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Industrial Chemical Monographs

COLLOID CHEMISTRY;
Principles and Applications

By

JEROME ALEXANDER, M.Sc.

Consulting Chemist and Chemical Engineer. Past Chairman, Committee on the Chemistry of Colloids (National Research Council); Fellow, Amer. Assn. for the Adv. of Science, and Amer. Inst. of Chemists, Mem. Amer. Inst. of Chem. Engineers; Amer. Inst. Mining and Metallurgical Engineers, etc.

THIRD EDITION



1830 1930

CHAPMAN & HALL'S
CENTENARY YEAR

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Originally Published as "COLLOID CHEMISTRY"
COPYRIGHT, 1919, 1924, BY
D. VAN NOSTRAND COMPANY

PUBLISHED IN GREAT BRITAIN BY
CHAPMAN & HALL, LTD.
ELEVEN HENRIETTA STREET
LONDON, W.C.2.

PRINTED IN THE UNITED STATES OF AMERICA
BY THE LANCASTER PRESS, LANCASTER, PA.

PREFACE TO THIRD EDITION

To meet the increasing demand for this little book, there has been prepared a Third Edition, greatly enlarged in both the theoretical section and in the practical applications. An Appendix has been added giving some experimental suggestions which constitute a modest laboratory manual, based mainly on materials and apparatus readily obtainable in the kitchen or household, or else at any drug store. The Appendix describes many simple experiments which go directly to the root of the principles involved. Montaigne once said that he liked peasants, because they were not sufficiently educated to reason incorrectly.

If any purist of pedagogic tendencies were to point out that the book includes items and data not strictly of colloidal nature, it may be said that Nature, herself, is delightfully oblivious to definitions, rules, laws, metes and bounds established by scientists for their own convenience. And often what might in strictness be considered as extraneous matter may add interest, zest and a background which leads to better appreciation of material unquestionably pertinent.

It is interesting to compare the 1907–1916 Decennial Index of "Chemical Abstracts" with the 1917–1926 Decennial Index; for this comparison indicates, although it by no means measures, the great increase of interest in colloid chemistry during the decade. The former Index contains only twelve columns of titles under "Colloids," while the latter contains twenty-seven columns under that heading alone, besides a

very great number of other papers dealing with colloid phenomena, indexed under such headings as "adsorption," "Brownian movement," "disperse systems," "gelatin," "micelles," "particles," "ultrafilters," etc.

The author gratefully acknowledges his indebtedness to very many writers and experimenters whose names and works are often mentioned specifically. While some of the ideas advanced are believed to be novel, no claim of priority is made or implied; for what is of most importance to the advance of science is not "*Who* is *first*, right?", but "First, *what* is right?". And there is usually some divergence of opinion as to what *is* right. The older literature abounds in forgotten or over-looked work of importance, some of which, despite the fact that it may have appeared long in advance of its time, has a surprisingly modern aspect. Frequently, things which we have seen, heard or read, and then apparently forgotten, lurk in our subconscious minds and influence our future thought.

JEROME ALEXANDER.

NEW YORK,
November, 1929.

PREFACE TO SECOND EDITION

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

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

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

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

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

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

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

JEROME ALEXANDER

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

PREFACE TO FIRST EDITION

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

J. A.

NEW YORK,
Nov. 1, 1918

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CHAPTER I

INTRODUCTORY

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

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

"Although chemically inert in the ordinary sense, colloids possess a compensating activity of their own, arising out of their physical properties. While the rigidity of the crystalline structure shuts out external

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

* This statement clearly shows that Graham appreciated the fact that the same substance (here silicic acid) could exist in either the colloidal or the crystalloidal state. The contrary erroneous statement has often been made, even by authors who quote this very statement of Graham.—J. A.

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

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

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

Colloid Chemistry Defined

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

as we now know, means a certain very fine state of subdivision. While there are no sharp limitations to the size of particles in colloidal dispersions, it may in a general way be stated that their sphere begins with dimensions somewhat smaller than a wave length of light, and extends downward well into dimensions which theory ascribes to the molecules of crystalloids. (See Table II, p. 38.)

Suspension vs. Solution

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

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

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

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

R. A. Millikan (see his book, "The Electron") has proved that what we call an "electric current" consists of a stream of particulate units carrying a negative charge (called *negative electrons*). Their number is so great, that Millikan estimates that if we were to set two and one half million people to work counting the electrons which pass in *a single second* as an electric current through an ordinary incandescent bulb, and they were to count steadily at the rate of two per second, day and night, without stopping for any cause whatever, it would take them 20,000 years to accomplish the task. Furthermore, it has been shown

that light is given out in little puffs, pulses, or *quanta* (Planck's quantum theory), this being due to the jets of energy given off by "excited" planetary electrons in atoms, when the electrons jump from some exterior "quantum position" to one further in (Bohr—Sommerfeld).

It would seem, therefore, that nature does many, if not most things, by leaps, only they are such tiny or rapid leaps, that they elude ordinary observation.

The recently evolved "wave mechanics" of L. de Broglie, Schrödinger, Heisenberg and others aims to explain phenomena not amenable to older theories, e.g. the *photoelectric effect*, which is that electrons knocked out of certain metal surfaces have an energy dependent only on the *wave-length* of the light, not on its *intensity*. In epitome it may be said that radiant energy includes two factors—a material corpuscle and a wave system with a maximum crest. Considered as a *vibration* the energy of the particle is the frequency of vibration (ν) times Planck's constant (h), while considered as a *mass* it is mc^2 (c being the velocity of light in vacuo); that is, $h\nu = mc^2$. From this de Broglie deduces that the wave-length (λ) associated with a mass m, moving with a velocity v, equals Planck's h, divided by the particle's momentum; that is, $\lambda = (h/mv)$. Schrödinger introduces the concept of emission frequency as due to pulses or *beats* (in the acoustical sense) resulting from two or more vibrations coexisting in an atom. Special treatises must be consulted regarding these new developments, which may reconcile Newton's corpuscular theory with the light-wave theory of Young and Fresnel.

CHAPTER II

MATERIAL UNITS AND THE FORCES DOMINATING THEM

There are many perfectly sane, capable, and earnest people who have not been trained to follow, or who cannot follow mathematical reasoning, even when all the successive steps are given in painful detail—which good mathematicians seldom do, since they assume the reader possesses a good mathematical background. Thus in one of his treatises, J. Clerk Maxwell, after establishing a certain equation said: "By inspection, we see that"—and then he jumped to another equation. The writer, then a student, worked a full hour before he discovered how the second equation was derived from the first. We can therefore appreciate the English school-boy's description of algebra as "a low form of cunning."

However, it is encouraging to know that we can enjoy the beauty of a cathedral without understanding all the details of the scaffolding by aid of which the structure was built, although most people will readily grasp the general principles involved in the scaffolding, provided they are not stunned by details. Simple mathematics is simple reasoning. Thus most people will agree that $2 + 2 = 4$, although in certain financial circles they say $2 + 2 = 22$. Complicated mathematics involves complicated reasoning, or, what amounts to the same thing, conducting simultaneously many simple lines of reasoning—which many persons find confusing.

But even skilful mathematicians may run into

trouble when they attempt to apply mathematics to the solution of natural phenomena. Take the simple case of the greyhound running at 600 yards per minute, chasing the rabbit running at 500 yards per minute, that is 100 yards per minute slower than the greyhound. If the rabbit has a head start of 100 yards, the greyhound should overtake him in just one minute. However, if we remove this problem from the desk to the field, and actually set a real greyhound after a real rabbit, surprising things are apt to happen. Thus, before being caught, the rabbit may pop into his hole. Or a hawk may swoop down and snatch him off before the greyhound gets him. Or a barbed wire fence may let the rabbit pass but hold up the greyhound. Or the greyhound might run a thorn into his foot and lose speed or even stop altogether.

The disgusted mathematician will tell you that all this is not in the problem. Of course not—but it may occur in nature. Really, in framing a statement about a problem, whether we put it into the form of a mathematical equation or not, we make the following basic assumptions: *First,* that what we *do* say corresponds to the actual facts; *Second,* that we have included *every* factor exerting an effect. The first may be carefully safeguarded; where we get into trouble it is generally because there are factors we do not think of, know of, or even imagine as existing. Nature is so full of unexpected or unthought of influences, that we must add to our conclusions what the certified public accountant adds to his report—E. and O. E. (errors and omissions excepted).

Next to accurate observation and due allowance for all influential factors involved, perhaps nothing is more

important in scientific matters than the mental separation of seasoned facts from the theories designed to systematize and explain them. For facts are hard, stubborn things that survive the theories whose downfall they may cause.

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

Divisibility of So-called Elements

Among the disconcerting discoveries of recent times may be mentioned those connected with radio-activity, which eventually led to the demonstration that electricity consists of discrete particles, and that our supposedly infrangible elements are complexes of positive and negative electrons, and that some of these complexes are breaking up spontaneously and uncontrollably, while others may be shattered by the terrific impact of alpha particles moving at the rate of 10,000 miles or more per second.

Then the basic assumption of Dalton's atomic theory fell, when T. W. Richards, J. J. Thompson, Aston, Dempster, Harkins and others showed that

with many of the elements, the atoms are not all alike, but have different atomic weights.

TABLE OF ISOTOPES

According to F. W. Aston *

Element	Atomic Number	I.C.T. Atomic Weight	Minimum Number of Isotopes	Mass Numbers in Order of the Intensities of the Mass-Spectrum Lines
H	1	1.0077	1	1
He	2	4.00	1	4
Li	3	6.939	2	7, 6
Be(Gl)	4	9.02	1	9
B	5	10.82	2	11, 10
C	6	12.000	1	12
N	7	14.008	1	14
O	8	16.000	1	16
F	9	19.00	1	19
Ne	10	20.2	2	20, 22
Na	11	22.997	1	23
Mg	12	24.32	3	24, 25, 26
Al	13	26.96	1	27
Si	14	28.06	3	28, 29, 30
P	15	31.024	1	31
S	16	32.065	1	32
Cl	17	35.458	2	35, 37
A	18	39.91	2	40, 36
K	19	39.095	2	39, 41
Ca	20	40.07	2	40, 44
Sc	21	45.10	1	45
Ti	22	47.9	1	48
V	23	50.96	1	51
Cr	24	52.01	1	52
Mn	25	54.93	1	55
Fe	26	55.84	2	56, 54
Co	27	58.97	1	59
Ni	28	58.69	2	58, 60
Cu	29	63.57	2	63, 65

* From International Critical Tables Vol. 1.

TABLE OF ISOTOPES.—*Continued*

Element	Atomic Number	I.C.T. Atomic Weight	Minimum Number of Isotopes	Mass Numbers in Order of the Intensities of the Mass-Spectrum Lines
Zn	30	65.38	4	64, 66, 68, 70
Ga	31	69.72	2	69, 71
Ge	32	72.38	3	74, 72, 70
As	33	74.96	1	75
Se	34	79.2	6	80, 78, 76, 82, 77, 74
Br	35	79.916	2	79, 81
Kr	36	82.9	6	84, 86, 82, 83, 80, 78
Rb	37	85.44	2	85, 87
Sr	38	87.62	2	88, 86
Yt	39	89.0	1	89
Zr	40	91	3	90, 94, 92
Ag	47	107.880	2	107, 109
Cd	48	112.41	6	110, 111, 112, 113, 114, 116
In	49	114.8	1	115
Sn	50	118.70	7, (8)	120, 118, 116, 124, 119, 117, 122, (121)
Sb	51	121.77	2	121, 123
Te	52	127.5	3	128, 130, 126
I	53	126.932	1	127
Xe	54	130.2	7, (9)	129, 132, 131, 134, 136, 128, 130, (126, 124)
Cs	55	132.81	1	133
Ba	56	137.37	1	138, (136)
La	57	138.91	1	139
Ce	58	140.25	2	140, 142
Pr	59	140.92	1	141
Nd	60	144.27	3	142, 144, 146, (145)
Hg	80	200.61	2, (6)	(197–200), 202, 204
Bi	83	209.00	1	209

It is startling to learn, for example, that lithium consists of a mixture of atoms having atomic weights of 6 and 7, chlorine of atoms having atomic weights of 35 and 37, and that krypton has six *isotopes*, as they are called. In an address before the Chemical Society (London) Aston remarked:—"Though as a chemist I view with some dismay the possibility of eighteen different mercuric chlorides, as a

physicist it is a great relief to find that nature employs at least approximately standard bricks in her operations of element building." And, to the endless disgust of small boys, Harkins has pointed out the possibility of 63 different kinds of calomel.

Some of our other new discoveries cast doubt upon what were heretofore accepted as facts. Thus the recognition of vitamines and certain salts as food essentials has necessitated the re-examination of conclusions drawn from some previous experiments on food values, which in some cases showed simply the minimum quantities of food needed to supply the necessary amount of vitamines or salts. The incompleteness of mere calorie-fat-protein-carbohydrate specifications is now well recognized.

Chemical vs. Physical Forces

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

The difference between chemical and physical attraction is explained in many elementary text books by taking the example of iron filings and flowers of sulphur. From their physical mixture the iron may be separated magnetically or the sulphur dissolved out by carbon bisulphide; and the two ingredients may be separately identified in the microscope. If they are heated, however, the non-magnetic chemical

Physical Units			*Physical Data*	*Biological Units*
Material Unit	Order of Complexity	Approximate Size Limits		
Proton *	0?	2×10^{-8} Å.		
Electron †	0?	3.8×10^{-5} Å.	Atomic nuclei—Light atoms, about 5×10^{-5} Å.	
Atomic nucleus		H—2×10^{-8} Å. Gold—4×10^{-7} Å.	Gold, about 3×10^{-4} Å. (Rutherford.) Shortest known X-rays—0.0057 $m\mu$ (0.057 Å.).	
Atoms	1	0.1–0.6 $m\mu$ 1–6 Å. U.	Dia. H atom—1.08 Å. U. (Bohr). Smallest distance between C atoms in diamond—1.53 Å.	
			X-ray data of crystal units. { Ni—2.76 Å.; Fe—2.86 Å.; Na—4.30 Å.; NaCl—5.56 Å.	
			Ultramicroscopic limits—about 2 $m\mu$.	
Molecules	2	0.2–5 $m\mu$		*Moleculobiont* (Hypothetical simplest life)
Molecular groups	3	0.5–10 $m\mu$	Amplitude of Brownian motion of Pt hydrosol at 19° C. Av. particle size = 25 $m\mu$ = 2100 $m\mu$ in 0.0065 sec. (323 μ per sec.).	
Primary colloidal particles	4	2–20 $m\mu$	Connecting zone between shortest ultraviolet and	20 – 70 $m\mu$—Genes

longest X-rays 60–8 $m\mu$.

Secondary colloidal particles	5	5–100 $m\mu$	Average Free Paths: CO_2 = 61.5 $m\mu$; NH_3 = 66.0; N = 92.9; O = 99.3; H = 160.0; He = 300.0	50 ± $m\mu$—Bacteriophage
Microscopically resolvable particles	6	Over 100 $m\mu$	Microscopic limits for resolution about 250 $m\mu$. Visible Spectrum: Violet— about 4,000 Å.; Blue— 4,700 Å.; Green— 5,200 Å.; Yellow— 5,800 Å.; Orange— 6,000 Å.; Red— 6,500 Å.	2 ± μ = Cocci (round bacteria); 0.2 – 3.5 μ—Chromosome; 5 μ – 15 μ—Cell nucleus
Visible particles	7	Over 50 μ	Limits of visibility—8.000 Å. Longest infra red from Hg vapor—0.313 mm. (313,000 $m\mu$). Shortest Hertzian waves 2.0 mm. (2,000,000 $m\mu$).‡ Electro-magnetic vibrations of alcohol—70.0 cm. Hertzian wireless waves 100 m.—30,000 m.	7 μ – 25 μ—Cell

N—number of molecules in 1 gram molecule = 60.62×10^{22}.
h—Planck's constant of action = 655×10^{29} erg seconds.
e—charge of the electron = 4.774×10^{-10} electrostatic units.

Human voice	60—12,000	vibrations per second.
Audible sound	16—30,000	" " " (human).
	60,000±	" " " (mice).
Mechanically detectable	90,000	" " " (Koenig).

2.5 mm. *Drosophila melanogaster* (the "fruit fly")

The estimates for the sizes of the cell, cell nucleus, chromosomes and genes apply to *Drosophila melanogaster*.

* Rutherford's estimate from experiment.
† Lorentz, from electromagnetic theory.
‡ Nichols and Tear.

compound FeS is formed, from which CS_2 extracts no S. Furthermore, while Fe and S may be physically mixed in any desired proportions, in the chemical compound FeS they combine in the definite proportions of 56 parts by weight of Fe to 32 parts by weight of S, and any excess of S may be dissolved out by CS_2.

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

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

Do Colloids Form Chemical Combinations?

The answer depends upon what is meant by "chemical combination." It is generally understood to mean combination in fixed, definite proportions, resulting from precise union of atoms, radicles or molecules. Now suppose that a real definite chemical compound were formed at some edge or corner of a large molecular mass of indefinite size—would it be fair to call the whole huge mass a chemical compound? If we spill a drop of nitric acid on our sleeve, do we thereby make nitrate of coat? If we stick a postage stamp on a letter, do we thereby make stampate of envelope or envelopate of stamp? Sodom and Gomorrah might have been saved by the presence of ten

good men; but even a larger number of definite molecules cannot entitle a huge cluster to the saving grace of a chemical name. It is hardly fair to distort the accepted meaning of the term "chemical compound," because nature permits molecules to have many and strong residual attractions. After all, we must accept Nature as she is, and not try to force her into a stoichiometric straight-jacket.

The Sub-microscopic Structure of Matter

A whole series of complexities underlie even the smallest particle of matter visible in the most powerful microscope. Negative electrons, and protons or positive electrons are the only material units not at present *known* to be complex. While the number of steps in this series may vary in individual cases, in many instances the degrees of aggregation shown in the Table on pp. 14–15 may be definitely traced.

Taking Shapleigh's estimate of the diameter of the galaxy of 300,000 light years = approximately 2.5×10^{21} cm., we see that in an exponential range of 37 * we may pass from the smallest known material unit, the proton, to the outermost confines of the universe. This indicates the extent of the variations in real values represented by the pH exponential figures so often used to express the effective acidity or alkalinity of colloidal solutions. When using Sörenson's convenient pH symbolism we must remember that it is an *inverse exponential function.*

* That is, the proton has a diameter of the order of 10^{-16} cm. and the galaxy a diameter of the order of 10^{21} cm., the exponential spread being 37.

Hydrogen Ion Concentration

The expression pH demands some explanation. It is a convenient way to express the reaction of any fluid, but is dangerous because it does not do this directly; for it is an inverse logarithmic function, deprived of its minus sign, as will be seen directly.

Pure water dissociates slightly according to the equation

$$H_2O \rightleftharpoons H^+ + OH^-$$

the reaction being reversible. It has been found that at 22° C. the concentration of hydrogen ions in pure water equals $\frac{1}{10{,}000{,}000}$ moles per liter, a fact usually expressed by the symbolism C_{H^+} (concentration of hydrogen ions) equals 10^{-7} moles per liter. Since for each H^+ ion in water there is an OH^- ion, $C_{OH^-} = 10^{-7}$ under the same conditions.

	Degree of normality	C_{H^+}	Equivalent pH value
HCl	1.0	8.0×10^{-1}	0.10
	0.1	8.4×10^{-2}	1.07
	0.01	9.5×10^{-3}	2.02
	0.001	9.7×10^{-4}	3.01
	0.0001	9.8×10^{-5}	4.01
Acetic acid	1.0	4.3×10^{-3}	2.37
	0.1	1.6×10^{-3}	2.87
	0.01	4.3×10^{-4}	3.37
	0.001	1.6×10^{-4}	3.87
Caustic soda	1.0	0.90×10^{-14}	14.05
	0.1	0.86×10^{-13}	13.07
	0.01	0.76×10^{-12}	12.12
	0.001	0.74×10^{-11}	11.13

Now, for convenience, Sörensen proposed to disregard the minus sign, and to use simply the numerical

value of the exponent of 10 to express the reaction represented by the corresponding C_{H^+}. The table* on p. 18 will make this clear:

This table shows that the lower the pH value, the greater the *effective reaction* of acidity, which is something quite different from the *total* acidity. Thus equal volumes of normal hydrochloric acid and of normal acetic acid will neutralize equivalent volumes of normal alkali, but the normal acetic acid has a much lower degree of acidity or hydrogen ion concentration, and therefore a higher pH value.

Not only does the pH value run *opposite* the H ion concentration, but the variations are exponential or logarithmic, not arithmetical. The step between pH 5 and pH 6 is vastly less than the step between pH 5 and pH 4, as may be seen from the following table:

pH value	Number of times H (or OH) ion concentration exceeds that of pure water	
1	1,000,000	
2	100,000	
3	10,000	
4	1,000	
5	100	acid side
6	10	
7	0	pure water————————
8	10	
9	100	alkaline side
10	1,000	•
11	10,000	
12	100,000	
13	1,000,000	

Homogeneity and Heterogeneity—Phases

Lewis and Randall ("Thermodynamics," p. 9) describe a *homogeneous system* as one in which there are

* "Die Wasserstoffionen Concentration," by Prof. Leonor Michaelis.

no apparent surfaces of discontinuity; and a *heterogeneous system* as one consisting of two or more distinct homogeneous regions or *phases*, which appear to be separated from each other by surfaces of discontinuity. The celebrated Phase Rule of J. Willard Gibbs [Trans. Conn. Acad. Sci., *3*, 228 (1876)] is that the number of degrees of freedom (F) of a system as a whole (in other words the number of independent variables upon which it depends) equals the number of variables essential to determine the state of the individual phases, minus the sum of the phases outside the first.

Thus in a system of n phases whose individual states are controlled by x variables,

$$F = x - (n - 1) = x - n + 1$$

But as Zsigmondy pointed out (Colloids and the Ultramicroscope, p. 3) and as the above table showing the serial complexity of matter indicates, the practical distinction between homogeneity and heterogeneity depends entirely upon the refinement of our means of observation. In many cases we assume phases to be homogeneous to simplify our calculations; but when a substance is finely subdivided or dispersed, the influence of specific surface (exterior or rind surface) becomes an important factor, the phases neglected or submerged for our convenience urgently demand consideration, and the number n in Gibbs' equation must be increased.

A typical instance of the break-down or failure of a "law" or formula was brought out by Millikan in his work on weighing the electron. He caught electrons on tiny oil droplets, and calculated the increase in weight,

after he had observed the added velocity of their fall. Now Stokes' formula is based on the assumption that the air or other fluid in which a sphere is falling, is *homogeneous;* and in most practical cases, air and water behave as if they were homogeneous. But the oil droplets used by Millikan were so tiny, that they fell through the "holes" between the air molecules. These holes are fixed by the molecular mean free paths, that is by the average jumps of the molecules between collisions. Consequently, the droplets fell much more rapidly than Stokes' law said they should, and Millikan had to figure out and apply a correction.

