure of gelatinous precipitates was obtained by Weiser and Cunningham[5] in the course of an ultramicroscopic study of the various types of sulfur precipitates which are formed by the coagulation of Selmi's sulfur sol with different electrolytes. Thus, reversible gelatinous precipitates result on precipitating the sol with strongly hydrated lithium or sodium ion and plastic irreversible flocks with the weakly hydrated potassium or barium ion. Ultramicroscopic study of the gelatinous clumps shows them to consist of an agglomerate of ultramicroscopic particles surrounded by an envelope of water. The film of adsorbed water, together with the water entrained during the agglomeration process, gives a flexible hydrous mass, the gelatinous precipitate. Ultramicroscopic observations of the change taking place when a weakly adsorbed, highly hydrated cation is removed from a gelatinous sulfur clump by displacing it with a more strongly adsorbed, less hydrated cation reveal a marked shrinkage as the result of loss of adsorbed water and the coalescence of the particles, giving a ball of sulfur which may occupy a volume not more than $1/500$ that of the original clump. Motion pictures taken of this change in physical character of the clumps disclose clearly the optical effects produced by the outflow of the adsorbed and entrained water and the coalescence of the ultramicrons.

JELLIES

Structure

Since certain oxides and salts may be precipitated in either a gelatinous or jellylike form by suitable variations in conditions, it would seem to follow that the structure of the two types of inorganic gels is essentially the same. Jellies result when a gelatinous material separates sufficiently slowly and uniformly. An aqueous inorganic jelly consists of myriads of highly hydrous or gelatinous particles enmeshed into a network or sponge structure that entrains all the liquid phase.

Formation

Precipitation of sol. Since highly dispersed particles that adsorb water strongly are of primary importance for the formation of hydrous jellies, it would seem that the most promising method of preparing jellies with a low ratio of solid to liquid phase would be to precipitate hydrous substances from colloidal solution. Investigations in the author's laboratory have disclosed that jellies are formed from sols by precipitation at a suitable rate without agitation, in the absence of a medium that exerts an appreciable solvent or peptizing action. If the concentration of the sol is too low, no jelly or only a very soft jelly can result. If the velocity of precipitation is too great, contraction is likely to occur with the formation of a gelatinous precipitate instead of a jelly. The effect of the presence of salts on jelly formation is, therefore, determined in large measure by the precipitating and stabilizing actions of the ions in so far as these affect the rate of precipitation. In general, a slow rate of precipitation favors the formation of a uniform jelly rather than a gelatinous precipitate, provided that there is little or no tendency of the particles to grow as a result of the solvent action of the electrolyte. The favorable concenration for different electrolytes is in the immediate region of their precipitation concentration. A little below this value, no precipitation or only a slight precipitation takes place; whereas above this value, coagulation is usually so rapid that a gelatinous precipitate is formed instead of a jelly. The reason is that time is not allowed for the uniform mixing of the colloid with coagulant, and the slow uniform precipitation necessary for the building of a uniform jelly structure is replaced by rapid uneven coagulation and the consequent contraction that distinguishes a gelatinous precipitate from a jelly.

The accuracy of the deductions has been demonstrated by the author[6] in the formation of jellies of alumina, chromic oxide, stannic oxide, and cupric oxide. A notable example is hydrous chromic oxide which forms a firm jelly containing but 0.18% Cr_2O_3, and a soft jelly containing 0.09% Cr_2O_3. The formation of such dilute jellies can result only when the particles are very hydrous and when the conditions of precipitation allow time for the building up of an enmeshing network. Holmes and Fall[7] accomplished the slow precipitation of hydrous "ferric arsenate" in the form of a jelly by allowing ammonium hydroxide or sodium acetate to diffuse slowly through a membrane into the sol.

Dialysis of Sol

Prolonged dialysis of certain oxide and arsenate sols[8, 7] causes them to coagulate to firm uniform jellies. From the point of view outlined in the foregoing section, the formation of jellies by dialysis of a hydrous sol is readily understood. Dialysis merely removes the stabilizing ion slowly and uniformly below the critical concentration necessary for stability; and precipitation in the jellylike form results just as if a suitable concentration of electrolyte were added to the sol.[9]

Precipitation from Solution

Jellies formed by precipitation from concentrated solutions according to von Weimarn's procedure (p. 137) are usually non-uniform semi-solid masses that entrain all the liquid phase. When dilute solutions are mixed that precipitate immediately, gelatinous precipitates rather than jellies ordinarily result. The reason is evident when we consider the impossibility of getting the instantaneous mixing of the solutions which is essential for uniform precipitation throughout the mixture. One part is precipitated before another is mixed with the precipitant, and the uniformity characteristic of a jelly is lost. Moreover, the mixing itself tends to destroy the jelly structure. The results are, therefore, not unlike those obtained when a sol capable of forming a jelly by slow precipitation is coagulated too rapidly by the addition of excess electrolyte. To obtain a jelly from a sol, it is necessary to add such an amount of electrolyte that thorough mixing is possible before appreciable coagulation takes place. From these considerations, it follows that precipitation of a hydrous substance, as a result of double decomposition, might form a jelly instead of a gelatinous precipitate if thorough mixing of the solutions could be effected before precipitation began and if the precipitation, once started, proceeded at a suitable rate. Such conditions do not obtain as a rule, but they are entirely possible theoretically. Thus the precipitation may be the result of a stepwise process, one step of which proceeds at a suitably slow rate. It is further possible to have a reaction that goes very slowly at low temperatures but with marked velocity at higher temperatures. This would not only allow mixing without precipitation, but would also make it possible to control the subsequent rate of reaction by a suitable regulation of the temperature. Such a favorable combination of circumstances obtains when a manganese salt of a strong acid and KH_2AsO_4 are mixed.[10] Similarly, the rate of precipitation of hydrous silica from silicate of soda can be adjusted to give a uniform, perfectly transparent jelly by suitable regulation of the concentration, *p*H value, and temperature of the interacting solutions.[11]

PROPERTIES OF GELS

Vapor-pressure Relations: 1. Isobars

If the hydrous gels are not hydrated, they would be expected to give smooth curves for change in composition (*a*) with change in vapor pressure at constant temperature (isotherms), (*b*) with change in temperature at constant vapor pressure (isobars). On the other hand, if the gels are hydrated, the dehydration curves should be stepwise in form. Typical isotherms and isobars are shown in Fig. 99*A* and *B*. I is typical of the curves for the definite crystalline hydrates and hydroxides such as $CaSO_4 \cdot 2H_2O$, $CaSO_4 \cdot 0.5H_2O$,[12] $Mg(OH)_2$, and $Ca(OH)_2$ which undergo reversible dehydration. At the other extreme are the hydrous gels such as the hydrous oxides of iron, chromium, and titanium in which none of the water is held in a definite stoichiometric ratio, but varies continuously without any indication of steps (III). Occupying an intermediate position (II) are the hydrous hydrates or hydroxides such as $WO_3 \cdot H_2O$, $Al_2O_3 \cdot 3H_2O$, β-$Fe_2O_3 \cdot H_2O$,[13] and $Cu(OH)_2$ which do not rehydrate after decomposition and give isotherms and isobars without sharp breaks. The rounded corners result from variations in particle size, lattice distortion, lattice strain, and strong adsorption by the hydrate and its decomposition product, the anhydrous oxide or a lower hydrate. In some instances, it is difficult to tell from the form of the dehydration curve whether or not the gel is a hydrate. This may be decided, as a rule, by the simultaneous application of dehydration studies and x-ray diffraction analysis. To illustrate, some observations on alumina gels[14] will be considered.

It is now known that alumina gel thrown down from an aluminum salt solution in the hot, or by the action of amalgamated alumina on hot water, is hydrous γ-$Al_2O_3 \cdot H_2O$ or γ-$AlO(OH)$ (böhmite). If the reactions take place in the cold, the hydrous γ-$Al_2O_3 \cdot H_2O$ first formed changes spontaneously first into α-$Al_2O_3 \cdot 3H_2O$ (bayerite) and then into γ-$Al_2O_3 \cdot 3H_2O$ (gibbsite). In Fig. 100 is given the dehydration isobar of γ-$Al_2O_3 \cdot 3H_2O$, and in Fig. 101 the x-ray diffraction patterns of several alumina preparations. The two types of information show that γ-$Al_2O_3 \cdot 3H_2O$ loses $2H_2O$ to give γ-$Al_2O_3 \cdot H_2O$ as an intermediate product which in turn goes over to γ-Al_2O_3 and finally to α-Al_2O_3 at higher temperatures. The rounded step corresponding to the trihydrate is followed by a continuous curve which gives no indication of a step corresponding to a monohydrate; but the x-ray data show that this compound is formed.

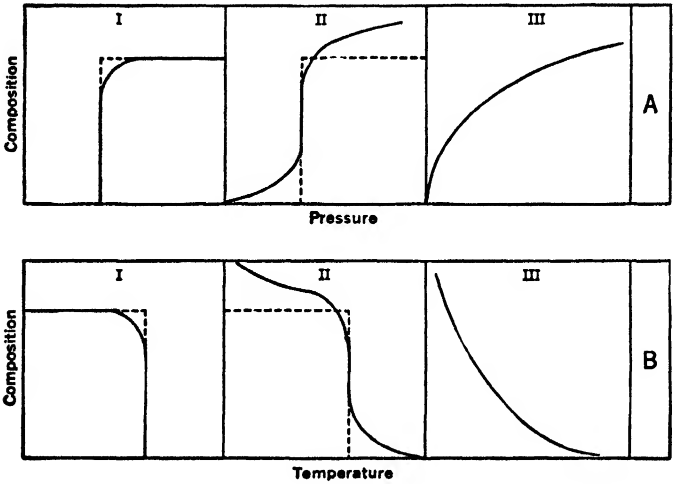

FIG. 99. Typical dehydration curves: *A*, isotherms; *B*, isobars.

Application of the phase rule to the two-component system monohydrate-oxide-water vapor, shows that the system should be univariant, giving an isobar[15] represented by the broken lines *AB* and *BC* in Fig. 100. Theoretically, the curve should drop to zero composition at a definite temperature, but, as we have pointed out, this never occurs with a colloidally dispersed hydrate; instead, a part of the water is lost below the true decomposition temperature of the mass of the hydrate, and the curve takes the rounded form *ADC*. Now, if the oxide formed by the dehydration of the hydrate is highly hygroscopic, it will adsorb most of the water vapor formed in the decomposition. Hence the actual dehydration measured is the loss of adsorbed water from the oxide. In such cases a bivariant type of curve is to be expected, as shown by the solid line *AE* in Fig. 100. Fricke and Severin[16] obtained this last type of curve for both α- and $\gamma\text{-}Al_2O_3 \cdot H_2O$.

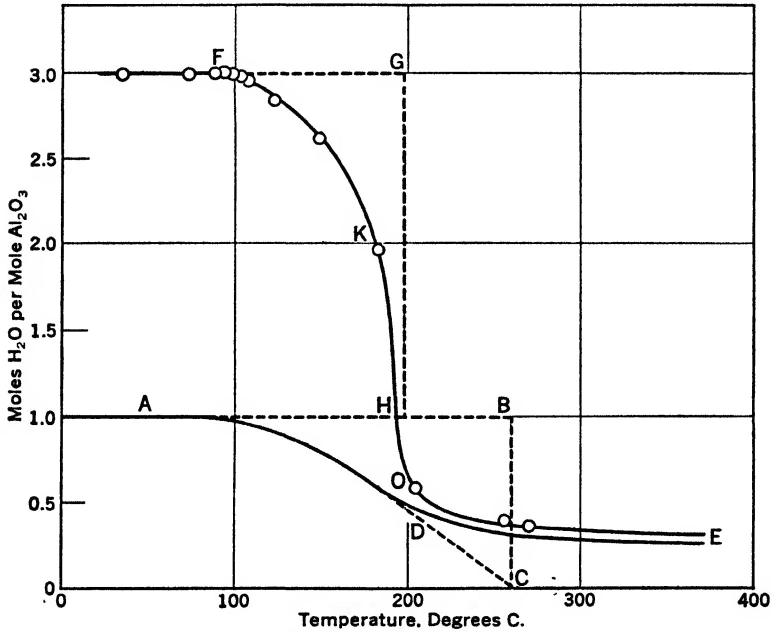

FIG. 100. Dehydration isobar of $\gamma\text{-}Al_2O_3 \cdot 3H_2O$. Solid curve, observed; broken curve, theoretical.

In a higher hydrate decomposing into a lower hydrate and, finally, into the anhydrous substance, it is apparent that, under the conditions noted above, the isobar alone will fail completely to detect the lower hydrate. The theoretical curves for a trihydrate decomposing into a monohydrate, and this in turn into the oxide, are given by the broken lines *FGHBC*✓(Fig. 100). Experimentally, the composition of the trihydrate remains constant only to point *F* where some water is lost, giving a small amount of water vapor and monohydrate. As this process continues along the line *FKH*, all the trihydrate decomposes rapidly to monohydrate. Then the lower hydrate loses water to the point *O*; hence the line *FKH* continues past the theoretical composition of the monohydrate to *O*. This decomposition of monohydrate gives the highly adsorptive γ-Al_2O_3, the presence of which causes the dehydration curve to follow the course *HOE* for the reasons given above.

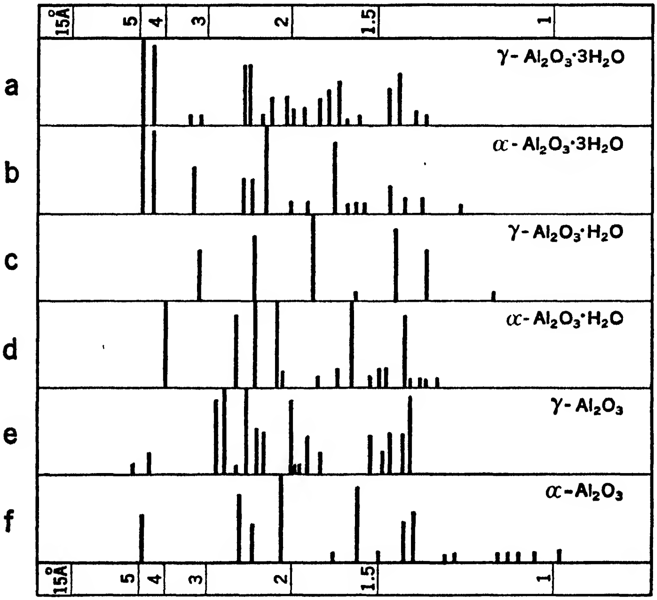

FIG. 101. Diagrams of the x-ray diffraction patterns of aluminas and their hydrates (or hydroxides).

Because of the extreme hygroscopicity of γ-Al_2O_3, the dehydration curve of γ-$Al_2O_3 \cdot H_2O$ shows such a marked variation from the theoretical curve that its existence as intermediate product in the dehydration of γ-$Al_2O_3 \cdot 3H_2O$ has not been detected by phase-rule technique. This is an extreme case, but it is not unique. Adsorption of water by the dehydration product is responsible for the shape of the lower portion of the dehydration isobar of all colloidal oxide hydrates and hydroxides.

α-$Al_2O_3 \cdot 3H_2O$ or bayerite is a metastable compound isomeric with gibbsite, the stable modification. The dehydration isobar of bayerite is similar in essential respects to that of gibbsite.

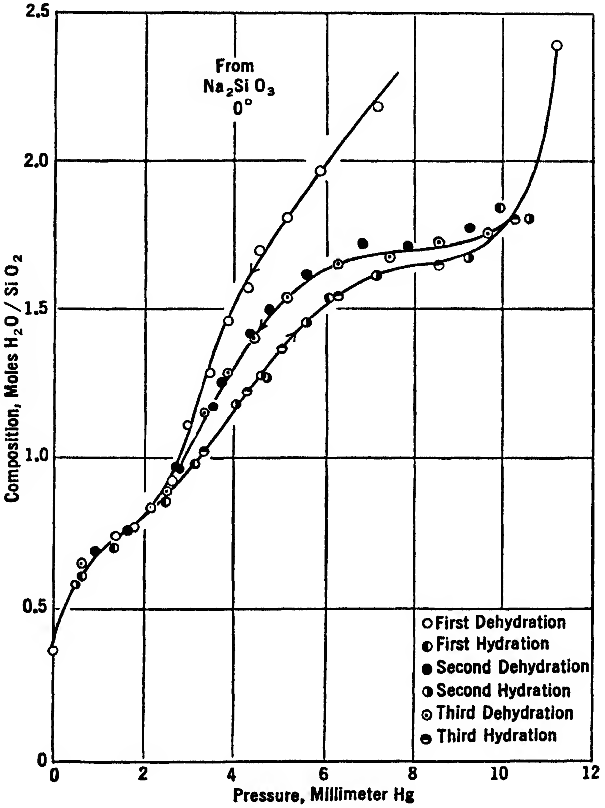

Fig. 102. Sorption-desorption isotherms for silica.

Vapor-pressure Relations: 2. The Adsorption Isotherm; Hysteresis

In Chapter 4 reference was made to the use of the adsorption isotherm in estimating the surface area of inorganic gels. In this connection no mention was made of the phenomenon of *hysteresis* in adsorption-desorption, discovered by van Bemmelen[17] in his classical experiment on the adsorption-desorption of water by silica gel more than 50 years ago. The curve in Fig. 102 illustrates the phenomenon.[18] This is the 12-degree isotherm plotted from data obtained in a modern apparatus[19] making use of the McBain-Bakr[20] silica spring balance to observe changes in weight. It is apparent that the hysteresis loop is reversible, a phenomenon first demonstrated conclusively by Rao.[21]

Cohan[22] has classified and analyzed critically the several theories which have been proposed to account for sorption-desorption hysteresis: (*a*) the incomplete wetting theory, (*b*) the cavity-with-constricted-neck theory, and (*c*) the open-pore theory. All the theories are alike in assuming the existence of some kind of capillary structure in the gel. Any theory to explain hysteresis must account for the fact that the assumed structures are modified or destroyed by the simple procedure of aging the parent sol at the boiling temperature before coagulating the sol to a gel.[18]

Aging; Syneresis

For want of a better term, *aging* signifies the changes in properties which a freshly formed inorganic gel undergoes on standing. The term is used especially in connection with gels of the hydrous oxides. In general, a newly formed gel is very highly hydrous, is easily dissolved or peptized by certain dilute acids and alkalis, shows a high adsorption capacity for ions, and gives a diffuse x-ray diffraction pattern. On standing at room temperature, the gel gradually becomes less hydrous; the solubility, peptizability, adsorption capacity, and catalytic activity decrease in many cases; and bands or lines appear in the x-radiogram. This gradual change in properties is frequently attributed to a transformation from one allotropic modification to another; but, more often, it is due to growth and agglomeration of minute particles into larger granules and agglomerates with a consequent decrease in specific surface. The absence of diffraction lines in the x-radiogram of a freshly formed gel, and their appearance with gradually increasing sharpness in the aged gel, are probably due in some instances to an actual change from the amorphous to the crystalline state; but usually the appearance of lines is the result of a gradual increase in crystal size from crystallization centers too small to show a pattern, to crystals large enough to diffract the x-rays. Certain hydrous oxides such as chromic oxide give no x-ray diffraction pattern even on aging for years at ordinary temperatures, but they exhibit all the other changes in properties which are associated with the loss in specific surface accompanying the growth and agglomeration of the minute particles that precipitate initially.

The freshly formed hydrous oxides of iron, chromium, aluminum, osmimum, etc., when aged rapidly by heating to temperatures around 500°, evolve enough heat to cause the whole mass to become incandescent. This behavior, which may be termed the *glow phenomenon*, disappears on allowing the oxides to stand and is not observed when the precipitates are heated slowly. The glow is the visible manifestation of the coalescence of primary colloidal particles into larger masses, involving a marked decrease in surface energy.[23]

The aging of jellies may manfest itself by contracting and exuding liquid without breaking. This phenomenon, known as *syneresis*, was first observed by Graham[24] with silica jellies; it occurs to a greater or lesser extent in all jellies. Since the jelly-forming process consists in the coagulation of the hydrous particles into an enmeshing network, the syneresis which follows the initial set is the visible manifestation of further slow coagulation and agglomeration which squeeze out some of the entangled liquid. Thus the more rapid the set, the sooner the jelly starts to synerize, and the more rapid is the initial velocity of the process.

Silica is unique among the inorganic jellies in possessing, when freshly formed, an elasticity of the same order of magnitude as gelatin jelly.[25] Moreover, silica jellies vibrate like a rigid body under certain conditions. Holmes, Kaufmann, and Nicholas[26] obtained jellies in a glass tube that gave tones two octaves above middle C when the vessel was struck. The vibration frequency was much lower when the tube was coated with vaseline to prevent the jellies from touching the glass. The frequency was increased by decreasing the concentration of silica and by the presence of excess mineral acid, factors which increase the tension and thus the effective rigidity. The same factors increase the rate of syneresis, indicating that both vibration and syneresis have a direct relation to tension.

Thixotropy and Rheopexy[27]

Thixotropy. If a suitable amount of electrolyte is added to a fairly strong sol of, e.g., ferric oxide,[28] alumina, chromic oxide, or stannic oxide, and the mixture is allowed to stand quietly, it will set to a jelly which is no more cloudy than the original sol. If the resulting jelly is then shaken, a sol is re-formed which will set again on standing; and the process may be repeated as often as desired. This isothermal reversible sol-gel transformation has been termed *thixotropy*,[29] which is derived from the Greek and means literally "to change by touching." The phenomenon is observed only with fairly strong hydrous oxide sols; but bentonite sols[30] containing less than 1% of solid are thixotropic provided that an optimum particle size is obtained by removing the larger particles with the centrifuge. If the larger particles are not removed, the concentration must be above 4%. Gelatin sols will likewise liquefy reversibly at constant temperature if shaken before the structure has become too firmly fixed.

For thixotropic behavior in inorganic colloidal systems, the ζ-potential on the particles must be reduced only to the point where they will stick together to form a loose network structure when the sol is allowed to stand. If the ζ-potential is reduced too far, a gelatinous precipitate is obtained at once or a jelly results which is broken up to give a gelatinous precipitate on shaking. Other important factors are the size and shape of the colloidal particles. In general, small particles which are plate- or rod-shaped favor thixotropic behavior. Hauser and Le Beau[31] consider that the sol-gel transformation is caused by the particles taking up equilibrium positions in relation to one another. Such equilibrium is reached without the particles actually coming in contact when the overall attraction of the particles for one another is compensated by the overall repulsion arising from the electrical charge, solvation, etc.[32]

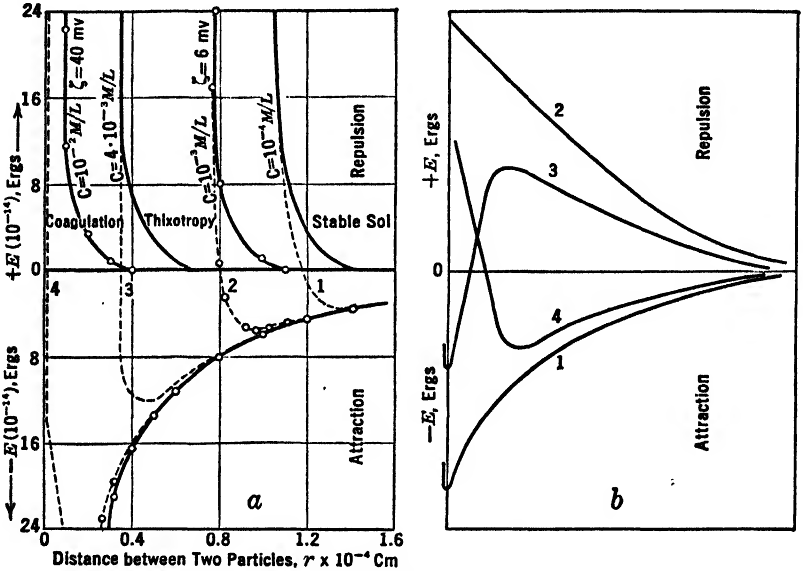

FIG. 103. Types of potential curves showing the relation among adhesion, coagulation, and thixotropy (*a*, after Freundlich; *b*, after Hamaker).

The relationships among adhesion, coagulation, and thixotropy may be represented diagrammatically as in Fig. 103*a*, constructed by Freundlich.[33] The abscissa is the distance between two particles *r*, and the ordinate is the potential energy of the repelling forces $+E$ and the attracting forces $-E$. The curve of attraction extends with small but appreciable values up to about 1 μ. The upper four continuous curves represent the potential energy of repelling forces at four different concentrations of potassium chloride. The distance to which such forces are effective diminishes with increasing electrolyte concentration. To test whether an equilibrium exists between attracting and repelling forces, the corresponding values of potential energy are shown in the broken curves 1, 2, 3, and 4. If a curve of this kind has a minimum, it means that an equilibrium exists between the two forces for the value of r which corresponds to the minimum. The absence of a minimum in curve 1 shows that the repelling forces predominate and a stable sol exists. The minimum value in curve 2 is not well defined, but in curve 3 it lies at a value of $r = 0.5\ \mu$. Accordingly, a large amount of liquid exists between the particles, and the equilibrium system whose particles are motionless because of the balance between the repelling and attractive forces constitutes a thixotropic gel. In curve 4 the minimum value is found at such a small value of r that but little liquid is enclosed between the particles, as in the coagulum from a sol.

The relationships among sol stability, thixotropy, and electrolyte coagulation are apparently more complicated than the potential curves of Fig. 103*a* would suggest. Hamaker[34] recognizes four different types of potential curves (Fig. 103*b*), considered as a superposition of the London-van der Waals attraction (p. 38) and electric repulsion. In curve 1 of Fig. 103*b*, the attractive force predominates over the repulsive force whatever the distance between the particles; in curve 2, the reverse of 1, the electric repulsion is stronger everywhere than the London-van der Waals attraction; in curve 3, intermediate between 1 and 2, the repulsive force is greatest when the particles are separated by a large distance but the attraction predominates when they are close together; and in curve 4, the reverse of 3, the attraction is strongest at large distances and the repulsion predominates at small distances. According to Freundlich, curve 3 of Fig. 103*a* or curve 4 of 103*b* is useful in explaining the phenomenon of thixotropy. Hamaker points out that an equivalent though somewhat more complicated curve 3 of Fig. 103*b* may also account for thixotropic behavior.