Interfacial Anomalies*

In all free surfaces the exterior molecules occupy a position quite different from the interior molecules, which are on all sides surrounded by their own kind. Part of the attractive forces of the surface molecules are directed inward, part toward adjacent surface molecules (thus forming a surface skin), and a residual unsatisfied portion outward. This residual affinity may be demonstrated by cleaving a piece of mica (muscovite) and instantly putting the new surfaces together. They exhibit considerable cohesion, although this represents but a fraction of the original attractive force, and is soon lost by further adsorption of atmospheric constituents. A fresh iron surface absorbs atmospheric constituents so quickly that, although a piece of cast iron broken under mercury is

* Among those whose work in this field is outstanding, may be mentioned Sir W. B. Hardy, G. Fridel, W. D. Harkins, I. Langmuir, N. K. Adam, Devaux. Papers by all but the last two are in Vol. 1 of Alexander's Colloid Chemistry, Theoretical and Applied. (Chem. Cat. Co.)

amalgamated at its new surfaces, the same iron if broken above the mercury and instantly dropped in, is not amalgamated at all. (P. W. Bridgman.)

Residual Affinities

If the attractive forces existing between atoms were entirely balanced or satisfied by their chemical combination, then every chemical compound would behave as a perfect gas so far as concerns the factor a in the equation of van der Waals. But in all chemical compounds exist residual attractions or stray fields of force which exert a controlling influence on what are ordinarily termed the physical properties of the compound—its state (gaseous, liquid or solid), its cohesion, solubility, boiling point, conductivity for heat and electricity, dielectric constant, etc. This residual attraction is responsible for the phenomena we call adhesion and adsorption, and its range of effective action (of the order of 10^{-8} cm.) is much less than the diameter of a molecule.

Langmuir says that molecules usually orient themselves in definite ways in the surface layer, since they are held there by forces acting between the surface and particular atoms or atomic groups in the adsorbed molecule. This accounts for the influence of chemical composition on adsorption commented on by Bechhold and others. Harkins (J. Am. Chem. Soc. 1920, 42, 706) points out that in organic compounds this orientation depends upon the dissymmetry of the molecule. "An entirely symmetrical molecule (or atom in the case of monatomic liquids) would not orient at all, but such a molecule or atom does not exist. Molecules as symmetrical as those of the short

chain saturated paraffins, carbon tetrachloride, etc., would not be expected to show such evidence of orientation as those molecules which may be considered as heavily loaded, from the standpoint of the stray electro-magnetic field, at one end of the molecule and very light, in the same sense, at the other."

A Simple Principle Underlying the Colloidal State

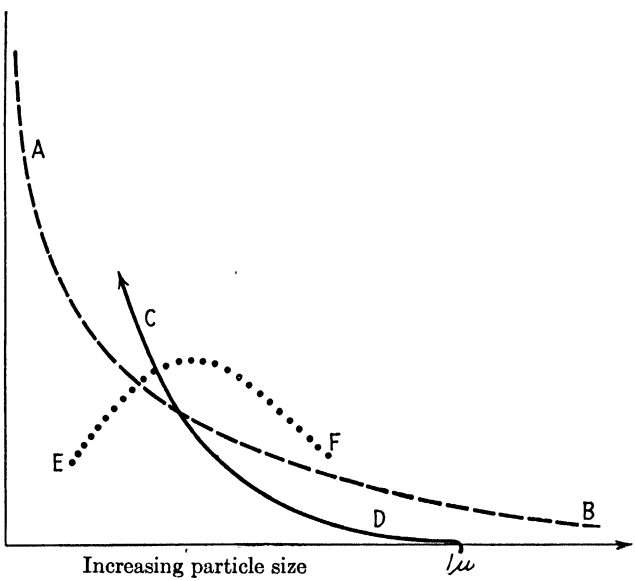
The anomalous properties exhibited by matter in colloidal dispersion, as we follow it beyond the limit of microscopic resolvability to molecular dispersion, may be understood by considering two properties—(1) *specific surface* and (2) *kinetic activity.*

Specific surface (exterior or rind surface per gram) will vary considerably with the actual shape of the particles. If we assume an average spherical shape and plot specific surface against particle size, we obtain an hyperbola. For with infinitely large particles the free surface per gram approaches zero, and with infinitely small particles the free surface per gram approaches infinity; and the areas of spheres vary inversely as the squares of their radii. Therefore the curve is asymptotic to both axes and varies as d^2; that is, it is hyperbolic.

The mean velocity of translation * of particles is likewise subject to great variations; chemical nature, physical structure, viscosity of the dispersing medium, temperature; incidental ions, solutes, or impurities, all exercise their effects. But with the same substance, under the same conditions, the kinetic motion, beginning as the well-known Brownian motion at the limit of

* There is a kinetic motion of revolution as well as of translation, the observed translatory kinetic motion being a net result.

microscopic resolvability, increases at first slowly and then with gradually accelerating rapidity as subdivision proceeds; so that the curve of kinetic motion, plotted for convenience of comparison on the same axes as that of specific surface, soon rises rather abruptly, and cuts the latter (see Fig. 1). Motion tends to vary with *mass*, and the mass of a given substance varies inversely as the cube of the particle diameter (i.e. as d^3 or its *volume*).* The kinetic motion curve, therefore tends toward a *cubic* hyperbola.



AB = free surface per gram; CD = kinetic motion curve; EF = rise and fall of colloidal characteristics.

Fig. 1.—Relation between kinetic activity and specific surface.

* The formulas for momentum (MV) and for kinetic energy ($\frac{1}{2}MV^2$), where M is mass and V is velocity, both depend on *volume;* for mass varies as volume varies.

The Zone of Maximum Colloidality

In following the gradual dispersion of a substance from gross visible particles all the way down to true molecular subdivision, it is obvious that in the colloidal zone there is a transition from a state where the kinetic activity is *small* as compared to the specific surface to a state where the kinetic activity is *large* as compared to the specific surface. In the heart of the colloidal zone there is usually observable an indefinite portion of the curve which has been termed the *zone of maximum colloidality* (J. Alexander, J. Am. Chem. Soc. 43, 434 (1920), wherein colloidal properties, such as viscosity, are most marked.

The zone of maximum colloidality appears in a wide variety of substances—in steel (J. Alexander), in duralumin (Merica, Waltenberg & Scott), in dyeing (R. Auerbach). In his H. M. Howe Lecture (before the Am. Inst. Min. & Met. Engr. 1924) Prof. Albert Sauveur stated facts which disclose its existence in heated steel, which showed maximum strength over a certain temperature range. On adding water to acetone solutions of nitrocellulose, F. Sproxton (3d Report on Colloids, etc., Brit. Assoc. Adv. Science, 1920) found that the viscosity rose to a maximum and then fell. Sulfur at 150° has a viscosity of 8; at about 200° it rises to over 50,000, and at 400° it drops to 150. Viscose in ageing passes through a maximum of viscosity.

Further instances are given in Alexander's Colloid Chemistry, Theoretical and Applied, Vol. I, from which the following quotation is taken (p. 25):

"A most striking example of optimum dispersion is found in living matter. Figuratively speaking, if all

chemical substances comprising our organism were in true or crystalloid dispersion, reactions would proceed so rapidly that we would, so to say, live ten years in ten minutes. On the other hand, if coarse dispersion prevailed, it would take ten years to live ten minutes. Every organism is dependent on the coordination of its reactions *in point of time*, and this leisurely procedure depends largely on *degree of dispersion*, which keeps chemical reaction velocities within certain speed limits through its regulation of free surface and kinetic activity. Life lies between lysis and coagulation. The colloidal zone is, as it were, a vital metronome tolling off the tempo of life."

Just before gases liquefy, they show, at the critical point, an opalescence, cloudiness, or turbidity, which Albert Einstein proved by sheer mathematical analysis, to be consequent on the existence there under the action of the laws of probability (Boltzmann's Entropy Probability Theorem) of molecular aggregates of such size and number, that they scatter enough light to produce a Faraday-Tyndall effect, just as a searchlight does in a foggy atmosphere. The phenomenon is commonly seen when steam blows out into the air, as when a locomotive puffs. The bluish haze which appears just before the white "steam" contains colloidal aggregates of the condensing water molecules. (See also p. 83, under Meteorology.)

We may therefore *pass upward* into the colloidal state as molecules *aggregate or become larger*, or pass *downward* into the colloidal state as coarse particles are *more finely ground or dispersed.* Thus Martin H. Fischer showed that in taking sodium salts of the fatty acids beginning with sodium formate and passing

through the acetate, propionate, etc., up to the stearate and oleate, we find that the water holding capacities of the salts increases steadily.* His results may be tabulated as follows:

No. of Carbon Atoms								
1...	Sodium	formate.....	molecular dispersion					
2...	"	acetate.....	"		"			
3...	"	propionate..	"		"			
4...	"	butyrate....	"		"			
5...	"	valerate....	"		"			
6...	"	caproate....	shows signs of holding water					
8...	"	caprylate ...	1 mol.	gives a jelly	with		250 c.c.	of water
10...	"	caprate.....	1 "	"	"	"	"	500 c.c.
12...	"	laurate.....	1 "	"	"	"	"	4,000 c.c.
14...	"	myristate...	1 "	"	"	"	"	12,000 c.c.
16...	"	palmitate...	1 "	"	"	"	"	20,000 c.c.
17...	"	margarate ..	1 "	"	"	"	"	24,000 c.c.
18...	"	stearate.....	1 "	"	"	"	"	27,000 c.c.
20...	"	arachnate...	1 "	"	"	"	"	37,000 c.c.

On the other hand, Victor Lenher reduced silica to colloidal solution by continued grinding; and colloidal gold may be produced by the Bredig or the Svedberg method of electrical spattering, as well as by the Faraday-Zsigmondy method of reducing gold chloride.

The above facts justify Svedberg's classification of methods for the formation of colloids into (*a*) *aggregation methods*, (*b*) *dispersion methods*.

Critical Velocity

At the Toronto meeting of the British Association for the Advancement of Science, Sir Ernest Rutherford, in order to illustrate the repulsion of a positively

*L. Lascary [Koll. Z., *34*, 73 (1924)] found that the effect of sodium soaps on surface tension *increases* with molecular weight to sodium myristate, above which it *decreases*.

charged alpha particle by a positively charged nucleus, made use of an electro-magnet swung from the ceiling with its positive pole down, and another similar magnet fastened to a table beneath, with its positive pole up. If the swinging magnet passed sufficiently near the fixed one, it was swerved from its course. In attempting to show that a direct, head-on hit would result in a repulsion, the magnet was swung from too far back on the first attempt, with the result that its high velocity carried it over the fixed magnet. A second, less violent swing, resulted in a rebound.

This observation gave rise to the following reasoning: Suppose we turn upward the *negative* pole of the magnet on the table, and try swinging the positive pole of the other magnet over it at varying velocities. It is obvious that while at low speeds, the swinging magnet will be *held* by the fixed one, there is some critical speed above which it will swing past and *not* be held.

This same factor of *critical velocity* makes itself felt in many catalytic and enzyme actions, which, in general, proceed more rapidly with rise of temperature, up to a certain point varying with the particular case; after which further increase of temperature results in a decline in activity. We may here consider that throughout, increase in temperature brings about an increase in the *total number* of the essential molecular impacts or meetings; but that after reaching the critical temperature, owing to increase in average molecular velocities, the number of *successful* molecular meetings begins to diminish. To put it figuratively, a catalyst resembles a Judge who may marry or divorce molecules, if they appear before him and do not rush

off without waiting for "due process of law." And like the Judge, a catalyst may become "tired," or buried under other matters, and refuse to consider the domestic relations of waiting molecules.

The Relation of Colloidal to Other Forces

Mendelćef in his suggestive paper, entitled "A Chemical Conception of the Ether," intimated that gravitation might be explained on the basis of etherial impact acting from all sides; for from this assumption the Newtonian laws of gravitation may be easily developed. This is evident from the following considerations:

Assuming that the ether is a subtle gas whose particles move with approximately the speed of light, and that mass represents the ability of a substance to reflect the motion of ether particles, then any body, if alone in the universe, would be struck equally on all sides by the ether particles and if at rest would remain at rest, but if in motion would tend to maintain its rate of motion. This is *Newton's first law;* but it is obvious that if the motion of the body is large as compared with the motion of ether particles, then the moving body will appreciably increase in mass; for it will anticipate the blows of ether particles coming from the direction of its motion, and receive a diminished impact from those coming from the opposite direction (*relativity effect*).

As soon as we introduce a second body into our calculation, then each body *shadows* the other *in proportion to its mass* or ether-stopping capacity. This means an excess of ether pressure on the unshadowed side, so that the bodies attract each other

directly as their masses. But since the areas of spheres vary inversely as the squares of their radii, it is obvious that a body removed to twice the distance will have only $^1/_4$ the shadowing effect; at three times the distance only $^1/_9$ the shadowing effect, etc. That is, the attraction between the bodies *varies directly as their respective masses and inversely as the square of the distance between them* (*Newton's second law*).

E. Cunningham ("Relativity and the Electron Theory") has shown that a material ether is not inconsistent with relativity, and the objective view of gravitation is much more appealing than recourse to "fields of force" without a material substratum, although, as Herbert Spencer pointed out, explanations of this kind simply transfer the enigma of Nature one step further back.

M. Le Sage in 1784 had expounded the same theory of gravitation, and Prof. S. P. Langley (inventor of the airplane) had a translation of Le Sage's work published by the Smithsonian Institution. It is possible that the nature of chemical attraction may be explained as a gravitational force modified because the reacting units are so close together that their size, shape and internal structure become material factors. We seem to be working toward the view maintained by Faraday and no doubt by many others, that there is one ultimate kind of force. In fact Albert Einstein has just published (Jan. 1929) his "unified field theory" wherein he combines the gravitational field formulae of his general theory of relativity, with J. Clerk Maxwell's vector formulae covering the electro-magnetic fields of light.

P. V. Wells (J. Wash. Acad. Sci. 1919, 9, 361) suggests the following classification of forces:

1. *Electronic Forces*—Maintain positive nucleus, and negative or valence electrons in equilibrium as a single system.

2. *Atomic Forces*—Maintain two or more atoms in equilibrium as a single system.

3. *Molecular Forces*—Maintain two or more molecules in equilibrium as a single system.

4. *Molar Forces*—Maintain two or more masses in equilibrium as a single system.

Electronic forces are thus responsible for atoms; atomic forces, for their chemical combination into molecules; molecular forces, for most physico-chemical and colloidal phenomena; and molar forces, for ordinary physical and astronomical phenomena. "Each group of forces," says Wells, "may be regarded as the residual fields of force remaining unsaturated in the smaller systems constituting the components of the system under consideration. . . . Molecular systems have lost so much of their discreteness that combinations of molecules do not follow the laws of definite and multiple proportions. In such phenomena as molecular association and surface structure, the discreteness of atomic constitution begins to give place to statistical continuity. Moreover, in these phenomena the force are relatively so weak that molecules are not usually regarded as permanently grouped together."

Thus adsorption, molecular association, and condensation would be considered as molecular phenomena; and while polymerization may start that way, in it atomic forces predominate.

In reading over the numerous practical applications of colloid chemistry we will later consider, it must be remembered, then, that most of the reactions lack

that preciseness indicated by the present meaning of the term "chemical compound." Slight deviations from previous conditions may involve a material difference in results, and until we understand and can give proper weight to all the underlying factors, many of our successful methods will remain "cooking recipes." Colloid chemical research is letting in a flood of light upon many reactions not amenable to the ordinary stoichiometric laws of chemistry, though in some cases they may closely approach these laws.

Solution vs. Colloidal Solution

When the attraction of the molecules of a liquid for those of a solid exceeds the attraction of the molecules of the solid for each other, then the solid is dissolved or peptized by the liquid. If the dispersion is profound enough, the solute may go into true or crystalloidal solution, but if the molecules of the solute cling to each other to a considerable extent, they may form groups of colloidal dimensions, and there results a colloidal solution.*

The degree of dispersion in which a substance exists in a solution naturally affects its kinetic activity, its speed of diffusion, and even its ability to diffuse. Thus sodium stearate is not a good protector nor even a good detergent until it is dissolved in sufficiently heated water; and in tanning and dyeing the degree of dispersion governs fixation capacity and speed. In the case of a kinetically balanced equilibrium, as with blood sugar, difference in diffusion speed may raise or lower the percentage of dextrose in the blood.

* Indeed, with most solutes and with most solvents, too, there is a certain degree of molecular association, as it is called. Liquid water is mainly dihydrol $(H_2O)_2$. Some molecules are themselves of colloidal size.

An interesting case is the action of selenium oxychloride on barium sulphate. As Lenher discovered, this remarkable solvent, which dissolves such diverse substances as rubber and gelatin, converts the highly insoluble barium sulphate into a colloidal jelly. Molecular groups having a great tendency to dissolve are sometimes able to drag into solution with them attached groups which would otherwise be insoluble. Thus many aniline dyes and even oils are sulphonated in order to make them "soluble" in water, where they usually form colloidal dispersions.

The Nature of Adhesion

Our principal adhesives, such as gums and glues, are substances which because of the makeup of their molecules possess powerful residual fields of force and are therefore capable of attaching themselves to other substances possessing residual fields of the opposite charge. They must besides have sufficient residual force to cling powerfully to adjacent molecules of their own kind. Thomas Graham long ago remarked that colloids as a rule adhere better to each other than to crystalloids. One reason probably is that colloids possess a plurality of residual fields which may have different charges at different points. They are also highly polar.

Adhesion is purely a matter of surfaces. Glue will stick paper to wood, but not to paraffin or to wood having a paraffined surface. It is true that glue will hold paper to paraffin or to bright tin until the adhesive dries; then the powerful attraction of the glue particles for each other as they are dehydrated breaks the weak bond between the glue and the paraffin or

metal, although it is unable to break the bond with the paper to which the other face of the glue layer clings tightly.

The orientation of molecules in surfaces may be a material factor in wetting of the surface and in adhesion. An experiment reported by Devaux is illuminating. He floated a lens-shaped drop of molten fatty acid on the surface of some hot water, and allowed it to cool and solidify there, so that the upper surface of the lens cooled in contact with air, while the lower surface cooled in contact with water. After careful drying, the lower surface could be wet by water, but the upper surface could not. Apparently the hydrophile or friendly-to-water ends of the fatty acid molecules were turned outward in the surface that had cooled in contact with the water, while the hydrophobe or "greasy" ends were turned outward in the surface which had cooled in contact with the air. It would seem that the direction in which the molecules of fatty acid turn or orient themselves at the surfaces depends upon which of their "ends" shows a greater attraction for the molecules of the exterior medium (air and water) than for the mass of fatty acid molecules on the interior of the drop. Since these attractions are the result of residual electronic fields, the phenomenon may be called *electroversion*. It shows how the nature of a medium may effect the behavior of particles dispersed in it.

Surface Forces in Grinding or Pulverizing

It is not an easy or inexpensive operation to dry grind most substances below 200 mesh. As subdivision proceeds, the total free surface increases enor-

mously, and apart from the inherent difficulty of breaking up a very fine particle, the tendency of the fragments to reunite or "cake up" begins to assert itself. The finer the particles the greater this tendency, and it is increased by pressure. It is to a large measure overcome by wet grinding, because the adsorption of fluid or solutes at the new surfaces tends to prevent their reunion.

The " Colloid " Mill

This is essentially a high speed disintegrator arranged for wet grinding, and the patents of Block, Plauson, China and others relate chiefly to mechanical details. A readily absorbable substance (a deflocculator or protective colloid) is added to the liquid in the mill, and stabilizes the colloidal dispersion as it is formed.

Block's machine, has a very high speed rotor eccentrically placed in a casing of circular cross section. The high peripheral speed of the rotor forces the material to be pulverized, practically under pressure, into the space between the rotor and the casing, where most of the atomization occurs, the material to a large extent grinding against itself.

Colloid mills can be used to make emulsions, and colloidal solutions of cellulose and highly concentrated colloidal mercury have been made with it. It is said to be used in the soap industry for speeding up saponification; in the dairy industry for homogenizing milk and cream; in producing colors, inks, rubber goods, etc. No doubt it will produce many desirable results, but since high speed takes power and means wear, the commercial advantages of the mill remain to be dem-

onstrated. (See e.g. 8th Report on Progress of Applied Chemistry, Soc. Chem. Ind., 1923, page 340).

A few years ago a so-called "colloid mill" was demonstrated before a technical-scientific gathering; dried milk powder mixed with water was reconverted into milk, a cresol-soap solution was made into an emulsion with water, and a red pigment converted into a suspension which promptly settled out. After the burst of applause which followed this evidence of the potency of the mill, discussion was called for; and some one had the timerity to point out (1) that simple stirring with a teaspoon would suffice to reconvert the milk powder into milk; (2) that simple stirring in a bucket of water with a stick would suffice to make an equally perfect emulsion of the cresol-soap solution; (3) that the red pigment suspension had already settled out, and was therefore not colloidal. This awoke the audience to the fact that, in many cases at least, satisfactory results may be had by intelligent use of simple, well-known apparatus, without any need of paying extravagant prices or royalties. Indeed, the proper preparation of what goes into the apparatus is generally of much greater importance than the type of mill used.

CHAPTER III

CLASSIFICATION OF COLLOIDS

The broadest classification of colloids is that of Wolfgang Ostwald (*Koll. Zeitschr.*, Vol. 1, page 291), who grouped them according to the physical state (gaseous, liquid or solid) of the subdivided substance (dispersed phase), and of the medium in which the particles of the subdivided substance are distributed (dispersion medium).* Table I below shows the nine resulting groups and gives some instances of each.

Ostwald's classification, however, is more theoretical

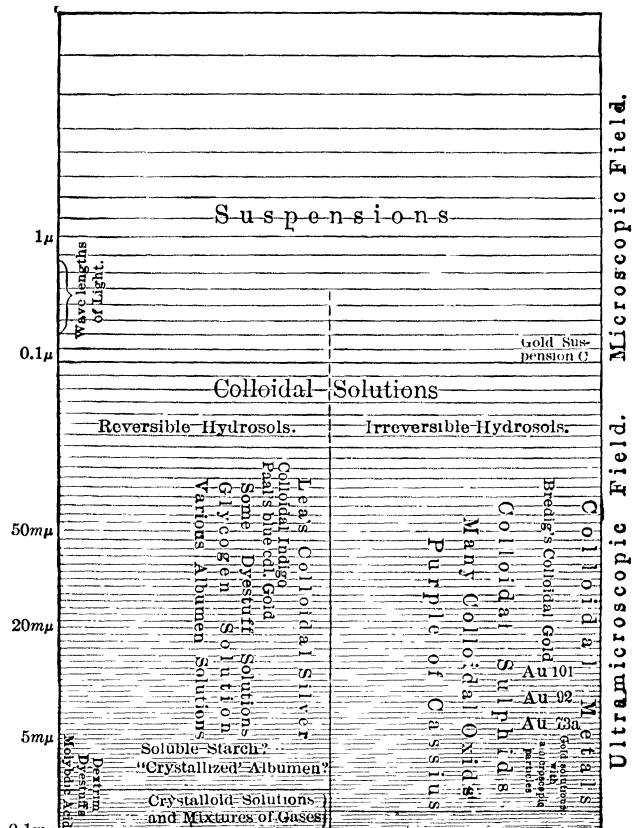
TABLE I

Dispersed phase.	Dispersion medium.	Example.
Gas.....	Gas.....	No example, since gases are miscible in all proportions.
Gas.....	Liquid.....	Fine foam, gas in beer.
Gas.....	Solid.....	Gaseous inclusions in minerals (meerschaum, pumice), hydrogen in iron, oxygen in silver.
Liquid.....	Gas.....	Atmospheric fog, clouds, gases at critical state.†
Liquid.....	Liquid.....	Emulsions of oil in water, cream, colloidal water in chloroform.
Liquid.....	Solid.....	Mercury in ointments, water in paraffin wax, liquid inclusions in minerals.
Solid.....	Gas.....	Cosmic dust, smoke, condensing vapors (ammonium chlorid).
Solid.....	Liquid.....	Colloidal gold, colloidal sodium chlorid, colloidal ice in chloroform.
Solid.....	Solid.....	Solid solutions, colloidal gold in ruby glass, coloring matter in gems.

* G. Bredig proposed to call colloids "microheterogeneous systems." W. Ostwald called them "dispersed heterogeneous systems," which expression was contracted by P. P. von Weimarn into the term "dispersoids."

† A. Einstein, "Turbidity near the Critical State," Ann. Phys., **33**, 1275 (1910); also Alexander, Vol. I, p. 323.

TABLE II



Classification of Colloidal Solutions

according to the size of the particles contained in them and according to their behavior upon desiccation.

than practical, for the properties of colloids are dependent mainly upon the specific nature of the dispersed substance and its degree of subdivision. Following Hardy, Zsigmondy divided colloids into two classes, the *reversible* and *irreversible;* the former redissolve after desiccation at ordinary temperatures, whereas the latter do not.

Table II, taken from Zsigmondy,* illustrates this classification, and shows how colloids having the same particle size or degree of subdivision may nevertheless act quite differently because of specific differences in the nature of the dispersed substances.

With the reversible colloids (gelatin, gum arabic, albumen), there is a more intimate union between the two phases; in fact it is probable that with them we have really a mixture of (1) a dispersed phase of water subdivided in the solid, with (2) a dispersing phase of the solid finely subdivided in water. The reversible colloids are therefore called *emulsoids* and the irreversible colloids *suspensoids.* Colloids of the reversible type are also said to be *hydrophile* or *lyophile,* while the irreversible colloids are *hydrophobe* or *lyophobe.*†

No sharp line is to be drawn, however, for besides intermediate or transition cases between the two classes, there may be recognized two groups of irreversible colloids, roughly defined by their behavior upon concentration:

First: The *completely irreversible,* which coagulate while still quite dilute and separate sharply from the solvent with the formation of a pulverulent precipitate rather than a gel (i.e., pure colloidal metals). Chem-

* "Colloids and the Ultramicroscope," J. Wiley & Son, Inc. (Translation by J. Alexander.)

† Hydrophile = water-loving; hydrophobe = water-hating. Lyophile = solution-loving; lyophobe = solution-hating.

ical or electrical energy is needed to bring them back again into colloidal solution.

Second: The *incompletely reversible* which, when quite concentrated, form a gel that may be easily redissolved or *peptized* by comparatively small amounts of reagents, unless the evaporation has proceeded too far (i.e., colloidal stannic acid).

CHAPTER IV

CONSEQUENCES OF SUBDIVISION

As the subdivision of a substance proceeds, the area of its effective surface increases enormously, as may be seen from the following Table III adapted from Ostwald. Consequently surface forces, such as adsorption, capillarity and surface tension, become enormously magnified and of primary importance. Furthermore, the so-called radius of molecular attraction ($\rho = 50\ m\mu$) is well within the colloidal field, so that the specific attractive forces of the particles also enter as a controlling factor. In fact, before substances can unite chemically their particles must be first brought into proper subdivision and proximity,* by solution, fusion, ionization or even by mere pressure, as was demonstrated by W. Spring,† who caused fine dry powders to combine chemically by high pressure. If the degree of subdivision is not profound enough to permit of the combination of isolated atoms or ions with each other, chemical combination in the strict sense may not occur, but there may be produced "adsorption compounds" resulting from the union of atomic or ionic mobs in indefinite or nonstoichiometric proportions, under the influence of more or less modified chemical forces. The combination of arsenious acid and ferric oxid which Bunsen regarded as a

* It is a striking fact that absolutely dry sodium is not attacked by absolutely dry chlorin. M. Raffo and A. Pieroni observed that colloidal sulphur reduced silver salts energetically, whereas even fine precipitated sulphur did not form silver sulphide in the cold, and did so only partially upon boiling.

† In 1914 the Société Chimique de Belgique gathered and reprinted the work of this brilliant and prolific investigator, in two large volumes.

TABLE III. RESULT OF PROGRESSIVE DECIMAL SUBDIVISION OF A CUBE

Length of edge.	Number of cubes.	Total surface.
1 cm. = 0.3937 in.	1	6 sq. cm. = 0.93 sq. in.
1 mm. = 0.0394 in.	1,000	60 sq. cm. = 9.3 sq. in.
0.1 mm. = 0.0039 in.	1,000,000	600 sq. cm. = 93 sq. in.
0.01 mm. = 0.0004 in.	1,000,000,000	6000 sq. cm. = 6.46 sq. ft.
1 μ = 0.001 mm.	1,000,000,000,000	6 sq. m. = 64.58 sq. ft.
0.1 μ = 0.0001 mm.	1,000,000,000,000,000	60 sq. m. = 645.83 sq. ft.
0.01 μ = 0.00001 mm.	1,000,000,000,000,000,000	600 sq. m. = 6458.33 sq. ft.
1 $m\mu$ = 0.001 μ	1,000,000,000,000,000,000,000	6000 sq. m. = 1.48 acres
0.1 $m\mu$ = 0.0001 μ	1,000,000,000,000,000,000,000,000	6 hectares = 14.83 acres
0.01 $m\mu$ = $\frac{4}{10,000,000,000}$ in.	1,000,000,000,000,000,000,000,000,000	60 hectares = 148.26 acres
*0.001 $m\mu$ = $\frac{4}{100,000,000,000}$ in.	1,000,000,000,000,000,000,000,000,000,000	6 sq. kilometers = 1482.6 acres = $2\frac{1}{3}$ sq. miles

* These subatomic dimensions are 1000 times larger than the theoretical size of electrons

$$1\ \mu = \frac{1}{1,000}\ \text{mm.};\quad 1\ m\mu = \frac{1}{1,000}\ \mu.$$

basic ferric arsenite, 4 Fe_2O_3, As_2O_3, 5 H_2O, has been shown by Biltz and Behre to be an adsorption compound; and Zsigmondy proved "purple of Cassius" to be an adsorption compound of colloidal gold and colloidal stannic acid by actually synthesizing it by mixing the two separate colloidal solutions. Zsigmondy's proof has been further confirmed by A. Huber (Physikal. Zeit. (1924), *25*, 45) who examined the purple of Cassius with the X-ray spectrometer and found that none of the gold is in chemical combination.

The effect of increasing subdivision upon the particles in colloidal solutions is illustrated in Table IV, adapted from Zsigmondy. Tables V and VI were prepared by Zsigmondy to illustrate visually the relation of the sizes of colloidal particles to well-known microscopic objects on the one hand and to the theoretical sizes of molecules on the other.

TABLE IV

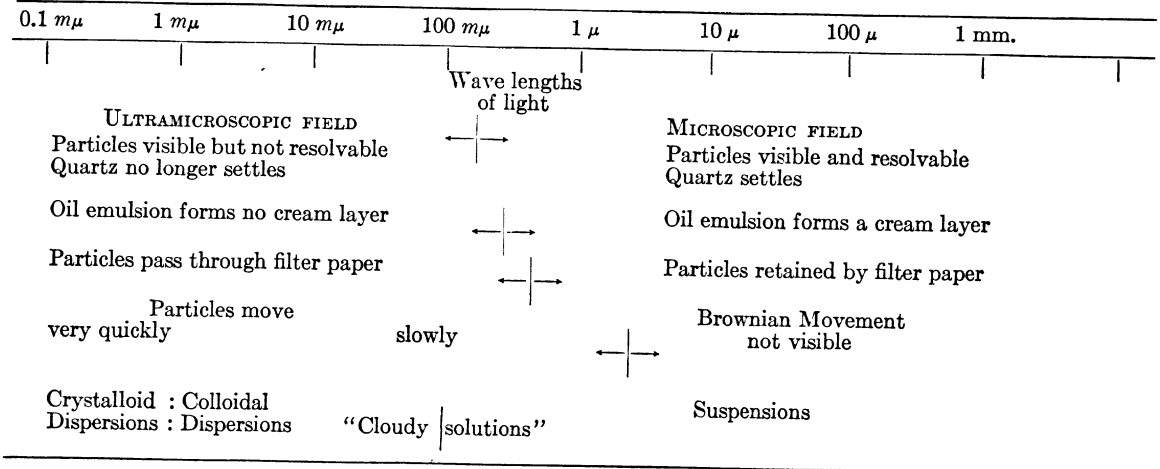
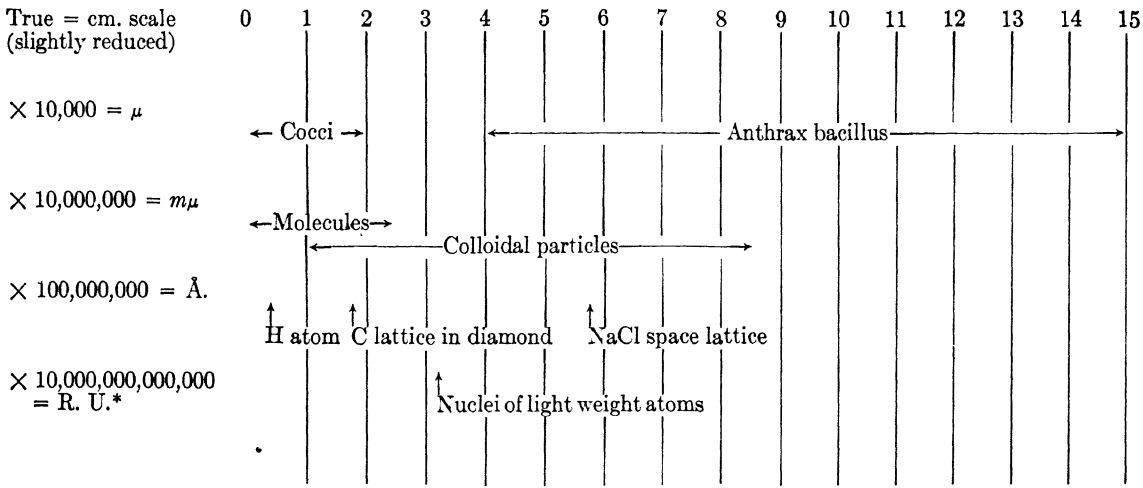

0.1 mμ
1 mμ
10 mμ
100 mμ
1 μ
10 μ
100 μ
1 mm.
Wave lengths of light
Ultramicroscopic field
Particles visible but not resolvable
Quartz no longer settles
Oil emulsion forms no cream layer
Particles pass through filter paper
Particles move very quickly
Crystalloid : Colloidal Dispersions : Dispersions
"Cloudy" solutions
slowly
Microscopic field
Particles visible and resolvable
Quartz settles
Oil emulsion forms a cream layer
Particles retained by filter paper
Brownian Movement not visible
Suspensions

CHART SHOWING SIZES OF VARIOUS UNITS AT VARIOUS MAGNIFICATIONS

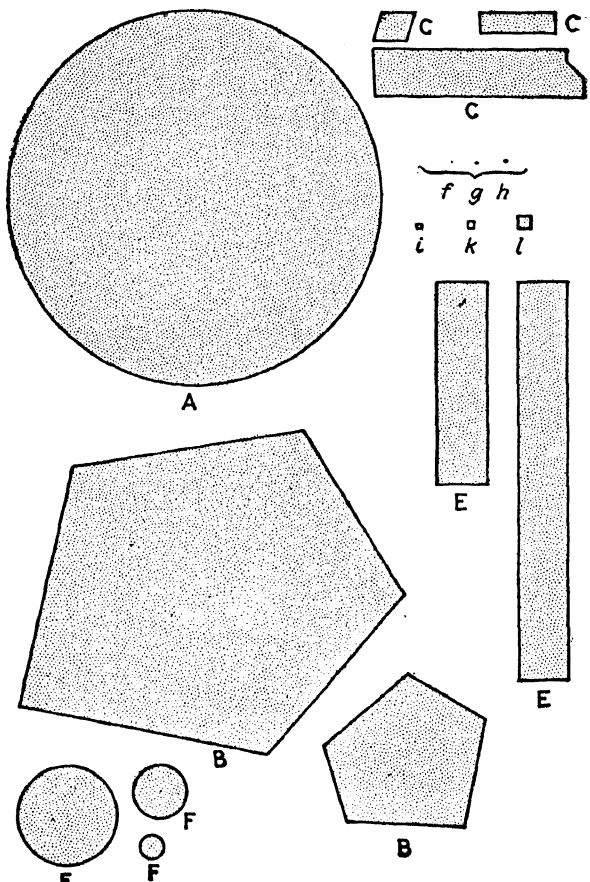


* In dealing with the extremely minute sizes involved in describing nuclear diameters, it is convenient to use a unit of measurement one million times smaller than 1 $m\mu$. This I have termed a "Rutherford Unit" (R. U.), and therefore 1 R. U. $= \frac{1}{100{,}000}$ Å. $= \frac{1}{1{,}000{,}000}\, m\mu$.

From Alexander, Vol. 1, p. 15.

TABLE V

LINEAR MAGNIFICATION 1: 10,000



A. Human blood corpuscles (diameter 7.5 μ, thickness 1.6 μ).
B. Fragment of rice starch granule (according to v. Höhnel) 3–8 μ.
C. Particles in a kaolin suspension.
E. Anthrax bacillus (length 4–15 μ, width about 1 μ).
F. Cocci (diameter about 0.5–1 μ, rarely 2 μ).
f, g, h. Particles of colloidal gold solutions Au_{73a}, Au_{92}, Au_{97} (0.006–0.015 μ).
i, k, l. Particles from settled gold suspensions (0.075–0.2 μ).

CHAPTER V

THE ULTRAMICROSCOPE

As this instrument revolutionized colloid research, a brief description of it is essential.

It is a matter of every-day experience that the unseen motes and dust particles in the air become visible in a beam of bright light, especially against a dark ground, and in this simple fact lies the principle of the ultramicroscope.

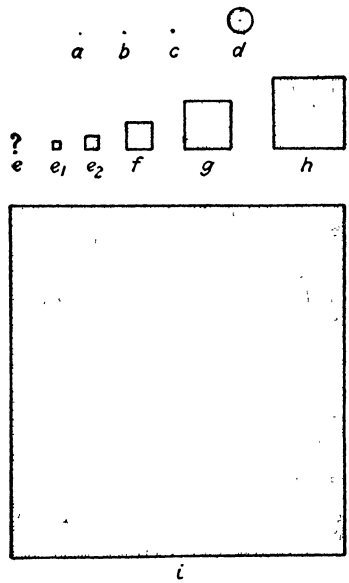
Faraday and later Tyndall made use of a convergent beam of light to demonstrate the optical inhomogeneity of solutions; for in fluids not optically clear, the path of the beam becomes more or less distinctly visible, because of the light scattered by the particles present. In this manner can be recognized much smaller quantities of matter than by spectrum analysis—in fact less than 10^{-8} mg. (1/10,000,000) of metallic gold can thus be detected with the naked eye.

Prof. Richard Zsigmondy while experimenting with colloidal solutions conceived the idea of examining this light cone microscopically. His preliminary experiments having demonstrated that he could thus see the individual particles in various hydrosols, he sought the assistance of Dr. H. Siedentopf, scientific director of the Zeiss factory, in Jena, where was produced the first efficient ultramicroscope.

The ultramicroscope consists essentially of a compound microscope arranged for examining in a dark field an intense convergent beam of light cast within or upon the substance under examination. The light

TABLE VI

LINEAR MAGNIFICATION 1 : 1,000,000



a–d —*Estimated Molecular Dimensions*

a. Hydrogen molecule—dia. 0 1 *mμ.*
b. Alcohol molecule—dia. 0 5 *mμ.*
c. Chloroform molecule—dia 0 8 *mμ.*
d. Molecule of soluble starch—dia. about 5 *mμ.*

e–h.—*Gold Particles in Colloidal Gold Solutions*

e. Gold particle in Au_{16} (too small to determine).
e_1. " " " " , about 1 7 *mμ.*
e_2. " " " " , " 3 0 *mμ.*
f. " " " Au_{73a}, " 6 *mμ.*
g. " " " Au_{92} , " 10 *mμ.*
h. " " " Au_{97} , " 15 *mμ.*
i. Gold particle in settled gold suspension.

seen by the eye represents, therefore, the light diffracted, scattered or reflected upward by the substance or by particles within it.

If within a thin beam of light from a projection lantern we scatter successively powders of different substances in various degrees of fineness (mica ground to pass 60, 100 and 160 mesh; lampblack; powdered oxid of zinc; flake and powdered graphite), some of them will produce only a homogeneous illumination of the beam in which no isolated particles can be seen, whereas with others, the individual particles are distinctly visible.

Passing the beam through a beaker of distilled water, nothing can be seen; but upon the addition of a few drops of colloidal gold solution, which appears quite clear to transmitted light, the path of the beam through the fluid immediately becomes visible. This Tyndall effect,* as it is called, might be considered a criterion of colloidal solution were it not that very minute traces of colloidal impurities can produce it and it is often exhibited by solutions generally regarded as crystalloidal—those of many dyestuffs for example; furthermore with increasing fineness of subdivision the Tyndall effect decreases, disappearing as molecular dimensions are approached.

Just as in the cosmic field our most powerful telescopes fail to resolve the fixed stars, which are nevertheless *visible* as points of light of varying brilliancy, so, too, in the ultramicroscopic field, we can *see* particles much smaller than the resolving power of the

* Also known as the Faraday-Tyndall effect. It is commonly shown by every searchlight at night, and when the sun "draws water" or throws a beam of light into a partly darkened room, the observer looking across the beam.

microscope (that is, smaller than a wave length of light) provided only that they diffract sufficient light to affect the retina. Based upon the experience of astronomers we may be able greatly to increase the sensitiveness of the ultramicroscope by fortifying the eye, so to speak, with the photographic plate, using at the same time tropical sunlight or ultraviolet * light for illumination.

In the original form of the ultramicroscope, as perfected by Siedentopf and Zsigmondy, which is the one best adapted for the examination of transparent solids, a side illumination is effected by a microscope objective with micrometer movements, which throws an intense but minute conical beam of light into the fluid contained in a little cell having quartz windows at the side and top. Above this cell a compound microscope is adjusted vertically, so that the narrowest part of the light cone occupies the center of the focal plane. If the fluid under examination is optically clear or if it contains particles so small that they cannot diffract sufficient light to create a visual impression, the light cone cannot be seen. If enough light is diffracted, the light cone becomes visible, being homogeneous if the particles are too small or too close together to be individually seen, and heterogeneous if the particles can be individually distinguished. Particles or dimensions beyond the resolving power of the microscope (about $\frac{1}{4}\ \mu$) are for brevity termed *ultramicrons*. Ultramicrons that can individually be made visible are called *submicrons* (or hypomicrons) while those so small that they produce an unresolvable light cone are termed *amicrons*.

*This has recently been done by T. Svedberg.

Small primary colloidal particles Zsigmondy terms "*protones.*" If protones aggregate they yield secondary colloidal particles or "*polyones.*"

Knowing the percentage of gold present in a colloidal gold solution and assuming a certain specific gravity and uniform shape for the gold particles, the average size and mass of a single particle of colloidal gold can be calculated, if the number present in a given volume be first counted. In this manner Zsigmondy has shown that the smallest particles of colloidal gold which can be individually distinguished with bright sunlight are approximately 5 $m\mu$ in diameter, that is, five millionths of a millimeter; still smaller particles exist but they produce only an unresolvable light cone. Magnified 1,000,000 times such a tiny gold particle would be about ¼ inch in diameter, while a human red blood corpuscle would be about 25 feet across, and a hydrogen molecule a speck barely visible. The gold particles in the unresolvable light cone must therefore closely approach molecular dimensions. In fact, by allowing amicrons to grow into visibility in a suitable solution and then counting them, Zsigmondy has recently shown that some of the particles of colloidal gold have a mass of $1\text{–}5.10^{-16}$ mg., indicating a size of 1.7 to 3 $m\mu$.

Various other types of ultramicroscopes, mainly modifications of dark field illumination, have been developed by Cotton and Mouton, Ignatowski (made by Leitz), Siedentopf (cardioid condenser, made by Zeiss) and others, and besides being useful in examining colloidal solutions, they have enabled pathologists to see and discover ultramicroscopic bacteria (spirochetes, infantile paralysis).

Bausch & Lomb Optical Co. of Rochester, N. Y., are now producing a useful ultramicroscope.

CHAPTER VI

GENERAL PROPERTIES OF COLLOIDS

The optical properties of colloids and their simulation of chemical compounds have been already referred to. The other general properties of colloids may be considered under the following headings:

1. Colloidal Protection.
2. Dialysis, Ultrafiltration and Diffusion.
3. Electric Charge and Migration.
4. Pectization (Coagulation) and Peptization.
5. Viscosity.

Colloidal Protection

Without an understanding of the underlying principles, isolated facts have long lain like individual gems scattered or even lost in the wide fields of human experience. A theory is necessary to string them together, each in its proper place, to form a beautiful necklace; or rather, a theory to serve as a matrix that forms of them a cutting drill, with which we may bore into the hard rocks of the still unknown.

Continually, throughout chemical literature, the use of protective substances crops up, only to be buried again or to be hidden in the *oubliette* of some rule-of-thumb formula. The *aurum potabile* of the alchemist was made by reducing gold chloride in the presence of ethereal oils. Then followed the use of solutions of tin which stabilized the gold sol by the stannic oxide simultaneously produced, giving the rich purplish red solution known as the *purple of Cassius.* In 1794

colloidal gold produced *in situ* was known as a dye for silk; in 1821 egg-white, isinglass, and starch were used as protectors for gold sols; and the *Lehrbuch* of Berzelius (1844) contains several recipes for producing gold sols of various shades. In 1856 Faraday * reports the discovery of jelly (evidently isinglass or gelatin) as a protector to colloidal gold; and, finally, Zsigmondy (1898), then unaware of the preceding work, rediscovered gold sols.†

Thomas Graham was probably the first to recognize colloidal protection, as such. (See Zsigmondy, "Colloids and the Ultramicroscope," p. 43.) In his paper on diffusion (see Chapter II), Graham describes the dialysis of crude caramel, obtained by heating raw sugar to 210–220° C. a colored substance diffuses away, leaving behind the portion richest in carbon, which, in 10 per cent solution, is gum-like and forms a weak water-soluble jelly. When thoroughly dry this dialysis residue can be heated to 120° C., and still remain completely soluble; but it becomes insoluble if evaporated to dryness on a water-bath. Both the soluble and the insoluble caramel have the same empirical formula, $C_{24}H_{15}O_{15}$.‡ The liquid caramel is quite tasteless, neutral in reaction, and is extremely sensitive to crystalloid reagents. Traces of mineral acids, alkali salts, and alcohol make it pectous; the precipitated caramel yields a brownish-black powdery substance, insoluble in hot or cold water. Graham then states: "The presence of sugar and of the intermediate brown substances protects the liquid caramel in a remarkable degree from the action of

* *Phil. Trans.*, **1857**, p. 145.

† "Colloids and the Ultramicroscope," **1909**.

‡ We would now write H_{30} instead of H_{15}.

crystalloids, and accounts for the preceding properties not being observed in crude caramel."