Rheopexy. Thixotropic sols, containing distinct rod- or platelike particles which set spontaneously rather slowly, may be made to set rapidly by rolling the container gently between the palms of the hands or by tapping it gently in order to facilitate the orientation of the particles. For example, a vanadium pentoxide[35] sol which set spontaneously in 60 minutes solidified after the rolling procedure in 15 seconds. Similarly a 1.3% bentonite sol which set spontaneously in 25 minutes solidified in 15 seconds after gentle tapping of the container.[30] This phenomenon has been named *rheopexy*[36] from the Greek *pectos,* meaning "curdled" or "solidified."

The application of thixotropic behavior on a large scale is found in the so-called drilling fluids used in drilling for petroleum.[37] In this operation, the drill passes through layers of clay, quartz, etc. If the boring fluid is water alone, the mixture in the hole will be a concentrated suspension of clay, etc., which may easily settle down for one reason or another and "freeze" the drill. This may be prevented by using as a boring fluid a thixotropic suspension of bentonite which sets, at the worst, to a soft gel which is easily liquefied again.

One of the important functions of a drilling fluid is to seal off gas formations by the hydrostatic head of the fluid column. For this purpose, weighted drilling fluids are employed which not only furnish a pressure exceeding that of the gas but will penetrate the formation to a slight extent, thus preventing entrance of gas by diffusion or solution. Ambrose and Loomis[37] calculate that, if the gas pressure is 1500 lb/sq in at 2750 ft, the drilling fluid weight per gallon must be at least 10.46 lb/gal, and should be at least 2 lb/gal heavier to furnish a reasonable excess pressure. Clay suspensions of this density are entirely too viscous for pumping; hence a suitable drilling fluid is made by adding 2–3% of bentonite to mixtures of substances such as barium sulfate and hematite whose suspensions alone have a low viscosity. "Baroid" is a technical mixture of this kind.

Diffusion in Jellies—the Liesegang Phenomenon

The rate of diffusion in dilute jellies is almost the same as in pure water, but in concentrated jellies it is much slower. A number of interesting reactions have been carried out in transparent jellies such as gelatin and silica jellies. The usual method of procedure consists in adding one electrolyte to the solution before the jelly sets, after which a solution of a second electrolyte is poured on the jelly and allowed to diffuse into the mass where the interaction takes place. If a crystalline precipitate is formed by the reaction, the crystals will be much larger and better formed than if the solutions are mixed directly. For example, Hatschek and Simon[38] obtained large gold crystals by reducing gold salts in silica jelly with several different reducing agents; and Holmes[39] prepared magnificent crystals of a number of metals and salts. The function of the jelly is to prevent rapid mixing of the reacting solutions, thereby avoiding rapid precipitation and the consequent formation of amorphous particles or small crystals.

Reactions in jellies sometimes lead to the formation of the so-called *Liesegang rings* or *rhythmic bands* of precipitates, instead of large crystals. The phenomenon was discovered by Liesegang,[40] who placed a drop of silver nitrate on a glass plate coated with moist gelatin containing potassium dichromate and obtained a series of concentric rings of silver chromate. If the reaction is carried out in a test tube, a series of parallel bands results.

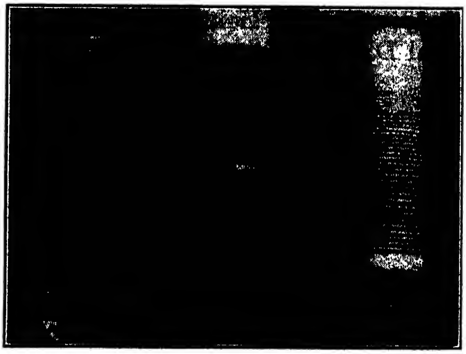

FIG. 104. Rhythmic bands of manganous sulfide in silica gel (Tower).

The rhythmic-banding process has been observed repeatedly with a number of substances in several different types of jellies. Figure 104 is a photograph of Liesegang rings of manganese sulfide in silica gel, obtained by Tower.[41] The nature of the jelly is important in certain cases. For example, silver chromate readily forms bands in gelatin but not in agar, and copper chromate readily forms bands in slightly basic silica jelly,[39] whereas silver chromate and lead chromate give bands in silica only under rather favorable circumstances.[42] It should be emphasized that the presence of a jelly is not essential for rhythmic banding. Thus Morse[43] prepared the bands with a large number of salts in aqueous solution in the absence of any colloidal material. It is easier to get the phenomenon in capillary tubes than on a larger scale.[44]

✓ (Morse claims that periodic precipitation from aqueous solutions can be explained in the light of two well-known facts: (1) that slightly supersaturated solutions may persist for an indefinite time before precipitation; and (2) that highly supersaturated solutions will persist for only a short time before precipitation. This explanation goes back to Wilhelm Ostwald,[45] who first accounted for rhythmic banding by assuming supersaturation up to a certain point followed by rapid precipitation. In its original form, Ostwald's explanation proved inadequate, for it assumed a definite metastable field for supersaturation and did not include any specific effects due to the nature of the jelly. Moreover, Hatschek[46] showed that periodic precipitation sometimes results in jellies containing crystals of the precipitated substances which should be expected to prevent supersaturation. Other theories have been proposed by Holmes,[47] Wolfgang Ostwald,[48] Bradford,[49] and Sen and Dhar;[50] but none is entirely satisfactory for all cases.[51])

In spite of the limitations of Wm. Ostwald's theory in its original form, the mechanism which he formulated lies at the basis of every periodic precipitation. Fischer[52] points out that certain salts exhibit an induction period, and these alone will give rhythmic precipitates in water. On the other hand, all salt solutions show an induction period in the presence of gelatin, agar, and dyes, and all can be made to give rhythmic precipitates, the ease with which this occurs varying with the nature and concentration of the colloidal material. In certain cases the actual formation of the rings or bands may be the coagulation of a sol rather than a release of supersaturation. This would account for Hatschek's observation that rhythmic bands may form in gelatin containing crystals of the precipitated substances. A more probable explanation is that the crystals formed in the presence of gelatin adsorb it and so are prevented from seeding a supersaturated solution of the substance.) There is nothing unusual about this behavior. Indeed, gypsum does not precipitate readily from its supersaturated solution in the presence of gypsum nuclei formed in the presence of ammonium acetate, probably because of an adsorbed film of acetate on the surface of the crystals.[53]

Reactions in jellies are important as offering a plausible explanation of certain formations in nature. Thus gold salts may have become reduced to gold in gelatinous silica which subsequently became quartz. Similarly, agate has probably been produced from gelatinous silica into which iron and other salts have diffused and deposited rhythmic bands.[54] The concentric layers in gallstones are a manifestation of the Liesegang phenomenon.[55] Photographs of some synthetic banded gallstones are reproduced in Fig. 105. The bands resulted from the diffusion of bile pigments into a gel of cholesterol containing calcium ion.

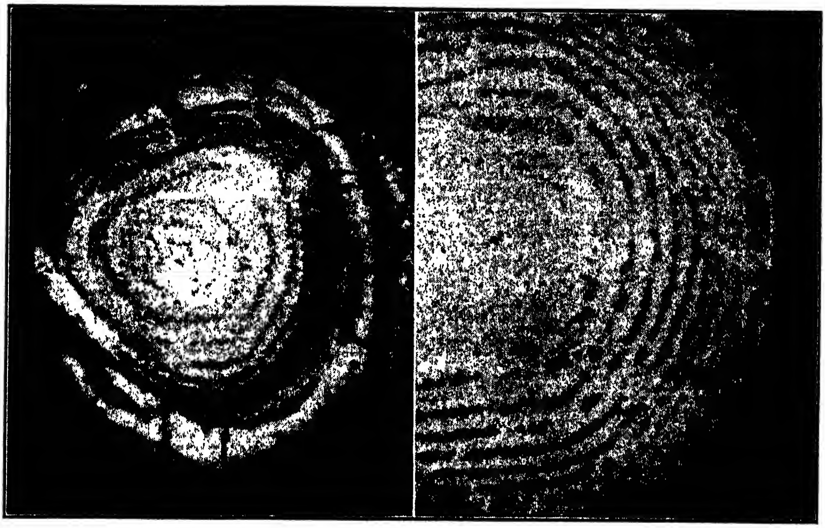

FIG. 105. Synthetic banded gallstones.

ORGANOGELS AND AEROGELS

The water in hydrogels may be replaced to a greater or lesser extent by organic liquids giving organogels. For example, Graham claimed to remove practically all the water from silica hydrogel by repeated immersion in absolute alcohol. Actually, it is quite difficult to remove all the water,[56] but Furth and Purse[57] showed that a gel containing but 0.57% water associated with 30.3% alcohol can be obtained by passing dry air saturated with alcohol vapor over the hydrogel; and Rao and Doss[58] reduced the water content to 0.21%, associated with 7% alcohol, by extracting the gel with absolute alcohol in a Soxhlet extractor.

Removal of all the water from gels by heating causes them to lose most of their adsorbing power for liquids and vapors, as a result of coalescence of particles and the consequent decrease in porosity. Kistler[59] has demonstrated, however, that it is possible to replace the liquid in a gel by a gas with little or no shrinkage. The method consists in displacing the liquids successively by liquids that are completely miscible with the preceding and succeeding one (e.g., water, alcohol; or water, alcohol, ether), the last one having a low critical temperature. The resulting jelly is then placed in an autoclave with an excess of liquid and heated above the critical point. On allowing the gas to escape, a coherent expanded *aerogel* is obtained. A silica aerogel having an apparent density of 0.02 was prepared in this way as a slightly opalescent but quite transparent glassy solid. The method is general, and aerogels have been made of silica, alumina, tungstic oxide, ferric oxide, stannic oxide, nickel tartrate, cellulose, nitrocellulose, gelatin, agar, and egg albumin.

Thoria aerogel is an excellent catalyst for the conversion of aliphatic acids and esters to ketones.[60]

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CHAPTER 20

Gels II: Organic Jellies

STRUCTURE

In the previous chapter it was concluded that inorganic jellies consist of myriads of highly hydrous or gelatinous particles enmeshed into a network or sponge structure in which both the solid and liquid phases are continuous. This concept is essentially the same as the micellar theory of the structure of organic jellies proposed by Frankenheim and Nägeli.[1] According to this theory, distensible bodies such as gelatin, agar, and rubber are assumed to consist of small anisotropic, crystal-like, molecular aggregates which retain their identity even when the substance goes into (colloidal) solution. The micelles, as Nägeli called the molecular aggregates, take up water in such a manner that they are surrounded by a water layer, the thickness of which is determined by the relative intensity of the attraction of the micelles for water and for each other. Zsigmondy's earliest investigations with the ultramicroscope led him to conclude with Nägeli that the jelly structure is granular or flocculent; but later he observed a fibrillar structure in addition to the granules encountered in dilute gels of gelatin, agar, and hydrous silica.[2] The fibrils or threads are quite sharply defined in soap jellies studied by Bachmann and later by McBain and coworkers,[3] and in barium malonate jellies studied by Flade.[4] Flade noted the crystalline character of the fibrils and suggested that jellies in general probably consist of a network of crystalline threads. Gortner [5] prepared a jelly of dibenzoyl cystine which was found to consist of minute crystalline needlelike fibers, and Büchner [6] observed a similar structure with myricyl alcohol jelly in chloroform. Bradford [7] champions the theory that the reversible sol-jelly transformation is merely an extreme case of crystallization.

Although the solid phase in certain jellies may consist of crystalline fibrils, the solid need not be definitely crystalline, and the individual particles need not be fibrillar in shape. Laing and McBain [3] consider that the colloidal particles in soap sol and jelly are the same; but in the sol they are independent and in the jelly they are linked together to form a filamentous structure. The formation of the soap curd is looked upon as a phenomenon analogous to crystallization that is distinct from the process of jelly formation.[8] In certain starch-water jellies, Meyer[9] observed a net structure made up of turbid drops or globules. Similarly, gelatin in aqueous alcohol appears to give a net structure made up of globules rather than of filaments.

To summarize: some people consider that all organic jellies are made up of a framework of amorphous threads; others, that they are composed of crystalline threads; and still others fail to find any threads or filaments at all but observe an irregular grouping of particles. Doubtless all are right in specific cases. Indeed, it is not unlikely that there are various arrangements of molecular aggregates in different jellies and perhaps in the same jellies. It is probable that the process of gelation and the jelly structure are more complex in a heterogeneous mixture of complex groups such as are found in gelatin sol or jelly than in the inorganic jellies or in soap jellies. The orientation of the particles may result in fibrils in certain instances and in more or less irregular arrangements in others. In some the fibrils may consist of definite crystals, whereas in others the crystalline characteristics may be entirely lacking. In all cases it seems probable that the particles are highly hydrous as a result of adsorption or absorption and that they are linked together, forming an irregular mesh or network in the interstices of which liquid is entrained. In both inorganic and organic jellies both the solid and liquid phases appear to be continuous, the solid framework being comparable to a sponge rather than to a honeycomb.

FORMATION

Cooling of Sol

Certain substances like gelatin and agar swell in water at ordinary temperatures but are not peptized to form sols until the temperature is raised. Cellulose aceate behaves the same way in benzyl alcohol. At the higher temperatures, the liquid phase serves the double rôle of peptizing agent and dispersing medium. On cooling such a sol system, a jelly results provided that the concentration is suitable. Thus a sol containing 1% of pure gelatin does not gel until around 10°, and gelation does not take place at any concentration above 35°. The "melting" and "setting" temperatures are not definite, but comparable results can be obtained by choosing some arbitrary standard of viscosity or elasticity. The "setting" temperature is found to be in the neighborhood of 5–10° lower than the "melting" temperature; in other words, a hysteresis range exists in which the system may be either sol or gel. This range is much smaller for gelatin than for agar; an agar jelly must be heated to about 95° before it liquefies, and the resulting sol must be cooled below 35° before it sets once more.

The temperature of gelation of gelatin sols is influenced by the *p*H and by the presence of neutral salts. Pectin jellies are usually obtained in acid solutions containing sugar. If alcohol or glycerol is substituted for sugar, jellies will form in the absence of acid; [10] and they may be made in alkaline solution.[11]

Pure warm sols of gelatin appear almost homogeneous in the ultramicroscope, but, on cooling, they become heterogeneous with the particle size amicroscopic to submicroscopic, depending on the concentration. The appearance of visible particles is not dependent on the formation of a jelly since these may be seen before the jelly sets and in dilute sols that do not set. When a jelly results on cooling a sol, the process consists in the formation of highly hydrous molecular aggregates which are linked together to form a more or less rigid network. Bogue [12] believes that the aggregates not only grow in size but also become more hydrous on cooling. This might be expected in view of the usual increase in adsorption at lower temperatures.

Swelling

Practically all substances which form the so-called elastic jellies will swell in a suitable liquid or in the vapors of such liquid. Thus dry gelatin, fibrin, and starch will swell in water at ordinary temperatures, forming jellies that are peptized at higher temperatures to give sols. Albumin swells in water but not in alcohol, benzene, ether, or turpentine. Vulcanized india rubber swells in various organic solvents such as benzene, toluene, and xylene, but not in water; soaps swell in water and in many organic solvents.

Some substances like gum arabic swell continuously at ordinary temperatures until the entire mass is peptized to give a sol, whereas others like gelatin and rubber approach [13] a maximum of swelling without sol formation.

Swelling pressure. Whenever a dry jelly takes up water, the system occupies less volume than the water plus dry jelly.[14] On the other hand, the dry jelly considered alone undergoes marked expansion on taking up water, and the swelling may exert a very high pressure.

Rocks have been split by inserting dry wooden wedges in a seam and moistening the wood. In some experiments on dried seaweeds, Reinke[15] found that water was taken up against a pressure of 41 atmospheres, the volume increase amounting to 16%. Similarly, Rodewald[16] found that starch swells against a pressure of 2500 atmospheres, and Schull[17] showed that certain dry seeds will withdraw water from saturated lithium chloride solution which has an osmotic pressure of 965 atmospheres. Posnjak[18] made some observations on the amount of water with which gelatin is in equilibrium at various pressures and on the corresponding behavior of raw rubber in different organic solvents. In all experiments, the amount of liquid taken up decreases with increasing pressure. The data do not enable us to determine what pressure would be necessary to prevent any swelling or to remove all the adsorbed liquid from a swollen jelly; these values would probably be very high in every case. Some idea of the magnitude of the swelling pressure of gelatin may be obtained by coating a glass plate with gelatin which has absorbed the maximum amount of water and observing the degree to which the glass plate is bent by the drying film of gelatin.[19] The strain is frequently sufficient to break the plate or pull pieces of glass off the surface.

Effect of *p*H and salts. The effect of *p*H and salts on swelling has been investigated extensively with gelatin. Loeb[20] found that the swelling approaches a minimum value at the isoelectric point, increasing on either side of $pH = 4.7$. At the same time, the swelling is not determined by the *p*H value alone. For example, at $pH = 3$, the order of swelling in different acids is: HI > glycerophosphoric > sulfosalicylic > H_2SO_4 > HCl; in more acid solutions, the swelling is greater in hydrochloric acid than in sulfuric acid.

Salts influence the swelling of gelatin, some increasing and some decreasing it. For sodium salts, the swelling follows the order of the lyotropic series: CNS > I > Br > NO_3 > ClO_3 > Cl > acetate > citrate > tartrate > SO_4; the swelling is less in the last four than in pure water. Salts cut down the swelling caused by acids or alkalis. Cations influence the swelling in the order: Cs > Li > Rb > K > Na > NH_4.[21] This is not the lyotropic order; and, when the amount of swelling is plotted against the lyotropic numbers (p. 297) of the cations, the resulting curve shows a minimum. These observations are explained by assuming the absence of a parallelism between the hydration of the cations and their adsorption by gelatin.

Fibrin behaves much like gelatin in the presence of salts, but agar swells less in any salt solution than in water.

Theory of swelling. Procter and Wilson[22] applied Donnan's theory of membrane equilibrium (p. 247) in interpreting the effect of pH on the swelling of protein jelly. It is assumed that the H^+ ions of an acid in which the jelly is immersed combine with the protein giving positively charged micelles, the anions of the acid being the counter ions. Within the jelly, the intermicellar solution contains H^+ and anions, A^-, and the solution surrounding the jelly contains like ions. At equilibrium, the distribution of ions between the jelly j and surrounding solution s is given by the equation of products:

$$[H^+]_s \cdot [A^-]_s = [H^+]_j \cdot [A^-]_j$$

In the surrounding liquid at equilibrium let

$$x = [H^+] = [A^-]$$

and in the jelly, let

$$y = [H^+] \text{ in the intermicellar liquid}$$

and

$$z = [A^-] \text{ corresponding to the positive charges on the protein}$$

from which

$$y + z = \text{total } [A^-] \text{ in the intermicellar liquid}$$

The equation of products then becomes:

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

Since

$$2y + z > 2x$$

it follows that

$$2y + z = 2x + e$$

where e is the excess of concentration of diffusible ions in the jelly phase over the concentration in the surrounding solution. This excess causes water to pass into the capillary spaces of the jelly by osmosis and forces swelling of the jelly. In other words, the anions tend to diffuse into the outer solution and carry the positively charged micelles with them. But the micelles are a part of an elastic structure which resists the outward pull of the anions. According to Hooke's law, the value e of this pull is:

$$e = CV$$

where C is a constant for the bulk modulus of elasticity (p. 333) of the gelatin, and V is the increase in volume.

Procter and Wilson have tested this theory experimentally for gelatin and hydrochloric acid and have found good agreement between observed and calculated values for the amount of swelling. Moreover, in accord with the theory, the addition of neutral salts to acid-swollen jellies causes them to shrink since the cation concentration y in the jelly is increased without increasing z.

The application of the Donnan theory to the swelling of gelatin is certainly a step forward in explaining the mechanism of the swelling process, although it is not helpful in interpreting the swelling of such substances as rubber in organic liquids or the swelling of isoelectric gelatin.[23] Moreover, it will not account for the enhanced swelling of polysaccharides and gelatin by such organic substances as thiourea, resorcinol, benzene sulfonates, and small amounts of propyl and butyl alcohols.

GENERAL PROPERTIES

Water Relationships

The elastic organic hydrogels lose water continuously in dry air just like the inorganic hydrogels. A striking difference in the behavior of the two is that the dehydration of the inorganic jellies is not reversible whereas dry plates of the elastic jellies will take up moisture and swell again in moist air.

The state of water in hydrophilic jellies has been the subject of investigation by a number of people, and the results of their work have been summarized by Gortner.[24] From the findings obtained by thirteen different experimental techniques, the conclusion is reached that part of the water in hydrophilic colloid systems differs in certain physical properties from water in bulk. Such water is said to be "bound" in the sense that the molecules have been so reduced in activity that they may be exposed to low temperatures without being oriented into the crystal lattice characteristic of ice. Jones and Gortner[25] found, for example, that, in a 2% gelatin jelly, 4.68 g H_2O/g dry gelatin fails to freeze between −10 and −30°; and even in the non-elastic silica and ferric oxide gels, 0.80 g H_2O/g dry material does not freeze above −50°.[26]

The forces which bind water to the surface in hydrophilic particles appear to be similar in nature to those which cause the association of water molecules in bulk and which immobilize the molecules of water in the crystal lattice of ice. More specifically, it is now almost certain that the binding is by means of hydrogen bonds.[27]

Gortner has emphasized the parallelism between "bound water" in protoplasmic material and biological behavior, and he suggests that the water relationships in the biocolloids may determine to a large degree the vital activities of organisms. The bound $\rightleftarrows$ free water equilibrium is of primary importance for winter hardiness and drouth resistance in plants, for winter hardiness in insects, and for the regulation of cell activities generally in both plant and animal organisms.

Like inorganic jellies, jellies of gelatin, agar, etc., contract and squeeze out water on standing. This syneresis in both types of jellies probably results from agglomeration of colloidal particles to form denser aggregates which can adsorb and entrain less water than the freshly formed system.

Elasticity

The elasticity of gelatin jelly has been studied most extensively because of the ease with which it may be molded into any desired shape and because comparable samples are readily obtained. The values for the modulus of elasticity observed by different people agree fairly well. Leick[28] obtained values that range from 2.42 g/mm^2 for a 10% jelly to 29.4 g/mm^2 for a 45% jelly. The elasticity modulus is influenced by the presence of various substances in the jelly, just as these affect gelation. Thus, chlorides lower the value just as they lower the viscosity and setting temperature of the sol, whereas glycerol and cane sugar have the opposite effect on each of the constants. The volume of a jelly does not change when it undergoes extension.

The elasticity of gelatin jellies is perfect only for small loads applied for a short time. The stress required for maintaining a given deformation decreases with time but never becomes zero; that is, the jelly exhibits partial relaxation.[29] Strain produces optical anisotropy in the jelly which does not disappear on removal of the stress.[30] Apparently the particles in a strained jelly become cemented in their constrained position and so cannot move after the stress is removed. Similar observations have been made with india rubber, cotton, wool, silk, and other fibers.[31]

A gelatin jelly becomes warmer when it is stretched and cooler when compressed, just as rubber does. The compressibility of gelatin is 10×10^{-6}, which is approximately ten times greater than that of solids at ordinary temperatures.[32] The compressibility increases with rising temperature, and, when the jelly liquefies, it becomes 48×10^{-6}, the value for water.

Optical Properties

The double refraction produced in a jelly when subjected to strain (see above) is possessed also by very dilute sols of gelatin, gum, collodion, etc. There appears to be no satisfactory explanation of the ultimate cause of the optical phenomenon, but it seems reasonable to assume that the appearance of strained elastic sols and gels in polarized light is due to the effect of the stress on the elastic semi-solid or solid phase. With some jellies it is possible that the double refraction is a property of the crystals which compose the solid framework.

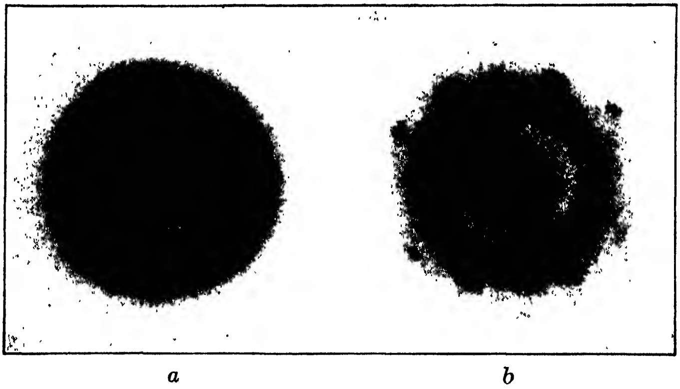

Fig. 106. X-radiograms of (*a*) unstretched rubber, (*b*) stretched rubber.

The double refraction in sols and jellies subjected to strain should be distinguished from that which occurs in certain sols when no external stress is applied (p. 180).

X-ray diffraction investigations on organic gels show that many of them are crystalline. To illustrate, the x-radiogram of unstretched rubber[33] is an amorphous band pattern, as shown in Fig. 106*a*; whereas the stretched rubber gives a diagram of lines and points (Fig. 106*b*), characteristic of small crystals. Gelatin jellies exhibit a similar phenomenon.

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PART IV. EMULSIONS AND FOAMS

CHAPTER 21

Emulsions

Emulsions consist of drops of one liquid dispersed in the bulk of a second liquid. Emulsions that are quite stable result if a very small amount of oil is highly dispersed in a large amount of water. In such systems, the stability is due to the electrical potential on the colloidal droplets. This is evidenced by the fact that they behave in an electric field and toward electrolytes like typical hydrophobic sols.[1]

The electrical potential on dispersed droplets is insufficient to maintain stability except in very dilute and highly dispersed systems. In more concentrated emulsions, the droplets touch each other and run together unless a third component is added which forms a film around the droplets and prevents their coalescence. The third component is called an *emulsifying agent* or *emulsifier*.

The necessary requirements for a stable emulsion are: (1) the droplets of the dispersed liquid shall be sufficiently small so that they will remain suspended, and (2) the droplets shall be surrounded with a sufficiently viscous or plastic film to prevent their coalescence. An emulsifying agent or emulsifier is, therefore, any substance which goes into the oil-water interface and produces a film with the necessary properties. From observations with gelatin and cellulose nitrate as emulsifying agents, Holmes[2] concludes that the most satisfactory protecting film should be elastic and tough and should change little with age.

With any pair of non-miscible liquids, two sets of emulsions are possible: one in which oil droplets are dispersed in water, and a second in which water droplets are dispersed in oil. The term *oil* as applied to emulsions refers to the liquid other than water. In general, an emulsifying agent which tends to form a stable emulsion of oil in water will be unsatisfactory or less satisfactory for forming a stable emulsion of water in oil, and *vice versa.* For example, alkali soaps tend to give good emulsions of oil in water but not of water in oil, and alkaline-earth soaps tend to give stable emulsions of water in oil but not of oil in water.

The type of an emulsion may be of importance technically. An emulsion of creosote in water is much less satisfactory than an emulsion of water in creosote for treating wood.[3] Cod-liver oil emulsions are very properly of the oil-in-water type, since nothing would be gained by emulsifying flavored water in cod-liver oil. Emulsions of lubricating oil in water are mobile liquids, whereas stiff greases may be prepared by emulsifying water in lubricating oil.

Many of the dispersed droplets in most emulsions are much larger than the 0.5 μ which marks the upper limit of the colloidal zone. Nevertheless, emulsions should be considered colloidal systems since the emulsifying agent is either definitely colloidal or exhibits colloidal properties.

THE THEORY OF EMULSIFICATION

The Double Interfacial Tension Theory

To account for the formation of emulsions, Quincke[4] and Donnan[1] assumed that the emulsifying agent acts by lowering the interfacial tension between the two liquids and thus by concentrating at the interface. This concept has been extended by Bancroft[5] to explain the formation of the two types of emulsions. According to the double interfacial tension theory, the emulsifying film has a minimum thickness of three molecules: one molecule of water, one molecule of the emulsifying agent, and one molecule of oil. The film has two surfaces, one toward the water and the other toward the oil. Now, if the surface tension at the interface water-emulsifier is less than at the interface oil-emulsifier, the film will tend to bend so as to become convex on the water side, thereby tending to make an emulsion of oil in water. On the other hand, if the surface tension at the interface water-emulsifier is greater than at the interface oil-emulsifier, the film will tend to curve so as to become concave on the water side, thereby tending to give an emulsion of water in oil. In line with this, Bancroft pointed out that a small drop of olive oil on the surface of a sodium soap solution stands up because the oil tends to be emulsified, whereas a drop of olive oil on a calcium soap solution tends to spread out because it is trying to emulsify the water. Conversely, a drop of aqueous sodium oleate spreads readily on olive oil, whereas a drop of aqueous calcium oleate does not.

Briggs has formulated Bancroft's theory as follows: Oil-in-water emulsions result when the emulsifying agent at the interface is chiefly in the water phase, and water-in-oil emulsions are formed when the emulsifying agent at the interface is chiefly in the oil phase. Typical emulsifying agents are colloidal materials which are peptized strongly by one phase but not by the other, and which are adsorbed strongly at the interface. To illustrate, potassium and sodium soaps, gum arabic, gum tragacanth, gelatin, saponin, albumin, and casein are peptized readily by water but not by oil; hence they tend to form stable emulsions of oil in water. Conversely, calcium, magnesium, and zinc oleates, rosin and the resinates, lanolin, gum dammar, rubber, cellulose nitrate, and asphalts are peptized by oil but not by water, and they therefore tend to form stable emulsions of water in oil. Since most emulsiers will not peptize the second liquid spontaneously, the latter must be broken up into droplets by mechanical means.

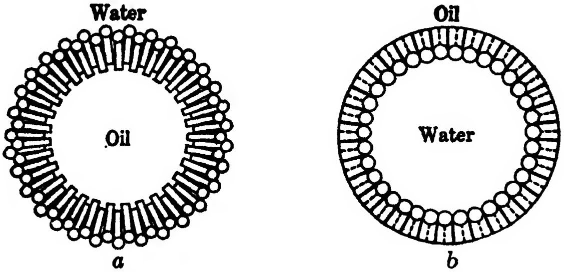

FIG. 107. Diagram of molecular orientation of the stabilizing molecules in oil-in-water and water-in-oil emulsions (Harkins).

Polar emulsifying agents such as the soaps are probably oriented in the surface film (p. 123) with the hydrocarbon end of the molecule toward the oil phase, and the carbonyl group with its metallic radical toward the water phase. Hildebrand[6] and Harkins[7] proposed a wedge theory of emulsification based on this molecular orientation. With a univalent base, the group soluble in the water is assumed to occupy more space than is necessary for the closest packing of the hydrocarbon chain; hence the film tends to be convex on the water side, giving an oil-in-water emulsion (Fig. 107*a*). With a bi- or trivalent base, on the other hand, the fatty acid radicals in the oil are assumed to spread out and occupy more space than the metallic radicals, making the interface convex toward the oil side and tending to give a water-in-oil emulsion (Fig. 107*b*). This "oriented wedge" model[8] is not satisfactory since simple molecules of soaps of the multivalent metals probably do not exist, and simple and regular monomolecular soap films probably do not form. Moreover, the size of the molecule of an emulsifying soap appears insufficient to give the assumed leverage action. The wedge hypothesis is limited in its applicability to polar emulsifying agents and is best considered as a special case of Bancroft's general theory. If an emulsifying agent is oriented at the interface, it will tend to form a stable emulsion of oil in water provided that the oriented molecules are chiefly in the water phase, and a stable emulsion of water in oil provided that the oriented molecules are chiefly in the oil phase.[5]

The most common emulsifying agents are gelatinous materials, but finely powdered solids may be used if they exhibit the necessary properties: (1) the particles must go into the dineric interface; hence they must be wetted sufficiently by both liquids in order to increase considerably the miscibility of the two liquids at the surface between solid and liquid (p. 75); (2) the particles must be wetted more strongly by one liquid than by the other; (3) the particles must form a coherent plastic film around the dispersed droplets. If the particles are wetted more strongly by water than by oil, they will tend to give emulsions of oil in water, whereas if they are more strongly wetted by oil than by water, they will tend to give emulsions of water in oil. Emulsification by solid powders, therefore, comes under the general theory. A few examples will illustrate the applicability of the procedure. Oil-in-water emulsions may be prepared by means of basic sulfates of copper, ferrous iron, and nickel.[9] Nitrobenzene may be emulsified in aqueous sulfuric acid with lead sulfate,[10] and chloroform in water with silver dichromate.[11] Insecticidal sprays have been made in which mineral oil is emulsified in water by means of kaolin, fuller's earth, or colloidal clay; [12] such sprays are less likely to "burn" the foliage than emulsions made with soap.[13] Emulsions of water in kerosene, turpentine, benzene, or toluene are obtained with soot as emulsifying agent,[14] and aqueous ammonium chloride in kerosene by means of lampblack.[15]

Applicability and limitations. The Bancroft double interfacial tension theory is the most useful theory we have at present to explain the formation and stability of the two types of emulsions. There are, however, many exceptions such as have been pointed out by Tartar and coworkers,[16] Seifriz,[17] and Woodman.[13] Water-in-oil emulsions are sometimes formed where the opposite type would be predicted, and *vice versa*. Moreover, the formation of such emulsions as ether in water with iodine as emulsifier, and benzene in water with methyl alcohol [18] as emulsifier, would not be predicted by the theory. If sufficient information were available concerning the various systems, it is possible that the exceptions would prove to be only apparent. In any event, the systems may be quite complicated, and it would not be surprising if one simple theory proved to be inadequate to explain all the observed facts. Roberts [19] has extended Bancroft's theory by considering the energy relationships which exist at the two interfaces by virtue of the adsorption of polar and non-polar molecules and of ions at the respective interfaces. A better understanding of emulsion behavior will follow from an increase in our knowledge of the interfacial tension forces on the two sides of the stabilizing film.

PREPARATION OF EMULSIONS

Two general methods of making emulsions have been recognized, especially by the pharmacist, who is frequently called upon to make oil-in-water emulsions with a gum as emulsifying agent. In the so-called American method, the gum is first peptized in water and then mixed in a mortar with oil which is added a little at a time; whereas in the Continental method, the solid gum is first ground with oil, and enough water to emulsify the mixture is added all at once.

The necessary conditions for emulsification are to get one phase in the form of fine droplets and to get the droplets coated with a protecting film. This may be accomplished by placing oil, water, and emulsifying agent in a bottle and shaking under suitable conditions. The process has been studied extensively by Briggs [20] with the system benzene-water-sodium oleate. Some observations with various ratios of benzene to 1% sodium oleate, with continuous shaking in a machine and with intermittent shaking by hand, are given in Table 65. The time recorded is that required to effect the emulsification. In the intermittent shaking, the mixture was allowed to stand 30 minutes between each shake.

The observations show that the number of shakes required for complete emulsification by the continuous procedure increases rapidly as the ratio of benzene to water rises. More striking is the enormous decrease in the number of shakes required by the intermittent process: in the 96% emulsion this is reduced from 48,000 to 80, and in the 80% emulsion from 6000 to 7, by allowing the mixture to stand between shakes. The continuous shaking breaks up both the benzene and aqueous phases. Since the aqueous phase is the continuous one in the emulsion under consideration, a shaking process which keeps the soap solution broken up will retard the emulsification. The dispersed drops of benzene are protected by a film of soap, whereas the water drops are not protected and coalesce rapidly. Accordingly, intermittent shaking, with short intervals of quiet to allow the aqueous phase to coalesce, gives much better results than continuous agitation. In the American method of preparing emulsions, the pharmacist uses intermittent stirring without realizing it when he adds the oil a little at a time instead of all at once. In the preparation of mayonnaise, oil, water (vinegar), and egg (the emulsifying agent) are whipped together by means of an egg-beater. Intermittent or leisurely whipping is preferable to continuous violent stirring for the successful preparation of this emulsion.

TABLE 65

Emulsification by Continuous and Intermittent Shaking

Continuous			Intermittent		
Vol. C_6H_6 in 100 vols.	Time (min)	Shakes	Vol. C_6H_6 in 100 vols.	Time (min)	Shakes
30	<1	<400	80	3.5	7
50	3	1,200	84	6.5	13
70	10	4,000	86	7.0	14
80	15	6,000	88	9.0	18
90	22	8,800	90	12.5	25
95	40	16,000	92	15.5	31
96	120	48,000	94	22.5	45
99	480 *	192,000	96	40.0	80

* Incomplete.

Not only is intermittent shaking better than continuous shaking in the preparation of emulsions, but too violent agitation [21] and agitation at a given intensity for too long a time [15] both tend to increase the size of the dispersed droplets.

In the Continental process, the initial grinding of the oil with solid gum arabic was found by Briggs to be for the purpose of increasing the interface between oil and water, by suspending in the oil a finely divided substance that is readily wet by water. The same results were obtained by grinding the oil with silica or glass and adding an aqueous dispersion of gum, but this gave an emulsion containing a foreign solid. Gum arabic plays the double rôle of finely divided solid and emulsifying agent. Sodium oleate or other water-peptizable colloid may be substituted for gum arabic. To make water-in-oil emulsions by the Continental method, an oil-peptizable colloid such as gum dammar or magnesium oleate is first ground in water, followed by addition of the oil.

Emulsions with very fine particles are sometimes prepared by a process known as homogenization in which the emulsion or a mixture of two liquids is forced by high pressure through small tubes and the fine streams are allowed to impinge against a solid surface. Milk and cream may be subjected to the homogenization process in order to render them more stable. Milk and cream are emulsions of butter fat as drops in water with casein as emulsifying agent. The fat globules in unhomogenized milk are about 2–10 μ in diameter and in cream 3–5 μ in diameter; homogenization reduces them to 1/10–1/100 their original size, thereby greatly increasing the interfacial area and the amount of stabilizing protein in the interface. The resulting homogenized cream will not "whip," and ice cream made from it is smoother than from the raw product. Briggs [20] has described a simple laboratory homogenizer which is useful for making highly dispersed emulsions.

Colloid mills (p. 158) are frequently used in the preparation of technical emulsions.[22] A special procedure for forming emulsions involves the use of high-frequency sound waves—the so-called ultrasonic waves.[23]

The stability of emulsions usually increases on standing quietly for an hour or so after they are formed. The reason is that time is required for the uniform distribution of the emulsifying agent around the droplets.

PROPERTIES AND STABILITY OF EMULSIONS

Determination of Type of Emulsion [13]

The type of emulsion may be determined from the properties of the external phase. An oil-in-water emulsion is freely miscible with water, whereas a water-in-oil emulsion will float on water. The mixing test devised by Briggs [24] is best made by adding a little water to one drop and a little oil to a second drop on a microscope slide and observing the behavior microscopically. In general, the continuous phase is the same as the bulk liquid when the mixing takes place readily.

A dye such as Sudan III which is oil-soluble but not water-soluble behaves differently when brought in contact with the two types of emulsion.[25] If the emulsion is the water-in-oil type, the dye dissolves uniformly when dusted over the surface, whereas if it is the oil-in-water type, the dye powder appears as a series of discontinuous specks. A colored water-soluble salt such as potassium permanganate gives similar discontinuous specks when the fine powder is dusted on a water-in-oil emulsion. The emulsion type in benzene-water systems has been determined by means of iodine.[24]

The conductivity of an emulsion is high when an aqueous solution is the continuous phase, whereas it is very low when an oil is the continuous phase. This marked difference in conductivity enables one not only to distinguish the two types of emulsions [26] but also to follow the transformation from one type into another (see next paragraph).

Reversal of Emulsion Types

An oil-in-water emulsion stabilized by a sodium soap is readily changed to an emulsion of water in oil by adding a suitable amount of a bi- or trivalent metallic salt.[27] For example, if calcium chloride solution is allowed to flow slowly with stirring into an oil-in-water emulsion, it breaks when sufficient calcium is added to give equivalent amounts of sodium and calcium soap; and it is changed to a water-in-oil system when a small excess of calcium salt is added. The process may be followed by inserting electrodes in the emulsion and observing the marked drop in conductivity when the reversal in type takes place.

The process is more complicated when mineral oil containing magnesium oleate is agitated with sodium oleate solutions. Parsons and Wilson [27] mixed equal volumes of oil and water in which the ratio of magnesium oleate to sodium oleate in equivalents was varied from 25 to 0.5. In every instance, the systems separated into three layers on standing: oil on the top, water on the bottom, and varying amounts of emulsion between. In many cases, especially in the concentration range 10 magnesium oleate to 1 sodium oleate, the middle layer was found to contain both types of emulsion, the upper portion being chiefly water-in-oil and the lower portion chiefly oil-in-water.

Roberts [19] explains the antagonistic action of calcium and sodium oleates by postulating that the calcium salt will tend to be adsorbed on the oil side of the interface water-oil and will try to pass its polar end into the water side, whereas sodium oleate will tend to be adsorbed on the water side and will try to pass its non-polar end into the oil. This competition for position across the interface will result in a mutual repulsion between the competing molecules so that each component nullifies the effect of the other when present in a critical ratio. If the calcium soap is present in excess of the critical ratio, the external phase will be oil, whereas if sodium soap is in excess, the external phase will be water.

Solid emulsifying agents may act antagonistically toward each other in much the same way as the alkali and alkaline-earth soaps. For example, carbon black alone gives a water-in-oil emulsion, and silica alone gives an oil-in-water emulsion; but a mixture of carbon black and silica in suitable proportions gives no emulsion at all.[28] An emulsion of water in kerosene stabilized by carbon, zinc hydroxide, or lead oxide is reversed by the addition of hydroxyl ion.

Tartar and associates[16] found that the type of emulsion is influenced by the concentration of the emulsifying agent and the temperature. For a given concentration of emulsifier, a critical temperature exists, in the neighborhood of which reversal of type takes place. Near the inversion temperature, dual systems of emulsions are sometimes obtained in which, for example, larger water drops suspended in oil contain small droplets of oil.

It has been calculated that the maximum space which small spherical droplets can occupy when packed as closely as possible is 74% of the total volume; it is argued, therefore, that an emulsion must reverse on passing through 74% volume concentration. This proves not to be the case experimentally, stable emulsions containing as much as 99 volumes of paraffin oil or of benzene having been emulsified in 1 volume of aqueous soap solution. This is readily accounted for when it is remembered that the dispersed particles are not uniform in size; moreover, since they are easily deformed by pressure, they are not necessarily spherical in shape. In general, it is more difficult to prepare a concentrated emulsion than a dilute one, and a failure to make an emulsion above 74% by volume is frequently attributed to reversal rather than to experimental error. Bhatnagar[29] claimed to have observed reversal at high concentrations, but Bancroft[30] showed that Bhatnagar was determining the point at which his method of emulsification broke down.

Ion antagonism in biological systems. The antagonistic action of sodium and calcium salts in the process of emulsification suggested to Clowes[27] a possible relation to certain biological problems. Loeb found that the fertilized eggs of a sea urchin, *Fundulus heteroclitus*, do not develop to embryos when transferred to a solution of sodium chloride having the same concentration as sea water; but the destructive action of the sodium chloride is neutralized by adding calcium chloride in the ratio of 1 or 2 moles of the calcium salt to 200 of the sodium salt. Small concentrations of other bivalent cations have an effect similar to calcium. It is a striking fact that the optimum ratio of sodium chloride to calcium chloride is approximately the same as it is in nature, in sea water, and in the blood of animals. A similar relationship was observed by Osterhout [31] and others with certain seeds and plants and by Chambers and Reznikov [32] and Heilbrunn and coworkers [33] with amoeba.

Considering protoplasm as consisting of lipoids (oil) and water, it is conceivable that it will exist as an emulsion of oil in water in the presence of sodium salts, and as an emulsion of water in oil in the presence of calcium salts. From this point of view, it would follow that a critical ratio of sodium and calcium salts is one which produces a balance between the two types of emulsions that is most favorable for life and growth. In support of this hypothesis, Clowes, working with oil, water, and soap, showed that the ratio of sodium and calcium salts necessary to produce a balancing between the two types of emulsions is about the same as that in sea water. Osterhout found that the specific conductivity of the seaweed, *laminaria,* is increased by the addition of sodium salts and decreased by the addition of calcium salts. Now, if one has a labile emulsion in a critical state, its conductivity should be increased by converting it chiefly into an emulsion of oil in water, and decreased by changing it chiefly into an emulsion of water in oil. Clowes [34] was able to duplicate Osterhout's results by impregnating filter paper with an emulsion of oil, water, and soap to which he afterwards added salts of sodium and calcium.

The antagonistic action of ions in the precipitation of sols by electrolytes has already been discussed (p. 277). The similarity to the biological phenomena suggests that the antagonistic action of salt pairs may be due to their effect on the permeability of the colloidal membrane surrounding the cell. Gortner and coworkers [35] observed an antagonism between ions in their effect on the absolute charge at interfaces.

Breaking of Emulsions

Two general procedures may be employed for breaking emulsions: destruction of the emulsifier and cracking of the emulsifying film.

Destruction of the emulsifier. The emulsifying agent may be destroyed by addition of some chemical that reacts with it. Acid will break an emulsion stabilized by sodium oleate since it changes the soap into oleic acid which has no emulsifying action. Similarly, an emulsion stabilized by sodium oleate is broken by the addition of a suitable amount of alkaline-earth or heavy-metal salt. This converts the sodium soap to a soap of bi- or trivalent metal which, as we have seen, acts antagonistically to sodium soap and renders the emulsion instable.

Cracking of the emulsifying film. The cracking of the film may be accomplished in a variety of ways, one or more of which may work with specific emulsions: (1) addition of an emulsifier which tends to form an emulsion of the opposite type, (2) agitation with an excess of the dispersed phase, (3) addition of salts with multivalent ions opposite in sign of charge to the drops, (4) "salting out" by an excess of salt which may dehydrate swollen films, (5) heating, (6) freezing, (7) electrophoresis with a high potential, (8) centrifuging, (9) jarring, (10) filtration.

When an antagonistic emulsifying agent is employed to break an emulsion, it is necessary to avoid an excess, or a reversal of type occurs. Oil field emulsions have been broken by adding salts with multivalent cations,[36] by electrophoresis,[37] and by heating.[38] Emulsions formed in reciprocating engines have been broken by filtration[39] through filter beds of calcium or magnesium carbonate under pressures not higher than 50 lb/sq in. The centrifuge is useful in separating creams; and emulsions are sometimes broken by centrifuging, especially if the density of the two phases differs considerably. Jarring an emulsion may cause it to crack. This is done in making butter from cream. The churning also produces a foam, and the fat goes into the walls of the foam cells and coalesces to give the semi-solid product known as butter. Vibration may cause a technical emulsion such as mayonnaise to crack during shipment. To avoid this, trucks in which it is transported are sometimes equipped with special springs to reduce the road shock.[40]

Crude petroleum emulsions. Crude petroleum emulsions are frequently encountered in the oil industry and must be broken before the product is subjected to the refining processes. The emulsions are of the water-in-oil type; hence the emulsifying agent is probably a colloidal material readily peptized by oil, such as asphalt. Since not all asphalt-base oils readily form emulsions of water in oil, Sherrick[26] suggests that the emulsifying agent may be asphaltic materials adsorbed on clay which will form tough elastic membranes around the water drops.

A common method of cracking such emulsions consists in treating them with suitable amounts of water-soluble colloids such as sodium oleate or the sodium salts of certain sulfonic and naphthenic acids.

Mixtures of such water-soluble materials, sold under the trade name "Tret-O-Lite," have been very widely used for cracking petroleum emulsions.

Since the emulsions are negatively charged, they have been destroyed, as already pointed out, by electrophoresis with a high potential and by the addition of electrolytes with strongly adsorbed cations. Electrolytes are useless unless they can be conveyed through the oil to the water. This is accomplished by selecting a substance that is partly soluble in both phases; Dodd[41] found both acidified phenol and kerosene-acid sludge to work quite satisfactorily with certain emulsions.

The cracking of some emulsions is accomplished by steaming or by direct heating to 350–500°. Centrifugal treatment is frequently successful, especially if the stability of the emulsion is first reduced by some other procedure. Ayres[42] reports an emulsion that was too stable to be broken by centrifuging but was cracked in transit by the vibration of an express train.

Color of Emulsions; Chromatic Emulsions

Emulsification of two transparent liquids yields a milky-white mixture if the index of refraction of the two phases is not the same. On the other hand, the emulsion will appear homogeneous and transparent if the index of refraction of the two phases is the same. To illustrate, emulsions of kerosene or olive oil in water are milky, whereas emulsions of glycerol in carbon tetrachloride (containing calcium oleate or gum dammar) are fairly transparent. Similarly, glycerol and amyl acetate give a creamy emulsion, whereas a suitable mixture of glycerol and water (with the same index of refraction as amyl acetate) and amyl acetate (containing cellulose nitrate) gives a transparent emulsion.[43]

Holmes and Cameron[43] treated a milky emulsion of glycerol in acetone (containing cellulose nitrate) with benzene a little at a time, in order to bring the two phases to the same index of refraction. This increased the transparency and at the same time gave an emulsion that was yellow when viewed from the side and blue by transmitted light. Further additions of benzene raised the refractive index of the continuous phase, which caused the yellow to change to a beautiful pink and the blue to green. More benzene changed the pink to lavender and then to peacock blue. Finally, the emulsion became milky, but the colors were restored in the reverse order by the cautious addition of acetone. Similarly, the whole chromatic scale of colors was obtained by adding carbon disulfide cautiously to an emulsion of glycerol in amyl acetate with cellulose nitrate as emulsifier.

The structural colors in the above-mentioned emulsions are due to the "Christiansen effect."[44] Immersing clean powdered glass in carbon disulfide and adding benzene stepwise, Christiansen observed that the transmitted light was first red, then yellow, green, and blue, in order. The reason for the color is that the dispersion of light by the liquid mixture differs from that of the glass; hence there is an agreement of refractive index only for certain wave lengths which are transmitted, giving colored light. Bodroux[45] observed the phenomenon by substituting a second liquid phase for glass, for example, with mixtures of sodium chloride, ethyl acetate, and water, or of sodium bromide, propyl alcohol, and water. Holmes and Cameron prevented the second liquid phase from settling by means of an emulsifying agent. In general, emulsions possessing structural colors may be secured by means of the following: (1) a continuous phase consisting of two completely miscible liquids (*a*) having relatively low index of refraction and low optical dispersive power and (*b*) having relatively high index of refraction and high optical dispersive power; (2) a dispersed liquid (*c*) having an index of refraction intermediate between that of (*a*) and (*b*). The chromatic range of colors results by the cautious stepwise addition of (*b*) to a milky emulsion of (*c*) in (*a*).

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CHAPTER 22

Foams

Foam or froth consists of globular liquid films enclosing vapor or gas. Foams are like emulsions in that adsorption films surround the dispersed phase in both systems. Foams differ from emulsions in two respects: (1) the dispersed phase is a gas in foams and a liquid in emulsions; (2) the gas bubbles in foams are, in general, much larger than the dispersed droplets in emulsions. Foams must be regarded as colloidal systems because the thicknesses of the films surrounding the gas bubbles are of colloidal dimensions or the films exhibit colloidal properties.

Foams are of practical importance in the lathering of soap solutions and in frothing processes of ore flotation; they are sometimes quite objectionable in the boiling of liquids, in evaporation and distillation processes, and in steam boilers. Foulk [1] points out that: "Even man's social nature is influenced by foams; to such an extent, indeed, that it sometimes demands a stable foam as in beer and soda water and sometimes an instable one as in champagne and ginger ale." This chapter will be concerned with the necessary conditions for foam formation and stability and with the prevention and destruction of foams.

FORMATION AND STABILITY OF FOAMS

The gas bubbles in a foam or froth are surrounded by a more or less viscous film. To get a foam on shaking a liquid with air, it is essential, therefore, that there be a distinct surface film; in other words, that the concentration in the surface shall differ appreciably from the concentration in the body of the liquid.[2] In general, a pure liquid will not foam.[3] In a criticism of Foulk's theory of film formation outlined in the following paragraph, Hazelhurst and Neville [4] maintained that a pure liquid will foam because they obtained foams with some liquids which they assumed to be pure. On the other hand, Foulk and Barkley [5] showed conclusively by three different methods that highly purified water, benzene, nitrobenzene ether, acetone, *n*-heptane, and methanol possess no film-forming properties. Addition of a few hundredths percent of water to the highly purified organic liquids was sufficient to restore their film-forming properties. Although a pure liquid will not foam, all true solutions will foam provided there is a definite increase or decrease of surface tension with concentration (cf. p. 16). Similarly, a sol will foam provided that the colloidal particles concentrate in the interface or are forced out of the interface.

Foulk[1, 6] considers that the liquid films surrounding the gas phase in foams result when two already-formed surfaces approach each other on the liquid side. The mechanism of foam formation proposed by Foulk is represented diagrammatically in Fig. 108. *A* is a solution which gives a surface film that is more concentrated than the body of the solution. The denser hatching on the surface and around the bubble represents, on an exaggerated scale, the higher concentration of the surface film. The bubble rising from position 1 to position 2 pushes up a portion of the surface film as shown. In this position, the two surface layers are pictured as having ceased their approach toward each other because any nearer approach would cause them to merge and give a uniform concentration of the three layers: the two surfaces and the interior one of bulk concentration. The tendency to merge is opposed by the forces which produced the differences in concentration in the first place. The conditions represented in *B* are the same as in *A*, except that the surface concentration is less than the bulk concentration of the solution. If the upward thrust of the rising bubble is insufficient to overcome the resistance to mixing of the surface layers, a spherical film is formed. A foam is a mass of such spherical films.