In dilute potash the pectous caramel becomes gelatinous and dissolves again on heating. Caramel is 600 times less dialysible than sodium chloride (ordinary table salt), and 200 times less than sugar. Referring to the analogy between caramel and anthracite coal, Graham states: "Caramelization appears the first step in that direction—the beginning of a colloidal transformation to be consummated in the slow lapse of geological ages."

A most important contribution of Zsigmondy, however, was his demonstration that stable though highly sensitive gold sols could be made without the use of protectors provided the presence of coagulators was avoided, and also the proof that these sensitive sols could be stabilized by the addition of gelatin, gum, and the like. Then only did the full import of colloidal protection begin to dawn and the use of the principle, as such, begin to be understood and developed. Zsigmondy also synthesized the purple of Cassius by simply mixing the pure colloids of gold and stannic acid, thus proving that here the stannic acid takes the part of a protector.

Von Meyer and Lottermoser* had just previously re-discovered protective action as such, calling attention to the fact, long utilized by practical photographers, that albumin stabilized silver sols. Lottermoser† later said that "on the addition of very stable colloids, as albumin, gelatin, agar, or gum arabic, to a silver sol, no precipitation is caused by electrolytes

* *J. prakt. Chem.*, **56** (1897), 241.

† "Anorganische Kolloide," **1901**, p. 50.

until the stable colloid is coagulated. The less stable silver sol is thus protected against the electrolyte by the more stable colloid; it becomes more like the latter in its behavior."

Gold Number

With his pure but sensitive ruby-red gold sols (gold content about 0.005 to 0.006 per cent), Zsigmondy then established the relative protective value of a number of protective substances. The "gold figure," compiled from the results of Zsigmondy and Schryver (see below), indicates the number of milligrams of protector which just fail to prevent the coagulative color change from red to violet of 10 cc. of the colloidal gold solution upon the addition of 1 cc. of 10 per cent sodium chloride solution. It must be remembered that the relative protective values were determined with gold, and while they are generally maintained, they may be different with other substances, especially those that coagulate the protector or adsorb it poorly. A substance fixed by adsorption often does not behave as it does when free, so that stability and protective power are not necessarily parallel functions.

Substance	Gold Number
Gelatin	0.005 to 0.01
Russian glue	0.005 to 0.01
Isinglass	0.01 to 0.02
Casein (in ammonia)	0.01
Egg-globulin	0.02 to 0.05
Ovomucoid	0.04 to 0.08
Glycoprotein	0.05 to 0.1
Amorphous egg-albumin	0.03 to 0.06
Crystallized egg-albumin	2.0 to 8.0
Fresh egg-white	0.08 to 0.15
Gum arabic	0.5 to 4.0

Gum tragacanth	2.0 ±
Dextrin	6.0 to 20.0
Wheat starch	5.0 ±
Potato starch	25.0 ±
Sodium oleate	0.4 to 1.0
Sodium stearate at 100 degrees	0.01
Sodium stearate at 60 degrees	10.0
Deutero-albumose	∞
Cane sugar	∞
Urea	∞
Stannic acid sol (old)	∞

Zsigmondy, following W. B. Hardy, classified colloid sols into two broad classes, based on their behavior on desiccation—the reversible or resoluble, and the irreversible or irresoluble sols. These correspond roughly with the groups hydrophile-hydrophobe (Freundlich), lyophile-lyophobe (Perrin), and suspensoid-emulsoid (Wo. Ostwald). Although some salts (citrates, sulfocyanates) may act as protectors, protection is generally accomplished by adding a reversible or emulsoid colloid to an irreversible one, which thereupon acquires reversible properties—that is, it becomes insensitive to electrolytes, redissolves after desiccation (at any temperature that does not render the protector insoluble), and passes through ultrafilters that would otherwise hold it back.

The generally accepted explanation of this phenomenon is that advanced by Bechhold,* that the protector is adsorbed at the free surfaces of the protected particle. Zsigmondy supports this view, although he was unable to detect ultramicroscopically any sign of the adsorbed layer or any diminution in the Brownian motion. This is not surprising, as the

* *Z. phys. Chem.*, **48** (1904), 385.

protecting layer is probably only a few molecules thick. Another possibility is that the protector, following its adsorption, may change the net charge of the particles.*

Experimentally, it is a most surprising fact that certain minimal quantities of protectors actually sensitize instead of protect, and may themselves even produce flocculation. Thus, according to Bechhold,† 0.0003 to 0.0001 parts of gelatin per million will flocculate gold sols or oil emulsions. The work of J. Billiter ‡ indicates that this is due to the fact that in such cases the minute amount of added protector brings the other colloid to or near the isoelectric point, where, as Hardy has shown, all colloids are especially susceptible to coagulation.

From what has been said it is evident that although, in general, oppositely charged colloids precipitate each other, if an excess of a positive protective reversible (emulsoid) sol is quickly added to a negative irreversible (suspensoid) sol, the protector is adsorbed and protects before precipitation can occur. If, however, only a very small quantity of the protector is used, or, what amounts practically to the same thing, if the protector be added very slowly, precipitation may occur before protection can be established—that is, precipitation may depend upon the speed of mixing as well as on the relative proportions mixed. This gives us also an explanation of the curious "zones of

* Millikan ("The Electron"; also Alexander, Vol. 1, p. 181) was able to have colloidal droplets of oil, mercury, etc. "capture" *as many as 150 electrons.* All "charges" therefore, are not necessarily due to chemical "ions."

† "Colloids in Biology and Medicine," *translated* by J. G. M. Bullowa

‡ *Z. phys. Chem.*, **51** (1905), 142.

precipitation" investigated by Neisser and Friedmann, H. Bechhold, Teague and Buxton, A. Lottermoser,* and J. Biltz.

It is not at all strange that the behavior of a sol should be in large measure controlled by the nature of the outer layer or skin of its particles. Adhesion, as is well known, depends upon the nature of the outside layers, and so in fact does chemical action; for, while the nucleus of an elemental atom is mainly responsible for its atomic weight, its chemical behavior is governed by its outer ring or layer of electrons.

It would be a long task to discuss the numerous cases where colloids are used, wittingly or unwittingly, in scientific, medical, or technical practice, as protectors, deflocculators, and emulsifiers; or where they must be removed because their presence is detrimental. Problems of this kind abound in such widely diverse fields as photography, metallurgy, brewing, rubber, paper, glass, filtration, cooking, cement, agriculture, tanning, paints, pharmacy, biology, etc. Colloidal sols exist everywhere in the organism, and no reaction takes place there without being influenced by their presence.

To illustrate the working of protection, compare precipitates of silver chloride and tin or lead "trees" made in the presence and in the absence of gelatin, or divide a lead acetate solution into three parts, adding a little hot gelatin solution to the last. The first will give with hydrochloric acid a curdy precipitate of lead chloride; the second will give with sodium chloride (which is less highly ionized than HCl) a turbid lead chloride sol; while the gelatin-

* See paper by A. Lottermoser in Alexander's "Colloid Chemistry, Theoretical and Applied," Vol. I (Chemical Catalog Co., 1926).

containing solution will, preliminarily at least, show no visible turbidity with sodium chloride.

Simple colloidal protection has long been known. Let us now consider some newer aspects of this remarkable phenomenon—namely, double or plural protection, autoprotection, and cumulative protection.

Double or Plural Protection

In 1908, while experimenting with milk, it seemed that casein might be an adsorption product containing protein and calcium salts. Accordingly, an attempt was made to produce a colloidal precipitate of calcium phosphate in the presence of such protectors as gelatin and gum arabic. The protector was added first to the sodium phosphate alone and then to the calcium chloride alone; but in neither case could a precipitate be obtained which approached casein in fineness or stability.

Upon following mentally the course of the formation of colloidal calcium phosphate in the body, the idea was conceived that, since in the organism all reacting fluids hold protectors, perhaps the result could be obtained by adding some protector to *both* of the reacting solutions. The experiment was at once tried, and yielded, with gelatin as protector, a colloidal calcium phosphate which could be precipitated by both acid and rennin. Upon emulsifying some olive oil in the mixture, a stable artificial milk was obtained. Thus was developed the principle of double or plural protection, for which a U. S. patent was secured. (U. S. P. No. 1,259,708.)

The literature contains several instances where this principle has been used in a more or less empirical

manner. These were found subsequent to taking the patent. Thus, Carey Lea produced some of his colloidal silver by the following formula:

Solution 1		Solution 2	
Water	800 cc.	Water	800 cc.
20 per cent Rochelle salt solution	200 cc.	20 per cent Rochelle salt solution	200 cc.
40 per cent silver nitrate solution	50 cc.	30 per cent crystalline ferrous sulfate solution	107 cc.

Solution 2 was then added to Solution 1. The Rochelle salt here acts as a protector.

In the photographic field the so-called Lippmann "grainless" emulsion is made by the following formula:

Solution 1		Solution 2	
Gelatin	75 grains	Gelatin	75 grains
Potassium bromide	3 grains	Silver nitrate	45 grains
Water	8 oz.	Water	8 oz.

The ingredients are mixed in the order given; and after allowing the gelatin to swell, the solutions are heated to 95° F. Then Solution 2 is added to Solution 1.

Lobry de Bruyn * found that, upon adding gelatin to both reacting solutions, precipitation may in many cases be inhibited, a colloidal dispersion resulting. Thus, under these conditions potassium bichromate and silver nitrate give a brick-red coloration but no precipitate. In general, Lobry de Bruyn used 0.1 to 0.05 *N* solutions, protecting them with 5 to 10 per cent of gelatin.

The value of this principle in producing colloidal precipitates is obvious, especially for colors, insecticides, pharmaceutical preparations, etc. It is also of

* *Rec. trav. chim.*, **19** (1900), 236; *Ber.*, **35** (1902), 3079.

the highest importance in biology and medicine, and may serve to explain many anomalies in physiology, pathology, and related branches, where things happen *in vivo* that are not duplicated *in vitro*. Almost no reactions occur in the organism which are not controlled by the protective colloids everywhere present.

Autoprotection

Many substances are naturally prone to assume the colloidal state, and in a large number of these it appears that the molecular aggregates first reaching the colloidal degree of dispersion where surface forces predominate, adsorb the less aggregated groups or isolated molecules, and thus the advance toward visible crystallization is delayed, or, for all practical purposes, entirely inhibited. Such a condition occurs in sulfur and also in pure iron, where one allotrope, γ-iron, seems to be adsorbed by α-iron (ferrite). Ammonium salts, in particular, and some oleates exhibit the phenomenon. The globulitic stage is often a precursor to crystallization, but conditions may prevent emergence from this stage. Lactose acts this way. Several remarkable cases of autoprotection have been reported and these will be briefly considered.

W. B. Hardy * found that 5-dimethylaminoanilino-3, 4-diphenylcyclo-1, 2-dione, upon cooling from its solutions in organic solvents, gives gels that gradually become crystalline. Gortner and Hoffmann † report that dibenzoyl-l-cystine forms even in 0.2 per cent solution a rigid gel, which in the course of several weeks crystallizes almost completely. So powerful is

* *Proc. Roy. Soc.* (*London*), **87A** (1913), 29.

† *J. Am. Chem. Soc.*, **43** (1921), 2199.

its gelatinization that this dilute solution makes as strong a jelly as a 5 per cent solution of gelatin. Camphorylphenylthiosemicarbazide acts similarly, its solutions in organic solvents forming, on quick cooling, gels that gradually become crystalline.*

Cumulative Protection

The general rule in colloidal protection is that anything which removes, coagulates, or destroys the protector, or disperses it crystalloidally, will cause the protected dispersion to coagulate. Thus, on adding ferric chloride to olive oil emulsified with gum arabic, the gum is coagulated and loses its emulsostatic action, so that the oil separates out—the emulsion "breaks." On the other hand, anything that protects the protector—that is, stabilizes it against coagulation, crystalloidal dispersion, or destruction—will tend to stabilize the protected sol. Thus, some ammonia in a gelatin-protected sol would tend to prevent the coagulation of the gelatin by formaldehyde, and an antiseptic would prevent its dispersion by bacteria or enzymes which, as the work of E. Zunz indicates, may convert protectors into coagulants. The rennin coagulation of milk seems to be of this nature, the enzyme converting the protective lactalbumin into a coagulant.†

This introduces a new idea—cumulative protection. In many cases we must expect to find that the protector of the protective colloid is itself a colloid, and there is no reason to doubt that cumulative protection may extend through a series of several colloids, or

* Forster and Jackson, *J. Chem. Soc.*, **91** (1907), 188; E. Hatschek, *Kolloid Z.*, **11** (1912), 158.

† Alexander, *8th Intern. Cong. Appl. Chem.*, **1912**.

colloids and crystalloids, giving a structure which, like a house of cards, may collapse if any one of its essential supports is removed.

This aspect of protection does not seem to have been recognized or investigated experimentally as such, and it offers a wide field for research. As instances of its practical operation may be mentioned glasses, alloys, and the gluten of wheat and rye flours. Many protein and similar complexes may be built up in this fashion.

Dialysis

Colloid solutions possess a small but definite diffusibility through colloidal septa (parchment paper, bladder) as was recognized by Graham, who found that "tannic acid passes through parchment paper about 200 times slower than sodium chlorid; gum arabic 400 times slower." * Graham's original form of dialyzer may be made from a wide-mouthed bottle whose bottom has been removed.† The mouth is closed by a piece of bladder or parchment paper tightly bound on, the solution to be dialyzed is poured in, and the bottle immersed about halfway in water contained in a larger vessel. Most of the crystalloids diffuse through the membrane into the outer water, which should be frequently renewed, while most of the colloids remain in the original bottle, and may be thus obtained in a purified condition. Improved modern dialyzers consist of parchment or collodion sacs or

* It is commonly but erroneously stated, even in text books, that colloids do not diffuse or dialyze. The extent to which dialysis occurs depends mainly on the fineness of the colloidal particles, the nature of the septum, and *time*.

† A lamp chimney will answer very well, and a piece of kid glove will serve as a septum.

thimbles, or even of whole bladders, which have the advantage of a larger dialyzing surface.

Ultrafiltration

H. Bechhold found that he could make filtering membranes of varying degrees of permeability by forming them from jellies of varying concentration. He used principally collodion dissolved in glacial acetic acid and afterward immersed in water, and gelatin jellies hardened in ice-cold formaldehyde. The jellies were formed and hardened on pieces of filter paper, which were supported from below by nickel wire cloth, and clamped between two flanges. The liquid to be subjected to ultrafiltration is intro-

TABLE VII

Suspensions.
Prussian blue.
Platinum sol (made by Bredig's method).
Ferric oxid hydrosol.
Casein (in milk).
Arsenic sulphid hydrosol.
Colloidal gold hydrosol (Zsigmondy's No. 4, particles about 40 $m\mu$).
Colloidal bismuth oxid (Paal's "Bismon").
Colloidal silver (Paal's "Lysargin").
Colloidal silver (von Heyden's "Collargol," particles about 20 $m\mu$).
Colloidal gold hydrosol (Zsigmondy's No. 0, particles about 1–4 $m\mu$).
Gelatin solution, 1 per cent.
Hemoglobin solution, 1 per cent (molecular weight about 16,000).
Serum albumin (molecular weight about 5000 to 15,000).
Diphtheria toxin.
Protalbumoses.
Colloidal silicic acid.
Lysalbinic acid.
Deuteroalbumoses *A*.
Deuteroalbumoses *B* (molecular weight about 2400).
Deuteroalbumoses *C*.
Litmus.
Dextrin (molecular weight about 965).
Crystalloids.

duced in the chamber thus formed and forced through the prepared septum by appropriate pressure, which may run up to 20 atmospheres or more and may be produced by a pump or by compressed gas (air, nitrogen or CO_2). Table VII (page 64), prepared by Bechhold, shows various colloids arranged in order of the diminishing size of their particles in solution, and was obtained by using ultrafilters of varying degrees of porosity or permeability.

By means of ultrafiltration through ultrafilters of appropriate permeability, not only may colloids be separated from crystalloids, but colloids having particles of different sizes may be separated from each other.

Great care must be used in gauging the size of the pores in ultrafilters. Thus Prof. Richard Zsigmondy in Chapter XIV, on "Filtration Experiments," of his book "Colloids and the Ultramicroscope" (Wiley & Sons, 1909), says:

All three kinds of filters (Maassen, Pukall and Chamberland) contain pores large enough to allow the passage of gold particles of about 30 $m\mu$ and less. The pores of a cell are of very different sizes, the Chamberland cell containing, for example, large pores, which allow the gold particles to pass through, and others which retain most of them. The size of the pores is, however, not the sole criterion in filter experiments. It is of especial importance in coarse filters, whether the particles to be filtered are held to the surface of the cell by adhesion or "adsorption" (A), or not (B).

(A) In the first instance the substance to be filtered gathers upon the outside surface (and to a certain extent in the deeper pores), and prevents the other

particles from forcing their way through; first, because the pores are made smaller; second, because the particles held fast to the surface of the cell repel the freely moving particles following the course of the current.*

(B) When adhesion or adsorption does not take place, all colloidally dissolved substances pass freely through the cell, providing the pores are large enough.

In the presence of a protective colloid, e.g., egg albumen, all the gold particles pass smoothly through, whereas in the absence of protectors, matters proceed as in case (A). The fact that protected gold particles of 30 $m\mu$ and over easily pass through Maassen and Pukall filters should be of interest to bacteriologists. The Chamberland filter, too, contains, besides the very small pores chiefly present, others which permit the passage of particles of the size mentioned.

Another point of great importance to bacteriologists has been emphasized by Professor H. Bechhold, who found that lecithin emulsions whose droplets were several μ in diameter passed through ultrafilters capable of retaining hemoglobin, and whose pores were less than 30 $m\mu$ (pressure 150 g./cm.^{2}). Bechhold explains that the droplets assume a filiform shape in their passage, reforming on their exit.†

Bechhold says in the latter reference, p. 832:

Therefore the diameter of the pores of the ultrafilter gives no definite idea of the diameter of a retained

* This action may be due to the well-known negative electric charge of the particles, which apparently also affects the adhering gold particles.

† See Bechhold's "Colloids in Biology & Medicine," Bullowa's translation, Van Nostrand; also Vol. I of Alexander's "Colloid Chemistry, Theoretical and Applied," Chem. Cat. Co., 1926, articles on Ultrafiltration and Electro-ultrafiltration by Bechhold.

particle as far as *emulsions* are concerned, whose disperse phase has a low surface tension against the dispersing phase.

Since the work of Heilbronn, Chambers, Seifriz and others shows the great changes in viscosity which micro-organisms exhibit during mitosis, and since changes in the milieu may produce similar changes, we must observe many precautions before hazarding an opinion about size deduced from filtration experiments. Alteration of the pH of the milieu may modify the charges of particle and of filter, and even reverse them. Salt ratios and antagonism must be considered, as well as anything leading to formation of surface films. And these or other factors may influence the viscosity of protoplasm. Professor H. Schade illustrates a phagocyte passing in filiform fashion through an orifice very much less than its average diameter, and appearing in its usual guise after it emerges on the other side of the membrane. (See Alexander, Vol. II, p. 664.)

Diffusion

Diffusion through a septum is, of course, involved in dialysis. If, however, diffusion occurs *into a jelly*, many interesting phenomena may develop, especially if the jelly adsorbs any of the diffusing substances or contains substances which can react with them.

Owing to the enormous surface they present, colloidal gels exhibit a powerful adsorptive action. In fact, even when percolated through such a relatively coarse-grained septum as sand, most solutions issue with a materially reduced content of solute, and benzopurpurin solutions may be thus decolorized.

Further, if a solute hydrolyzes into ions having different degrees of adsorbability or different rates of diffusibility, they may be actually separated by diffusion through a colloidal gel.

This phenomenon is nicely exhibited by what may be termed a "patriotic test tube," prepared by filling a tube about two-thirds full with a slightly alkaline solution of agar containing a little potassium ferrocyanid and enough phenolphthalein to turn it pink. After the agar has set to a firm gel, a solution of ferric chlorid is carefully poured on top, and almost instantly the separation becomes evident. The iron forms with the ferrocyanid a slowly advancing band of blue, before which the more rapidly diffusing hydrochloric acid spreads a white band as it discharges the pink of the indicator. After the lapse of a few days the tube is about equally banded in red, white, and blue.

Even then the tubes do not cease to be of interest, for if they are allowed to stand several weeks the pink color is all discharged and there develop peculiar bands or striations of blue, apparently due to the fact that the iron ferrocyanid temporarily blocks the diffusion passages, which are gradually opened again after a layer of the blue salt has diffused on from the lower surface. (*Liesegang's rings.**)

Not only may ions be thus separated, but if two solutes in the same solvent possess different rates of diffusion or different degrees of adsorbability, they also may be separated from each other by diffusion through a colloidal gel or septum. (*Differential Diffusion.*)

* Liesegang's rings, named after Raphael Ed. Liesegang, are of importance in mineralogy (agates), geology (ore deposits), and biology (rhythmic banded structures).

Electric Charge and Migration

The particles of practically all colloidal solutions possess an electric charge, and under the influence of an electric current (difference of potential) move toward the electrode having the opposite charge. (*Electrophoresis.*) In general, when two substances are brought into contact, the one having the *higher* dielectric constant becomes *positively* charged, whereas the one with the *lower* dielectric constant becomes *negatively* charged (Cohen's Law). Since water has a high dielectric constant (80), most substances suspended in pure water become negatively charged and wander to the anode. On the other hand, if suspended in oil of turpentine, which has a low dielectric constant (2.23), they become positively charged and wander to the cathode.

If, however, electrolytes are present, Cohen's law is superseded by other controlling factors, such as the adsorption of ions, which may give their charge to the suspended particles. In fact Hardy found that in pure water albumin was amphoteric; in the presence of a trace of alkali it acquired a negative charge and migrated to the anode; but a trace of acid gave it a positive charge and it then migrated to the cathode. The following table shows the usual charge and migration tendency of a number of *aqueous* colloidal solutions.

The electrically charged particles tend to, and usually do, surround themselves with ions of the opposite charge, forming thus an *electric double layer*, as it is called. Or polar molecules may be oriented at the interface between the particle and the dispersion medium.

Charged + Migrate to Cathode (− Pole)	Charged − Migrate to Anode (+ Pole)
1. Hydrates of Fe, Cu, Cd, Al, Zr, Ce, Th.	1. Sulphids of As, Sb, Cu, Pb, Cd. Halides of Ag.
2. Titanic acid.	2. Stannic acid, silicic acid.
3. Colloidal Bi, Pb, Fe and Cu (Bredig's method).	3. Colloidal Pt, Au, Ag, and Hg, I, S, Se.
4. Albumen, hemoglobin, agar.	4. Gum arabic, soluble starch, gamboge, mastic, oil emulsion.
5. *Basic Dyes:* Methyl violet, Bismarck brown, methylene blue, Hofmann violet.	5. *Acid Dyes:* Eosin, fuchsin, anilin blue, indigo, soluble Prussian blue.

Pectization and Peptization

Briefly stated, pectization means the coagulation of a colloidal sol, and peptization its redispersion. If a small quantity of an electrolyte is added to a pure ruby red colloidal gold solution, the latter changes to a blue or violet color, and deposits its gold as a fine blackish coagulum or precipitate. By watching in the ultramicroscope the coagulation of very dilute milk by dilute acid, the individual particles of the colloidal casein may be seen to gather gradually together into groups, whose motion becomes progressively less as their size increases, until they are no longer able to stay afloat, and finally coagulate in large grape-like clusters. Hardy believes that the particles of colloids adsorb the oppositely charged ions of electrolytes present; at the *isoelectric point* (that is, when there is no excess either of positive or negative charges on the particles) coagulation occurs. If, however, an *excess* of electrolyte be added *all at once*, the isoelectric point may be passed before coagulation occurs, and the particles acquire a charge

opposite to the one they had originally. Under such conditions, no coagulation may result.

Burton epitomizes the difference in action of various electrolytes as follows: "Two remarkable results are evident on comparing the coagulative powers of various electrolytes on colloids of different kinds; first, the coagulation depends entirely on the ion bearing a charge of sign opposite to that of the colloidal particle; and, second, with solutions of salts, trivalent ions have, in general, immensely greater coagulative power than divalent ions, and the latter, in turn, much greater than univalent. Acids and alkalis in particular cases act more strongly than the corresponding salts."

High-tension electric discharges may also effect the coagulation or precipitation of a finely subdivided or dispersed phase; which fact was utilized by Sir Oliver Lodge in dispelling fogs, and by Cottrell in coagulating smelter and similar fumes.

Peptization.—So strong is the analogy between digestion and colloidal disintegration that Thomas Graham, the father of colloid chemistry, coined the word *peptization* to express the liquefaction of a gel. He first speaks of the coagulation or pectization of colloids. "The pectization of liquid silicic acid," he states, "and many other liquid colloids is effected by contact with minute quantities of salts in a way which is not understood. On the other hand, the gelatinous acid may be again liquefied, and have its energy restored by contact with very moderate amounts of alkali. The latter change is gradual, 1 part of caustic soda, dissolved in 10,000 water, liquefying 200 parts of silicic acid (estimated dry) in 60 minutes at 100 degrees. Gelatinous stannic acid also is easily

liquefied by a small proportion of alkali, even at the ordinary temperature. The alkali, too, after liquefying the gelatinous colloid, may be separated again from it by diffusion into water upon a dialyzer. The solution of these colloids in such circumstances may be looked upon as analogous to the solution of insoluble organic colloids witnessed in animal digestion, with the difference that the solvent fluid here is not acid but alkaline. Liquid silicic acid may be represented as the 'peptone' of gelatinous silicic acid; and the liquefaction of the latter by a trace of alkali may be spoken of as the peptization of the jelly. The pure jellies of alumina, peroxide of iron and titanic acid, prepared by dialysis, are assimilated more closely to albumen, being peptized by minute quantities of hydrochloric acid."

Peptization is in reality deflocculation, a dispersion of groups into separate particles which once more acquire active motion and remain afloat or in solution. The detergent action of soap and dilute alkalis is due to the fact that they deflocculate adhering particles of "dirt."

Viscosity

Viscosity depends largely on the relation between kinetic motion and free or specific surface. It may be measured by time of flow from an orifice under a fixed head or pressure (Ostwald or Engler types), or by measuring the force needed to shear layers of liquid past each other (Couette or MacMichael types). Crystalloid solutions exhibit low viscosity; the rapid motion of their particles aids flow. The relatively coarse suspensions are likewise not viscous, because of deficiency of active surface. In the colloidal zone

we find maximum viscosity, which falls off on either side (zone of maximum colloidality, see p. 23 et seq.).

Slowly moving particles exhibit inertia to the commencement of flow, and this accounts for what is known as "plasticity" or "yield value" of viscous materials. Theoretically everything should have some yield value, though in many cases it is not measurable, especially over limited time,* and with relatively slow rates of flow.

Surface Tension

The volume (and weight) of a drop of a liquid is so uniform, under uniform ordinary conditions, that medicines of various kinds are commonly prescribed to be taken in doses of so and so many drops. This does not mean, however, that drops of different kinds of liquids are alike in volume. By dropping alcohol, water, mucilage, mercury, and other liquids from the same medicine dropper, it will be seen that the drops of water are larger than those of alcohol, while mucilage gives still larger drops. If a definite number of drops of each liquid is collected in the same small measuring tube, it will be seen that the volumes differ considerably.

Why is this?

By making the drops form slowly, we see that they hold together, just as if they were surrounded by an

* See J. Alexander, "Glue and Gelatin," p. 98 et seq.

Thomas Graham said (Proc. Roy. Soc. Lond., 1864): The ultimate pectization of silicic acid is preceded by a gradual thickening in the liquid itself. The flow of liquid colloids through a capillary tube is always slow compared with the flow of crystalloid solutions, so that a liquid transpiration-tube may be employed as a colloidoscope. With a colloidal liquid alterable in viscosity, such as silicic acid, the increased resistance to passage through the colloidoscope is obvious from day to day. Just before gelatinizing, silicic acid flows like an oil.

invisible, flexible, distensible skin or bag. As the growing drop becomes heavier and heavier, the skin tears near the dropper tip, but instantly heals itself up to make a new bag bottom for the next drop. Meanwhile, the torn top of the "bag" surrounding the falling drop, has instantaneously closed itself to round out a sphere. This "skin" or "bag" effect is consequent upon the fact that the molecules at the outside are situated quite differently from those on the interior of the drop. The inside molecules are surrounded equally on all sides by their fellows, while the molecules in the surface film have only the relatively slight attraction of the air on the outside, and therefore stick or huddle together to make a surface *skin*. The tenacity of this skin is a measure of the *surface tension*, the force which holds the skin together.

Naturally, the specific gravity of the liquid (weight per unit volume) enters into our calculation, for the *weight* of a drop is what causes it to tear loose. If we *weigh* a definite number of drops, or *count* the number of drops given by a definite weight or volume of a liquid, we can calculate the surface tension.* A carefully made dropper which enables us to count the exact number of drops given by a definite volume of liquid is called a staglomometer or *drop-measurer* (Traube) or a *tonometer* (Kopaczewski).

Since the attraction between the exterior medium (air, in the cases we have been considering) and the material composing the drop, is a factor in determining the strength of the interfacial film (that is, the surface

* For detailed treatment of surface tension, see Alexander's "Colloid Chemistry, Theoretical and Applied," Vol. I (Chemical Catalog Co., 1926), especially the papers of Prof. Wm. D. Harkins and of Sir Wm. B. Hardy.

tension), it stands to reason that we must always specify *against* what medium the surface tension is measured. This can be readily shown by simple experiments. Thus if a drop of butter or fat be placed on a cup of hot water, it floats as a spheroid (a sphere flattened by weight of the drop) because the attraction between the fat particles for each other exceeds the attraction of the water surface for the fat. If we now increase the attraction between the fat and the water by dissolving some soap in the water, the conditions are reversed; the fat is dragged out into a thin skin on the surface of the water and upon slight agitation goes into a fine dispersion or emulsion. We have made oil and water mix, contrary to the old saw which says they won't.

From this it is obvious that if two substances have a low surface tension against each other, they will tend to "wet" each other. Water won't wet oil—until we add soap to reduce their surface tension against each other. That is why soap and alkalis make water wet greasy dishes, and emulsify the grease.

If we dip a perfectly clean capillary glass tube into water, the water will wet the interior of the capillary, and surface tension will drag a column of water to a considerable height in the capillary, and support it there. From the height of the "capillary rise," at equilibrium, the surface tension water/air may be calculated.*

* The general formula is

$$\gamma = \tfrac{1}{2}rhgd$$

where γ is the surface tension; r, the diameter of the capillary; h, the capillary rise; g the force of gravity (a constant, 980); and d, the density of the liquid (in this case, water, for which $d = 1$). For exact details, see Harkins' paper, *lib. cit.*, p. 246.

CHAPTER VII

PRACTICAL APPLICATIONS OF COLLOID-CHEMICAL PRINCIPLES

The practical applications of colloid chemistry are so manifold and widespread that they touch every branch of science and technology. Whole books may be and have been written on many of the most restricted fields, while the scientific literature teems with monographs and articles, directly on, or applicable to, colloid-chemical subjects. In what follows, it will be possible therefore to give not an exhaustive, but only a most general survey, intended primarily to show the ubiquity of colloid phenomena; and many important topics must be dismissed with a most rudimentary discussion, altogether incommensurate with their importance.

Practically all the substances we meet with in our everyday life are colloids, and we are mainly colloids ourselves. The foods we eat, the clothes and shoes we wear, the wooden furniture we use, the houses we live in with their windows, carpets and floors, the metals and rubber of our automobiles as well as their leather or leather substitutes, the very books and newspapers we read, and the paper and twine that our purchases come wrapped in—all are largely if not entirely composed of colloids or matter in the colloidal condition. Consequently, problems in colloidal chemistry appear in every branch of science, industry and technology.

It is intended here to give in outline a sketch of a number of these applications, stressing more particu-

larly those that have biological technological bearings, but including others that show the operation of the colloid-chemical principles involved. In order to bring some coherence into this extensive survey, the topics are gathered into more or less related groups as follows:

I

Astronomy
Meteorology
Smokes and Dusts
Perfumes
Geology
Mineralogy
Gems

II

Agriculture
Clay
Ceramics and Refractories
Flotation

III

Dyeing
Shower-proofing of Fabrics
Nitrocellulose and Its Products
Paints, Pigments and Varnishes
Emulsions

IV

Soaps
Lubrication
Coal
Colloidal Fuel
Petroleum
Asphalt
Fire Foam
Insecticides

V

Filtration
Sewage Disposal
Photography
Brewing
Tanning
Paper
Rubber

VI

Foods	Ice Cream
Baking	Confectionery
Milk	Gelatin and Glue

VII

Glasses	Boiler Scale
Metals and Alloys	Cement, Mortar and Plaster
Electro-deposition of Metals	

VIII

Chemical Analysis	Antiseptics and Bacteriology
Pharmacy and Therapeutics	Biology and Medicine

Astronomy

As matter in colloidal state is so common on our relatively minute earth, it is but natural to expect to find many instances of colloidal dispersion in the immensity of the Universe.

Cosmic dust is widely distributed throughout space, and as it is gathered up by the superior attraction of the larger heavenly masses (suns, planets, etc.), which in any system grow at the expense of the smaller masses, fresh quantities are continually produced by the collisions of bodies in space, as well as the disintegration of meteorites, comets, asteroids, etc.

According to Isabel M. Lewis of the U. S. Naval Observatory, a swarm of meteors or "shooting stars" (which are quite different from the large meteorites or fire balls) consists of minute dust-like particles which for the most part do not weigh as much as a

single grain. If we could view them outside our atmosphere, they would appear as a cloud of dust reflecting the sunlight, their luminescence being caused by the friction of their rapid passage through our atmosphere. Particles of colloidal size, which probably accompany them through space, tend to be retarded by the viscosity of our atmosphere.

The zodiacal light also seems to be consequent on a cloud of colloidal matter generally believed to surround the sun. Lars Vegard recently advanced the view that the upper atmosphere contains minute crystals of frozen nitrogen, to which he attributes the blue color of the sky, as well as the green color of aurora borealis. (See Philosophical Transactions, Oct. 1923.)

This view was recently modified by Prof. J. C. McLennen, who showed that the green aurora color is due to a mixture of helium and oxygen.

The "Planetesimal Hypothesis" of Chamberlin and Moulton (see paper by Prof. W. D. MacMillan in Alexander, Vol. I, p. 447) is replacing the Laplace theory of nebular rotation to account for the formation of the solar system, even though the latter was bolstered up for a while by Helmholtz' "contraction theory" to account for solar radiation. This indicated that the sun still had about 20,000,000 years of "life." However, geological and astronomical evidence indicated that the sun must be much older than Helmholtz' view would permit. The view advanced by Chamberlin and his co-workers is in essence this:

About ten or twenty billion years ago, our sun, then quite similar to what it now is, was "side-swiped" by another passing star, which may in fact have passed

many millions of miles away, but still near enough to tear loose from the sun in a pulsating fashion, enormous masses of matter. Part of this was carried off by the visiting star, part fell back into the sun, and part remained scattered throughout the area of our present solar system, where, in the slow course of time, the larger masses gathered or "swept up" the smaller ones, forming our planets and their satellites. The meeting of two stars, while rare, becomes a certainty if long enough periods of time are considered, and the age of our galaxy runs into *eons*, an eon being a million billion (10^{15}) years. The pulsating nature of the "tides" raised in our sun may account for the orderly nature of our planetary distribution. This view accounts for the fact that our planets all revolve in one direction, and it furthermore allows for the persistence of colloidally dispersed residues, as well as "captured" matter. The retrograde moon of Jupiter is probably a "captured" satellite.

Heavenly bodies must occasionally meet in collision, and the terrific impact must add to the nebulous or cometary masses of colloidal matter which are distributed throughout space.* While most of these bodies are self-luminous, others are lighted up by neighboring suns. Light itself is invisible, but a beam of sunlight shot into a darkened room becomes evident by illuminating the innumerable motes in our atmosphere, most of which are colloidal. Some of these atmospheric nuclei, as C. T. R. Wilson has shown, are due to the deposit of moisture, etc., on ions or ionized particles, but others are without charge.

* In contradistinction to phenomena of such magnitude Prof. R. A. Millikan (Nobel prize winner) weighed the electron by catching these minute individual particles of negative electricity on colloidal oil droplets which he viewed in an ultramicroscope.

A few years ago when, as astronomers had foretold, the earth was about to pass through the tail of a comet, our yellow journals warned us to prepare for the end—but no one, not even the astronomers, noticed the slightest effect. The tail, whose length ran into millions of miles, was only a vast cloud of colloidally dispersed extremely tenuous matter, and its luminosity was simply a Faraday-Tyndall effect on a gigantic scale, but analogous to the beam which a searchlight or automobile headlight shoots through the atmosphere, especially if it is slightly hazy. The spectroscope indicates that the luminosity of the tail is due to reflected sunlight.

The tails of comets seem to consist almost entirely, and the nuclei and coma largely, of colloidally dispersed matter. The great comet of 1882 which made a transit of the sun was invisible against the solar disc (a position corresponding to attempted observation of colloidal particles in the ordinary microscope against a luminous background), but became visible again after passing beyond the sun's disc (a position corresponding to successful observation of the same colloidal particles in the ultramicroscope against a dark background, the eye of the observer being protected from the source of illumination).

The streaming of the cometary tails away from the sun may be due to the ionization of the constituent colloidal particles, and their consequent electrical repulsion. With colloidal particles the Brownian or kinetic motion is a factor to be reckoned with. J. Clerk Maxwell pointed out (1870) that the intensity of the action of the sun's rays on a particle depends upon its *surface*, which varies as the *square* of its

diameter, whereas the gravitation of the same particle to the sun depends upon its *mass*, which varies as the *cube* of its diameter. Theoretically in the case of a particle whose density equals that of water, the repulsion balances gravitation when the diameter reaches 0.0015 mm. ($= 1.5\ \mu$). As the diameter diminishes, the repulsive force gains the ascendancy, soon reaching a maximum and again diminishing, until when the particle has a diameter of only 0.00007 mm. ($= 70\ m\mu$) the two forces again balance each other.*

These figures, which refer to a substance having the density of water, are approximately of colloidal dimensions; but in the case of denser bodies the subdivision would be even more profound. It is therefore not surprising that, when the earth recently passed through the tail of a comet, no disturbance of any kind was noticed. The comet's tail is a vast celestial camouflage—its luminosity a macroscopic Faraday-Tyndall effect. From what is stated above we should imagine that in some cases the tail of a comet may point *away* from the sun, providing that its particles are of the proper size, and in fact Baade's comet, recently visible, showed this phenomenon. Comets have been seen with tails pointing both towards the sun and away from it.

The nebulæ, too, apparently consist of finely dispersed matter, rendered luminous by neighboring suns; although with them, as with the comets, part of the light may result from self-luminescence (incandescent gas, etc.).

* See Simon Newcomb's article on "Comet," *Encyclopedia Britannica*, 11th edition. Also Svante Arrhenius, "Worlds in the Making," Harper & Bros.

Meteorology

What we commonly call "weather conditions" are largely dependent upon the degree of dispersion of water in the atmosphere, and this dispersion is mainly effected and maintained by solar heat and electrical charges. When air carrying water vapor is chilled by rising to a higher level (which means reduced pressure and expansion), meeting a colder mass of air, or even by the alternation of night and day, the moisture it contains assumes the colloidal state as cloud, fog or mist; and as the coagulation of the dispersed water proceeds, these in turn may condense still further into dew, rain, snow or hail, depending upon conditions.

When steam under pressure blows off into the atmosphere, it appears clear some distance from the point of issue and does not become visible until it has condensed into colloidal dimensions. Then as its particles condense still further to drops (or else evaporate or are dispersed), it becomes invisible once more. White cloud particles are already larger than strictly colloidal size.

An interesting exhibition of the principles mentioned is found in the Hawaiian Islands, where the warm, moisture laden trade winds, blowing steadily from the northeast, are caused to ascend by the high volcanic mountains they encounter. As the air ascends, the diminution of pressure causes expansion; the expansion results in cooling; and the cooling leads to deposition of moisture on nuclei (dust, ions, etc.) in the atmosphere, evidenced in the formation of thick clouds at the higher mountain tops and heavy rains there and in the upper valleys. As the air passes on over the

mountains and descends to lower levels on the other side, the process reverses itself, and the clouds tend to melt away. A newcomer at Honolulu (locally a *malihini* or tenderfoot) seeing threatening clouds on the nearby hills, tucks an umbrella under his arm. But an old-time resident (*kamaaina*) takes no heed, for he knows that at most only some windblown sprinkles will reach the city.

As the water particles in a cloud aggregate, the total specific or "free" surface diminishes, but must continue to hold the total electric charge because the charge distributes itself superficially. This means that the charges on the outside of the individual droplets increase enormously until the lightning discharge occurs.* We have all noticed how a nearby lightning flash is promptly followed by an increased fall of raindrops whose condensation gave it birth. The condensation of the moisture particles usually shows itself by the cloud assuming a dark gray or bluish-black shade.

Many water droplets are formed about ions or electrons and carry an electric charge. As the droplets aggregate the charge accumulates on the outer surface, so that in a large cloud, with an enormous number of droplets, very high potentials may result. Indeed if the aggregation of the water droplets is not sufficient to obscure the sky, and the charges are very numerous, we may have a "bolt out of the blue"—not an uncommon phenomenon.

We do not know to what extent electrical conditions on the earth affect the dispersion of substances in its

* It is possible that in the gymnotus and other "electric fish," an aggregation of colloids in their special glands, due to nervous influences, may underlie the high potential and shock.

atmosphere; but since half of the earth is always heated by the sun while the other half is cooler, thermoelectric currents are continually circulating about the earth. Variations in solar radiation, due to sun-spots and the like, cause violent electric and magnetic storms which are intimately connected with the aurora, and other atmospheric phenomena (ionization, electrical charge of dispersed particles).

Colloidal ice often occurs at high levels * and may be the cause of halos, perihelions and periselenes ("sun-dogs" and "moon-dogs"), etc. In many elevated regions (Idaho) there occur frost fogs called by the Blackfoot Indians "pogonip" or "white death," where finely divided ice, like hoar-frost on a gigantic scale, deposits on trees in huge masses, and is a contributing cause of pneumonia.

Since changes in barometric pressure must affect the CO_2 tension of the blood and tissues, and since this means a variation in the turgidity of the body colloids which incidently affects the circulation (see p. 215), we have here one basis for the popular impression that the "weather" influences our feelings. Other factors are of course at work (e.g., evaporation of water from the skin, etc.), but physicians know that with persons suffering from neurotic and rheumatic affections (e.g., arthritis), the effects of weather conditions are noticeable. Change of altitude may have a similar effect.

The blue color of the sky is caused by diffraction of

* Just recently Captain Stevens and Lieutenant Johnson of the United States Army, on reaching an altitude of 39,000 feet in an airplane, reported a temperature of 76° F. below zero, and "that the ice particles were visible by the billions, hanging in mid-air, their reflections seeming to form caves."

the sunlight by the earth's atmosphere. Were it not for this gigantic Faraday-Tyndall effect the sun would appear to us as a fiery ball set in a black star-sprinkled sky. The varying shades of bodies of water ("blue Mediterranean," "green" ocean, black, yellow, white, red rivers, etc.) are largely due to the diffraction caused by finely dispersed substances. When we look through a great length of the atmosphere, distant objects such as mountains seem to have a blue tone.

> 'Tis distance lends enchantment to the view,
> And robes the mountain in its azure hue.

So the poet Thomas Campbell beautifully puts it in his "Pleasures of Hope." Though atmospheric gases exercise some effect, without colloidal dust we would have less romantic twilight, and darkness would fall rather sharply as the sun sank below the horizon.

The blue-whiteness of snow, which sometimes even assumes a positive blue tint, is due to the reflection of light from its interior surfaces, the color being a structural one. [See J. Alexander, Science, 41, 465 (1920).] As Bancroft has pointed out, the blue color of many birds' feathers is due to their colloidally fine structure. A certain green tree toad owes its color to a structural blue, which on passing through a layer of yellow oil droplets in the skin appears green. If preserved in alcohol, which dissolves out the oil, the toad turns blue.

The tremendous explosive eruption of the volcano Krakatoa in 1883 projected colloidal dust and ashes so high that they gradually spread entirely around the earth. Besides causing glorious "golden sunsets," such fine dust is by many believed to exert a

noticeable influence upon weather conditions. While many particles in such dust greatly exceed colloidal dimensions, it must be remembered that the effects of fine subdivision do not end abruptly with the usual colloidal limits of 5 to 100 millimicrons. Test plates taken in an airplane, show that pollen grains are numerous at an altitude of 15,000 feet (Hay fever).

The daily papers of February 23, 1929, reporting on the blizzards sweeping Europe, state that black snow fell at Ruschuk, the phenomenon being attributed to volcanic dust. Red dust from the Sahara has caused "bloody" rains and snows. On April 26–27, 1928, Lemberg reported a heavy shower of mud, attributed by Profs. Arctowski and Stenz to dust blown from the arid soil of southern Russia. They estimate that 1,500,000 tons of dust fell in Poland alone. (See also p. 94.)

One more curious function of colloidal atmospheric dust must be mentioned. As Kendall has shown, the proper functioning of the thyroid gland depends upon the presence of a small quantity of thyroxin, an iodine-containing organic compound. This means that iodine must be found in traces in the soil, from which all food directly or indirectly comes. The original source of iodine is the sea, and although some of it exists in geological deposits of sea salt, a continual source of supply to the soil is to be found in the colloidal sea-salt dust, which forms from the ocean's spray and is carried thousands of miles inland before being washed down by the rain. The incidence of goiter and cretinism (largely due to iodine insufficiency) is most marked in interior mountainous (Switzerland, Idaho, Wyoming) regions where the least amount of sea-salt

dust is apt to be carried. Thus it would take a person 1,000 years to drink enough of the water of Lake Superior to give the iodine needed for his thyroid gland.

Smokes, Fogs and Dusts
(Aerosols)

Fogs, mists, and clouds, whether of water or dust, exercise a potent influence on terrestrial climate, flora and fauna, for they govern to a considerable degree the amount of solar radiation reaching the earth's surface. According to one theory, glacial periods were, in part at least, due to such influences.

By interfering with the normal passage of solar radiations, as well as by furnishing nuclei for the deposit of moisture to form fog, coal smoke, if present on a large enough scale (as in some parts of England), may exert an effect upon weather conditions. It is quite probable that a noticeable improvement could be made in the atmospheric conditions of London, if some way could be found to reduce materially the generation of nuclei from the enormous numbers of smoky domestic, factory, locomotive, and steamship fires. Public health would also be benefited, since the dust and fog interfere with beneficial ultraviolet solar rays. This is one reason why the "country" is healthier for children than the "city."