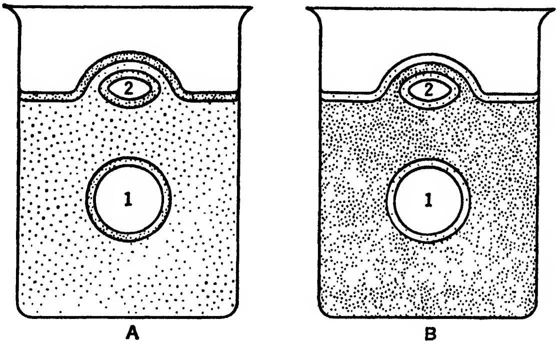

FIG. 108. Diagram of the balanced-layer mechanism of foam formation (Foulk).

This so-called balanced-layer mechanism of foam formation emphasizes the necessity of a surface film and explains, therefore, the absence of foaming tendency in a pure liquid. In a masterful fashion Foulk[7] has defended his balanced-layer theory of film formation against the criticisms of Hazelhurst and Neville.[4]

Foam Formers

Molecular solutions. To determine foam stability Bartsch[8] measured the duration of the foam which results on shaking 10 ml of solution in a cylindrical vessel 25 cm long and 1.5 cm inside diameter.

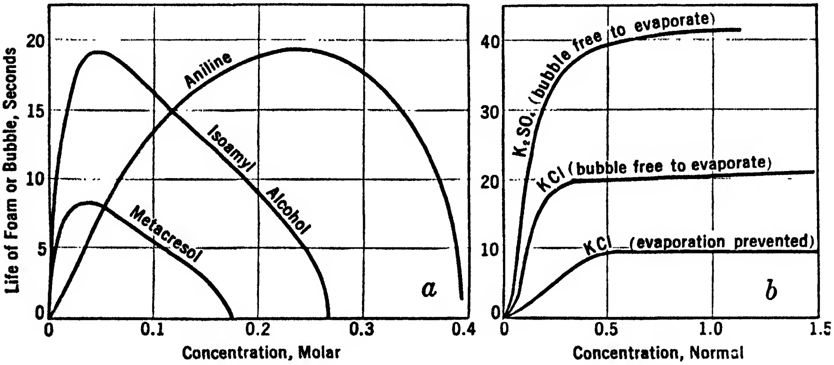

FIG. 109. Influence of dissolved solutes on the stability of foams and bubbles.

Talmud,[9] on the other hand, blew individual bubbles 1.5 mm in diameter by passing air through a capillary tube under the solution and measured the time a bubble rested on the surface. The two methods give similar results. Solutions of inorganic salts give such instable foams that Foulk[6] determines their foaminess by means of a dynamic foam meter which consists essentially of an arrangement for blowing air through a porous septum into the bottom of a column of solution. The height of the resulting foam collar measures the foaminess of the liquid.[10]

Aqueous solutions exhibit an optimum concentration for giving the most stable foam or bubble. This is illustrated in Fig. 109*a*, for three different solutions. The stability range is fairly broad, and the maximum stability is frequently attained at relatively low concentrations. This is illustrated further in Table 66 which records the maximum duration D of the foam obtained with a number of alcohols and acids, and the optimum concentration C and surface tension γ at the optimum concentration for giving the most stable foams. It is rather surprising that the critical concentrations of the several solutions possess surface tensions which are not far apart. So far as these observations go, however, it appears that the solutions with the lowest surface tensions tend to give the most durable foams.

Inorganic electrolytes which raise the surface tension give stability curves which flatten out at higher concentrations. This is illustrated by some of Talmud's results, shown graphically in Fig. 109*b*. The two curves for the life of bubbles obtained in potassium chloride solution show that the stability is increased when the solvent is allowed to evaporate from the bubble wall.

TABLE 66

FOAM-FORMING PROPERTIES OF SOLUTIONS

Aqueous solutions of	D (sec)	C (mole/l)	γ (dynes/cm)
Ethyl alcohol	5	0.28	66
Propyl alcohol	11	0.32	56
Isobutyl alcohol	12	0.09	56
Isoamyl alcohol	17	0.036	54
Tertiary amyl alcohol	10	0.034	61
Heptyl alcohol	8	0.0007	68
Octyl alcohol	5	0.0003	64
Formic acid	4	0.45	70
Acetic acid	8	0.20	69
Propionic acid	11	0.25	61
Butyric acid	18	1.00	33
Valeric acid	9	0.015	64
Caproic acid	13	0.0075	57
Heptylic acid	16	0.0015	60
Caprylic acid	12	0.00025	66
Nonylic acid	5	0.00007	70
Benzyl alcohol	10	0.10	59
Meta-cresol	9	0.025	62
Anilin	11	0.10	62
Para-toluidine	6	0.04	63

Talmud attributes the varying stability of foams formed with different solutions to the size, solubility, and degree of orientation of solute molecules in the film and to the degree of hydration of the polar groups in the molecules.

Colloidal solutions. Foams formed with molecular solutions are relatively instable. For a fairly permanent foam, the film must be sufficiently viscous in itself or must be stabilized by introducing finely divided solids into the interface. Many hydrophilic colloids such as soaps, saponin, and proteins give copious and quite stable foams. Johlin[11] found that 0.019 *N* sodium oleate gives the longest-lived foam, and this concentration causes the greatest lowering of the surface tension of such solutions. Preston and Richardson[12] showed, however, that unknown factors in addition to surface tension and surface viscosity determine the foaming power of soap solutions. The stability of such foams is due in part to the colloidal acid soap which concentrates in the interface.[13] The addition of glycerol which is frequently recommended for making good soap-bubble solutions is said to act by increasing the viscosity of the liquid and by making the films soft and flexible. Dewar[14] kept soap bubbles for long periods by maintaining the conditions constant. A black horizontal film 20 cm in diameter lasted more than a year (a black film is too thin, 5–15 mμ, to give colors by interference); a corresponding bubble lasted 95 days. Bubbles 4.0 ft in diameter were blown, but these lasted only a few hours.

The surface viscosity of saponin solutions is several hundred times that of the bulk of the liquid, and such solutions give quite stable froths because of the rigidity of the bubble walls. In carbon dioxide fire extinguishers, carbon dioxide is generated by the action of solutions of aluminum sulfate and sodium bicarbonate in the presence of saponin or an extract of licorice root.[15] A froth of carbon dioxide stabilized by hydrous aluminum oxide and saponin or licorice extract serves to extinguish the fire. Ferric acetate solutions give stable froths because of hydrolysis with the liberation of acetic acid, a froth former, and of hydrous ferric oxide which is adsorbed at the interface and stabilizes the froth.

As we have seen, protein may concentrate at the surface of a protein sol to such an extent that it is coagulated by shaking the sol (p. 305). Foams formed with protein sols may be quite stiff and permanent. Examples are meringues prepared from egg white, and "marshmallow" whips made from solutions of gelatin and sugar. The foaming power of gelatin sols varies with the *p*H value and is a maximum at the isoelectric point.[16] Beer gives a stable froth because of the presence of colloidal albumoses which concentrate in the interface.[17] Shaking a rennet solution cuts down its power to coagulate milk because the rennet concentrates at the surface. On the other hand, shaking does not inactivate a rennet solution containing saponin, since the saponin prevents the rennet from going into the interface.[2]

Foam Stabilizers

Finely divided materials that may or may not be of colloidal dimensions will stabilize foams provided that they will go to the interface and make a viscous film. As already mentioned, aqueous solutions of ethyl alcohol and acetic acid will foam, but the films are too fragile for the foam to last. A little lycopodium powder will stabilize the alcohol foam, and a little lampblack the acetic acid foam. Similarly, a small amount of clay added to a sodium oleate solution which is too dilute in itself to lather will yield a persistent froth on shaking.[18]

The amount of solid which concentrates in the foam film and the stability of the resulting foam depend on the nature of the solid particles, the degree of subdivision of the particles, and the concentration of the solution. Bartsch [8] found that the stability of an isoamyl alcohol foam was not changed by such materials as feldspar and quartz which do not go into the interface; whereas sulfide ores such as zinc blende, molybdenite, and galena which go into the interface have a marked stabilizing action. Foulk [7] has observed that finely divided silica cuts down the foaminess of sodium chloride solutions. Although silica does not go into the interface, it might not be expected to increase the foaminess of sodium chloride solutions, but it is not immediately obvious why it should decrease film formation in such solutions. The degree of subdivision of the solid is very important. Galena particles may be ground sufficiently fine so that they will stabilize an isoamyl alcohol foam for several hours.

Collectors

If a small amount of insoluble oil such as oleic acid or kerosene is shaken with water, bubbles of air coated with a thin film of oil are formed. This film is not viscous enough to give a stable froth, but, if a pulverized sulfide ore is introduced into the mixture, the solid particles concentrate in the interface, giving a stable foam of "armored" bubbles. The Minerals Separation Company took out patents in 1905 for the flotation of ores by the use of a fraction of 1% of an oil, and millions of tons of ore are handled by this general process annually.[19] Better results are obtained by the use of an oil containing some soluble constituent which acts as a foam former in place of a straight insoluble oil. To illustrate: kerosene alone does not froth with water, and the foam formed by adding fine particles which are wet by kerosene is relatively instable; but if a small amount of cresol, a foam former, is dissolved in the water before adding the kerosene and solid particles, a fairly stable foam results.

Oils which are effective in carrying certain solid particles into the interface and making stable foams are called *collectors*. In flotation practice, essential oils containing high percentages of alcohols and ketones of the hydroaromatic series such as terpineol, menthol, eucalyptol, or borneol have proved quite satisfactory. Essential oils that are widely used include Australian eucalyptus oil, pine oil, and pine tar oil with or without the admixture of such substances as mineral oils, α-naphthylamine, and potassium xanthate. The essential thing is that both a suitable foam former and a suitable collector be present in the right proportion.

Selective adsorption is the mechanism whereby sulfide particles are concentrated in the foam in the technical ore-flotation process. The sulfide particles adsorb the collector and are carried into the interface, whereas the gangue material like feldspar and silica does not adsorb the collector and so is not carried up by the froth.[15] Colloidal foam formers such as gelatin, saponin, and soap cut down the amount of ore which concentrates in the foam in spite of the fact that such agents increase the frothing enormously. The reason is that the foam-forming colloids are adsorbed by the sulfide particles; this cuts down the adsorption of the collector and so decreases the amount of sulfide which goes into the foam.

FOAM PREVENTION AND DESTRUCTION

In certain laboratory and technical processes, foam formation is so troublesome that methods of controlling it are quite important. In general, the life of a persistent foam is shortened by the addition of some material which gives fragile, short-lived films. The higher alcohols, especially caprylic, heptylic, and nonylic, are good foam eradicators; and isoamyl valeriate and mixtures of it with isoamyl alcohol exhibit a marked tendency to prevent foam formation. In making *p*H measurements on protein or tannin solutions with the hydrogen electrode, a trace of one of the higher alcohols will minimize the foaming. The protein and gummy substances in raw sugar give long-lived foams when shaken in water; in sugar analysis, such foams may be broken by a drop of ether. In concentrating maple sap by boiling, the foam may be broken by allowing it to come in contact with a piece of fat. The foam which results on boiling certain liquids may be destroyed by blowing over the surface a current of cold air or other gas which causes a sudden condensation of the vapor within the bubbles. The same procedure is said to break up the foams in yeast fermentation vats.

Foulk[6] made the interesting and important observation that the foaming of a solution of sodium sulfate which is negatively adsorbed at the interface is completely prevented by a trace of soap which is strongly positively adsorbed. This antagonistic action of positively and negatively adsorbed foam formers was found by Foulk to be a general phenomenon. He records the observation that a little soap prevented the formation of foams during the concentration of heavy brines worked up in the West for potassium salts.

In the evaporation of brines by boiling, marked foaming may take place as the concentration continues, because of the presence of traces of surface-active organic impurities. To prevent this at Deep Springs Valley, California, strips of lead fastened to the steel shell of the container were allowed to dip into the brine.[20] This served to eliminate the offending organic impurities, probably by oxidation with hypochlorous acid formed by electrolytic action between the lead and iron.

The foaming ("priming") of boiler waters is a major problem in steam engineering. The foaming is due in large measure to the dissolved salts such as sodium chloride and sodium sulfate, but the presence of finely divided solid matter—loose scale and sludge—may stabilize the foam to a certain extent. Foulk and coworkers[21] have made an extended study of the effect on boiler-water foaming of such solids as calcium carbonate, calcium phosphate, magnesium hydroxide, and the hydrous oxides of iron and aluminum. By working with one solid at a time, it was found that some materials increase the foam stability, whereas others either have no effect or decrease it. To illustrate, calcium carbonate produced in the boiler by the decomposition of the bicarbonate cut down the stability of the foam formed on solutions of sodium chloride or sodium sulfate; on the other hand, the precipitate formed by pumping sodium carbonate into calcium chloride in the boiler had no effect, and that produced by pumping calcium chloride into sodium carbonate increased the stability. Similarly, magnesium hydroxide precipitated by adding sodium hydroxide to magnesium chloride outside the boiler and pumped into the boiler increased greatly the foaming of the salt solutions, whereas the precipitate formed by adding magnesium salt to sodium hydroxide greatly reduced the foaming. Foulk suggests that the striking difference in the behavior of the precipitates formed by the two procedures may result from a difference in the sign of the charge on the particles, so that one type is attracted to the steam bubbles and the other is repelled by them. Another factor is the physical characteristics of the precipitates: calcium carbonate and magnesium hydroxide, like barium sulfate,[22] may differ appreciably in crystal size and physical structure, depending on which ion is in excess during the precipitation process. In line with this, Foulk[21] showed that a calcium carbonate which increased the foam stability when first formed lost this property after aging by several hours' contact with boiling water or by a few minutes' contact with water at high pressures (temperatures). This aging might be expected to cut down the foam-stabilizing power by increasing greatly the size of the primary crystals and hence the form of the agglomerates. It is not obvious, however, how a solid can reduce the foaming of a molecular solution unless it lowers the concentration of the solution by adsorption. In general, antifoams depend not only on their own nature but also on the nature of the foam-producing substance. Therefore, a given substance can be an antifoam towards foam-producing substance *A*, but not necessarily towards foam-producing substance *B*.

Castor oil is a good antifoam, cutting down or preventing foam formation in boilers; it is, therefore, not a collector of calcium carbonate sludge. "Blowing-down" is the practical method of keeping dispersed and suspended matter below the critical foaming point in steam boilers.

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PART V. AEROSOLS AND SOLID SOLS

CHAPTER 23

Aerosols: Smoke and Fog

Aerosols[1] are dispersed systems of solid or liquid in gaseous media. They include a variety of natural and artificial systems which are termed *smoke, dust, fog, cloud, mist, haze,* and *fume.* In general, smoke and dust are aerosols of solid in gas, whereas fog, cloud, and mist are aerosols of liquid in gas. But there is no sharp line of demarcation between the two. Thus smoke may contain both liquid and solid particles, and fog and cloud may result by condensation of vapors on solid nuclei. Whytlaw-Gray[2, 3] classifies aerosols on the basis of the volatility of the dispersed phase. The particles are nonvolatile in most dusts, smokes, and some industrial fogs such as tar fogs, whereas the particles are volatile in the majority of natural systems such as country fogs, clouds, and mists, in which the particles consist of water or of dilute aqueous solutions of hygroscopic nuclei.

Aerosols are much less stable systems than hydrosols. Thus, most dusts settle rather rapidly, smokes coagulate and settle out, and clouds and fog dissipate by evaporation. This instability results from the low density and low viscosity of the dispersion medium which offers but little resistance to the motion of the particles or to molecular diffusion.

DUST AND SMOKE

Formation

Aerosols, like hydrosols, are formed by processes of disintegration or dispersion and by condensation. Dusts are usually formed by dispersion methods, and smokes by condensation methods.

Dispersion methods. Air that has not been specially treated always contains particles of solid. In large cities the number of particles per cubic centimeter may be in the hundreds of thousands, and in the open country in the hundreds. In the cities these are derived largely from combustion processes, whereas in the open country they are chiefly dust particles from plowed fields and from roads, and particles of plant or animal origin, including pollen. Volcanic dust and cosmic dust may spread over wide areas. In recent years dust storms in Texas, Oklahoma, and Kansas picked up large amounts of surface soil in the form of dust and scattered it as far east as the Atlantic seaboard.

Solids may be disintegrated into dust by grinding, decrepitation, and explosive action. In ordinary grinding processes, it is said to be impossible to get particles smaller than about 10^{-4} cm. This accords with the fact that hydrosols are prepared with difficulty by the mechanical grinding of solids in water. The most prolific source of dust produced by man is the grinding operations such as those in the manufacture of flour, fertilizer, cement, coal, lime, chalk, gypsum, pigments, glass and pottery materials, rubber fillers, and meals. Other dusts are produced in the surface-grinding, polishing, and sand-blasting industries.

Certain crystals such as barytes and sodium chloride that contain liquid are disintegrated into fine dust particles on rapid heating, owing to the gas pressure developed in them. This process, known as *decrepitation,* may be used to separate a mineral such as barytes from non-decrepitating ones such as quartz, galena, and pyrites. A similar phenomenon takes place on releasing the pressure from a saturated solution of gas in a molten solid. This happens when molten lava saturated with steam at high pressure is suddenly thrown into the atmosphere. A noteworthy example[4] was the eruption of the volcano Krakatoa in 1883, which threw high into the atmosphere an enormous amount of very fine dust which was carried entirely around the world by the winds, forming a layer 5 to 15 miles above the earth's surface. Because most of the blue light was scattered by this enveloping cloud of fine particles, red light chiefly was transmitted. This manifested itself through the years 1884–5 by producing bright red sunsets which diminished slowly in brilliance as the dust settled to the earth. On account of the great distances which fine volcanic dust may travel, it may be confused with cosmic dust resulting from the burning of meteors in the earth's atmosphere.[5]

With the exception of volcanic eruptions, the most complete disintegration of solids is accomplished by the disruptive action of explosives. Familiar examples are the dust clouds raised by blasting in mining and quarrying operations. In the mining and handling of coal, large quantities and high concentrations of dust result not only during blasting but also in the subsequent screening operations. During World War I, toxic smokes were formed by exploding shells containing the poisonous materials.

Condensation methods. Smokes are formed by condensing the vapor of a high-boiling substance, diluting it rapidly, and cooling it with a large volume of air or other gas. They may also be prepared by chemical reactions at ordinary temperatures under suitable conditions.

The phenomenon of condensation of vapors, both in vacuum and in the presence of another gas, has been considered in connection with the preparation of hydrosols, especially by the arcing process (p. 148). In the preparation of smokes by the physical condensation method, great care must be taken in order to obtain reasonably reproducible aerosols. Whytlaw-Gray [3] obtained fairly satisfactory sols of stearic acid by heating the substance in a stream of air which was cooled rapidly by dilution with cold air in a large chamber. Aerosols of iodine, anthracene, acetanilide, diphenylamine, etc., may be prepared by a similar procedure. If the materials were evaporated directly into the chamber and distributed by stirring, the resulting aerosols coagulated at once to give non-uniform, coarser particles.

To prevent growth of particles, the cooling must be quite rapid. With substances of very low vapor pressure such as stearic acid, zinc, and arsenic, rapid cooling produces such a high degree of supersaturation that nuclei are precipitated rapidly throughout the mass of vapor. Slower cooling, on the other hand, results in growth on foreign nuclei or spontaneously formed nuclei to give relatively coarse particles.[6]

Smokes may be formed by the interaction of gases which give a solid at ordinary temperatures. A uniform, high degree of dispersion is obtained if thorough mixing can be accomplished before the gases react appreciably. For example, hydrogen sulfide and sulfur dioxide may be mixed and then exposed to light which speeds up the reaction with the formation of a uniform sulfur smoke. Ammonia and hydrogen chloride, which react immediately, give a smoke with coarser and less uniform degree of dispersion.

A highly dispersed, reproducible, and quite stable smoke for experimental purposes is best prepared by the photochemical decomposition of dilute iron carbonyl [$Fe(CO)_5$] vapor in air.[7]

In industry, true smokes occur chiefly in metallurgical operations in which metals or metallic oxides are volatilized by heat, as in the "distillation" of zinc, or as a result of unavoidable side reactions which occur in most smelting operations. Domestic and industrial flue smokes are not true smokes since they consist of both solid and liquid dispersions. The "blue haze" of forest fires and the "blue" smoke of cigarettes are true smokes resulting from combustion. Aitken [8] has shown that atmospheric haze is due entirely to very finely dispersed solid particles. The darker-colored smokes from combustion processes contain larger particles of carbon, coke, partly burned coal, tar, ash, water, etc. A true carbon smoke results from the complete thermal decomposition of hydrocarbons or other volatile carbon compounds which give no liquid products.

Properties

Stability. Aerosols differ from other colloidal systems in being comparatively instable. Volcanic dusts and atmospheric haze are the only solid-in-gas dispersions that have very long life. The stability results from their high degree of dispersion, their high dilution, and the effect of air currents. Stabilization of aerosols by the action of protecting colloids is conceivable theoretically but has not been accomplished practically. Moreover, the electrification of the particles is, in general, insufficient to keep them from colliding. Not more than 30% of the particles in ordinary smokes possess a charge. Fuchs[9] found that strongly charged monopolar aerosols do not aggregate; but the system has a tendency to expand, the particles migrating to the walls of the vessel where they lose their charge and remain attached.

The kinetics of the coagulation of smokes has been investigated by different workers whose results have been summarized by Whytlaw-Gray. With many smokes the coagulation process follows the simple law: $1/n_2 - 1/n_1 = K(t_2 - t_1)$, where n_1 and n_2 represent the number of particles present per cubic centimeter at times t_1 and t_2, and K is constant. The theory of coagulation worked out for sols by Smoluchowski (p. 278) has to be modified somewhat, because the sizes of the dispersed particles are comparable with the mean free path of the molecules in the gaseous medium, and because the mobility defined by Stokes's law does not take into account the discontinuous nature of the surrounding gas. The coagulation constant K for a homogeneous smoke is found to be:

$$K = \frac{4}{3}\frac{RT}{\eta N}\left(1 + A\frac{l}{r}\right)$$

where R is the gas constant; T, the absolute temperature; N, the Avogadro number; η, the viscosity of the medium; l, the mean free path of the gas molecules; r, the radius of the particles; and A, a constant.

The Smoluchowski theory appears to apply very well to smokes if they approach the ideal conditions of being uniformly sized spheres which coagulate to form progressively larger spheres. The real problem is to prepare a suitable, uniformly dispersed smoke; the stearic acid and ferric oxide smokes, above referred to, approach ideal smokes when properly made. As already pointed out, the ordinary domestic and factory smokes are highly heterogeneous in composition and particle size, consisting of loosely built aggregates of microscopic dimensions or of irregular chains made up of small units.

Dusts, in general, consist of larger particles and settle more rapidly than smokes. Moreover, the number concentration in typical dust systems is usually low: but, on account of the particle size, they reflect light and show a high optical density. The larger particles collide and stick together, forming complexes, but the process is so slow that it plays only a minor rôle in the life history of most dusts.

Optical properties. Smokes show the Tyndall phenomenon even when very dilute. The blue of tobacco smoke and the blue haze are a Tyndall blue. Reference has been made in Chapter 12 (p. 176) to the Tyndallmeter, a form of ultramicroscope for quantitative investigations on smokes.

The blue of the sky is attributed by Lord Rayleigh[10] to the scattering of the sun's rays by particles of dust, water, and ice, and even by the molecules of nitrogen and oxygen. Other color effects in the sky, apart from the blue, are likewise caused by the presence of solid and liquid particles. Twilights and sunsets would be less brilliant if it were not for dust motes in the atmosphere. A spectacular illustration of the effect of selective absorption by dust has been mentioned in connection with the color effects which followed the eruption of Krakatoa.

Photophoresis. Particles dispersed in a gas migrate under the influence of light rays. This phenomenon is called *photophoresis*. Particles of gold and silver dispersed in nitrogen and particles of camphor and turpentine dispersed in air are repelled by light, whereas sulfur and selenium particles in argon, and cigar and wood smokes, are attracted by light. Whether a particle will be attracted or repelled depends on its capacity to absorb or transmit radiant energy. With a strongly absorbing particle, the illuminated side will be heated more than the opposite side, so that the impact between the gas molecules and the heated surface will be greatest toward the light and the particle will move away. On the other hand, weakly absorbing particles will be heated more strongly on the side that is not illuminated, and such particles will move toward the source of light. Arrhenius[11] suggests that a considerable amount of very fine dust or smoke may be driven from the earth to the sun by the radiation pressure of the sun's light.

Particle charge. In considering the stability of ordinary solid-in-gas aerosols, it was mentioned that most of the particles may possess little or no charge. Those which do, derive the charge from coming in contact with gaseous ions originally present in the gas or formed during the preparation of the aerosol.

Dust blown about by the wind becomes electrified,[12] the sign of the charge depending on the chemical composition of the particles. Non-metallic elements and acid-forming oxides become positively charged, and metallic elements and basic oxides, negatively charged. Salt particles assume a positive or negative charge, depending on which ions they adsorb the more strongly.

The particles in neutral smokes may become charged by the action of ultraviolet light or by radioactive radiation. They may also be charged by placing them in an electric field of sufficient intensity (p. 367).

Inflammability. The rate of oxidation of a solid increases with its degree of subdivision. Accordingly, a combustible dust or smoke will burn with explosive violence if ignited under the proper conditions. Wheeler[13, 1] investigated the inflammability of a number of dusts obtained from factories in Great Britain. From the results of this work he grouped the dusts into three classes as follows:

Dusts belonging to the first class ignite easily (match flame) and propagate the flame readily. They include the following substances arranged roughly in the order of inflammability: sugar, dextrin, starch, rice, cork, soy bean, wood flour, malt, oat husk, flour-mill grain, maize, tea, compound cake, storage grain, rape seed, and chicory.

Dusts of the second class are ignited readily; but, for the propagation of the flame, they require a source of heat either of large size and high temperature (electric arc) or of long duration (Bunsen burner). Included in this class are: copal gum, leather, "dead" cork, cocoanut oil milling, rice milling, sawdust, castor meal, oil cake, grist milling, mustard, shoddy, and shellac.