Carl Barus [Smithsonian Contribution 1309 on "Atmospheric Nucleation," Washington, 1905] kept a continuous record of atmospheric nucleation for several years and found that the number of nuclei varied from about 2,000 to 100,000 per cubic centimeter. Such nuclei may be produced by violently agitating liquids, by heated bodies (red-hot metal or glass, a clear non-

luminous Bunsen flame), by chemical activity (smokeless oxidation of phosphorus at about 13 deg.), by evaporation (e.g., of sulphuric acid or naphthalene), by high potential (charged metal), and by certain kinds of radiation (ultra-violet light, X-rays, radioactivity). Barus says that the nuclei are at the outset simply dust particles small enough to float in the air, but larger than the order of molecular size, upon which water condenses. Most of them carry an electric charge. Atmospheric nucleation varied greatly from day to day and during the day, but was on the average greatest at the winter solstice (December 21) and least at the summer solstice (June 21).

In flames, the burning matter is largely in colloidal state, and when a combustible dust suspended in air approaches colloidal dimensions, its free surface becomes so great that it may burn with extreme rapidity if started by a static or frictional spark or the like (*explosive aerosols or dusts*).

Sodom and Gomorrah were probably destroyed by a colloidal cloud of petroleum ignited by local fires or lightning. Analogous phenomena are known in the Caucasus Mountains to-day.

The electrical precipitation of colloidal and finely dispersed substances from air, smoke, furnace gases, etc., by the Cottrell process is too well known to be described in detail here. Unexpected sources of profit are being found in the fumes compulsorily collected from cement kilns (potash) and from smelters (arsenic, selenium, etc.). Many dusts and mists (including sulphuric acid, which is a very good nucleator) that had defied ordinary bag-house methods are readily separated out by the high tension current. Sir Oliver

Lodge even suggested that ships might thus clear their path of fog for some distance ahead.

Recently W. D. Bancroft and L. F. Warren demonstrated that electrified sand, scattered by an airplane, could cause the coagulation of fog and clouds, thus producing even a slight localized "rain."

One case where smoke is intentionally produced is in the use of "smudge pots," which are burned in orchards in the spring or early summer when indications are that the tender blossoms or fruit are about to be injured by frost. This remedy is, of course, ineffective in very cold weather, but often serves to prevent what agriculturists term a light frost, which has for its precursors a still, clear atmosphere and a temperature approximating the freezing point. Frosts of this kind do not occur on cloudy or windy nights.

In the absence of smoke, the freezing process seems to proceed as follows: With falling temperature frost may deposit directly, or a dew-like deposit of water forms on leaves, buds, fruit and similar surfaces, and is congealed into ice crystals or "frost" when the slight heat liberated by the condensation radiates into the surrounding cold atmosphere; the freezing is facilitated by the evaporation of part of the deposited water. While the heat generated by the burning smudge oil is a large factor, the smoke liberated furnishes throughout the entire lower atmosphere innumerable nuclei upon which moisture deposits, with the liberation of some heat and the formation of a protective fog blanket that tends to check terrestrial radiation. The combination of all these factors is usually sufficient to ward off the threatened calamity.

These views are strengthened by the observations of

Lieutenant B. H. Wyatt (Science, Sept. 21, 1923, p. 223) who, during the recent total eclipse of the sun, took observations while flying in an airplane in a comparatively clear layer at an altitude of 13,000 ft. "During totality the recording thermometer at this altitude showed a rise of three and one half degrees Fahrenheit instead of the anticipated drop period. The humidity fell from sixty-three to fifty-two per cent." This seems to indicate a liberation of heat upon the condensation of moisture, providing he did not enter a different stratum of air.

The author recently suggested that if the place and time of the formation of hail could be reasonably forecast, from meteorological observations and experience, at least a mitigation of the damage might be effected by burning nuclei-forming rubbish on a large scale to produce nuclei in the upper atmosphere, which would lead to formation of a larger number of *smaller* hailstones, whose weight and "whipping" and destructive power decreases as the cube of their diameters. A relatively small mass of matter can be made to produce an incredibly huge number of nuclei, and while the gigantic forces of nature cannot be denied or stifled, they might be thus *diverted* so as to diminish damage, which, especially in the West and Northwest runs into many millions annually in wheat alone.

The recent war resulted in an enormous development of the use of artificial smokes and fogs in military and naval offensive and defensive operations. While in the old days attacks or retreats had often been made under cover of natural fog or mist, now soldiers crept to the attack under the protection of a

smoke barrage, and on sea destroyers laid down a smoke screen, or steamers sought, like the cuttlefish, to escape submarines in colloidal clouds of their own making. In the air natural clouds were lurking places for airplanes and dirigibles, and many air craft, especially Zeppelins, produced colloidal clouds in which they were lost to view.

Perfumes

Without attempting to go into the question of what constitutes the sense of smell from a nervous or psychological standpoint, it may be said that the sensation of smell or odor is aroused only by the transmission of material particles which must be very small, since they pass readily through paper, textiles and the smallest crevices, and are held back only by airtight surfaces like glass or metal. Some gases have distinct odors, but from the fact that Barus ["The Structure of the Nucleus," Smithsonian Contribution 1373, Washington, 1903] was able to demonstrate the presence of colloidal nuclei in gasoline, benzol and carbon disulphide vapors, it is obvious that the presence of such particles is much more common than has been believed. It is a question whether these nuclei arise from molecular association or from the condensation of vapor on smaller atmospheric nuclei. The persistency of naphthalene nuclei and their tendency to reach a fixed diameter led Barus to remark that "it is probable that the vapor pressure of naphthalene, however small, is the cause of this long maintenance of the supply of nuclei, and one may suspect that other bodies with strong odors and which show a tendency to slow sublimation will be found in like degree nuclei-producing."

Ambergris evidently owes its body-producing effect in perfumes to the formation by it of nuclei which have the power of strongly condensing the vapors of the ethereal oils, etc., which constitute the odoriferous ingredients of perfumes. Thus Barus found that paraffin nuclei, made by shaking a benzol solution of paraffin, disappeared with relative rapidity. This field offers an interesting vista of research, which may lead to a cheaper or superior substitute for ambergris, among other things.

In modern society, smell is a sense that is largely *tabu*, although throughout the whole animal kingdom it is of prime importance and utility. Wild animals are guided largely by it, and insects seem to be also. While some odors are due to molecularly dispersed particles, in many cases we have to deal with colloidal particles; and it will be of interest to investigate the permeability of septa to smells. The odors of many substances are due to impurities. Thus absolutely pure sulfuretted hydrogen, carbon disulfide and phenol are without marked odor, as are also pure indol and skatol.

Geology

Coming back to solid earth, let us consider the ordinary properties and behavior of the earth's solid constituents. These depend more upon their state of physical dispersion than upon their chemical constitution, as may be seen by considering Atterberg's classification of minerals according to the size of their fragments:

	Diameter
Boulders	2 m. to 20 cm.
Pebbles	20 cm. to 2 cm.
Gravel	2 cm. to 2 mm.
Sand	2 mm. to 0.2 mm.
Earth	0.2 mm. to 0.02 mm.
Loam	0.02 mm. to 0.002 mm.
Clay	smaller than 0.002 mm.

The finer particles are more readily blown about by the wind and carried and deposited into sedimentary beds by water; they are more soluble and are more easily leached and decomposed by "weathering." In mass the finer particles are less permeable to water, but possess a much higher capillarity and water-holding capacity, besides a powerful fixing or decomposing action on diffusing substances. Thus if dilute potassium sulphate solution is percolated through a column of fine sand, free sulphuric acid is found in the percolate.

A few instances may be mentioned to show the tremendous masses of finely divided matter carried great distances by the winds. Hellman and Meimardus report that about March 8–10, 1901, a cyclonic storm central over Tunis sucked up dusts raised from the deserts of southern Algeria to such high levels, that about one-third of the 1,800,000 tons that fell in Europe, was deposited north of the Alps. Great quantities fell into the Mediterranean Sea and 150,000,000 tons was estimated to have fallen on the African Coast. E. R. Miller and A. W. Winchell reported on a storm of dust-discolored snow over an area of 100,000 square miles (from Dubuque, Iowa, to Chelsea, Vermont) and estimated that the million or so tons deposited must have come from the arid South-

west (Arizona, New Mexico) and must have been carried over 1,000 miles at high altitudes *before* it began to fall.

The expeditions led recently by Roy Chapman Andrews into western China and Manchuria report on the tremendous erosive effects of wind and water on the soils there and on the huge dust storms.

Prof. Y. Wada states that on March 4, 1915, a "sand mist" consisting of dust from the interior of China moistened by accumulated water, deposited a one-fourth inch layer of dust at Etchu Province, Japan.

Between January and April it is common to meet at sea, west of Africa, falls of dust from the Sahara, which probably accounts for the legend of a "Sea of Darkness" lying between the Canaries and Cape Verde Islands. In 1898 the S. S. "Roslin Castle" sailed through about 900 miles of dense haze in that region, and S. S. "Tintagel Castle" was detained thirty hours by it.

The eruption of Mount Pelée, which destroyed Martinique and 30,000 of its people, cast exploded ash so high that for several days the fall continued. The S. S. "Roddam," lying nearby, received a heavy coat. Scientific men arriving a week later found the air full of fine ash, some of which was still afloat then; ten weeks later another explosion scattered white ash over the whole West Indies.

Fine deflocculated clay is carried thousands of miles by rivers, and when finally coagulated by the salts of the ocean forms new land. Geological evidence shows that this process has added about a thousand miles to the length of the Mississippi River, and owing to the enormous areas under cultivation (which permit more

soil to be carried off) it is going on perhaps faster than ever. Its results may be seen at the mouth or delta of every large river—the Nile, Ganges, Hwang-Ho, Amazon, Euphrates. The great weight thus accumulated at certain weak places in the earth's crust may cause slip along lines of geological fault. The recent (1923) destructive earthquake in Japan is believed to have had such an origin.

The presence of fine particles in water produces many beautiful effects in nature. This is marked in limestone glaciated regions, and seems to be due to the fact that the cold glacier water dissolves quite a bit of atmospheric carbonic acid and takes up some limestone in solution (as bicarbonate), the mineral being afterwards thrown out in colloidal state as the temperature of the water rises. This appears to be the case at Lake Louise in the Canadian Rockies, for the coarser material brought down from the Victoria Glacier is deposited at the head of the Lake. Variations in color of the water, as in Lake O'Hara, "Blue River," etc., involve differences in depth and in light effects, and probably also in physico-chemical condition leading to variation in acidity and rate of temperature change, which would affect the particle size of the precipitated calcium carbonate. Analogous effects exist along the "Blue Mediterranean," and in the famous "Blue Grotto" of Capri, also in Lake Geneva and in Swiss glacier streams.

Fine particles generally have been deposited in huge thick beds by glacial and other prehistoric waters, which have mostly graded them according to size. Such deposits, when cemented by pressure, dehydration or igneous or metamorphic action, became slate,

shale, sandstone, etc. When they enclosed pebbles, the result was "pudding stone," and these frequently served as a matrix for fossils and as a means to preserve fossil footprints, ripple marks, and even rain splashes.

Eozoon, long thought to represent the fossilized remains of primeval plant life, is probably nothing but an instance of rhythmic precipitation (Liesegang's rings), which often occur when precipitates are formed by diffusion into colloidal gels.

Mineralogy

Agates, onyx and dendrites are types of minerals formed by rhythmic precipitation (Liesegang's rings), and ore bodies may be deposited by similar segregating action. Some minerals are themselves colloidal gels (e.g., opal, flint, bauxite) or result from other minerals by weathering with subsequent gel formation (e.g., kaolin from kaolinite, serpentine from diabase). Lenher has recently shown that mere trituration is sufficient to bring silica into colloidal solution, and it seems that many quartz minerals have been deposited, in part at least, from colloidal solution. The same applies to stalactites and stalagmites, for with a fluctuating carbon dioxide content, especially in the presence of protectors like humus, some colloidal calcium carbonate will be formed.

Gems

Many gem stones owe their beautiful colors to impurities colloidally dispersed in them—the emerald to chromium, the ruby to iron, the amethyst probably to manganese, the topaz to iron, etc. The varying

shades of diamonds seem to be due to similar causes. Opals are gels with interior reflecting planes. The shade and even the color of many gems can be changed by subjecting them to the action of X-rays or radium, which apparently act by bringing the dispersed particles into a different state of aggregation, usually coarser.

Pearl scales, when examined in the dark field, show the inhibited crystallization characteristic of crystals formed in the presence of a protective colloid, which here is the slime or mucin of the mollusc. There is no reason to doubt that colloid research will lead to the synthetic production of mother-of-pearl, and perhaps even of substitutes for the real pearl itself.

Since the writing of the above there has appeared in "Chemie et Industrie," Vol. 8, p. 782 (1922), a paper by Clément and Rivière, describing the production of artificial mother-of-pearl, by precipitating calcium carbonate under chosen conditions in a colloidal medium. Imitation pearls have been made by coating transparent hollow glass beads on the inside with a lacquer containing finely comminuted scales (pearl essence) of a certain silvery fish, and then filling in with wax. Recently, colloidally precipitated calomel has been used in place of fish scales.

CHAPTER VIII

PRACTICAL APPLICATIONS (Continued)

AGRICULTURE

Although from time immemorial farmers have classified soils on the basis of their physical and physiological character as "light" or "heavy," "rich" or "poor," "productive" or "unproductive," etc., it is only within comparatively recent years that chemists have begun to realize the full importance of the rôle played by the colloids, especially the organic colloids of the soil.

The constituents of the soil fall into three classes:

1. Mineral fragments, consisting mainly of silica and silicates, resulting from the disintegration of rocks by weather, water, heat, freezing, etc.

2. Organic material, including bacteria, and that mixture of plant and animal debris known as humus.

3. Soil solution, which is water with its various solutes.

The fact that colloids occur in all three of these classes should serve to reconcile the older hypothesis that the colloidal behavior of clay is due to fine particles, with the more recent view that it is due to a jelly-like "ultra-clay" which surrounds the particles. Both conditions exist and exert an influence. The "ultra-clay" evidently consists largely of colloidal humus, for the smallest particles, with which it exhibits its main effects, have the largest percentage of organic matter.

Among the natural agencies tending to increase the size of the minute soil particles may be mentioned

heat with its drying or evaporative effect, freezing, and the coagulating or flocculating action of soluble inorganic salts and some organic substances present in the soil. On the other hand, included in that little known class of substances vaguely described as "humus," there are numerous organic substances derived from the bacterial, plant, or animal débris, or exuded by the roots of plants, which act as protective colloids (*Schutzkolloide*) and tend to produce and maintain the hydrosol, or deflocculated condition. (See P. Ehrenberg, "Die Kollide des Ackerbodens," Zeits. angew. Chem., 1908, **41**, 2122.) In an excellent paper on the mechanics of soil moisture, L. J. Briggs (U. S. Dept. of Agric., Bureau of Soils, Bull. No. 10, 1897) pointed out that very small quantities of certain organic substances, such as are continually being produced in the soil by the decay of organic matter, greatly decrease the surface tension of solutions, thus counteracting to a large extent the effects of the surface application of soluble salts which would tend to draw moisture to the surface by increasing the surface tension of the capillary water of soils. It is well known, however, that an excess of salts will ruin a soil physically, as is evident after flooding by sea water or the excessive application of chemical fertilizers. Of interest in this connection is the recent work of the Bureau of Soils, U. S. Department of Agriculture, carried out by Cameron, Schreiner, Livingston, Gile, Davis, and their co-workers. Thus plants grown in the unproductive Takoma soil were greatly benefited by green manure, oak leaves, tannin and pyrogallol. The injurious effects of quinone and some other organic substances may be due to their ability to precipitate

or flocculate the protective colloids of the soil; for as Lumière and Seyewetz have shown (Bull. Soc. Chim., 1907, 4, 428–431; J. S. C. I., 1907, 703), quinone renders gelatin insoluble.

The fact observed by Fickenday (J. Landw., 1906, **54,** 343) that more alkali is required to flocculate natural clay soils than kaolin suspensions, he attributes to the protective action of the humus present (see Keppeler and Spangenberg, J. Landw., 1907, **55,** 299).

Many factors oppose the agriculturally undesirable tendency of humus to deflocculate clay, which would permit the rain to wash it away: (1) In suitable concentrations humus and clay act as oppositely charged colloids, and mutually precipitate each other; (2) the lime present in most soils forms with the humus a gel of the insoluble calcium humate, which sticks the soil particles together. Generally an excess alkalinity due to soda produces the evil effects found in the heavy, sticky alkali soils.

When all these factors are properly balanced, the soil is in good *tilth,* which Sir E. J. Russell defines as that "nice crumbly condition suitable for a seed bed." This permits proper drainage and circulation of air essential to bacterial activity and plant growth. Humus acts as a stabilizer. It makes the soil less sensitive to the ruinous coagulating effects of an excess of salts. Thus 15 to 20 per cent. of humus will almost obliterate the difference between a clay soil and a sandy soil. "Humic acid" is a mixture of allied substances rather than a definite chemical entity. Its calcium "salt" exercises a buffer action by combining with injurious acids and liberating the harmless, insoluble humic acid.

Many important properties of a soil, such as permeability, capillarity, absorption, moisture content, etc., are dependent not so much upon the chemical composition as upon the sizes of its constituent particles. In coarse sand, for example, the amount of water is greatest at the bottom and smallest at the top, whereas in fine clay the distribution is much more uniform. Clay consists of particles 0.002 mm. (2 microns) in diameter and smaller. Over about 18 per cent. clay gives a heavy soil, while under about 4 per cent. means a sandy soil of low water-retaining capacity.* The effect of lime is so marked that a dressing of calcium carbonate will make an 18 per cent. clay soil act like a 12 to 14 per cent. soil, partly through the formation of calcium humate gel, which cements the finer particles into the desirable crumbly condition.

This also makes ploughing much easier; thus in the 1921–22 report of the Rothampsted Experiment Station it is stated that chalking heavy soil may reduce the power needed for ploughing by as much as 15 per cent.

Apart from the activity of bacteria, earth-worms and the like, the movement of substances in the soil is effected by diffusion and seepage of soil water. The forces acting may be divided into three groups, although, of course, there is no sharp line of demarcation between them: (1) Molecular forces of the order of 1,000 atmospheres; (2) capillary forces of the order of 3 to 4 atmospheres; (3) gravity. This corresponds roughly to the classification of soil water by Bouyoucos, as follows:

* The application of colloidal clay or bentonite might be useful in such cases.

Gravitational water—"super-available."
Free water—very available.
Unfree water { capillary-absorbed—slightly available.
combined { solid solution / hydration } —unavailable.

The leaf system of plants is continually evaporating moisture, and the resulting hydration and osmotic "pull" is sufficient to raise a column of water even to the top of the tallest sequoia tree. It is registered as a root pull of about 7 to 8 atmospheres. The water evaporated by plants is continually replaced by rain, but in dry weather there results a struggle for water between the plant and the soil. The percentage of water left in the soil when the plant can no longer protect itself against desiccation by taking up soil moisture is called the *wilting coefficient.* Its value varies with different plants, and the great influence of particle size of the soil may be seen from the following table of the shrinking coefficient of Kubanka wheat (after Briggs & Shantz):

Soil	Wilting coefficient
Fine sand	2.59
Fine sandy loam	9.66
Clay loam	16.3

An important factor in the struggle between the "root pull" of the plant and the "back pull" of the soil is the speed with which water can diffuse toward the roots. Cultivation of the soil above the roots exposes a greater soil surface to the air, and the resulting increased evaporation there causes increased upward and sidewise diffusion streams, which not only supply water to the roots at increased speed, but also carry the necessary plant food. As Bechhold observed

(Kolloid-Zeit. **27**, 29, 1920), soluble salts follow diffusion streams. Thus if a piece of plaster of Paris be dipped in sulphate of copper solution and then dried, the copper will be found almost quantitatively in the exterior layers. W. Kraus (Kolloid-Zeit. **28**, 161, 1921) showed that this "capillary phenomenon" of salt concentration is due to evaporation at the exposed surfaces. The plant is therefore enabled to make its necessary growth with less water, and as this growth generally is greatest in the wet season, *cultivation* or *tillage* by losing some water may actually enable the plant to enter the dry season with a reserve store of soil water in the soil, which in turn is made more rapidly available in the dry season by further cultivation. (J. Alexander, Science 1921). Cultivation also kills off competing weeds and aids soil bacteria which produce plant food in available form.

Contrary to popular idea, colloids do diffuse, albeit more slowly than substances molecularly dispersed, so that the roots may absorb soil colloids which diffuse toward them. While, of course, chemical reactions may go on in the soil, ionizable or hydrolyzable salts are apt to be split up and their fractions segregated by the action of selective adsorption and differential diffusion, giving results that cannot be simulated by simple aqueous solutions. Changes in effective reaction (hydrogen ion concentration) and other conditions affect the state of the soil colloids, and as their active free surface varies, they may hold or release adsorbed substances. Protectors also exert their influence.

In very permeable or sandy soils, especially if deficient in lime which holds the humus as a gel, the

alumina, iron and humus are apt to assume the sol form and be washed down by the rain to a lower stratum, where, by desiccation or electrolyte precipitation, they gradually form an insoluble rock-like layer known as a *pan*. Such a pan acts as an impermeable septum, shutting off the soil beneath from air and water, preventing diffusion between it and the top soil, and often causing swampy conditions.

A. S. Cushman [U. S. Dept. Agri., Bureau of Plant Industry, Bull. No. 104] showed that fine grinding of feldspar greatly increased the amount of potash available under the action of water. A coarse powder whose free surface was 43 sq. cm. per cc. yielded only 0.013 per cent., whereas a fine powder with a free surface of 501,468 sq. cm. per cc. yielded 0.873 per cent. of potash and soda, an increase of 6,700 per cent. Even then these fine particles averaged about 0.1 micron in diameter, which is about the upper limit of colloidal dimensions. In the soil they undergo further disintegration whereby still more of their potash becomes available. The availability of phosphate rock is greatly increased by fine grinding.

The formation and past history of a soil have much to do with determining its properties, as may be seen from the following remarks on loess soils, kindly given me by Prof. Frederick K. Morris.

Loess is a fine dust which has been carried by wind. It may be dropped when the wind slackens, or it may be washed out of the air by rain and held in place by vegetation. The true wind-borne loess is commonly associated with finely bedded water-borne silts, with which it should not be confused.

Loess is obtained by the wind from any widely exposed area of fine unconsolidated sediment which

has no vegetation cover. The outwash aprons issuing from glaciers; the floodplains and deltas of summer-withered rivers; the badlands and playa-floors of deserts; the dry bottoms of shrinking lakes; areas of residuary soil on which the vegetation has been killed, especially through change of climate; areas exposed by ploughing in regions of light rainfall, are the typical sources of loess. Loess is therefore especially abundant in basin-lands adjoining deserts, along the margins of formerly glaciated regions, and where large lakes extended during Pleistocene time. The principal loess regions are: China north of the Yangtze river; Siberia north of the Khangai and Sayan slopes; southern Russia; Hungary; northern Germany; and in the United States, the central and northern Prairie Plains, parts of the Columbia and Snake River Plateau, and parts of the Great Basin and the Southwest Basin states.