Dusts of the third class are inflammable but do not propagate a flame under ordinary factory conditions. This class includes tobacco, spice milling, bone meal, coal (foundry blacking), lampblack, retort carbon, cotton seed, charcoal, brush carbon, and bone charcoal. It is, of course, well known that coal dust is explosive under suitable conditions. The coal dust examined by Wheeler was probably too coarse to propagate the flame. The explosive character of coal has been attributed to the rapid production of inflammable gas from the heated dust; but the explosion of dust-air mixtures may be initiated and maintained by direct combustion of the coal itself, if the particles are sufficiently fine.

The inflammability of dust clouds is made use of in powdered fuel[1] which may be projected into a furnace where it burns rapidly and completely.

Elimination of Dust and Smoke

Smokes and dusts have become a serious problem, especially in congested industrial areas. In 1916, 109.8 tons per month of solid matter were deposited from the air in the city of Pittsburgh, as compared with 59.6 tons in St. Louis and 52 tons in Cincinnati.[14] In 1936, 239 tons of solids per square mile were deposited in Glasgow; 683 tons in Liverpool; and 284 tons in London.[15] Since greater London occupies an area of 700 square miles, approximately 200,000 tons of solid matter fall on the city each year. When it is recalled that the polluted air in such typical industrial cities contains not only soot, tar, and ash, but sulfur dioxide and sulfuric acid as well, the seriousness of the problem is readily comprehended.

In smelting plants valuable materials may "go up in smoke" from the stacks; and in cement plants valuable potassium compounds are lost, to say nothing of the contamination of the surrounding air and the undesirable effect upon plants on which the particles fall.

In granite cutting, and to a certain extent in mining operations, highly dispersed siliceous dusts are formed. When large amounts of such dusts get into the lungs, a fatal disease called silicosis develops.

For purposes of cleanliness, economy, and health, it is desirable to avoid industrial pollution of atmospheric air. The methods that have been employed for the removal of suspended particles include: (1) sedimentation in large chambers, (2) centrifugal separation, (3) filtration through fabrics or other porous layers, (4) washing with water, (5) electrical precipitation. Sedimentation processes are effective only for removal of the larger particles. Filtration through fabrics is effective but is open to the disadvantage that the filtering area must be very large because of the low permeability of an effective medium and the increasing resistance which accompanies the deposition of a dust layer. Considerable difficulty was encountered during World War I in stopping highly dispersed toxic gases, such as diphenylchloroarsine, by filtration in gas masks. Washing of gases with water is a very effective way of removing from them suspended particles and objectionable fumes. This method is employed widely in gas works and to a certain extent in the treatment of flue gases. In air-conditioning plants, the control of humidity by water-spraying devices accomplishes the removal of suspended particles. Hay-fever patients find almost immediate relief on entering a room from which pollen is removed by "air conditioning." Electrical precipitation, which was suggested by Lodge[16] and put on a commercial basis by Cottrell,[17] is the most extensively used procedure for removing dispersed materials from gases.

The Cottrell process. The principle of the Cottrell process is as follows. If a needle-point electrode and a plate electrode are connected to the two sides of a high-potential, direct-current line, the air space between the electrodes becomes charged with electricity of the same sign as the needle point, irrespective of whether it is positive or negative; and an insulated body brought into this space receives a charge of the same sign. A floating particle receiving this charge will move to the plate at a rate proportional to its charge and the difference in potential between the electrodes.

In commercial practice, a direct current of 20,000–75,000 volts potential is applied to a system of electrodes in the stack containing the gases to be treated. For the plate electrodes any smooth conducting surface may be used, and for the point electrodes asbestos or mica is twisted up with wires or otherwise attached to suitable supports in such a way that the current has to pass only a short distance by surface leakage over them. Moisture or acid fumes settling on the electrode material effect the conduction. If the gases do not supply this coating, special treatment of the material is necessary before the electrodes are placed in the stack.

The Cottrell process has been very successful, especially in smelting plants and cement plants. To illustrate: At Anaconda, Montana, 76 tons of dust containing 42% As_2O_3 are collected daily in a stack 72 ft in diameter at the base and 572 ft high. At a single cement plant in Riverside, California, 350,000 tons of dust were collected during a 12-year period;[18] this installation saved the citrus orchards in the vicinity of the plant. Cottrell precipitators have proved quite successful in the removal of the various solid and liquid particles in flue gases from both industrial and domestic chimneys, but they do not remove gases such as sulfur dioxide. Suitable modifications of the apparatus have been made for determining in the laboratory[19] the concentration of smokes and for avoiding loss of dust when burning grain or other material in the process of analyzing it for iodine content.[20]

FOG AND CLOUD

Formation

A fog results whenever a vapor is saturated suddenly, so that more or less uniform condensation takes place throughout the mass. In the laboratory, fog formation is readily accomplished by allowing a jet of steam to emerge into a cooler atmosphere or by an adiabatic expansion which effects the cooling. In the latter process, if a volume of air V_1 previously saturated with water vapor at a temperature t_1 is expanded adiabatically to volume V_2, the expansion ratio (V_2/V_1) causes a lowering of the temperature from t_1 to t_2. In dust-free air saturated with water vapor, C. T. R. Wilson [21] observed no condensation until the expansion ratio reached 1.25 (supersaturation, $S = 4.2$), and a fine rain resulted. The same phenomenon took place until the expansion ratio reached 1.38 ($S = 7.5$), when a more or less dense fog was produced.

The formation of highly dispersed aerosols of liquid in gas is accomplished only in the presence of a large number of nuclei on which saturated vapors may condense. In both natural and laboratory fogs, the nuclei may consist of dust or smoke particles, very hygroscopic substances, or ions. In Wilson's experiments with dust-free air between $V_2/V_1 = 1.25$ and 1.38, the condensation nuclei are ions existing in the gas or produced by the sudden expansion. From 1.25 to 1.28, the negative ions in the air are the nuclei; from 1.31 to 1.34, the positive ions serve as centers of condensation. Since the number of such ions is small, the condensation results in a small number of relatively large drops—rain. At values of 1.38 and above, the ions of water itself supply the necessary nuclei, and a larger number of small particles precipitate to give a fog or cloud. The ionization of the air may be increased greatly by exposure to x-rays, cathode rays, radium emanation, ultraviolet light, spark discharge, or silent discharge. By exposing air saturated with water vapor to such sources of ions, dense fogs will result by adiabatic expansion, for $V_2/V_1 =$ 1.25–1.34 ($S = 4.2$–6.8), a range in which rain only will form in the absence of the foreign ions. This principle was utilized by Wilson [22] in the so-called fog-track apparatus for rendering visible the paths of single α- and β-particles passing through supersaturated air.

Ionic nuclei may result from a number of chemical reactions such as the oxidation of phosphorus and iodine, the interaction of ammonia and hydrochloric acid, and the decomposition of ozone. It is believed by Helmholtz and Richarz[23] that fog formation in the vicinity of these reacting materials is due to condensation on ions. Engler and Wild[24] claim, on the other hand, that phosphorus pentoxide, iodine pentoxide, and ammonium chloride smokes furnish the condensation nuclei for fogs in these cases, and Pringal[25] considers that the nuclei attributed to ozone are oxides of nitrogen. It is probable that both the ions and the dispersed reaction products serve as nuclei. The same is true when fumes are formed by the violent action of water with sulfuric acid, metallic sodium, or phosphorus pentoxide.

The precipitation of water on an ion as nucleus takes place, according to J. J. Thomson,[26] because electrification of a drop of liquid tends to decrease the vapor pressure.

The fumes resulting from the action of moist air on hydrochloric acid, phosphorus pentachloride, silicon tetrafluoride, arsenic trichloride, and stannic chloride, at ordinary temperature, do not contain charged particles.[27] The condensation takes place on highly hygroscopic particles of liquid or on solid reaction products.

Natural fogs are formed in clear but damp air when it is cooled to a temperature below its dew point. The necessary cooling is caused by: (*a*) the loss of heat to a clear sky by long-wave radiation from the ground at night, or (*b*) the motion of warm damp air into some region where the surface of the earth is cold. The condensation takes place to some extent on solid nuclei which are not hygroscopic, but more frequently fogs are formed by precipitation on nuclei of very hygroscopic materials. For example, sodium chloride and sulfuric acid nuclei take up water, giving solutions with very low vapor pressure, so that water is highly supersaturated in their presence and condenses out on them. Sea fogs doubtless result from condensation on nuclei derived from sea water, and many nuclei formed in the air everywhere are believed to come from the evaporation of droplets of sea water projected into it by breaking waves and carried far and wide by the winds. In addition to such condensation nuclei, domestic and industrial furnaces supply a variety of solid and semisolid particles as well as nitrous and nitric acids, ammonia, and sulfuric acid on which water vapor will precipitate. Sulfuric acid is a very active fog former, but, fortunately, not a great amount of it is present in the air. It will be recalled that sulfur trioxide carried into water or dilute sulfuric acid by an air stream is not appreciably absorbed but is converted into a mist that is stable to acids and alkalis.

The reason is that the sulfur trioxide vapor first comes in contact with water vapor rather than liquid and reacts with the vapor to give minute droplets of dilute sulfuric acid in the form of a fog. These droplets do not dissolve because they are insulated from the absorbing liquid by a gas film.[28] The successful absorption of sulfur trioxide is accomplished in a liquid having a very low vapor pressure, such as 98% H_2SO_4. Acetic anhydride, chlorine heptoxide, and nitrogen pentoxide act in the same way as sulfur trioxide.

Fogs are usually dispersions of water in air, but tar fogs in crude coal gas and coke-oven gas are obtained by the decomposition of coal. The nuclei are "carbon" particles on which liquid tar, together with water (solution of ammonium salts), condenses. Oil fogs are found in the exhaust from gasoline motors and are produced from the lubricants of gas compressors. In the manufacture of sulfuric acid (oleum), the waste gases carry droplets of the acid condensed on dust particles in the form of fog.

Properties

The limits of radius of fog droplets are set by Bennett[29] at 4×10^{-4} to 3×10^{-3} cm with a velocity of falling from 0.2 to 11 cm/sec; and the upper limit of radius of cloud drops at 1×10^{-2} cm with a velocity of falling of 121 cm/sec. This distinction between fog and cloud on the basis of particle size is more or less arbitrary. Bancroft[30] says that, for most purposes, it is sufficient to say that a cloud becomes a fog when one is in it.

Fogs and clouds are ordinarily dissipated by evaporation when the vapor pressure falls below the saturation value, but Frankland observed dense fogs around London when the degree of saturation was only 50–80%. Frankland explained the existence of these so-called dry fogs by a coating of oil from coal smoke around the drops, which retarded their evaporation. The presence of tarry or sooty matter in the air is responsible for the yellow to black color frequently observed in city fogs.

The droplets in industrial fogs, like the particles in dust and smoke, may be removed by electrical precipitation. Indeed, the sulfuric acid industry and the sulfide roasting industry were among the first to use the Cottrell process for destroying very persistent acid fogs.

Fog or mist may be broken up by forcing it through a series of small apertures and causing the stream to strike a flat surface.[31] The droplets are apparently brought into contact by this process and coalesce to larger drops which adhere to the flat surface. This method, which is the mechanical analog of the Cottrell electrical process, has been used for the separation of tar, carbon disulfide, etc., from coal gas.

The problem of the dissipation of natural fogs has received considerable attention in recent years, but little practical progress has been made. The most promising suggestions appear to be: (1) warm the fog sufficiently to evaporate the water droplets; (2) introduce a very hygroscopic substance such as calcium chloride into the fog, thereby removing sufficient water vapor to ensure subsequent evaporation of the droplets;[32] (3) coagulate the fog or cloud by scattering, from an airplane, sand charged electrically with the sign opposite to that on the cloud.[33] Fog and cloud elimination by these methods has not progressed beyond the experimental stage. Their utilization on a large scale is delayed because of the cost.

The concluding paragraphs of this chapter are quoted from a summary of Vincent J. Schaefer, giving an account of the most recent work of the General Electric Company on weather research.

"Considerable progress is being made toward reaching a better understanding of the factors related to the development of rain and snow in the atmosphere. The field of experimental meteorology received much attention in the fall of 1946 when a method was developed[34] to simulate natural supercooled clouds under controlled laboratory conditions. It was shown that a very small quantity of solid CO_2 introduced into a supercooled cloud could be used to trigger off the instability which is the inherent property of such clouds. Subsequent studies showed that at least 10^{16} ice crystals could be formed per gram of dry ice when it was put into air below 0°C which was supersaturated with respect to ice.

"It was demonstrated[35] that profound changes could be produced in supercooled natural clouds when dry ice was introduced into them. Dry ice produces ice crystals in clouds up to a temperature of 0°C. Subsequent developments showed[36] that silver iodide particles could also be used as a sublimation nuclei and ice crystals would form on them in clouds supercooled to a temperature between −4°C and −10°C. The critical temperature is apparently related to the particle size of the silver iodide, the larger particle being effective at the warmer temperature.

"A considerable variety of finely divided natural dusts have been found[37] to act as sublimation nuclei. These include clays, volcanic dust, and certain other finely divided particles which become airborne and then serve as active nuclei if the water-vapor content of the air containing them becomes supersaturated with respect to ice and the temperature reaches values between −15°C and −25°C.

"Unlike the effect produced by dry ice which requires that the ice crystals formed must remain in saturated air colder than 0°C, sublimation nuclei, such as silver iodide, certain clays, and similar active air-borne particles, can be introduced in warm air and will subsequently produce snow crystals whenever their environment becomes saturated with water vapor and cold enough for active sublimation to occur.

"Langmuir has advanced a theory[38] which explains in considerable detail the processes which probably are necessary to start the precipitation cycle in cumulus clouds. The theory shows that many actively growing cumulus clouds having a vertical development of a mile or more can be induced to shed their moisture earlier than normal by introducing a few large drops of water into the convective region. The drops grow rapidly, break apart, and these in turn grow to an unstable size (5 mm dia.) to produce more particles. This mechanism is a type of chain reaction and provides a good explanation for the sudden downpour that is a characteristic property of rain from cumulus clouds.

"Much activity is underway in the field of cloud physics and a much better understanding of the precipitation process and related weather phenomena may be expected within the next few years."

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CHAPTER 24

Solid Sols

SOLID DISPERSED IN SOLID

Colloidal systems of solid dispersed in a solid medium are frequently encountered in nature and are often synthesized in certain industrial operations. Blue rock salt, natural obsidians, black diamond, and certain gem stones are natural solid-in-solid systems, and such systems are of importance in such widely diversified arts as ceramics, photography, and metallurgy. A few examples will be considered briefly.

Glasses and Enamels

Many transparent colored glasses owe their color to colloidally dispersed substances, usually metals or their oxides. One of the earliest known of these is gold ruby glass first prepared by Kunkel in 1679 by adding purple of Cassius (p. 376) to molten glass. The ruby glass is readily obtained by melting a lead or barium glass and adding a small amount of gold as gold chloride. If the melt is cooled quickly, the glass will be colorless; but if cooled slowly, or if the cold glass is heated rapidly to a temperature well below the melting point, it assumes a beautiful clear red color. Ultramicroscopic observations of Zsigmondy and Siedentopf[1] showed that the red color is due to myriads of colloidal gold particles of the size to transmit red light. If the temperature is too high or the time of heating too long, the red color may change to violet and then to blue, owing to growth or agglomeration of particles. Similar color changes in gold hydrosols are well known. The addition of some stannous oxide to the glass acts as a protecting agent, retarding the transformation from red to blue on prolonged warming.[2]

The amount of gold in ruby glass is quite small, 0.01% giving a pink color and 0.1% a bright red. There are some billions of gold particles per cubic centimeter, the weight of the particles being of the order of 10^{-15} grain, and their diameter from 4 to 30 mμ. Rooksby[3] detected gold by x-rays in a glass containing 0.1% gold.

Cheaper forms of ruby glass, such as are used in danger signal lights, contain copper or selenium as the dispersed phase. Copper either as metal or oxide always gives green to greenish-blue tints when added to glass in the ordinary way. When the oxidation of the element is prevented by the presence of a reducing agent and the glass is cooled slowly or subjected to repeated heating followed by cooling, an intense ruby color is produced. Glasses with particles of quite widely different sizes are recognized technically. In the true ruby glass, the particles are of ultramicroscopic dimensions; in the opaque copper-red hematinon, they are microscopically visible; and in aventurine glass, they exist as spangles visible to the naked eye. From analogy with gold ruby glass, one would expect the color of the glass to be due to colloidal copper, and this has been confirmed by x-ray diffraction examination.[3]

Selenium imparts a red to pink color to moderately alkaline glasses, the color being a purer red with potash than with soda glasses. Most selenium ruby glass is now obtained by adding both selenium and cadmium sulfides and melting in a reducing atmosphere. X-ray examination shows the color to result from precipitation of a solid solution of CdS and CdSe.[3] In strongly alkaline melts, selenium gives a chestnut-brown color and the glass is optically empty.[4] Tellurium colors glass coral to purple-red in low concentrations, and a steel blue in higher concentrations.

The addition of silver to glass as a surface stain yields the beautiful yellow color which characterizes a silver hydrosol having the finest particles. For enamels, silver is added to the mass of the glaze and not as a surface stain. A yellow stain of silver on a cobalt-blue enamel gives a green. Bancroft[5] points out that this is the ceramic analog of the green tree-frog which has no green pigment whatsoever, the green color resulting from a structural blue overlaid with a yellow pigment.

Certain gem stones, both natural and synthetic, may owe their color to colloidally dispersed solid. The red color of the ruby (Al_2O_3) may be due wholly or in part to chromic oxide.[6] In support of this, Stillwell[7] showed that a red modification of chromic oxide exists which is stable in alumina to over 30%, and stable in most glasses only to about 1%. α-Alumina is colored red by chromic oxide, and β-alumina is colored green. Papish[6] analyzed some natural rubies and found too little chromic oxide to account for all the red color; a part of the color must therefore be due to iron in some form.

Enamels are vitreous materials which adhere by fusion to the surface of metals or pottery. The base of enamels is generally a colorless glass in which is suspended particles of an opaque metallic oxide or salt. The dispersed phase is usually stannic oxide, but titania, zirconia, arsenic trioxide, calcium phosphate, cryolite, and fluorspar have been substituted for stannic oxide. All these compounds are colorless, and their addition renders glass opaque owing to the difference in refractive index. Thus, natural stannic oxide has a much higher refractive index for yellow light than glass has. The addition of antimony oxide to a lead glass gives an opaque yellow product, the second phase being lead antimonate, sometimes called Naples yellow.

Opalescence in certain glasses is produced by the introduction of suitable amounts of arsenic trioxide, stannic oxide, calcium phosphate, cryolite, or mixtures of aluminum- and fluorine-bearing compounds. The phenomenon results from the presence of highly dispersed particles in the glass. Silverman[8] attributes the opalescence of aluminum-bearing glasses free from alkali chlorides or sulfates to the presence of finely divided, positively charged particles of colloidal alumina. The addition of alkali chlorides or sulfates to the fused melt causes agglomeration of the particles and produces alabaster glasses in which opalescence is no longer visible, the glasses transmitting white light instead of fiery light.

Colored Salts

Purple of Cassius is a colloidal dispersion of gold in stannic oxide. Similarly colored sols result by suspending such solids as magnesia, lime, barium sulfate, calcium sulfate, zinc oxide, or alumina in a dilute solution of chloroauric acid and reducing the gold salt, followed by drying and igniting the resulting products.[9] Colored crystals of alkali halides are likewise formed by adding gold chloride to the fused salts and allowing them to cool.[10] The color appears after solidification and changes on cooling, the final color depending on the rate of cooling and the nature of the salt, being red-violet with potassium chloride, blue to green with potassium bromide, and yellow with potassium iodide. Ultramicroscopic observation discloses that the color results from the presence of colloidal gold.

Blue sodium chloride. The beautiful deep-blue color of certain natural deposits of sodium chloride has been attributed to colloidally dispersed sodium in the crystals. In support of this theory, artificial preparations that are quite similar in appearance to the natural salt may be made by methods which depend on dispersing the alkali metal in colorless salt crystals. This is readily accomplished with both sodium and potassium salts by heating the thoroughly dried crystals with the vapors of the metal at temperatures 50–80° below the boiling point of the metal [11, 12] or by exposing the colorless crystals to radiations [13] such as cathode rays, x-rays, ultraviolet light, or radium emanation, under the influence of which the salt is dissociated into free metal and halogen. The metallic vapors condense to ultramicroscopic crystals, imparting a blue color to the salt. Siedentopf showed that the gaseous metal diffuses into clefts in the crystal and deposits there in ultramicroscopic needle- or platelike, and in part pleochroic, sodium crystals. On dissolving in water, the color disappears, and the solution possesses a slight alkaline reaction.

The natural blue rock salt differs from the synthetic product in certain respects: (1) the solution of the mineral is not alkaline as a rule; [14] (2) the mineral loses its color at 200–300°, whereas a salt colored with sodium vapors requires a temperature of 500° or more; [12] (3) spectrophotometric data [12] show that, quantitatively, there is a distinct difference in color between the natural and the synthetic product. A survey [15] of the known facts indicates that the color of blue rock salt may be due to colloidal sodium but that it is more often the result of distortion in the normal crystal lattice as a result of the formation of sodium atoms or displacement of electrons. Radium emanation combined with pressure probably accounts for the blue of many natural salts deposits.[16] In support of this belief, most of the natural blue rock salt has been found in Australia, a country rich in radium ore.

By electrolysis of fused salts such as sodium chloride, Lorenz and Eitel [17] obtained colored liquids which were believed to be dispersions of metal in the molten salt and hence were termed *pyrosols*. Ultramicroscopic observations on a lead pyrosol at temperatures above 500° indicate, however, that the lead is in molecular solution and not colloidally dispersed in the melt; [18] it is quite likely that the alkali metal pyrosols are also molecular solutions. The colored crystals formed on cooling down the pyrosols are probably colloidal dispersions.

Photohalides. Photohalides is the name given by Carey Lea to the colored products formed by the action of light on silver halides. Lea [19] was the first to prepare these substances by incomplete chemical reduction of silver halide with such reducing agents as ferrous oxalate and pyrogallol. The converse of this process, namely, the incomplete oxidation of silver by halogen, will also give photohalides. Thus

Baur[20] prepared a colloidal photochloride by treating a silver sol with an amount of chlorine water insufficient to effect complete oxidation.

Lea believed the photohalides to be lakes or adsorption compounds of the normal halide with a subhalide or an allotropic form of silver. It is now known that the subhalides assumed by Lea do not exist and that his allotropic silver is colloidal silver. Conclusive evidence that the photohalides are dispersions of silver in silver halide is given by methods of preparation in which silver halide is brought in direct contact with colloidal silver. For example, Lea boiled freshly precipitated silver chloride with finely divided silver and obtained a red precipitate. Similar preparations are obtained by allowing silver to act on molten silver chloride,[17] by allowing colloidal silver to act upon flakes of silver chloride,[21] and by allowing silver chloride to crystallize from an ammoniacal solution containing colloidal silver.[22]

The photohalides possess certain of the properties of silver hydrosol, such as their wide diversity of color and their strong coloring power even in low concentrations. Lea obtained photochlorides which he described as pale flesh, pale pink, rose, copper, red-purple, dark chocolate, and black in color. For a long time there was opposition to the view that the various colors were due to dispersed silver since the metal was dissolved out of the photohalide by nitric acid only with great difficulty. Lüppo-Cramer[23] showed, however, that the silver was dissolved out if the particles were quite fine, but that little or no silver was removed if the particles were sufficiently coarse. He demonstrated further that the silver in photobromides prepared by mutual coagulation of silver sol and silver bromide sol was protected by the silver bromide from the solvent action of nitric acid in much the same way as gold in purple of Cassius is protected by stannic oxide from the solvent action of mercury.

The elucidation of the nature of the photohalides is of particular importance for the theory of the photographic process. Thus, through the work of a number of people, notably Lorenz[17] and Lüppo-Cramer, it has been found that the so-called "latent image" is an early stage of photohalide formation and consists, therefore, of silver extremely highly dispersed in silver halide. The silver particles furnish the nuclei for the subsequent development by suitable chemical reducing agents.

Alloys

Alloys may contain colloidally dispersed particles of solid which influence their properties. Pure metals tend to be coarsely crystalline and brittle. The addition of suitable foreign substances, which may be colloidally dispersed, tends to give a finer-grained structure and a harder product. Cementite, Fe_3C, is believed to have a grain-refining action in ordinary steel, and a similar effect is attributed to other metals such as vanadium, tungsten, molybdenum, chromium, and nickel in alloy steels. Even in the presence of foreign metal or compounds, coarsely crystalline structures ordinarily result on slow cooling of metals. For this reason, rapid chilling or quenching is often necessary to get sufficiently fine crystals.

Ordinary carbon steels are highly important but exceedingly complex alloys in which colloidal dispersions of cementite in iron may occur. Because of its importance and in spite of its complexity, steel is chosen to illustrate colloidal behavior in alloys. Alexander[24] points out that drastically quenched tool steel treated with nitric acid does not separate out iron carbide but gives a complex mixture of hydrocarbons. From this, it is concluded that the Fe_3C is so finely dispersed that the nascent hydrogen and the carbon released by the action of the acid are within the range of molecular attraction, which is of the order of 50 $m\mu$, and that the Fe_3C is colloidal.

Drastically quenched steel is too brittle for practical uses and must therefore have its hardness reduced by tempering. This consists in reheating the steel and keeping it at certain temperatures for various times to give it the desired properties. As soon as the temperature of the steel is high enough, the agglomeration of the Fe_3C begins again at the point where it was stopped by the previous chilling. Metallurgists recognize several forms of iron-cementite dispersions. In Table 67, compiled by Alexander, these forms are arranged in the order of their formation on progressive cooling.

From x-ray examination of austenite, it appears that the carbon atoms are dispersed in the lattice spaces between the γ-iron (ferrite) atoms, giving an "interstitial solid solution" which enlarges the unit cell and produces lattice strain. Instead of a solid solution of carbon in γ-iron, austenite may consist of ionized Fe_3C in γ-iron. Two changes tend to take place on cooling the hot solution of carbon or Fe_3C in γ-iron: (1) γ-iron tends to go to α-iron, the lower-temperature modification; and (2) Fe_3C molecules are formed which aggregate, finally giving microscopically visible particles. The increase in viscosity with decreasing temperature slows down the rate at which these changes can take place; hence, the structure actually obtained depends on the composition and speed of chilling of the original mass and the subsequent tempering and forging. Hardened steel may therefore contain some of all the constituents recognized by the metallurgist. In martensite and troostite, the Fe_3C appears to be in a colloidal state of subdivision, whereas in sorbite and pearlite the sol particles have coagulated into aggregates larger than colloidal.