The thickness of loess ranges from one to 300 feet, averaging 20 to 100 feet. It is massive, and locally shows a faint color-banding without bedding planes; locally grading into water-laid, stratified silts and gravels which are not true loess. The grains are angular and vary in size as shown in the following table (1, p. 459):

	Sample I		Sample II	
Fine sand	0.13 mm.	1.59%	0.10 mm.	1%
Very fine sand	0.065	27.44	0.063	25
Silt	0.033	50.97	0.030	54
Clay	0.0035	20.00	0.004	20

The grains are well interlocked, indicating a slow rate of accumulation; and locally an incipient cementation by carbonate cement has developed. Vertical tubules, which are attributed to the roots and stems of the plants which originally entrapped the dust, traverse the deposits; but the vertical cleavage of loess is only partly due to these holes; it is chiefly a jointing phenomenon, due to tension in the mass. Loess is characteristically rich in concretions, which

form in vertical positions due to precipitations of carbonates, chiefly of calcium, with less of $MgCO_3$ and $FeCO_3$, and still less of $MnCO_3$ and carbonates of alkali metals. The precipitates enclose the grains of loess, and so represent not only a filling of the vertical tubules, but a partial cementation of the loess. The irregular, knobby, vertical concretions have been called "loessmännlein" or "loesspüpchen." In some loess deposits they are quite absent. Porosity has been determined by Lowdermilk * as 47.8% (Barbour, loc. cit., page 462). Water travels much more freely in a vertical than in a horizontal direction in loess, because of the vertical tubules and vertical joints. Horizontally the only movement is through the very small and tortuous pores. The loess soils absorb water readily, and hold it. They are therefore rich in ground-water solutions. Being characteristically upland deposits, they are rarely in a position suitable for irrigation, and their high capacity for absorbing water renders irrigation unprofitable even where it is topographically possible. Loess soils are characteristically suitable for dry-farming and deep ploughing.†

Clays

The working properties of clays depend largely upon the size and the degree of dispersion and hydration of their constituent particles, and especially upon the proportion of colloidally dispersed particles. These factors are in turn influenced by the presence of protective colloids (e.g., humus), salts, and effective reaction (pH value, hydrogen ion concentration). Thus the clay of Mesopotamia is baked into bricks by mere exposure to the sun, whereas straw was necessary

* From *China Journ. of Science and Arts.*, Vol. III, p. 462; paper by C. B. Barbour (1925).

† See also Bryan, Kirk, "The Palouse Soil Problem," with an account of elephant remains in wind-borne soil on the Columbia Plateau of Washington, U. S. Geol. Survey Bulletin 790-B.

to make bricks out of the clay of Egypt (Exodus V). The straw may have been used as a fuel to burn the bricks, or else to improve the working quality of the clay, for recently patents have been taken out for "Egyptianizing" clay by the addition of tannin, extracts of straw and humus, etc. Glue and similar protective colloids deflocculate or "free out" clay and make it "cover" when used in paper-coating or kalsomining.

Bentonites are fine clays resulting from the dusts deposited by ancient volcanos. Some varieties form suspensions that readily settle, but others are so highly colloidal that they swell in water just like glue or gelatin. These grades are used for "beauty-clays" and cataplasms, as well as for many technical purposes.

Clay in general is flocculated by acids and by acid or neutral salts. Small amounts of alkalies and of alkaline salts deflocculate it, but larger amounts cause flocculation. Clay slip, prepared with a little sodium hydroxide or carbonate, can be readily poured or cast, even though it contains less water than a stiff mass of clay and water without alkali. On adding a little acid to such fluidified clay slip, the mass immediately becomes so stiff that it will not fall from the inverted vessel.

Each clay as found in nature bears within itself much evidence of its past geological history: the chemical and mechanical processes of past ages; lixiviation by glacial or other waters; subsequent sedimentation in still lakes or flats, or coagulation by saline waters; leaching out of some salts or soluble products; infiltration of other salts and of organic extractives; the pressure of overlying strata; thermal changes due to

solar heat, volcanic action, or metamorphic movements of the earth's crust, which may also cause pressure.

Ultramicroscopic examination gives a very good insight into the nature, working properties and impurities of clays. [See J. Alexander: J. Am. Ceramic Soc. 3, 612 (1920).] Some idea can be formed of the relative percentage of colloidal and coarser particles, and the influence of protectors and coagulating salts traced. Fire clays show the combined effect of the infiltration of protective substances (from peat, lignite or coal deposits) and of salts or acids resulting from the diffusive decomposition of ferrous sulphate (oxidized pyrites). To work properly, clays must have the proper proportion of coarser, finer and colloidal particles, so that by washing and blending clays and working upon them with reagents more powerful than those ordinarily found in nature, we have a wide range of possibilities.

Ceramics and Refractories

Following the principles above mentioned, the use of alkalis or alkaline salts to deflocculate clay and make a casting slip is general in the ceramic industry. Caustic soda and silicate of soda are largely used. If the clay mixture holds too much water, there will be excessive shrinkage upon drying; and if it is too hydrous, there will be too much shrinkage on firing. In either case the molded article will warp, and this must be prevented by proper selection, mixture and treatment of the clay used. To safeguard against warping, there is often added to the ceramic mixture some powdered burnt clay (broken pottery or grog).

When heated or "burned," clays become irreversibly dehydrated and harden into pottery, bricks, etc. Throughout the whole ceramic process, the pugging, blunging and aging of the clay, the molding and subsequent drying and burning, may be traced the influence of particle size and impurities, and their effects extend to the zone of actual fusion.

Fire clays have a preponderance of relatively large, consolidated or dehydrated particles, a result which may be brought about in nature by pressure, coagulating salts and a deficiency of organic deflocculators. They take up comparatively little water and therefore do not shrink much on drying. With clays exposed to high temperatures, the chemical composition, which influences the melting point, is vital.

There may be a "eutectic drop" in the case of the admixture of clays, just as there is with metallic alloys. Mixtures for Seger cones are based on the principles above referred to.

Flotation

The importance of flotation processes is evident from the fact that in 1918 over 70,000,000 tons of ore were thus concentrated. The understanding of the principles of flotation will be simplified by bearing in mind that, notwithstanding the presence of many disturbing and variable factors, there are involved two main triphasic systems:

1. *Ore/water/oil,* from which the true ore (usually a sulphide) must emerge with a film of oil which enables it to be taken up by the air bubbles and thus floated off with the froth, while the gangue is wetted and flowed off at a lower level.

2. *Air/water/oil,* which yields the bubbles to float the oiled sulphide.

The oil clings to the sulphide because the surface tension oil/sulphide is less than the combined surface tensions (σ) water/oil and water/sulphide.

That is, $\sigma OS < \sigma WO + \sigma WS$,
or $\sigma WO > \sigma OS - \sigma WS$.

The oils or some of their constituents distribute themselves at the interface water/air, and thus form stable bubbles, because the surface tension water/air exceeds the combined surface tensions water/oil and air/oil. That is,

$\sigma WA > \sigma WO + \sigma AO$
75 23 33 (approximate values)

The air bubbles forming the froth thus have a more or less stable surface film which is miscible with, though not necessarily identical with, the oil film on the sulphide, for selective adsorption may effect some segregation of the oil constituents. However, the oiled ore particles act like oil; they distribute themselves at the interface water/air, are thus attached to the air bubbles and lifted to the upper froth layer unless they are too heavy or are knocked off.

Some of the complicating factors will now be considered.

Water.—Dissolved air aids bubble formation by reducing the internal pressure of the water; so that temperature of the water is important. Most crystalloids, especially acid electrolytes, act beneficially, for they are adsorbed by and coagulate the fine slimes, clay, etc., which then tend to repel the flotation oil. This recalls the old-fashioned household expedient for avoiding the taste of castor oil, by moistening the

mouth and throat with orange or lemon juice. Some electrolytes, especially small quantities of alkalies, are very detrimental, because by reducing the surface tension between the water and the oil and the sulphide and the gangue, they tend to emulsify the oil, wet the sulphide and deflocculate the slimes. Humic substances, especially in the presence of alkali, and protective colloids in general, act in like manner; thus glue is very injurious. Colloidal clay or very fine gangue may have a similar action, for they may act as emulsifiers—"fat" clays emulsify oils, tars and asphalts.

Ore.—Some ores yield soluble substances which exert an effect, but as a rule the fineness of grinding is the most important factor. While the gangue must be fine enough to flow off readily under the conditions of operation, it should not be so fine as to cause the undesirable emulsification above referred to. The sulphide particles, if too large, are not lifted or are readily knocked off; if too small the bubble surface is covered by too small a weight of ore, and there is great loss in efficiency. The tiny ore particles should make a substantial armadillo-like covering about the air bubbles, which aids in the stabilization of the bubbles.

Oil.—Many substances used in flotation—e.g., cresols—are not oils at all, and many substitutes for oil have been patented. The rapid development of the flotation industry created a sudden demand for materials like pine oil which previously had a limited demand, and markets were thus turned topsy-turvy. Mixtures of substances may be used as "oil," for the foam-producing and the sulphide-oiling factors are not necessarily identical. The percentage of oil is

also important from an operative as well as from a patent standpoint.

The whole question of flotation demands intensive study and experience. Thus Callow estimates that with four different oils, three different oil percentages, two pulp densities and two temperature changes, there are possible about 60,000 different combinations of conditions.

CHAPTER IX

PRACTICAL APPLICATIONS (Continued)

DYEING

Four principal theories of dyeing have held the field: (1) The mechanical or physical theory; (2) the chemical theory; (3) the colloid-diffusion and adsorption theory; (4) the electrical theory. A complete historical review of these theories, with bibliography, is given by P. E. King in the First Report on Colloid Chemistry and Its Industrial Applications, published by the British Assoc. for the Adv. of Science, London, 1917. In the Second Report, London, 1918, W. Harrison discusses at some length the colloid chemical nature of the various textile fibers, as well as the electrical theory of dyeing.

There are many different types of dyes and thousands of different individual dyestuffs, and the various fibers, tissues, etc. (cotton, silk, wool, linen, jute, straw, paper, wood) all react characteristically. The phenomena of dyeing are, therefore, very numerous and complicated. In essence the conflicting theories are not so divergent as might be imagined; they differ mainly as to the classification of the attractive force between substrate and dye.

Since all forces of the nature involved are ultimately due to electro-magnetic fields of the atoms involved (or of their electrons), the attraction is essentially electrical or chemical; but since this attraction is exhibited only when the dye and substrate expose sufficient active free surface, the operation is "physical" or "colloidal." Although forces closely allied to those

of primary valency are involved, the compounds formed do not in general possess that preciseness connoted by the present meaning of the expression "chemical compound."

In some cases the colloid fiber adsorbs the dye, as with basic colors which dye silk and wool directly. In other cases there is necessary a *mordant*, which is first adsorbed and then fixes the color; e.g., for some dyes cotton must first be mordanted with an insoluble colloid precipitate formed *in situ* by tannin and tartar emetic. Certain dyes of opposite charge may mutually precipitate each other, and thus serve as mordants for each other; e.g., methylene blue and dianil blue 2 R; patent blue V and magenta. But a large excess of either dye may serve as a colloidal protector and either prevent the precipitate or make it colloidal. Grübler's stains owe their peculiar properties mainly to colloidal impurities (dextrin, etc.), so that the same dyes when spectroscopically pure, work differently.

Ultramicroscopic examination reveals the fact that many dyes are colloidal in solution, and the selective coloring of fibers, tissues, cells, nuclei, etc., probably represent the selective adsorption or precipitation of one colloid by another, a view sustained by the ultramicroscope researches of N. Gaidukov. Some dyes can be extracted from the dyed fiber by alcohol, which would hardly be the case if a true chemical compound were formed. There is an optimum degree of dispersion for each dye [zone of maximum colloidality (see p. 17)]. This is shown by the work of R. Auerbach [Kolloid Zeit. *34*, 109, (1924)] which indicates that if too coarse, the dye lacks diffusive power; and if too fine, it passes out of the fiber once more.

(J. Alexander, Am. Chem. Soc. Washington Meeting, 1924.) Temperature, and the addition of salts (Na_2SO_4), acids, colloidal protectors (boiled off silk liquor) and the like are used by practical dyers to control the degree of dispersion.

Colloid chemistry also throws much light upon many obscure points in the practical art of dyeing. It is possible to obtain much more level colors in old dye liquors than in fresh ones, and here it seems that colloidally dissolved substances are responsible, exercising a restraining action upon the absorption of the color. The addition of Glaubers' salt facilitates level dyeing, probably by its action as an electrolyte, producing a partial coagulation of the dyestuff, so that the particles of the latter, thereby made larger, are absorbed more slowly and evenly.

Congo red when dyed on silk or wool changes only in shade if the fiber is dipped in dilute sulfuric acid, whereas when dyed on cotton it turns blue in like circumstances. Upon following ultramicroscopically the changes produced in colloidal aqueous solutions of benzopurpurin, J. Alexander found [J. Soc. Chem. Ind. 1911, Vol. 30, No. 9] that the color change was accompanied by an aggregation of the dye ultramicrons. If a protective colloid such as glue was added to the dye solution before the addition of acid, the dye ultramicrons did not aggregate, and the color change could thus be modified or prevented. It seems, then, that silk and wool exercise a greater protective action on the adsorbed dye than does cotton, which harmonizes with the fact that proteins are in general better protectors than carbohydrates. This is also evidence against the chemical theory of dyeing in this case.

Shower-proofing Fabrics

If textile fabrics and the like are coated with a surface film of wax, aluminium stearate and so on, they are not wet by an ordinary shower, whose drops roll off "like water off a duck's back." With an untreated fabric the attraction between the fabric and water bursts the surface skin of air on the fabric and the surface film of the raindrop, which then spreads itself out on the fabric and is absorbed into its pores.

Remembering that as the attraction between surfaces increases the surface tension between them decreases,* this means that wetting occurs when the surface tension (σ) water/fabric is less than the combined surface tension water/air and air/fabric. That is,

$$\sigma WF < \sigma WA + \sigma AF,\dagger$$
$$\text{or } \sigma WA > \sigma WF - \sigma AF.$$

Since surface tension is only "skin deep," the surface tension water/fabric really becomes that of water/wax and is greatly increased. Therefore,

$$\sigma WF > \sigma WA + \sigma AF,$$
$$\text{or } \sigma WA < \sigma WF - \sigma AF,$$

the water is repelled and no wetting occurs.

Nitrocellulose and Its Products

When cellulose (cotton, purified paper pulp) is soaked in a mixture of nitric and sulphuric acid, it takes up from 10 to 13 per cent. of nitrogen, depending upon the purity and moisture content of the cellulose, the exact composition of the acid bath and the time and

* In fact, when the surface tension in a two-phase system becomes zero, solution or colloidal dispersion may occur.

† W = water, F = fabric, A = air, σ = surface tension.

temperature of nitration. The formation of a series of cellulose nitrates is generally assumed, although A. Müller suggested the existence of adsorption compounds. In any event the acid fixation curve is continuous, notwithstanding numerous attempts to separate out definite nitrates. Cellulose has a structure, the interior of a cotton fiber being less dense than the exterior, and since the nitration starts at the surfaces and leaves them comparatively undisturbed, its course will evidently be dependent upon the amount of free surface exposed. It has been found that by intensive grinding cellulose yields a colloidal solution in water.

The colloidal solutions that result from dissolving cellulose nitrate in various solvents or mixtures, are widely used as varnishes and lacquers to coat patent and artificial leather, metals, etc. Their degree of dispersion and therefore their viscosity is dependent upon the nature of the solvent, whose action may depend upon small percentages of substances which exercise a peptizing action. Thus old patents claimed that nitrocellulose dissolved in wood alcohol, because the "wood spirit" of those days contained ketones, small quantities of which are essential; for the nitrate is insoluble in pure methyl alcohol. According to F. Sproxton [Third Report on Colloids, etc., Brit. Assoc. Adv. Sci. 1920], if water be added in gradually increasing quantities to an acetone solution of cellulose nitrate, keeping the percentage of the solute constant, the viscosity rises to a maximum (both absolutely and relatively to the viscosity of the solvent) and then falls until it is practically the same as that of the solvent. This seems to be another illustration of the zone of maximum degree of colloidality [see J. Alex-

ander, J. Am. Chem. Soc. 43, 434, 1921], for the Tyndall effect becomes marked close to the position of maximum viscosity.

Celluloid

This is a transparent gel formed when nitrocellulose is kneaded with alcohol and camphor. In the subsequent sheeting, pressing and molding operations it undergoes a slow syneresis due to the loss of the alcohol and some of the camphor. Schüpphaus [Thorpe's Dict. Appl. Chem., vol. 1] thinks that there is some kind of chemical combination between the camphor and the nitrocellulose because the heat of combustion of the two ingredients is greater than that of celluloid itself. This, however, is no criterion, for as Prange has shown [Recueil des Trav. Chim. des Pays Bas, 9, 121 (1890)] colloids may set free heat if their particles aggregate, and heat is liberated when nitrocellulose and camphor are mixed. Furthermore, according to Sproxton, the optical rotation of a dilute acetone solution of celluloid equals the sum of the rotations of its two ingredients.

The view of Dubosc [Le Caoutchouc et la Gutta Percha, 1919, p. 9803] that celluloid is a camphorgel (nitrocellulose dispersed in camphor) seems well warranted by the facts. Its plasticity on heating to 80 deg. C. is attributed to the fusion of the dispersion medium, camphor, which diminishes the internal friction. The fact that camphor constitutes only about one-third the bulk of the celluloid does not militate against this view (as Sproxton suggests), for S. U. Pickering was able to emulsify 99 per cent. of petroleum oil in 1 per cent. of soap solution, obtaining an almost solid emulsion.

Explosives

The modern propellant explosives consist of nitrocellulose colloided with ether/alcohol, nitroglycerin, etc. The rate of burning of the grain is intimately connected with the external and internal surfaces of the explosive, the former being controlled by the size, shape and perforations of the pieces, and the latter by careful regulation of the manufacturing process. Variations in the original cellulose, the process of manufacture and the presence of traces of impurities may materially alter the stability and ballistic properties of the product as well as the viscosity of its solutions.

Blasting gelatin is a colloidal gel of 7 to 8 per cent. nitrocellulose with nitroglycerine, the former probably being the dispersed phase. There is evidently an optimum internal structure for this colloid, since its tendency to become insensitive on aging is a bane of the manufacturer. The use of a protective colloid seems indicated here; it will also probably tend to prevent the exudation of the dangerous nitroglycerine, which is especially apt to occur on freezing, and constitutes a serious danger on thawing or subsequent handling.

Paints, Pigments, Varnishes

When linseed oil, China wood oil, etc., begin to polymerize upon boiling, they form *isocolloids*, that is, a dispersion of the polymerized in the unpolymerized oil. Highly boiled China wood oil sets to a gel. The various varnish gums go into colloidal dispersion, and it seems not improbable that they may act as protectors to the boiled oil, keeping it from gelatinizing. What is known as the "break" in boiled oils is the

coagulum resulting from the albumin, etc., which must be filtered or settled out.

Varnishes must possess a very fine internal structure when dry, for they permit the swelling of gelatin protected by the varnish film. In most cases the internal spaces permit the formation of a cloudy dispersion or emulsion of water in the film, but with the most highly protective varnishes they are so fine that although as much as 5 per cent. of water be taken up, the film remains clear. The impermeability of the varnish film to most salts indicates the fineness of the pores; but since water absorption increases with diminishing salt concentration, it would seem that the salt by adsorption or swelling causes a diminution of the size of the pores. Normal solutions of NaCl, $MgCl_2$ and $CaCl_2$ prevent the ordinary varnish film from turning white, and greatly diminish the amount of water passing through.

Shellac contains about 4 per cent. of wax, which goes into colloidal dispersion in most solvents. In solutions over about $3\frac{1}{2}$ lbs. per gallon the wax does not readily settle out, but weaker solutions show a separation of wax-free *"French varnish"* or clear shellac solution.

Pigments vary greatly in their degree of dispersion which vitally controls their opacity, surface covering power, and oil-absorbing capacity. Because of the importance of the physical condition, mere chemical analysis is quite insufficient to rate pigments. The most finely subdivided oxide of zinc commands the highest price, chromates of lead vary in color from lemon yellow to orange and Prussian blues vary in shades as their particle size changes. The difference

between blanc fixe (precipitated $BaSO_4$) and ground barytes is enormous. Too great a degree of dispersion is harmful, for there is an optimum degree of dispersion on either side of which desirable properties begin to diminish. The cross-precipitation of BaS by $ZnSO_4$ yields a product so highly colloidal that it is furnaced and powdered to produce a more compact lithopone. The fact that a mixture of blanc fixe and zinc sulphide does not give the same degree of opacity as lithopone indicates that in the latter there is a close adsorption. Generally in making precipitated colors or color bases the degree of dispersion is controlled by temperature, colloidal or other protectors (or even coagulants), and the concentrations and speed of mixing of the reacting solutions. [See H. A. Gardner, J. Ind. Eng. Chem. *8*, 794 (1916).]

While *paints* are essentially mixtures of pigments, drying oils, and solvents, the presence of small amounts of other substances may be highly desirable. Thus E. G. Acheson [J. Soc. Chem. Ind. 30, 1426 (1921)] states that the addition of a minute amount of tannic acid causes a pigment to deflocculate readily on grinding in oil, and the use of about 2 per cent. of water emulsified by such a substance as silicate of soda has long been common in mixed paints to prevent hardening or settling in the can. Ware and Christman [J. Ind. Eng. Chem. 8, 879 (1916)] found that the addition of aluminium palmitate or oleate to paints helps this condition; these non-aqueous protective colloids aid in keeping the pigment in suspension, partly because they increase the viscosity of the oil. These authors also investigated the "livering," puttying, and skinning of mixed paints. Livering is attrib-

uted mainly to the formation of a zinc soap gel, the formation of which is aided by the presence of zinc resinate (formed from rosin used in the paint) and acid pigments.

An interesting application of colloid chemistry was made by Wheeler P. Davey, of the General Electric Co., who made a "*water japan*" by emulsifying japan base (mainly a solution of asphalt in a drying oil) in water containing ammonia and a protective colloid. Besides being cheaper and less hazardous than the ordinary japan made with petroleum solvents, the water japan is much less viscous and small pieces of metal may be coated by first heating them and dipping them *en masse* in baskets into the emulsion. As the japanned particles are negatively charged, they may also be deposited on the metal by making it the anode in an electric circuit. In both cases the japan base attached to the metal is free from solvent, and is baked as usual; "secondary drip" and scars due to mutual contact between the metal pieces are largely avoided by the wide latitude permitted in the composition of the base, for these changes do not seriously affect the viscosity of the emulsion.

Emulsions

An emulsion is a fine dispersion of one liquid in another. Since the interfacial tension between benzol and water is very high (about 35 dynes per sq. cm.), if benzol and water are agitated together, the benzol droplets tend quickly to unite, and the liquids separate into two layers. If there is a very small percentage of benzol, this process takes quite a while, especially if the benzol droplets are very small; so that the dilute emulsion has a limited life.

If however the aqueous phase consists of sodium oleate solution 0.01 normal or stronger, the interfacial tension is reduced to about two dynes per sq. cm., and vigorous agitation gives a stable emulsion. As J. Willard Gibbs showed, the sodium oleate, tending to reduce the interfacial tension, accumulates at the interface, and practically surrounds the emulsified droplets with a coherent film.