Hardenite and martensite are the hardest dispersions, the finer austenite and the coarser troostite, sorbite, and pearlite being softer. This may be an example of what Alexander[25] terms the zone of maximum colloidality, although the effect of the allotropic transformation cannot be overlooked. A similar phenomenon[26] takes place in the hardening of duralumin, an aluminum alloy containing 4% of Cu and 0.5% each of Mg and Mn. On heating at 500° long enough to ensure homogeneity of the system, followed by quenching and aging at room temperature, this alloy attains a maximum degree of hardness and then becomes softer again. This hardening results from the separation of $CuAl_2$ in the colloidal state from its supersaturated solution in aluminum. The hardness appears to depend on the amount of $CuAl_2$ formed and on a critical degree of dispersion.[27]

TABLE 67

NATURE OF STRUCTURES IN HEAT-TREATED STEEL

Iron-cementite dispersions			Microscopic appearance
Name *	Nature		
Austenite		Solid solution	Structureless streaks
Hardenite	↓ Increasing order of size	Colloidal	Structureless martensite
Martensite		Colloidal	Generally acicular, but varies; may be very fine
Troostite		Coagulation begun	Rounded or wooly (globulitic)
Sorbite		Coagulum	Fine pearlite, not readily microscopically resolvable
Pearlite		Coagulum	Laminated; may segregate into balls

* Hardenite is named for its intense hardness; pearlite for its pearly luster; the other dispersions are named after the metallurgists, Roberts-Austen, Martens, Troost, and Sorby, respectively.

The hardening action of cementite particles scattered through steel, and of $CuAl_2$ particles through duralumin, is believed by Jeffries and

Archer[27] to be a mechanical effect, the hard particles acting as *keys* which prevent motion along the slip planes as a whole.

From this brief survey, it would appear that the optimum dispersion of cementite in steel lies within, or just beyond, the colloidal zone. The proper tempering, therefore, requires considerable experience in the practical control of conditions. Manganese added to steel retards the coagulation of cementite sufficiently so that ordinary slow cooling gives martensite. The protecting action of tungsten is so great that "high-speed" tool steels containing this element maintain their hardness even when heated to low redness, at which temperatures ordinary tool steel loses its temper at once.

GAS DISPERSED IN SOLID

Colloidal dispersions of gas in solid are of frequent occurrence in nature. For example, volcanic ash[28] often consists of an obsidian glass filled with minute gas bubbles, so that large pieces will float on water. The blue color of many feathers is caused by the presence of minute bubbles in the horny part of the feather.[29] When the feather is viewed against a dark background, a blue results analogous to the blue of the sky. Both blue feathers and blue sky are due to suspended particles in a homogeneous medium; in the feathers, air bubbles are dispersed in a solid medium, and in the sky, solid or liquid particles are dispersed in a gas.

Floating soaps and bread contain gas suspended in a solid, but it is doubtful whether many of the bubbles are of colloidal dimensions. Aerogels (p. 323) are interlacing systems in which both the solid and gaseous phases are continuous. Meerschaum is a silicate mineral of this type. Porous silica gels occur as opals, as hydrophane, and as tabascheer.

Many crystals contain cavities filled with gas or liquid. Such crystals explode when the water is converted into steam by heating. This phenomenon of decrepitation has been discussed in connection with the preparation of solid aerosols and the separation of decrepitating from non-decrepitating minerals (p. 361).

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PART VI. APPLICATIONS OF COLLOID CHEMICAL PRINCIPLES TO CONTACT CATALYSIS AND DYEING

CHAPTER 25

Contact Catalysis

Contact catalysis deals with the chemistry of reactions at surfaces or at the interface between two phases. Since the reaction zone is larger the greater the extent of surface or interface, it is essential or advantageous in many cases to use the catalyst in the colloidal state in which there is a maximum extent of surface for unit mass of the catalyst. Thus platinum black is employed in the synthesis of sulfur trioxide from sulfur dioxide and oxygen, colloidal nickel reduced from the oxide in the hydrogenation of liquid fats, and a roughened, activated platinum gauze in the Ostwald process for the oxidation of ammonia to nitric acid.

The first portion of this chapter will be concerned with the general theory of catalytic action, and the last portion with a few applications of contact catalysis to technical processes.

THEORY OF CONTACT CATALYSIS

Specific Adsorption and Catalytic Activity

Most contact catalytic processes take place at a solid-fluid interface, and of these the larger proportion are at a solid-gas interface. In general, adsorption of one or more of the reactants is a necessary prerequisite for catalytic change. Langmuir[1] was the first to recognize clearly that catalytic activity results from primary or activated adsorption such as is frequently exhibited by active metallic adsorbents, and not to secondary or van der Waals adsorption (see Chapter 3). The increased concentration of the reactants as a result of adsorption is relatively unimportant as a rule. It is known that a mixture of oxygen and hydrogen is quite stable even under a pressure of 2000 atmospheres, which indicates that the marked action of platinum in catalyzing the combination is not due primarily to increase in concentration resulting from adsorption. Moreover, oxygen and hydrogen are adsorbed strongly by both platinum and carbon, but oxygen is much more active than hydrogen in catalyzing the combination of the gases.

If catalytic activity results chiefly from primary adsorption, as seems probable, one would not, in general, expect to find a parallelism between the observed total adsorption values and the catalytic activity of the adsorbent. This is well illustrated by some observations of Benton[2] on the adsorption of carbon monoxide, carbon dioxide, and oxygen by a number of oxide catalysts. A large difference was noted between the ratios of adsorption of carbon monoxide to carbon dioxide and of carbon monoxide to oxygen at 0° by the different catalysts. Assuming that in the case of silica the adsorption is wholly of the secondary type, the ratios furnish a means of distinguishing between the primary and secondary adsorptions (cf. Chapter 3). In Table 68 the several catalysts are arranged in the order of: I, total adsorption of carbon monoxide; II, secondary adsorption, calculated; III, primary adsorption; IV, observed catalytic activity in the combination of carbon monoxide and oxygen.[3] The tabulation shows the absence of any parallelism between total or secondary adsorption and catalytic activity;[4] on the other hand, the order for the primary adsorption of carbon monoxide and for the catalytic activity of the oxides is the same.

TABLE 68

COMPARISON OF ADSORPTION AND CATALYTIC ACTIVITY

	Order of catalysts
I. Total adsorption of CO	Co_2O_3 > hopcalite > SiO_2 > MnO_2 > CuO > Fe_2O_3 > V_2O_5
II. Secondary adsorption of CO (calculated)	SiO_2 > Fe_2O_3 > MnO_2 > Co_2O_3 > hopcalite > CuO > V_2O_5
III. Primary adsorption of CO	Co_2O_3 > hopcalite > CuO > MnO_2 > Fe_2O_3 > V_2O_5 > SiO_2
IV. Catalytic activity	Co_2O_3 > hopcalite > CuO > MnO_2 > Fe_2O_3 > V_2O_5 > SiO_2

The specificity of adsorption by metallic catalysts is shown in a striking way by some observations of Taylor and Burns.[5] Thus the ratios of adsorption of CO to CO_2 at 25° for several hydrogenation catalysts are: Cu = 10.0; Co = 3.6; Fe = 2.8; Pd = 288; Pt black = 10.6. Similarly, the ratios of adsorption of CO to H_2 are: Ni = 87 at 184°; Pt black = 3.3 at 110°; Cu = 12 at 25°. For oxide catalysts the adsorption ratios of CO to H_2 at $-79°$ are: hopcalite = 33; MnO_2 = 100; CuO = 34; Co_2O_3 = 19; Fe_2O_3 = 35; V_2O_5 = 17; SiO_2 = 28. The much stronger adsorption of carbon monoxide than of hydrogen by the oxide catalysts accounts for the preferential catalytic combination at oxide catalysts of carbon monoxide and oxygen in the presence of a large excess of hydrogen. With metals this preferential combination is less pronounced, the hydrogen being consumed with the carbon monoxide, especially at the surface of nickel and platinum. With copper, on the other hand, the adsorption ratio of carbon monoxide to hydrogen is larger, and a fair preferential combustion of carbon monoxide may be attained.

Mechanism of Activation by Adsorption

Contact catalysts in heterogeneous systems result from activation of one or more of the reactants as a result of oriented adsorption [1] or, possibly, multiple adsorption.[6] Activation by oriented adsorption consists in an alteration of the configuration of the adsorbed molecule or the opening up of primary valence bonds or secondary or residual valence bonds as a result of the primary valence forces on the surface of the catalyst. Since adsorption in this way does not usually lead to great molecular deformation, Burk [6] and Balandin [6] assume that activation results from suitable multiple adsorption, that is, the independent adsorption of the two ends of a molecule by active points on the catalytic surface. If these points are farther apart than the normal length of the molecule, sufficiently strong adsorption will cause stretching and distortion which are assumed to increase molecular reactivity.

Activation of elementary gases. Since monatomic hydrogen will reduce the same substances that catalytically active hydrogen will reduce, it is assumed that activated adsorption of hydrogen results in the formation of electrically neutral hydrogen atoms. Monatomic hydrogen does not react with nitrogen, and nickel is not a suitable catalyst for the synthesis of ammonia, although nickel is the most effective hydrogenation catalyst known. It is concluded, therefore, that an ammonia catalyst must contain some substance that activates nitrogen. The activated element is believed to be monatomic, electrically neutral nitrogen.[7] Taylor [8] is of the opinion that activation by adsorption of diatomic gases, generally, may consist in resolution into atoms, and that the adsorbed atoms are the active ones. Supporters of the multiple adsorption theory, on the other hand, believe that stretched molecules of hydrogen, say, may be more active than hydrogen atoms on the surface, since the bond catalyst —H would be stronger than the bond catalyst —H—H; hence the former would require activation for the hydrogen atoms to become reactive. From this point of view, an optimum degree of stretching of molecules would impart greater activity than complete resolution into atoms. Be that as it may, there is no doubt that active hydrogen which is atomic is formed by passing hydrogen containing small amounts of oxygen over platinum at temperatures below 120°.[9] This active, atomic hydrogen is instable but persists for a distance of 5 cm from the activating surface, reducing such substances as cupric oxide and the unsaturated group in olive oil. No such effect is obtained if the hydrogen is free from oxygen, indicating that the atomic hydrogen results from a reaction of hydrogen with oxygen at the platinum surface.

Specificity of catalytic action. Bancroft[10] points out that, theoretically, oriented adsorption of ethyl acetate might lead to three different reactions, depending on whether the ester is attached temporarily to the methyl group by one adsorbent, to the ethyl group by another, or to the carboxyl group by a third. In accord with this, Sabatier[11] claims that the action of alumina, titania, and thoria on ethyl acetate does give rise to three different sets of products. It is also known that ethyl alcohol decomposes in different ways at a nickel and an alumina catalyst:

$$C_2H_5OH \xrightarrow{Ni} CH_3CHO + H_2 \quad \text{and} \quad C_2H_5OH \xrightarrow{Al_2O_3} C_2H_4 + H_2O$$

With certain catalysts both reactions may take place simultaneously, giving varying amounts of C_2H_4 and H_2, as shown in Table 69.

Formic acid likewise undergoes decomposition in two different ways at nickel and at titania catalysts:

$$HCOOH \xrightarrow{Ni} H_2 + CO_2 \quad \text{and} \quad HCOOH \xrightarrow{TiO_2} H_2O + CO$$

Adkins and coworkers[12] showed that the method of preparation of oxide catalysts is just as important as, if not more important than, the particular metallic element in the oxide in determining the course which the reaction will follow. The conclusion is reached that the spacing of the surface atoms on the catalyst is the important thing, but it is not obvious why this should be unless one subscribes to the multiple adsorption theory of activation. Taylor[13] suggests that a catalytic oxide is a dual catalyst consisting of metal ion and oxygen ion, each having its own specific catalytic activity, the metal ion catalyzing hydrogenation and dehydrogenation processes, and the oxide ion, hydration and dehydration processes. Taylor[14] has given a more definite explanation of specific surface action in the catalytic decomposition of alcohol, as a result of his observation that a parallelism exists between the capacity of surfaces to induce dehydrogenation or dehydration, and the efficiency of such surfaces in promoting the recombination either of hydrogen atoms or of hydrogen atoms and hydroxyl radicals.

TABLE 69

Catalytic Decomposition of Ethyl Alcohol[11]

Catalyst	Composition of gas (%)		Catalyst	Composition of gas (%)		Catalyst	Composition of gas (%)	
	C_2H_4	H_2		C_2H_4	H_2		C_2H_4	H_2
ThO_2	100.0	trace	BeO	45.0	55.0	ZnO	5.0	95.0
Al_2O_3	98.5	1.5	ZrO_2	45.0	55.0	SnO *	0.0	100.0
W_2O_5	98.5	1.5	UO_2	24.0	76.0	CdO *	0.0	100.0
Cr_2O_3	91.0	9.0	MoO_5	23.0	77.0	MnO	0.0	100.0
SiO_2	84.0	16.0	Fe_2O_3	14.0	86.0	MgO	0.0	100.0
TiO_2	63.0	37.0	V_2O_5	9.0	91.0	Cu	0.0	100.0

* At beginning of run.

Intermediate compounds. In certain instances, contact catalysis is accompanied by the formation of definite intermediate compounds; indeed, Sabatier,[15] who has been an active worker in this field for 40 years, believes that the formation of intermediate compounds is a sufficient explanation of catalysis. In many catalytic processes, however, it seems altogether unlikely that any orthodox compounds could form as intermediate products; and in other cases, it is not obvious why intermediate compounds which are theoretically possible should be so reactive. Intermediate compounds appear to form, e.g., in the catalytic decomposition of hydrogen peroxide at a mercury surface;[16] when acetic acid is passed over heated barium carbonate;[17] and when carbon monoxide is oxidized in the presence of the mixed oxides of cobalt and nickel.[3] In the latter process, it is assumed that the oxygen carrier oxidizes the carbon monoxide and is, in turn, reoxidized by the oxygen of the air. This seems questionable, however, since the rate of oxidation of carbon monoxide by the higher oxides is relatively slow.

Poisoning of Catalyst

The term *poison* in contact catalysis is applied to anything that cuts down the velocity of a given catalytic reaction. Since the reaction takes place at the surface, a poison is anything that decreases the rate at which the substances reach the surface[18] or which prevents them from reaching it.[19] In general, any substance that is adsorbed more strongly than the reactants will cut down the adsorption of the latter and thereby slow down the reaction. Thus a small amount of carbon monoxide[20] reduces almost to zero the catalytic activity of platinum black on a mixture of ethylene and hydrogen. The poisoning results from the cutting down of the adsorption of hydrogen by the catalyst.[21] This phenomenon was investigated quantitatively by Pease and Stewart,[22] using a copper catalyst, with the results summarized in Fig. 110. It will be noted that but 0.05 ml of carbon monoxide will reduce by 88% the activity of a catalyst that adsorbs at less than 1 mm pressure, 1 ml of H_2, 2 ml of C_2H_4, and 5 ml of CO. Pease showed further that the vapor from 1 mm^3 of liquid mercury, introduced into 100 g reduced copper catalyst, inhibits completely the reaction between ethylene and hydrogen at 0° and renders it very slow even at 100°.

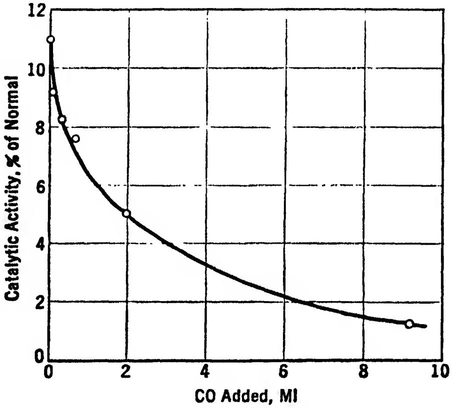

FIG. 110. Effect of carbon monoxide on the catalytic activity of copper.

In the decomposition of hydrogen peroxide solution by colloidal platinum, the catalyst is very susceptible to the action of poisons. For example, the addition to a given H_2O_2-Pt solution of $M/20,000,000$

HCN, $M/2{,}000{,}000$ $HgCl_2$, and $M/300{,}000$ H_2S reduces the rate of decomposition approximately one-half. Minute amounts of the same poisons likewise retard the hydrogen peroxide decomposition by enzymes such as hemase. Because of the analogous behavior, Bredig[23] termed colloidal metals *inorganic ferments*.

Autotoxic catalysis. If one or more of the reaction products is adsorbed so strongly on the active surface of the catalyst that the adsorption or rate of adsorption of the reactants is reduced, the process is known as *autotoxic catalysis*. Thus the accumulation of sulfur trioxide on the platinum surface in the contact sulfuric acid process slows down the reaction by cutting down the adsorption of sulfur dioxide and oxygen by the catalyst.[24] Similarly, adsorbed water slows down the catalytic dehydration of ether[25] and of alcohol,[26] and adsorbed hydrogen the catalytic dehydrogenation of alcohol. Indeed, nickel and copper are essentially dehydration catalysts in the absence of hydrogen, and hydrogenation catalysts in the presence of hydrogen. Hydrogen poisons a platinum wire for the catalytic decomposition of ammonia by the metal.[27]

Partially poisoned catalysts. Although the poisoning of catalysts is usually undesirable, Rosenmund and Zetsche[28] maintain that partial poisoning may be utilized to advantage in increasing the yield of certain products desired. For example, practically no benzaldehyde is formed on treating a solution of benzoyl chloride in pure benzene with hydrogen in the presence of colloidal platinum, but a good yield of benzaldehyde is obtained from the solution in ordinary benzene containing thiophene. It is claimed that pure benzene poisons the platinum completely, but the presence of thiophene partly counteracts this poisoning action, giving a suitable surface for the benzaldehyde synthesis.

In this connection, Adams[29] has shown that permanent poisons on the surface of catalysts may be employed to direct the catalysis. For example, the addition of ferrous chloride to a platinum catalyst promotes (see p. 392) the reduction of cinnamic acid to phenyl propyl alcohol, but, if the platinum-iron catalyst is poisoned to a suitable degree with zinc salts, the product is cinnamyl alcohol. The efficiency of the latter process varies with the extent of poisoning by the zinc salts.

The Nature of the Catalytic Surface

Non-uniformity of the catalytic surface. A great deal of experimental data tends to show that the surface of a catalyst is not uniformly active. As Taylor [30] points out, this is indicated in the first instance by observations on adsorption. For example, Hurst and Rideal [31] showed that the saturation capacity of a copper catalyst for carbon monoxide is 8.5 times as great as for hydrogen, and Maxted [32] found that mercury sols adsorb 3.5 times as many lead ions as mercury ions. If, at saturation, the surface is covered by a monomolecular layer of one substance, it is obvious that the surface is not covered by the second. One hypothesis is that the more strongly adsorbed substance is present in polymolecular layers, but it seems more reasonable to assume that the surface possesses variable adsorption capacity for different substances. This is indicated by the variation in the saturation ratio for adsorbed gases on different preparations of the same substances. Thus, as above noted, for the adsorption ratio of carbon monoxide to hydrogen on copper, Hurst and Rideal obtained the value 8.5 whereas Pease [33] got 2.86. Finally, the saturation ratio on the same preparation varies before and after heat treatment and before and after poisoning. Thus Pease showed that a copper catalyst poisoned with mercury changed the adsorption ratio of carbon monoxide to hydrogen from 2.86 to 19; heat treatment caused a change in the same direction.

Further indication of the non-uniform nature of the catalytic surface is furnished by a study of the action of poisons. Thus Pease and Stewart [22] found that adsorption of 0.05 ml of carbon monoxide on a copper catalyst, capable of adsorbing 1 ml of hydrogen at 1 mm pressure, reduced the rate of hydrogenation of ethylene by 90% and not by 3%, as the extent of adsorption would indicate. Apparently, all portions of the surface capable of adsorbing hydrogen are not equally effective in promoting catalytic hydrogenation; otherwise, the effect of the poison would be determined by the extent of surface it covers. More recently, Taylor and Liang [30] have confirmed the heterogeneity of the catalytic surface by techniques of measuring chemisorption of gases with increasing and decreasing temperatures at constant pressure.

Theory of the catalytic surface. From the above and other considerations, Taylor [30] proposed a theory of the catalytic surface that postulates the presence of active centers which are peaks of extralattice atoms of a relatively high degree of unsaturation. In a metal catalyst, "the surface of the granule may be regarded as composed of atoms in varied degree of saturation by neighboring atoms, varying from those one degree less saturated than interior atoms to those which are held to the solid surface by a single constraint." This theory of varying lattice saturation of the different faces of the crystal and of the edges, corners, and detached atoms of the particles accords well with the observations of adsorption and of the progressive changes in catalytic behavior under the influence of heat treatment and poisons.

Taylor's general concept of the nature of the catalytic surface has been a great stimulus to research in contact catalysis, and since its formulation it has been frequently adopted without question or has been modified to conform to the results of numerous investigations. To cite one example, Donnelly and Hinshelwood [34] found that the kinetics of the hydrogen-oxygen reaction on platinum, at atmospheric pressure, differs from Langmuir's results obtained at very low pressures. The differences are attributed to the presence of centers of varying activity on the catalytic surfaces. It is conceivable that, at very low pressures, most of the gas is adsorbed on the active centers which are relatively highly susceptible to poisons and may even be poisoned by too much of the reactant gas. At higher pressures, where the total adsorption is much greater, the larger proportion of the total reaction may be contributed by the less active centers because they are much more numerous and are less susceptible to poisoning.[35]

Although Taylor's concept of the catalytic surface has been useful, some investigators reject it or accept it with reservations. Thus Burk [6] points out that investigations on active centers do not necessarily lead to the conclusion that active centers are essential to catalytic activity [36] or that, when they exist, they are peaks of extra-lattice atoms, corners, edges, etc. Burk calls attention to the fact that the interface between minute crystals in a catalyst which must exist without assumption could and probably would serve just as well as the active centers assumed by Taylor. In this connection Bancroft [37] says: "Activation of charcoal by superheated steam would certainly take out the semi-detached atoms first and would not produce a good catalyst. Also, one does not see why a support should be so desirable for a catalyst if the active material is on a peak far from the support. The two essential features of Taylor's hypothesis are that only a small fraction of the catalytic surface is active and that the atoms or molecules are the semi-detached ones. Either of these assumptions may be true without the other one being true." In this connection Williams [38] points out that the catalytic activity of certain metals is directly associated with the orientation of the metal crystals with respect to the substrate. From this point of view, the active spots are due to a casual occurrence of metal crystals with suitable orientation. Catalysts may be formed in which all the crystals possess a single orientation and all spots are active.

Promoters. A *promoter* is a substance which, in itself, may possess but slight catalytic activity but which materially increases the activity of the catalyst to which it is added in relatively small amounts. If two substances are present in more or less equal quantities, the resulting product is called a *mixed catalyst;* if the non-catalytic material is in large excess, it is designated as a *catalyst support.*

Promoter action is a comparatively common phenomenon. Examples of promoted catalysts include the addition of: (1) molybdenum, tungsten, cerium, or, more especially, $K_2O—Al_2O_3$ or $Na_2O—Al_2O_3$ to active iron catalyst for the synthesis of ammonia; (2) bismuth, tungsten, or copper to active iron for the oxidation of ammonia; (3) copper or tellurium to nickel for the hydrogenation of oils; and (4) ceria to nickel for the hydrogenation of carbon monoxide and carbon dioxide to give methane. The mechanism of promoter action is not known definitely, but it is probable that the presence of the promoter increases or modifies the surface of the catalyst in some way. Taylor [35] suggests that the promoter acts by increasing the number of active centers as a result of an increase in the number of crystal faces, edges, and corners on the catalytic surface. Other assumptions are that the promoter acts: by furnishing an interface at which the reaction takes place, by increasing the velocity of activated adsorption,[39] by changing the ratio of adsorption of the two reacting gases,[40, 31] by activating one of the reacting substances which is not activated appreciably by the pure catalyst,[41] by decreasing the stability of an intermediate product,[42] by decreasing the adsorption of one of the reaction products below the point at which it has a poisoning action,[29] and by modifying the nature of the orientation of the crystals.

TECHNICAL APPLICATIONS

To illustrate the application of catalysis in industry, four technical catalytic processes will be considered briefly.

The Contact Sulfuric Acid Process

More than a century ago, Phillips obtained a patent for the use of spongy platinum as a catalyst for the oxidation of sulfur dioxide to trioxide. The process was not successful commercially because of the rapidity with which the catalytic material was poisoned. In 1875 Squire and Messel succeeded in making the process a technical success by using purified sulfur dioxide. Rapid development in the method did not come, however, until the opening years of the present century, when Knietsch [43] reported the results of his systematic investigations of the reaction velocities and the conditions of equilibrium in the reversible reaction: $2SO_2 + O_2 \rightleftharpoons 2SO_3 + 45{,}200$ calories. It was found that the most favorable temperature for the catalytic reaction with platinum is a little over 400°. Below this temperature, the velocity drops off rapidly, and much above this temperature, the equilibrium is displaced in the wrong direction since sulfur trioxide is decomposed to some extent at 500° and completely at 1000°. The results with platinum catalyst, under different conditions and with the less efficient burnt-pyrites and porcelain catalysts, are shown in Fig. 111. In these experiments, purified technical converter gas of the following composition was employed: $SO_2 = 7\%$; $O_2 = 10\%$; $N_2 = 83\%$. Curve I was obtained by passing the mixture over platinized asbestos at varying temperatures with a flow rate of 300 ml per minute; curve II with a flow rate of 30,000 ml per minute; and curve III using burnt-pyrites, Fe_2O_3 (CuO), as catalyst with a flow rate of 500 ml per minute. As the curves indicate, if the rate of flow is not too rapid the conversion at a platinum surface is almost 100% at a little above 400°. With pyrites, on the other hand, the reaction is too slow in the neighborhood of 400°; and, at the higher temperature of 550°, the conversion is less than 50%. Curve IV shows the low efficiency with broken porcelain as the catalytic agent.

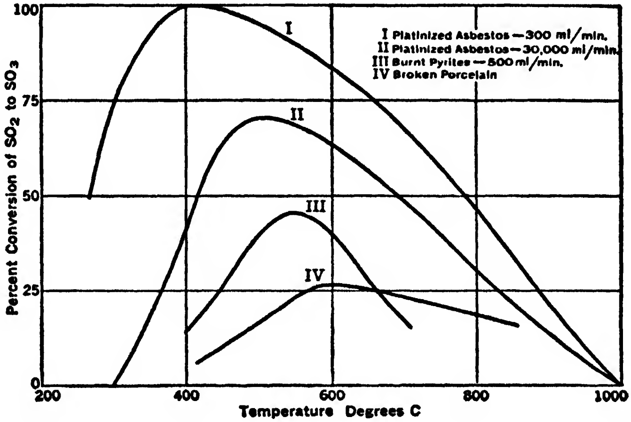

FIG. 111. Effect of temperature on the percentage conversion of sulfur dioxide to sulfur trioxide in contact with various catalysts.

An increase in the partial pressure of oxygen above the theoretical quantity necessary for complete conversion of sulfur dioxide to sulfur trioxide is desired, but there is a limit to the amount of air that may be admitted because of the diluting effect of the nitrogen. The optimum results are obtained when the quantity of excess air raises the oxygen content to the ratio $SO_2:O_2 = 2:3$, or 3 times the theoretical amount.

Because of the expense of platinum, a great deal of attention has been paid to obtaining the maximum yield with the smallest amount of contact material. To this end, the platinum black is precipitated on a support, usually asbestos,[44] silica gel,[45] or magnesium sulfate.[46] In general, the supporting material is impregnated with a platinum salt which is then reduced. In the widely used magnesium sulfate support, the partially calcined compound is sprayed with a solution of platinum salt and then heated in the presence of sulfur dioxide, thereby reducing the salt to platinum which is deposited as a thin film on the porous, dehydrated support. It is said that but 0.2 to 0.3% of platinum on the support gives an excellent contact material.[47]

One of the most serious problems in connection with the contact sulfuric acid process, using a platinum catalyst, results from the ease with which the catalyst is poisoned. Compounds of arsenic and mercury exhibit the most marked poisoning action, and compounds of selenium, antimony, bismuth, lead, tellurium, and zinc should not be present in any appreciable quantities. An amount of arsenic equal to but 1 or 2% of the platinum will frequently destroy the catalytic activity completely. It is therefore essential for the success of the technical process that the sulfur dioxide be freed practically completely from any arsenic that may be present, before it is brought in contact with the catalyst.

The most recent development in the preparation of sulfuric acid by the contact process consists in the substitution of vanadium compounds for platinum black. It has been known since 1895[48] that vanadium compounds will catalyze the sulfur dioxide oxidation, but they have come into technical use only in recent years, largely through the work of Jaeger and his associates. The contact masses contain as their active ingredients non-siliceous base-exchange bodies (p. 103) in which vanadium is present in the non-exchangeable nucleus. The presence of certain other compounds is said to promote the catalytic activity of the vanadium mixture. A typical method of forming the catalyst consists in adding a solution of ferric chloride or ferric sulfate to a solution of potassium vanadate in such amounts that the so-called ferric vanadate is precipitated. This is then incorporated in a gel by mixing with a solution of alkali silicate which is subsequently precipitated. Holmes and Elder[49] recommend that the iron-vanadium complex be peptized with excess ferric chloride before it is added to the water-glass solution, thereby obtaining a single precipitate consisting of catalyst, promoter, and support.

The Synthetic Ammonia Process

This process is based on the direct union of nitrogen and hydrogen in accord with the equation: $N_2 + 3H_2 \rightleftarrows 2NH_3 + 24{,}200$ calories.

TABLE 70

Equilibrium Data for Ammonia Synthesis

Temperature (degrees)	Per cent NH_3 at equilibrium at the following pressures (atmospheres)					
	1	30	50	100	300	1000
200	15.3	67.56	74.38	81.54	89.94	98.29
300	2.18	30.25	39.41	52.04	70.96	92.55
400	0.44	10.15	15.27	25.12	47.00	79.82
500	0.13	3.49	5.56	10.61	26.44	57.47
600	0.05	1.39	2.25	4.52	13.77	31.43
700	0.02	0.68	1.05	2.18	7.28	12.87

This reaction results in an equilibrium mixture, the composition of which varies with the temperature and pressure as shown by the data in Table 70, calculated from the experimental results obtained at the Fixed Nitrogen Research Laboratory.[50] It is apparent that the yield of ammonia should be highest at low temperatures, but the rate of the synthesis is so slow under these conditions that the process is useless technically. If the mixture is heated to 400–500°, so that the rate of synthesis is sufficiently great, the rate of decomposition of the resulting ammonia is so rapid that the equilibrium mixture contains less than 0.5% ammonia at 1 atmosphere pressure. Since the synthesis takes place with a decrease in pressure, raising the pressure increases the yield of ammonia.

The Haber process. The synthesis of ammonia was first realized technically by Haber,[51] who used a promoted iron catalyst at a temperature of 550° and a pressure of 200–250 atmospheres. The conversion efficiency under working conditions is in the neighborhood of 10%. This compels the adoption of a circulatory system in which the gases, after being freed from ammonia by absorption in water or by liquefaction, are returned to the incoming gases.

The most satisfactory contact material for the ammonia synthesis was developed by Larson[52] and his associates in the Fixed Nitrogen Research Laboratory. The catalyst which gives approximately 14% conversion efficiency at 450° and 100 atmospheres consists of reduced iron with K_2O and Al_2O_3 as promoters. The efficiency of the catalyst was found to depend both on the state of oxidation of the fused oxide from which it is obtained and on the nature and amount of promoter employed. The most active catalyst results by reduction of a fused iron oxide in which the ferrous:ferric ratio is 1:2 as required for Fe_3O_4. The best promoter is K_2O mixed with a somewhat acidic oxide, preferably Al_2O_3. K_2O alone reduces the conversion efficiency of pure iron, and Al_2O_3 alone raises it. The promoter probably acts both by retarding the sintering of the catalyst and by improving its quality.

The contact ammonia process is readily poisoned[53] by such substances as sulfur, selenium, tellurium, arsenic, boron, and their compounds; many organic compounds; lead, zinc, bismuth, tin; and oxygen, water vapor, and gaseous oxygen-containing materials such as carbon monoxide and carbon dioxide. Almquist and Black[54] showed that a catalyst poisoned by water vapor could be brought back to its original activity by displacement with the pure reactant gases. Oxygen held irreversibly was shown to be present as oxide formed as a result of interaction of a trace of water vapor with the active iron atoms on the catalytic surface.

The Claude process. The Claude process,[55] developed in France, differs from the German process in using temperatures of 600° and pressures of 800–1000 atmospheres. The maximum conversion claimed is 40%. No external heat need be applied after starting the process, and the bulk of the ammonia may be liquefied by cooling the gas, the residual ammonia with unchanged hydrogen being passed to a second catalytic unit where further conversion occurs. Thus, by placing a small number of catalytic units in series, an efficiency approaching 90% can be achieved without any circulatory plant.[56] Moreover, with the higher pressures, it is possible to use nitrogen-hydrogen mixtures of a somewhat lower order of purity. The high-pressure process introduces a number of technical difficulties, but these have been gradually overcome. In any event, the du Pont Ammonia Corporation is using the process exclusively.[57]

Mechanism. It is pretty generally believed that an iron nitride is formed as an intermediate product in the synthesis of ammonia at an iron catalyst. From a survey of the evidence, Emmett[58] suggests that the mechanism consists "in the reaction of nitrogen molecules with highly active surface iron atoms, forming some sort of surface nitride which, when brought into contact either with gaseous hydrogen molecules or possibly with hydrogen molecules adsorbed or momentarily combined with adjacent active iron atoms, will result in the formation of a surface NH or NH_2 group intermediate to the completion of the ammonia molecule."

Using deuterium as a "tracer element" in studying the mechanism of the ammonia synthesis, Taylor[59, 1] found more specifically that the synthesis involves the breaking of N—N bonds and H—H bonds and the making of N—H bonds. The making and breaking of H—H and D—D bonds were studied by following the rate of reaction between light and heavy hydrogen: $H_2 + D_2 \rightarrow 2HD$. This reaction was found to take place readily even at room temperature on promoted iron catalyst. The making and breaking of N—H bonds were followed by a reaction such as $NH_3 + D_2 \rightarrow NH_2D + HD$ which likewise takes place rapidly at room temperature on promoted iron catalyst. It appears therefore that the high temperature required in the synthetic ammonia process is due to the slowness of breaking N—N bonds. This conforms with the earlier observations of Emmett and Brunauer that no chemisorption of nitrogen by promoted iron catalyst takes place until the temperature is around 200°. When heavy nitrogen became available, a study was made of the making and breaking of N—N bonds in contact with various surfaces by following the reaction between light and heavy nitrogen. By means of a mass spectrograph, it was possible to follow the disappearance of masses 28 and 30 and the appearance of mass 29 with time. On iron catalyst this was slow in the temperature range of ammonia synthesis, whereas with the rarer osmium, the catalyst first used by Haber, it occurred freely even at 200°–300°C.

The Ostwald Nitric Acid Process

It was observed by Kuhlmann in 1839 that ammonia can be oxidized to nitric acid in the presence of platinum, but it was not until 1904 that Ostwald[60] put the process on a commercial basis. This process, in connection with the Haber ammonia synthesis, has given the world an inexhaustible source of nitric acid at a comparatively low price. These processes were the foundation of the chemical portion of the German war program in 1914.

The reactions involved in the Ostwald process are as follows:

$$4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O \qquad (1)$$

$$2NO + O_2 \rightarrow 2NO_2 \qquad (2)$$

$$3NO_2 + H_2O \rightarrow 2HNO_3 + NO \qquad (3)$$

The problem is complicated by the oxidation of some of the ammonia probably in the following way:[61]

$$4NH_3 + 6NO \rightarrow 5N_2 + 6H_2O \qquad (4)$$

Both reactions 1 and 4 are accelerated by platinum, but 1 takes place more rapidly than 4. The best results are obtained by keeping the reactants in contact with the catalyst as short a time as possible, which, Bancroft[62] points out, indicates that reaction 4 is a secondary and not a simultaneous reaction. If 1 and 4 took place simultaneously, the ratio of the products formed should be independent of the rate of flow.

In the technical process,[63] ammonia containing approximately 10 volumes of air, heated to approximately 300°, is passed through a converter consisting of cylinders made up of several layers of platinum gauze. For the best operation, the actual temperature of the gas is 1025°. The du Pont Company[64] has developed a plant, working at 7.8 atmospheres, in which a platinum-rhodium alloy is the catalyst. Pressure operation is made possible by the use of chrome-iron, which is not attacked appreciably by nitric acid.

In operations at atmospheric pressure, yields better than 90% of the theory from ammonia to 50% nitric acid can be obtained. Operation at 7.8 atmospheres gives equal or better yields of 60% acid. The increase in strength of the acid from 50 to 60% in the pressure synthesis halves the cost of concentration to 90% acid.[64]

Smooth platinum is not a good catalyst, but after being used for a time it becomes roughened and activated. When it is highly active, the period of contact with reactants need be no greater than 0.0006 second.[47] With platinum-rhodium catalyst, under operating conditions, the losses are said to be only one-half as great as with pure platinum.[63]

The platinum catalyst is poisoned by such substances as phosphine, acetylene, and hydrogen sulfide. An amount of phosphine as low as

0.00002% of the reactants reduces the yield 20%;[47] but an amount of acetylene up to 0.4%, and of hydrogen sulfide up to 0.07%, exerts no injurious effect on the catalyst.[65] Indeed, a small amount of hydrogen sulfide up to 0.07% inhibits[66] the poisoning action of phosphine and actually increases the conversion efficiency.[67, 65] Iron oxide, grease, oil, and tar have a marked poisoning action and must be avoided.

Sabatier's Hydrogenation Process

Isolated cases of hydrogenation in the presence of a catalyst were observed prior to 1897, but this date is significant since it marks the beginning of the systematic study of the phenomenon by Sabatier,[68] who developed it into a general hydrogenation process of wide applicability.[69, 53] Sabatier's work started with the observation that acetylene and ethylene combine with hydrogen in the presence of reduced nickel. This simple synthesis has been extended to include a large number of direct hydrogenations not only in the gaseous phase but in the liquid state as well.

The method of procedure employed by Sabatier and his collaborators, Senderens, Mailhe, Ipatieff, and others, is characterized by its simplicity, rapidity, and high yields. A mixture of pure hydrogen with the vapors of the material under investigation is passed through a tube containing the specific metallic catalyst maintained at a temperature commonly between 150 and 200°, and the products are collected in a suitable apparatus on their emergence from the tube.

As in all catalytic processes, the catalyst is of particular importance. The metals arranged in the order of their efficiency for hydrogenation are: nickel > cobalt > copper > platinum > iron. Of these, nickel when properly prepared (p. 27) is by far the most important.

The catalyst as well as the reactants must be pure. Traces of hydrogen sulfide, phosphine, arsine, and hydrogen chloride are active catalytic poisons. Electrolytic hydrogen, freed from traces of oxygen and moisture, is recommended. Under the most favorable circumstances, frequent renewal of the catalytic material is demanded because of gradual sintering or lowering of the catalytic activity due to poisons.

Sabatier classifies the hydrogenations in the presence of metallic catalysts under four headings which are given in order, with specific examples in the form of equations:

I. Reduction without fixation of hydrogen:

$$C_6H_5OH + H_2 \rightarrow H_2O + C_6H_6 \qquad (1)$$

$$CS_2 + 2H_2 \rightarrow 2H_2S + C \tag{2}$$

II. Reduction with simultaneous fixation of hydrogen:

$$2NO_2 + 7H_2 \rightarrow 2NH_3 + 4H_2O \tag{3}$$

$$RNO_2 + 3H_2 \rightarrow RNH_2 + 2H_2O \tag{4}$$

$$RCHO + H_2 \rightarrow R \cdot CH_2 \cdot OH \tag{5}$$

$$CO + 3H_2 \rightarrow CH_4 + H_2O \tag{6}$$

$$CO + 2H_2 \rightarrow CH_3OH \tag{7}$$

III. Fixation of hydrogen with unsaturated compounds:

$$C_2H_4 + H_2 \rightarrow C_2H_6 \tag{8}$$

$$CH_2{=}CHCH_2OH + H_2 \rightarrow CH_3 \cdot CH_2 \cdot CH_2 \cdot OH \tag{9}$$

$$C_{17}H_{33}COOH + H_2 \rightarrow C_{17}H_{35} \cdot COOH \tag{10}$$

$$C_6H_5OH + 3H_2 \rightarrow C_6H_{11}OH \tag{11}$$

IV. Hydrogenation accompanied by decomposition of the molecule:

$$(C_2H_5)_2O + H_2 \rightarrow C_2H_6 + C_2H_5OH \tag{12}$$

$$C_6H_5OR + H_2 \rightarrow C_6H_6 + ROH \tag{13}$$

Among the above are several reactions that lie at the basis of technical processes. Thus 5 may be used in the synthesis of alcohol from acetaldehyde, which in turn is made by the catalytic hydrogenation of acetylene; 6 is of importance in the technical production of methane from water gas;[69] 7, in the synthesis of methyl alcohol, using zinc oxide promoted with Cr_2O_3 as catalyst;[70] 10, in the hydrogenation of liquid oils to solid fats;[69, 71] and 11, in the preparation from phenol and *p*-cresol of cyclohexanol and *p*-methyl cyclohexanol, respectively, the starting point in the manufacture of isoprene and butadiene, the basis of synthetic rubber. For all the above reactions and reaction types except 7, nickel is probably the most satisfactory catalyst.

In the organic laboratory, sols of platinum and palladium dispersed in various solvents, such as water, alcohols, acetic acid, and hydrocarbons, are now quite generally used in the saturation of unsaturated organic substances. In general, protected sols are employed because of their greater stability, but the gain in stability is accompanied by a corresponding loss in catalytic efficiency.

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CHAPTER 26

Dyeing

Dyeing is the process by which a moderately fast color is imparted to a material by immersing it in a dye bath. All sorts of substances are dyed, but in a narrower sense the term dyeing refers only to the application of dyes on fibers. The dye bath is a molecular or colloidal solution of the dye. The bath is usually colored, but it may not be. Thus the indigo bath contains indigo white (reduced indigo), the blue color appearing after the indigo white is oxidized on the fiber.

Certain substances can be satisfactorily dyed by certain coloring matters only in the presence of what are known as *mordants*. In general, a mordant is a substance that is taken up strongly by a fiber and, in turn, takes up the dye strongly. In order to appreciate the importance of mordants in dyeing, one need but recall that Congo red, the first synthetic direct or substantive dye, was not discovered until 1884. Before this date it was impossible to dye cotton with acid or basic dyes except by means of mordants. Moreover, substantive dyes on cotton are in general much less fast to light and washing than the mordant colors.

The mechanism by which dyes are taken up by fibers and mordants is chiefly one of adsorption. In certain instances definite chemical compound formation or solid solution may predominate, but these constitute exceptions to the general rule. Because of wide variations in the nature of both fibers and dyes, the phenomena encountered in technical dyeing operations may be quite complicated, and many of them are not completely understood. A knowledge of the principles of colloid chemistry, however, has contributed greatly to an understanding of the dyeing process.

CLASSIFICATION OF DYES

Several classes of dyes are recognized by the dye industry.[1] In Table 71 are given the names of the various classes together with

TABLE 71

CLASSIFICATION OF DYES

Name	Distinctive characteristics	Examples
Basic	Salts of color bases that dye wool and silk direct; do not dye cotton satisfactorily without a mordant	Magenta, methylene blue, safranine, auramine
Acid	Salts of color acids that dye wool and silk direct; do not dye cotton without a mordant	Crystal ponceau, patent blue, erythrosin, eosin
Substantive (direct)	Salts of color acids that dye cotton direct; may also dye wool and silk	Congo red, purpuramine, curcumin S
Developed (diazotized)	Substantive color produced on the fibers by interaction of a diazotized base with an alkaline phenol or amine solution	*p*-Nitraniline red (diazotized *p*-nitranilin and β-naphthol), primuline red
Mordant	Do not dye wool, silk, or cotton in the absence of a mordant	Alizarin, chrome violet, alizarin black, coerulein
Vat	Reduction products are peptized by alkali and are then taken up by cotton in the absence of a mordant	Indigo, Tyrian purple, indanthrene blue
Sulfur	Reduced and peptized by Na_2S; dye cotton direct	Sulfur black, sulfur brown, direct sulfur blue
Miscellaneous	Organic dyes not belonging to the other classes; includes most of the natural dyes	Aniline black, logwood, quercitron, cochineal
Inorganic	Colored inorganic compounds produced on the fiber	Chrome yellow, Prussian blue, iron buff

a statement of the distinctive characteristics and typical examples of each. Under the conditions of use, the basic and acid dyes are more or less in molecular solution, whereas all the others are colloidally dispersed except the important mordant color, sodium alizarate or alizarin. The developed, vat, sulfur, and inorganic dyes may be considered substantive dyes since they dye cotton without a mordant; but since they possess other distinctive characteristics, it is simpler to classify them under different heads. In this brief survey of the dyeing process, consideration will be given to basic and acid dyes, substantive dyes, and mordant dyes, in the order named.

DYEING WITH BASIC AND ACID DYES

The basic and acid dyes are electrolytes which give true solutions in water. They dye both wool and silk directly, but in most instances they dye cotton satisfactorily only in the presence of a mordant. Wool and silk adsorb hydroxyl ion so strongly that, when they are dyed by basic dyes, there is a strong tendency for the color base to be adsorbed, leaving the acid in the bath; in other words, the adsorption is hydrolytic (p. 105). For example, in dyeing silk with rosaniline hydrochloride[2] all the red color-base is taken up by the fiber, leaving all the hydrochloric acid in the bath; with wool, a part of the acid is adsorbed; with silk, the tendency to adsorb the color base is so strong that the fiber may be dyed red from a colorless ammoniacal solution of the dye.[3] This behavior is the more remarkable in view of the fact that the color base is instable except when adsorbed on the fibers.[4] Acid dyes are generally used in acid solution which frees the dye acid that is taken up by the fiber. Crystal ponceau, however, is taken up as the acid salt from hydrochloric acid solution.[5]

The addition of acids, bases, and salts to solutions of acid and basic dyes influences their adsorption in accord with the rules for simultaneous adsorption from mixtures of electrolytes (p. 115). For the case at hand, these rules have been formulated by Pelet-Jolivet[6] and by Bancroft.[7] They may be summarized as follows:

1. Basic dyes (color in the cation) are taken up most strongly in an alkaline solution and least strongly in an acid solution.
2. Strongly adsorbed anions increase and strongly adsorbed cations decrease the amount of basic dyes taken up.
3. Acid dyes (color in the anion) are taken up most strongly in acid solution and least strongly in basic solution.
4. Strongly adsorbed cations increase and strongly adsorbed anions decrease the amount of acid dyes taken up.

Some observations of Briggs and Bull[8] illustrate the applicability of the rules for adsorption by wool of a typical basic dye, methylene blue, and a typical acid dye, lake scarlet ruby. One gram of wool was placed in 250 ml of a bath containing 75 mg of dye. After boiling 45 minutes, the dyed wool was removed, the *p*H value was determined, and the adsorption *x*/*m* was obtained from an analysis of the bath. The data are given in Tables 72 and 73. These results show that the adsorption of the basic dye is increased by increasing the *p*H value of the bath, whereas the adsorption of the acid dye is increased by decreasing the *p*H value. Sodium sulfate increases the adsorption of the basic dye and decreases the adsorption of the acid dye. At a given *p*H value, bivalent barium ion cuts down the adsorption of methylene blue more than the less strongly adsorbed sodium ion, and bivalent sulfate ion cuts down the adsorption of lake scarlet ruby more than the less strongly adsorbed chloride ion. The addition of sulfate to acid-dye baths which give up their color too rapidly has long been practiced by the commercial dyer. The sulfate tends to give a more even dyeing of the fabric by decreasing the adsorption as well as by retarding the rate of adsorption of the dye anion.

TABLE 72

ADSORPTION OF METHYLENE BLUE BY WOOL

0.1 *N* NaOH (ml)	Final *p*H	*x*/*m* (mg/g)	0.1 *N* NaOH (ml)	Final *p*H	*x*/*m* (mg/g)
0.0	4.50	4.0	+ 25 ml 0.1 *N* Na_2SO_4		
1.0	4.72	9.0	1.0	5.00	14.2
1.7	4.73	16.3	1.7	5.13	21.4
2.3	5.03	27.0	2.3	5.35	29.4
2.9	5.69	38.7	2.9	5.48	37.6
3.4	6.02	42.0	3.4	5.78	39.6
4.0	8.05	41.5	4.0	6.17	37.1
7.0	8.40	23.7			
10.0	9.81	11.9	+ 25 ml 0.1 *N* $BaCl_2$		
			1.0	4.80	4.3
+ 25 ml 0.1 *N* NaCl			1.7	4.96	8.4
1.0	4.80	6.4	2.8	5.05	10.8
1.7	4.80	11.6	4.0	5.35	15.6
2.3	5.12	17.1	6.0	5.50	17.0
2.9	5.29	21.4	8.0	6.06	17.6
3.4	5.66	28.9	10.0	6.70	28.5
4.0	6.18	46.9	12.0	7.61	32.3
			13.0	8.72	14.2

Apparent exceptions to the rules are frequently easy to explain. In Table 72, it will be noted that the adsorption of methylene blue falls off above a certain pH value. The reason is that the dye tends to become colloidal as the alkalinity of the bath increases (cf. p. 410). If the color base of a basic dye is instable or insoluble, one cannot use an alkaline solution; and if the color acid of an acid dye is instable or insoluble, one cannot use an acid solution. For example, the acid dye, alkali blue, is not used in acid solution because the dye acid is insoluble; but in an alkaline bath, less dye is adsorbed the higher the pH value in accord with the general rule.

TABLE 73

ADSORPTION OF LAKE SCARLET RUBY BY WOOL

0.1 N H_2SO_4 (ml)	Final pH	x/m	0.1 N HCl (ml)	Final pH	x/m
0.5	4.81	1.3	+ 25 ml 0.1 N NaCl		
1.0	4.40	10.6	0.5	4.90	10.0
1.5	4.13	28.1	1.0	4.55	20.9
2.0	3.84	40.9	1.5	4.15	35.7
2.8	3.50	57.5	2.2	3.77	49.1
4.5	3.14	65.8	3.3	3.28	65.9
			5.0	3.00	69.1
0.1 N H_3PO_4 (ml)					
1.2	4.98	10.8	+ 25 ml 0.1N Na_2SO_4		
2.5	4.55	22.6	0.5	4.55	8.6
4.2	4.25	39.0	1.0	4.05	18.9
5.5	3.93	48.6	2.0	3.80	31.0
7.0	3.62	47.8	3.0	3.36	44.0
8.8	3.45	64.6	5.0	2.88	54.5
12.5	3.11	68.7	8.0	2.70	62.0
20.0	2.75	73.9	15.0	2.37	68.5
			25.0	2.07	73.1

Because of the selective nature of adsorption, one might expect considerable variation in the tendency of acid and basic dyes to be adsorbed by wool and silk; and this proves to be the case.[8, 1] For example, azofuchsin G, naphthol yellow S, fast yellow, and indigo carmine dye wool strongly and silk very little or not at all; whereas rhodamine and new Victoria blue dye silk very strongly and wool only slightly. Between these extremes are azocarmine, fast acid violet A2R, azo yellow, fast acid violet 10B, patent blue A, and fast green, all of which dye the two fibers about equally well. In practice, satisfactory conditions for dyeing can usually be obtained by suitable adjustment of the *p*H value and the temperature. In general, silk is dyed more strongly relative to wool at lower temperatures and higher *p*H values. The basic dye, Victoria blue B, is adsorbed so strongly and therefore so rapidly from alkaline solution that an acid solution must be used to get satisfactory results with this dye.[8, 1]

DYEING WITH SUBSTANTIVE DYES

Direct or substantive dyes are salts of color acids, but, unlike acid dyes, they dye cotton as well as wool and silk directly. They differ from acid dyes also in being colloidal electrolytes, the anions aggregating to give colloidal micelles. Congo red, a typical substantive dye, is also a typical colloidal electrolyte, the constitution and properties of which were considered in an earlier chapter (p. 224).

Substantive dyes are taken up by fibers by adsorption from the colloidal dispersion, typical adsorption isotherms being obtained.[9] From neutral or alkaline solution, the dye salts are adsorbed as such,[10] whereas, from acid solutions, the color acid which is formed is taken up.

Briggs[11] recognizes that dyeing from such colloidal dispersions is a special case of the distribution of colloidal particles between an interface and the dispersion medium (pp. 74, 355). From this point of view, Briggs has formulated a special theory of substantive dyeing which emphasizes that the important factor in determining the adsorption is the stability of the dye sol. The addition of an electrolyte which tends to coagulate a dye will increase the adsorption, provided the dye remains colloidally dispersed; if the coagulation has gone too far, the fiber takes up less dye. Accordingly, the addition of a precipitating electrolyte will first increase to a maximum and then decrease the amount of dye adsorbed by the fiber. On the other hand, addition of a peptizing agent to the dye bath will decrease the amount of dye taken up by the fiber unless the peptizing agent is a second colloid which is itself strongly adsorbed by the fiber, i.e., a mordant.

In support of this theory, Briggs showed that the adsorption of such substantive dyes as Buffalo direct red and Erie red 4B is increased by sodium hydroxide, chloride, sulfate, or phosphate, the adsorption passing through a maximum with increasing concentration of electrolyte. The electrolytes below a certain concentration are therefore said to act as assistants toward the colloidal dyes. On the other hand, gelatin and albumin stabilize the dye and therefore act as restrainers, decreasing the adsorption. When both gelatin and salt are present in the dye bath, the assisting action of the salt is more or less neutralized by the restraining effect of the gelatin.

A dye salt that is partly in molecular solution and partly in true solution will behave toward electrolytes partly as an acid dye and partly as a substantive dye, one or the other behavior probably predominating.[11] Niagara violet appears to be a transition dye of this type; and methylene blue, ordinarily a basic dye, behaves like a colloidal dye when the pH value of the bath gets too high (p. 408).

The effect of addition agents on dyeing with substantive dyes has been summarized by Briggs as follows:

1. A substance which destabilizes the dye sol will act as an assistant up to the point of actual flocculation.
2. A substance which stabilizes the dye sol will act as a restrainer provided that it does not act as a mordant toward fiber and dye.
3. A stabilizing substance and a destabilizing substance may each exert their specific effects on the same dye bath.
4. Transition dyes exist which combine the characteristics of substantive dyes with their properties of acid or basic dyes.

MORDANT DYEING

Mordants[12] are substances which are adsorbed strongly by the fiber and, in turn, adsorb the dye strongly. In dyeing a mordanted cloth, it is usually the mordant rather than the fiber which adsorbs the dye. When a mordant adsorbs a dye in the absence of a fiber, the product is called a *lake*. The mordanting process and lake formation process will be considered separately in this section.

A typical example of a mordant dye is alizarin, the important coloring matter of the roots of *Rubia tinctorium*, or madder, a plant of Indian origin which was cultivated largely in France and Holland before the synthesis of alizarin from anthracene was accomplished in 1868. If a piece of cotton is dipped into an aqueous solution of alizarin, it assumes a yellow color that is easily removed by washing with soap and water; but if the cloth is first mordanted, it is dyed a fast color: red with alumina, reddish brown with chrome, orange with tin, and purple or black with iron. By treating the fiber with the so-called sulfonated oils before mordanting with alumina, there results the brilliant Turkey red, a color remarkable for its fastness to light and to the action of soap and water. The dyeing of Turkey red is a very ancient process, having been carried out centuries ago in India, using milk as fatty matter and *munjeet,* the Indian madder plant. The plant itself with its earthy incrustations furnished enough alumina to give the color lake. The art spread from the East through Persia and Turkey, reaching France and England in the latter part of the eighteenth century.

Wool, like cotton, can be dyed with madder only by the aid of mordants. The scarlet trousers of the French soldiers, introduced by Louis Philippe to encourage madder culture, and the scarlet uniform of the British soldier of Revolutionary War days were made possible by the use of the mordant alumina.

MORDANTS

Classification

Two classes of mordants are generally recognized: acid, and basic or metallic. The chief acid mordants are the tannins, albumin, certain fatty acids, such as oleic acid, sulfonated oils, and hydrous silica. The most important basic mordants are the hydrous oxides of chromium, aluminum, tin, and iron.

The Mordanting Process

When wool is boiled with a solution of alum or aluminum sulfate, some alumina and sulfate are fixed on the fiber. The nature of the process is indicated by some results of Paddon,[13] shown graphically in Fig. 112. Two-gram samples of well-washed wool were boiled for one hour in potash alum solution of varying strengths, after which the wool was removed and aliquot portions of the several baths were analyzed for both alumina and sulfate. The resulting curves are smooth and free from sudden breaks, indicating that the mordanting does not lead to the formation of definite compounds on the fiber but that the process is an adsorption phenomenon involving both alumina and sulfuric acid. It is probable that the acid is adsorbed by both the alumina and the fiber.

The maximum in the adsorption curve of alumina results from precipitation of some alumina by boiling the solutions of higher concentration, thereby cutting down the concentration of alumina so far as the wool is concerned.

Chrome, which is by far the most important mordant for wool, is not usually mordanted from sulfate solution but from sodium chromate solution in the presence of a salt of an easily reducible organic acid, such as sodium tartrate or lactate. This is equivalent to mordanting from a solution of chromium tartrate or lactate, and the resulting mordant is hydrous chromic oxide. Wool is seldom mordanted with iron (ferric oxide) or tin (stannic oxide).

Silk takes up the hydrous oxides less readily than wool; hence somewhat basic sulfate solutions are ordinarily used for the mordant bath. Silk treated with stannic chloride takes up 9–43% of SnO_2, depending on the concentration. The various combinations give x-radiograms of only SnO_2 and silk, indicating the absence of any crystalline compound of tin and protein. Silk is weighted by steeping it in a solution of stannic chloride and, after rinsing, putting it into a solution of sodium phosphate and subsequently into one of sodium silicate.

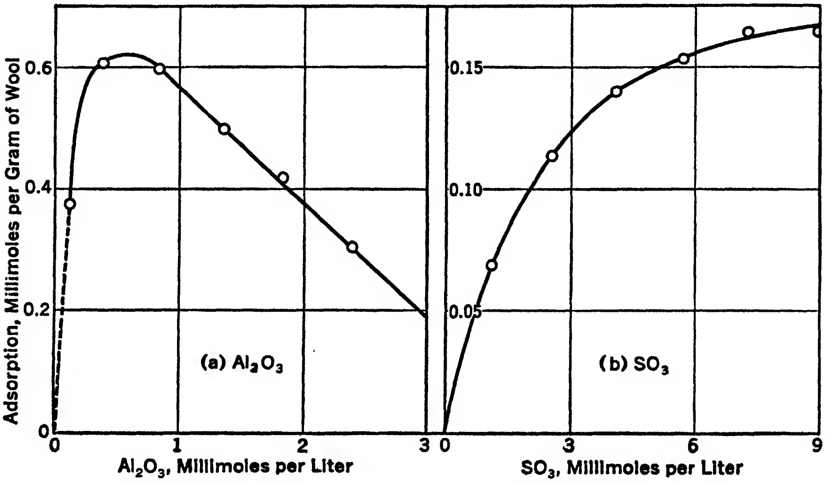

FIG. 112. Adsorption of Al_2O_3 and SO_3 by wool.

The adsorbing power of cotton for alumina is much less than that of silk, but it is possible to mordant cotton in either aluminum acetate solution or strongly basic alum solution. In mordanting cotton with iron, it is usually mordanted first with tannin followed by mordanting in ferrous sulfate solution and allowing the adsorbed ferrous hydroxide to oxidize.

Fibers are frequently mordanted with tannin, an important acid mordant. The course of the adsorption by wool and cotton under different conditions is shown in Fig. 113, constructed from data of Pelet-Jolivet[6] and Sanin.[14] Although tannin is strongly adsorbed by cotton, it is not held firmly and must be *fixed* before the dyeing process.

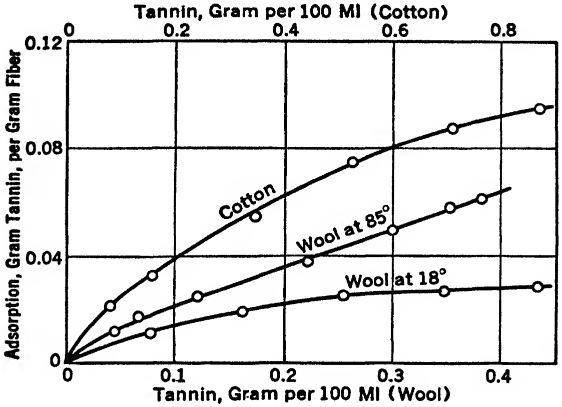

Fig. 113. Adsorption of tannin by wool and cotton.

Fixing

Any mordant which is not held sufficiently strongly by the fiber may be fixed by a suitable *fixing agent.* For example, sodium phosphate may be used for fixing alumina and tin; sodium arsenate, soap, and tannin for iron; sodium silicate and tannin for chrome and tin; alumina for sulfonated castor oil and other oil mordants; salts of antimony, tin, aluminum, and iron for tannin; substantive dyes such as chrysanine for basic dyes like methylene blue or safranine; etc. In other words, the acid mordants—tannin, fatty acid salts, arsenates, silicates, and phosphates—are used as fixing agents for the basic or metallic mordants, and the basic mordants are used as fixing agents for the acid mordants. It is possible that definite chemical compounds may form with certain mixtures, but in the vast majority of cases the fixing is due to the precipitation and adsorption of oppositely charged colloidal particles or to prevention of peptization by a strongly adsorbed ion.

COLOR LAKES

In the dyeing of mordanted cloth, the color is taken up chiefly by the mordant, giving a color lake on the fiber. The most common color lakes are formed with dyes and the hydrous oxides. For a long time, these were thought to be definite chemical compounds between the dye and the oxide. This belief was based largely on the observation that acid dyes are taken up to a great extent only by basic mordants and basic dyes only by acid mordants. It is now believed that, in many, if not most, instances, the dye is adsorbed by the hydrous oxide, and no definite chemical compound is formed. This is illustrated by some observations of Ackerman[15] shown graphically in Fig. 114. Since these typical curves are the same in form as those for the taking up of dyes by charcoal, they indicate the absence of chemical compound formation between dye and oxide, in these cases. Under certain conditions, the dye and oxide may combine to form definite compounds. For example, many mordant dyes, especially of the alizarin class, have been found to form chelate metallic compounds,[16] and others may form metallic salts of the dye anion.[17] It does not follow necessarily that the color lakes of these dyes are chelate compounds or salts. Certainly charcoal, which takes up most dyes strongly, does not form compounds with the dye ions.

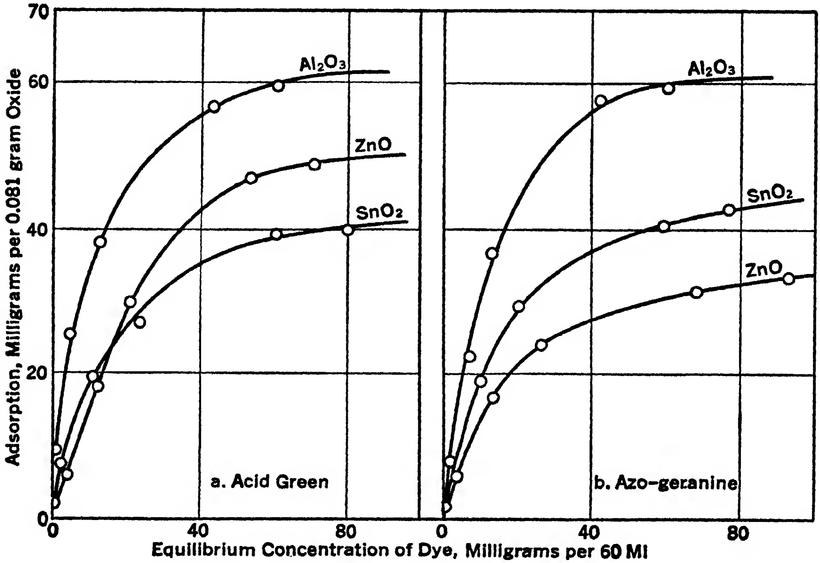

FIG. 114. Adsorption of dyes by hydrous oxides.

In the experiments summarized in Fig. 114, the concentration of the dyes was the only variable. Since the hydrogen-ion concentration is such an important factor in the fixing of dyes on fibers, it would be expected to influence the taking up of dyes by mordants.[17] Moreover, observations on adsorption of ions from mixtures of electrolytes would seem to indicate that the concentration of ions present in a dye bath, including hydrogen and hydroxyl, might be quite as important in determining the composition of a color lake as the concentration of the dye itself. Furthermore, the nature, physical character, and purity of the mordant would be expected to influence the composition of the lake. The importance of the several factors is strikingly illustrated in the alizarin lakes which will be considered in some detail.

The chief mordants for alizarin, the sodium salt of dihydroxyanthraquinone, are: alumina which ordinarily yields a red lake, chrome which yields a reddish brown, tin which gives an orange, and iron which gives a purple or black. Since alizarin dyes are taken up so strongly by the very highly dispersed hydrous chromic oxide, the observations with this adsorbent will be given.

Adsorption of Alizarin SW [18]

The sodium salt of alizarin monosulfonate is more suitable than alizarin for studying adsorption throughout a wide *p*H range, since the dye acid of the former is soluble and of the latter is insoluble.

Effect of the *p*H value. The results of a study of the adsorption of alizarin SW by chromic oxide, at varying *p*H values (cf. p. 117), are shown graphically in Fig. 115. For purposes of reference, the *p*H curve for the acid and alkali alone, in the same total quantity of water, is included in the figure. The length of a horizontal line drawn from any point on the curve for the *p*H of the mixture, "before adsorption" to the acid-alkali curve, gives the quantity of acid or base reacting with the dye at the point.

The adsorption curve is continuous, giving no indication of the formation of a compound at any *p*H value. As would be expected, quite a buffer effect is observed in the titration of the monosodium to the disodium salt. Moreover, there is a corresponding holding up of the adsorption-concentration curve in this region. This has two causes: the concentration of the hydroxyl ions is not increasing in proportion to the alkali added; and, at the same time, the concentration of the highly adsorbable dye ions is rapidly increasing. Just as was found with sulfate and with oxalate (p. 118), hydroxyl ion may completely displace the dye. A slightly higher concentration of hydroxyl ion is necessary for complete displacement of the dye than for complete displacement of either sulfate or oxalate. This indicates that the dye is more strongly adsorbed than either sulfate or oxalate, but not so strongly as hydroxyl.

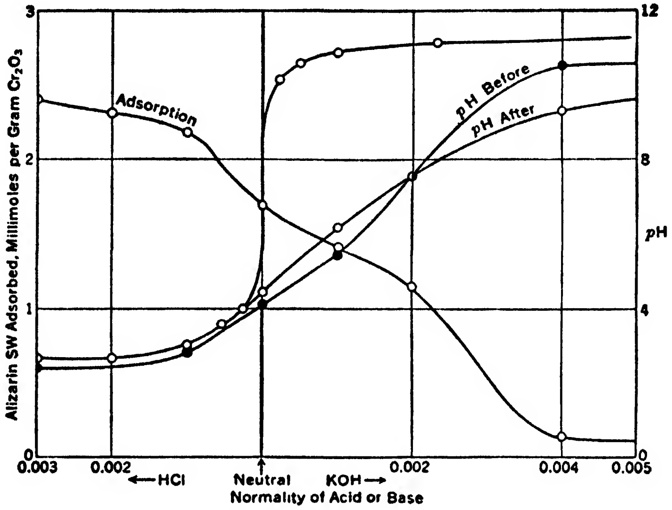

FIG. 115. Adsorption of alizarin SW by hydrous chromic oxide at varying *p*H values.

Simultaneous Adsorption of Alizarin SW and Other Ions

The effect of foreign ions on the adsorption of soluble dyes has already been described. Sulfate is frequently added to acid-dye baths which give up their color too rapidly, but a small amount of sulfate may be objectionable if the dye anion is not adsorbed sufficiently strongly. At one time Bancroft[7] believed that the purpose of adding calcium ion as calcium acetate to an alizarin bath is not to give a calcium aluminum alizarate or calcium chromium alizarate of some sort,[19] but to remove sulfate ion which cuts down the adsorption of alizarate ion. The difficulty with this explanation is that calcium sulfate is too soluble to account for the effect of calcium ion in this way.

Effect of sulfate at varying *p*H values. The effect of sulfate on the adsorption of alizarin SW at varying *p*H values was found by the same procedure used in determining the effect of sulfate on the adsorption of oxalate (p. 118). The data are summarized in Fig. 116. As in the case of oxalate, it will be noted that sulfate has little effect on the adsorption of alizarin SW anion in the neutral and basic solutions, since, under these conditions, the presence of the much more strongly adsorbed hydroxyl ion masks the relatively small effect of the sulfate. In the acid range, however, the effect of sulfate is quite marked. Since the dye anion is adsorbed more strongly than sulfate from the same concentration, one might expect sulfate to have little effect on the adsorption of the dye, but the behavior of the dye is similar to that of oxalate. In the acid solution, the effective concentration of the dye becomes very small because of the suppression of the ionization, and the action of sulfate manifests itself. If the sulfate adsorption has been determined in the series of experiments, the results would have been similar throughout to those obtained with sulfate and oxalate, viz., sulfate adsorbed more from the acid bath and dye adsorbed more

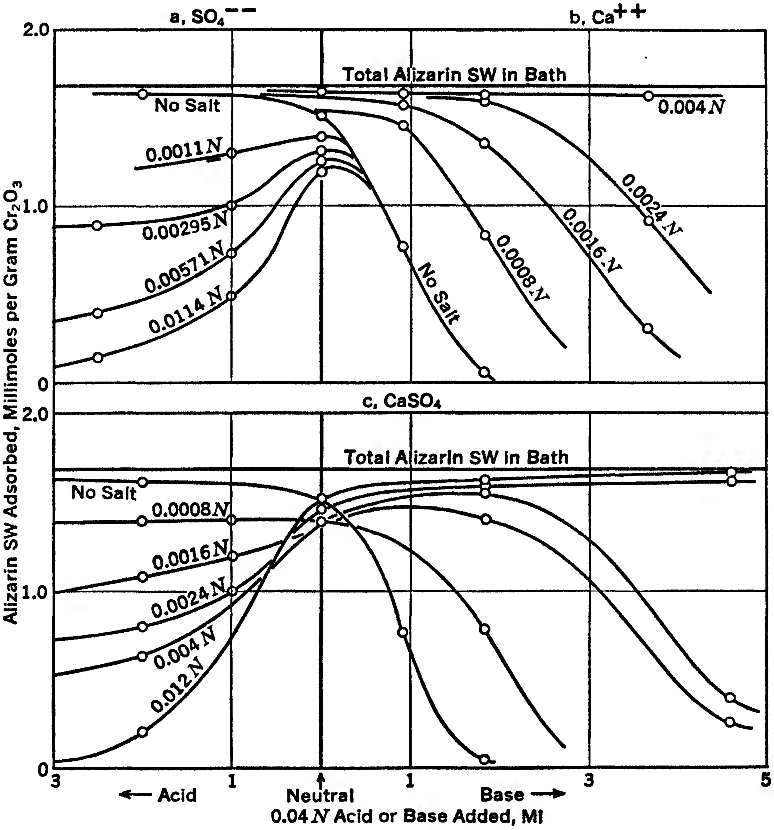

FIG. 116. Effect of sulfate and calcium ions on the adsorption of alizarin SW by hydrous chromic oxide at varying *p*H values.

from the neutral and the basic baths. Since acid baths are usually employed in dyeing with acid dyes, the retarding effect of sulfate is explained, even though the dye cation may be more strongly adsorbed than sulfate ion from the same concentration.

Effect of calcium ion at varying *p*H values. The results of the observation on the adsorption of alizarin SW in the presence of varying amounts of calcium ion, as well as of varying hydrogen-ion concentrations, are given in Fig. 116*b*. Just as the effect of sulfate ion is small in the presence of the relatively highly adsorbed hydroxyl ion, so the effect of calcium is small in the presence of the relatively strongly adsorbed hydrogen ion.

Effect of calcium sulfate at varying *p*H values. The foregoing experiments show that the effect of sulfate is large in the acid baths and negligible in the basic ones, and that the effectiveness of the calcium increases with the hydroxyl-ion concentration. One is led to conclude therefore that, if calcium sulfate were present, (1) the effect of sulfate would predominate in the acid solutions, and (2) the influence of calcium would be unaffected by sulfate in the basic baths. Direct experimental verification of these conclusions is given by the data plotted in Fig. 116*c*. If the curves *a*, *b*, and *c* are superimposed, it will be seen that *a* and *c* are alike in the acid range and *b* and *c* are alike in the basic range. These data show that the effects of the calcium and sulfate ions in the bath are practically independent of each other, and that each is dependent on the hydrogen-ion concentration.

Adsorption of Alizarin

Effect of calcium and sulfate ions at varying *p*H values. Sodium alizarate or alizarin is the dye used in commercial practice. The results of some observations of the effect of calcium and sulfate ions on the adsorption of alizarate ion from a sodium alizarate bath are given in Fig. 117. Since the bath must be basic in order for the dye to remain in solution, one would expect the effect of sulfate to be slight, as the observations show. On the other hand, the effect of calcium is marked and increases with its concentration. Hence, by the addition of a strongly adsorbed cation, one may use a slightly basic bath in which the alizarin is soluble and, at the same time, avoid the displacement of the dye anion by hydroxyl ion. This is the function of calcium ion in the formation of alizarin lakes on the fiber. That the effectiveness of calcium ion is not due to the direct precipitation of alizarin as calcium alizarate is evidenced by the fact that the quantity of calcium present may be greater than the equivalent of alizarin without the dye bath becoming exhausted. Moreover, the color of calcium alizarate is purple, and since the effect of calcium is to increase the red color by increasing the adsorption of alizarate ion, there is no justification for assuming the formation of purple calcium alizarate on the mordant.

From these observations on alizarin lakes and similar ones on the lakes of Congo red,[20] orange II,[21] and molybdenum blue,[22] the following conclusions were reached as regards the effect of the addition of salts on the lake-formation process:

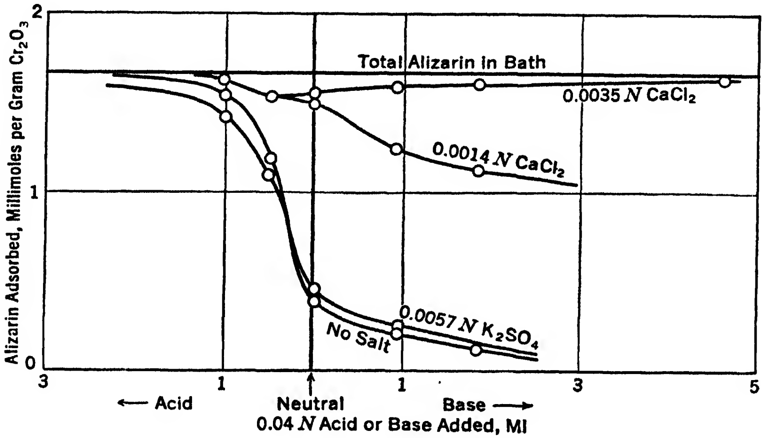

FIG. 117. Effect of sulfate and calcium ions on the adsorption of alizarin by hydrous chromic oxide at varying *p*H values.

1. The presence of a strongly adsorbed cation in the dye bath increases the rate and quantity of adsorption of acid dyes and has an opposite effect on basic dyes; the effect of the cation increases with increasing *p*H of the bath and with its own concentration.

2. The presence of a strongly adsorbed anion in the dye bath decreases the rate and quantity of adsorption of acid dyes and increases the rate and quantity of adsorption of basic dyes; the effectiveness of the anion increases with decreasing *p*H of the solution and with its own concentration.

3. If the dye bath is either acid or basic, the effects of foreign cations and anions are practically independent of each other, the influence of the cation predominating in the basic bath and of the anion in the acid bath.

Mechanism of the Formation of Alizarin Lakes

The alizarin lakes of the hydrous oxides are ordinarily formed by an exchange adsorption process in which the relatively strongly adsorbed alizarate ion displaces a more weakly adsorbed ion, such as chloride, from the hydrous oxide. Some experimental evidence in support of this conclusion is given in Chapter 7 (p. 102). If the adsorption capacity of the gel is satisfied with a strongly adsorbed anion such as hydroxyl, little exchange adsorption can take place, and lake formation is prevented. Since a bath must be slightly basic in order for alizarin to remain in solution, the necessary adsorption of alizarate ion for suitable lake formation from such baths takes place only in the presence of a relatively strongly adsorbed cation such as calcium.

Lakes are formed by the addition of sodium alizarate to positive hydrous oxide sols stabilized by preferential adsorption of hydrogen ion. If the accompanying anion is chloride, the amount of alizarate ion taken up by the coagulated oxide is equivalent to the amount of sodium chloride in the supernatant solution. The addition of sodium alizarate above the coagulation value reverses the charge on the sol, owing to preferential adsorption of alizarate ion. This was confirmed by Ackerman,[23] who showed further that the negatively charged lake was precipitated by an excess of sodium alizarate (cf. p. 258).

If a fresh gel of alumina, say, is formed rapidly in the absence of an anion such as chloride, it will adsorb alizarate ion direct from aqueous solutions of sodium alizarate or from alcoholic solutions of alizarin, yielding red lakes. It follows therefore that, depending on the conditions, adsorption of alizarate ion may be either exchange adsorption, direct adsorption, or both. The red color of alumina-alizarin lakes is neither the dark purple to purplish black of the alkali and alkaline-earth alizarates nor the orange of the alizarin acid, but is a bright red suggestive of the color of the alizarate ion in aqueous solution. The color of the lake is doubtless due to adsorption of the alizarate ion oriented toward the aluminum atom of the oxide. The ion associated with the alizarate ion and oriented toward the oxygen atom of the oxide may be sodium, potassium, ammonium, hydrogen, or calcium without materially modifying the color of the lake, except in so far as the extent of its adsorption influences the amount of adsorption of alizarate ion.

Opposed to the adsorption mechanism is the view of Morgan (p. 414) that the alizarin lakes are definite chelate metallic compounds. It is not known to what extent the above-described phenomena connected with the lake-formation process can be accounted for on the chelate compound theory.

Valko[24] regards adsorption as merely the first step in the taking up of a dye by a fiber. This is followed in time by chemical union in the modern sense between dye molecules and fiber molecules. In his article[24] Valko has passed over the subject of mordant dyeing, but, with his skill in interpreting colloid behavior in terms of modern physical chemical principles, one may anticipate that he will regard the adsorption phenomena outlined in the latter part of this chapter as only the preliminary step in the mordanting process. Be that as it may, a preliminary step may be too significant to be ignored; this is the case in mordant dyeing.

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