Taking Harkin's view of oriented adsorption, the hydrocarbon end of soap will direct itself toward the oily liquid, while the metallic end will point toward the aqueous phase. If, now, the fatty ends of the molecule can pack together closer than do the metallic ends, the interfacial film bends *toward the oil*, and we have an emulsion of oil in water. This is the case with sodium, potassium and cæsium soaps; and indeed Finkle, Draper and Hildebrand found that the size of the oil drops in emulsions, made with soaps of these alkali metals, varied as this theory demands [J. Am. Chem. Soc., *45*, 2780 (1923)].

If, however, a soap of a bi- or trivalent metal (calcium, aluminium, magnesium, lead or the like) be used, which has several hydrocarbon chains attached, then the interfacial film bends *towards the water*, and we have an emulsion of water in oil. Thus are explained the observations of G. H. A. Clowes on the reversal or inversion of emulsions and the variation in the number of drops when oil is dripped into various solutions from a staglomometer (drop measurer).

W. D. Harkins and his collaborators have developed the principles governing this oriented wedge theory of emulsions and the inversion of emulsions [see J. Am. Chem. Soc. *39*, 587 and 592–4 (1917); also "Science," May 23, 1924].

The preparation of stable emulsions is of importance in pharmacy (cod-liver oil, etc.) and cookery (mayonnaise, hollandaise sauce, etc.); and the biological importance (myelins, nerve tissue, fat depots, etc.) is obvious.

The "breaking" of undesirable emulsions (de-emulsification) is also of considerable practical importance. Thus many petroleums contain large amounts of emulsified water which must be removed. The basic method of F. H. Cottrell [U. S. P. 287,115 (1911)] makes use of high tension electric current [for details see J. Ind. Eng. Chem. *13*, 1016 (1921)]. Besides this filtration, chemical, and centrifugal methods are used to break the interfacial films and permit the droplets to coalesce. In some cases even as little as 0.001 per cent. of a protective colloid will do this, by coagulating the emulsostatic film. Freezing does the same thing in other instances. (For further details see W. Clayton's book on "Emulsions and Emulsification," Blakiston, 1923.)

CHAPTER X

PRACTICAL APPLICATIONS (Continued)

SOAPS

The orthodox view that soaps are simply alkali salts of fatty acids was considerably shaken when Lewkowitsch [J. Soc. Chem. Ind. 1907, 26, 590], after epitomizing the views of Merklen, said:

But whatever may be the outcome of renewed experiments, Merklen's views cannot fail to stimulate further research into the composition of soap, and thus help raise the industry of soap-making, which has too long been looked upon as a mere art, to the rank of a scientifically well-founded industry, the operations of which are governed by the laws of mass action, the phase rule, and the modern chemistry of colloids.

Merklen's views which aroused this comment are that commercial soap is a product of essentially variable composition which depends on (1) the nature of the fatty acids, (2) the composition of the "nigre" (in the case of settled soaps), (3) the temperature at which the boiling is conducted. It behaves like a colloid, and should not be regarded as a compound of fatty acids having chemically combined a definite amount of water, but is rather an "adsorption product" whose composition depends upon the environment in which the fatty acid salts find themselves at the moment of the finishing operation.

According to J. W. McBain [Third Report on Colloids, etc., Brit. Assoc. Adv. Sci. 1920], homogeneous solutions of soap are rarely met with during the process of manufacture, since their viscosity would be pro-

hibitively great, and must be held in check by the addition of caustic soda, salt, or other electrolytes, to bring the soap into a gel or even into coagulated form (soap curd). The soap is usually in the form of a dispersion of two soap solutions, soap-in-water, and water-in-soap, and may exist in the form sol/sol, sol/gel, or sol/curded-gel.

Most commercial soaps are of the sol/curded-gel type, but soft soaps may be of the sol/gel type. McBain regards soaps as colloidal electrolytes, that is, as salts in which one of the ions has been replaced by a heavily charged, heavily hydrated ionic micelle which exhibits a high conductivity.

Martin H. Fischer ["Soaps and Proteins"] has shown that the hydration capacity of soaps varies greatly with change in the fatty acid, and the base. Some soaps hold enormous amounts of water, while others hold very little, so that if the amount of water present exceeds the hydration capacity of the soap, free water separates or may remain emulsified (see p. 19).

Most soaps form crystalloidal solutions in alcohol, which ultramicroscopically are quite clear; but if a droplet of tincture of green soap, for example, be allowed to diffuse into a clear field of pure water held between a slide and cover glass in a dark-field condenser, the soap practically explodes into numberless actively moving ultramicrons. The colloidal nature of aqueous soap solutions is further indicated by their turbidity, viscosity, and gelatinization.

The *detergent action* of soap is due to its ability as a colloid to produce deflocculation. Hillyer [J. Am. Chem. Soc. 1903, 25, 511, 1256] showed that this action is not due to alkali freed by hydrolysis, and that

alkali itself does not wet oily matter. But all "dirt" is not oily, and W. Spring [Kolloid Zeit. 1909, 4, 161; 6, 11, 104, 164] in experiments with purified lampblack, iron oxide, alumina and silica, showed that soap makes such particles less adherent to the fabric, and to each other. The attraction of both fabric and "dirt" for soap exceeds the attraction of the fabric for "dirt" and of "dirt" particles for each other. In order that the soap may be adsorbed at the interfaces involved, it must be in colloidal dispersion, which requires hot water in the case of many soaps.

The practical working properties of various commercial soaps depend mainly upon the nature of the fatty acids in them. Thus sodium oleate is much more readily dispersible in water to colloidal dimensions than is sodium stearate, and even small amounts of oleate materially assist the higher fatty acid soaps to dissolve. In fact mixtures of fats or fatty acids show a "eutectic drop" in melting point, just as do alloys. From the oriented wedge theory of emulsions (see p. 124) it is evident that in an emulsion of oil in water, potassium soaps, having larger molecules (K) turned to the water phase than the sodium soaps (Na), tend to make a foam with smaller bubbles, which is therefore more stable. For this reason shaving soaps consist largely of potassium soaps.

H. Jackson [Cantor Lecture, J. Soc. Arts, 1908, 55, 1101] examined microscopically the supernatant fluid resulting from washing a piece of dirty cloth with soap and water, and found in it countless particles in a state of oscillatory motion (*"pedesis"*). This is really *Brownian motion*, first noted by the English botanist Robert Brown in particles approaching the

limit of microscopic resolvability. The ultramicroscope shows it to be largely due to bombardment of these larger particles by the still smaller and more actively moving colloidal particles, which in turn are activated by the motion of still smaller particles (water molecules), and so on. When an individual fiber was bathed in soap solution, the dirt particles gradually loosened and began to oscillate. Upon substituting salt solution for the soap, the particles flocculated and the motion ceased. An ultramicroscopic examination of the detergent action of soap is very interesting.

Transparent soaps are made by keeping the dispersion of the particles of the finished soap well toward the lower limit of colloidal dimensions. Among the factors that produce this effect are (1) the selection of the fatty acids; (2) quick chilling; (3) protective colloids; (4) the addition of alcohol, glycerol, sugar and the like, which tend to dissolve the soap crystalloidally. Frequently some of the fatty acid salts crystallize out in the clear matrix, marring the commercial appearance of the soap, and these crystals exhibit the dendritic or ramifying tendency common when crystallization occurs in the presence of colloids. W. D. Richardson [J. Am. Chem. Soc. 30, 1414] found that the fatty acids separated from the crystals had a higher melting point than those separated from the clear matrix.

To demonstrate the effect of the speed of chilling on particle size, J. Alexander melted a piece of commercial transparent soap and cast it into two cups, one of which was instantly chilled with ice, while the other was allowed to cool slowly while immersed in hot water. The quickly chilled piece was transparent and upon

ultramicroscopic examination showed much smaller ultramicrons than the slowly cooled piece, which was opaque. After several months standing the quickly chilled soap still appeared clear, whereas the other had large opaque spots. Upon ultramicroscopic examination the transparent piece appeared as before, but the slowly cooled piece showed perfectly resolvable crystals in a clear matrix.

Lubrication

The automobile has brought such an increase in the consumption of petroleum that a material curtailment in supply, if not actual exhaustion, lurks in the not far distant future. But we may look with confidence to colloid chemistry to supply the lubricants of that day.

The principle involved in lubrication is the maintenance, on each of the surfaces in contact, of an adsorbed layer of an easily deformable substance (usually a fluid) so that the surfaces can not come into actual contact, or "seize." Since the attractive forces at surfaces depend on their residual electrical fields, lubrication is affected by the chemical and physical nature of the surfaces as well as by that of the lubricant. Good lubricants are so strongly absorbed that great pressure and speed are necessary to tear them loose.

W. B. Hardy * [J. Soc. Chem. Ind. 1919, 38, 7 T] made some illuminating experiments with glass, which absorbs from the atmosphere rather more of its impurities than of the elementary gases, yielding a film about 1 millimicron (1×10^{-7} cm.) thick, that Lord Rayleigh termed "grease" because it has the properties of an oil. This "grease" tends to make pipettes

* See also his splendid paper in Alexander's Colloid Chemistry, Theoretical and Applied, Vol. I.

deliver inaccurately, so analytical chemists remove the absorbed layer by oxidation with bichromate and sulphuric acid.

For the same reason new or raw glass surfaces have mechanical properties different from those of a satisfied or neutral surface. Thus a finger bowl or tumbler does not give a musical note when rubbed with the wetted finger, unless the "grease" film is removed by vigorous rubbing with the finger tips until a peculiar clinging feeling is felt, due to "seizing" between finger and glass.

Experiments with cleaned glass surfaces have shown that water, ether, alcohol, benzene and strong ammonia do not prevent "seizing" even if the surface be flooded with them. A thin film of glycerin did not lubricate, but flooding the glass surfaces reduced the tangential force required to move them from 55 grams to 9 grams. Most acids, for example, sulphuric, acetic, oleic, lubricate better in thick layers.

Because animal oils, such as sperm or lard oil, are more highly adsorbed by metal surfaces than are petroleum oils, they have long been blended with the latter in considerable quantity to improve the lubricating value. It has been found, however, that such additions owe their value largely to the free fatty acids present which are highly adsorbed, and Southcombe and Wells patented the addition of about 1 per cent. of such acid to mineral oils, thereby effecting a great saving, by avoiding the cost of the blending oils.

Most lubricating greases are colloidal oil/water emulsions stabilized with sodium or calcium soaps. The so-called "cutting oils" which form stable emulsions with water are made by mixing petroleum with

water-soluble protective oils like turkey-red (sulphonated) oil. The thrust boxes of steamers which absorb the tremendous pressure of the propellers are lubricated and cooled by circulating an emulsion of oil and water.

The viscosity of oils, which is an important factor in lubrication, seems to depend to a considerable extent on the degree of molecular aggregation. Thus Dunstan and Thole (J. Inst. Petrol. Tech. 1918, 4, 191) found that mineral and fatty oils show an exceedingly fine heterogeneity in the ultramicroscope which they attribute to iso-colloidism.

Coal

Coal as the end product of a colloidal transformation, was first considered by Thomas Graham (see p. 54).

In recent years the complicated structure of coal has been given much attention. In banded bituminous coal the following constituents are recognized (M. C. Stopes, Proc. Roy. Soc. B, *90*, 470 (1919):

vitrain, brilliant, with conchoidal fracture.
durain, dull, hard coal.
clarain, bright coal.
fusain ("mother of coal" or "mineral charcoal"), is the most friable portion whose fineness controls the speed with which combustion spreads in the mass. When very fine it absorbs oxygen with avidity, and this may be a factor in *spontaneous combustion.*

Stopes and Wheeler (Monograph on Constitution of Coal, Brit. Dept. Sci. Ind. Res. 1918) define ordinary coal as a compact, stratified mass of mummified

plants (which have suffered arrested decay to varying degrees of completeness), free from all save a very low percentage of other matter. Although coal retains to some extent the structure and general chemical nature of the original plants, the presence in peat of Doppler-ite (a dark, apparently structureless jelly) indicates that part of the coal was probably in this state, which may account for some of the adsorbed substances found in coal.

Reinhardt Thiessen (U. S. Bureau of Mines, Bull. 117; Journ. of Geology, *28*, 185–208, 1920), divides the main constituents of coal into (1) *bright* or *glanz* coal, (*antharyxalon*) compact, pitchy jet-black, and of conchoidal fracture, formed from undisintegrated trunks and large limbs and retaining the original woody structure, and (2) *dull* or *matt* coal, less compact, dull grayish, and showing an irregular fracture; consisting of numerous small layers or chips of anthraxylon embedded in a dull matrix, the *attritus*, which is derived from assorted vegetable residues.

In the very nature of things, classifications of coal constituents must be rather arbitrary, but it is evident that the sub-microscopic structure of coal has much to do with its practical working properties.

"Colloidal" Fuel

"Colloidal" fuel consists of finely powdered coal, cheap tars and the like, dispersed in mineral oil and stabilized by a protective colloid or "fixateur" such as lime soaps or resinates, so that it may be stored, piped, atomized and burned practically like oil itself. As this new composite fuel may at one stroke relieve the drain on the earth's rapidly diminishing stores

of petroleum, and lead, as well, to the utilization of coal waste (culm, screenings), inferior fuels (peat, lignite), and even cellulose waste (slabs, sawdust), it may become a material factor in the conservation of our natural resources.

Coal or other combustible solid is prepared for dispersion by being pulverized so that about 95 per cent. passes through a 100-mesh screen, and 85 per cent. through a 200-mesh screen. This means, of course, that the bulk of the weight is in particles hundreds and thousands of times larger than colloidal dimensions. But the violent motion of colloidal particles aids in maintaining the Brownian motion of larger particles which helps to keep them afloat. A fluid fuel may be made containing as much as 40 per cent. by weight of powdered coal, and mobile pastes containing up to about 75 per cent. Mobile gels may be made from either liquid or paste.

Ordinarily between 0.5 and 1.5 per cent. of rosin or a saponifiable oil is used, and 0.1 per cent. exercises a noticeable effect. The amount is determined by the nature of the mixture and the degrees of permanence desired. The bulk of the particles does not begin to settle until the period of "life" has passed, the colloidal fuel having a limited "life" which may be regulated to meet requirements—days for power plants, weeks and months for central storage stations and ocean-going vessels. Heat and agitation revivify the liquid fuel; the paste form may be kept for years.

"Colloidal" fuel is heavier than oil or water and saves storage space by compressing a maximum thermal value per unit of space. It may be stored under

water to avoid evaporation, deterioration and fire risk. When sprayed into the hot fire-box, its oil-soaked solid particles are still further atomized by the sudden gasification of their imbibed oil. It possesses the advantages of fuel oil over coal in absence of smoke, dust and ash, practical elimination of labor in firing and filling storage space, thus saving time in "coaling" and in raising steam. The fire is likewise subject to instant control, and in naval operations a smoke screen may be readily produced by over-firing.

Another well-known colloidal fuel is "solidified alcohol," an alcogel usually stabilized by an alcohol-soluble protector. Thus the late Prof. Charles Baskerville found that certain percentages of calcium acetate yielded with alcohol an unstable gel, which is stabilized by stearic acid.

Petroleum

Colloidal phenomena are very marked in mineral oils. Many oils contain colloidally dispersed water which is difficult to remove. Cottrell devised a method of removing it with high tension current. He also was able to send viscous asphaltic oils through pipe-lines by emulsifying in them a certain percentage of water. The solid constituents of petroleum, especially the waxes, are largely in colloidal dispersion, some apparently serving as protectors to the others.* This phenomenon is common, being found in alloys, glasses, mixtures of waxes, fatty acids, etc. When the kerosene and lower boiling fractions are removed from such oils, the solids, on chilling with ice, often assume the form of a gel which may be broken up by

Bloom in oil seems to be in part caused by some colloidal constituent.

As Brooks and Humphrey have shown [J. Am. Chem. Soc. 40, 882 (1920)], the "acid tar" which forms when petroleum is refined with sulphuric acid represents the coagulation of a previously existing colloidal dispersion of asphaltic bodies and the like, and not a polymerization product of olefines. Even 100 per cent. acid at 15 deg. C. does not produce tars from pure olefines. In some cases impurities may be centrifuged out, but they are largely removed by absorption with fuller's earth, floridin, bentonite, bauxite or other adsorbents. Patrick's colloidal silica gel and activated carbons are now used to adsorb the petroleum dispersed in natural gas, which yields millions of gallons annually of the high-grade "casing head" gasoline.

Great care must be used in drilling oil wells, for if the oil sands below ground get *wet* with water, surface tension makes the sand repel the oil, which is then unable to diffuse toward the well-pipe. Once the sands are *oiled*, however, then water cannot wet them.

In oil shale the oil is so finely dispersed that it cannot be removed by mere pressure. Distillation is resorted to, though doubtful claims are made that grinding in the colloid mill will effect a separation.

Asphalt

Although most of the mineral matter in asphalt exceeds colloidal dimensions, as Clifford Richardson has shown, the great extension of free surface caused by its presence adds considerably to the viscosity, strength and wearing properties of the asphalt. The minerals here function somewhat like the fillers in

putties and lutes. Natural asphalts may be improved by the addition of colloidal clays.

Many years ago, H. Raschig, among others, patented the making of tar and asphalt emulsions by the use of water dispersions of clay. Later on Clifford Richardson found that colloidal clays, when used to emulsify asphalts or pitches, gave especially great strength and heat-resistance to the dried-out emulsion, and was granted patents for his discovery. Bentonite was among the colloidal clays used by Richardson, who used to exhibit two tubes containing spirals of the same asphalt, one with and the other without colloidal clay. The plain asphalt would melt and flow under temperatures which would not affect the asphalt reinforced with small percentages of colloidal clay, which, because of its great degree of subdivision and huge exposure of surface, produces effects out of proportion to its weight. These clay emulsions are useful because, while miscible with water and applicable to wet surfaces (roads, foundations, etc.), they become insoluble as they dry out, for they change from asphalt-in-water types of emulsions, to water-in-asphalt. The same relation exists between cream and butter.

L. Kirschbraun has patented the use of colloidal aqueous dispersions of asphalt, pitch, etc., which, when mixed with paper stock in the beater or on the way to the paper machine, may be flocculated out with alum or alum and sodium silicate, giving a highly waterproof and moisture-resisting paper. This asphalt dispersion is not sticky or adhesive under the conditions of pressure, etc., in the paper machine.

Among the many uses to which such emulsions are being put are protecting structural steel, patching

roofs and highways, making waterproof cork insulation, pipe coverings, paints, building and roofing papers, auto body parts, and especially making a large variety of moisture and waterproof containers and wrappers for foods, tobacco, etc.

"Fire-Foam"

"Fire-Foam" is a carbon dioxide froth made by mixing solutions of sodium bicarbonate and alum. A protective colloid such as liquorice, glue, dextrin, or saponin, is added to stabilize the foam and keep the bubbles in finely dispersed form. It kills fire.

Insecticides

Petroleum oils are readily emulsified in water for killing San Jose scale and similar parasites, by the addition to them of sulphonated oils. Sulphur, Bordeaux mixture and the like are maintained in fine dispersion by colloidal protectors, as are also such poisons as lead arsenate. Minute quantities of poisons are sufficient to kill insects and it is wasteful to supply more than the necessary dose. The colloidal poison is less apt to be noticed and rejected by the insect and clings better to the plant, and goes much further.

Even allowing for the necessity of a rather promiscuous distribution of insecticides, in general the use of coarse particles means that the factor of safety is exceeded hundreds if not thousands of times; and this means enormous economic loss.

The electric charge of the dispersed insecticide is of importance. Since the leaves of plants are mostly negatively charged, positively charged colloids tend to cling closely to them, as has been pointed out by Dr. William Moore.

CHAPTER XI

PRACTICAL APPLICATIONS (Continued)

FILTRATION

To secure commercially successful filtration, a filtering medium or septum must be used, which, under the application of a practicable pressure, will permit the fluid to pass and still hold back the solids. The pores of the filter may initially be small enough, or they may become so by the deposit of some of the precipitate itself or of some added substance, such as paper pulp, shredded asbestos (Gooch crucible), or the like. Exceedingly dense filters may require the application of high pressure to force the fluid through, and such high-pressure filters were termed by Bechhold *ultrafilters* because they could be made to hold back ultramicroscopic particles. Bechhold ("Colloids in Biology and Medicine," translated by Dr. J. G. M. Bullowa) used gelatin jellies hardened in ice-cold formaldehyde, or a glacial acetic acid solution of collodion coagulated in water. These septa were supported on fine-meshed wire cloth to withstand the high pressure used.

Zsigmondy has recently prepared *ultrafilters for analytical use*, which permit the rapid and successful filtration of troublesome precipitates [see Zsigmondy and Jander, Zeit. anal. Chem. *58*, 241 (1919)].

The so-called *stream-line filter* of Hele-Shaw consists of paper sheets tightly pressed together, with holes bored through the pack at right angles to the surface. Liquids are forced under pressure into one set of holes and pass between the sheets to the adjoining set. By

sufficient compression of the sheets, even Prussian blue may be filtered out of solution.

Anything that favors deflocculation of a precipitate or the formation of a fine or colloidal precipitate, such as protective colloids, dilute alkalis, and so on, works against clear filtration. Thus Zsigmondy found that a gold hydrosol, whose particles were 20 to 30 millimicrons, passed freely through Pukall and Maassen filters if egg albumen was present. In the absence of the protective albumen, the colloidal gold was absorbed by the filters, gradually clogging their pores until the filtrate, at first red, became colorless.

In technical practice, wherever possible, a coagulated precipitate is formed whose large particles are held back with comparative ease. Therefore, glucose liquors, for example, must be acid to filter well. Where protective colloids interfere with filtration, their protective action may be destroyed by coagulation, hydrolysis and the like.

Sewage Disposal

Sewage usually contains considerable amounts of deflocculating substances, such as soap, organic matter and the like, which tend to keep it full of colloidally dispersed particles. The successful treatment of sewage, backwaters, and trade effluents involves the separation from them of these colloids by coagulation, adsorption, filtration, or destruction (usually by bacteria in the septic tank). The old "ABC" method depended on the use of alum, blood, and clay (whence the name) to make a coagulum that would carry down suspended matter. Ferrous sulphate and lime (yielding a coagulum of ferric hydroxide) and alum are

also used as clarifiers and coagulants. H. M. Spencer (Chem. Age, Jan. 1924) uses a colloidal solution of aluminum hydroxide, which on dilution forms a gel.

In the *activated sludge process* it has long been known that the effective acidity of the sewage controls proper settling, and modern methods of p_H control aid in fixing the isoelectric point, most favorable to flocculation.

Filtration through sand, coke, and the like serves to adsorb colloidal impurities, but filters of this kind do not begin to function properly until they become coated with a gel-like slime containing many bacteria. There has been much discussion as to whether the action of the filter depends on activity of the bacteria in destroying and dispersing to the crystalloidal state the finely suspended or colloidal matter, or whether the removal of these substances is not an adsorption phenomenon due to the extended surface of the filter bed. Both effects exist, the latter being the more important, and depending largely on the action of the bacterial jelly that forms the surface layer.

Photography

The ordinary precipitate of silver bromide obtained by mixing equivalent amounts of potassium bromide and silver nitrate is flocculent and quickly settles. If the fresh precipitate (before or after washing) is shaken with a solution of gelatin containing a trace of potassium bromide, or better, yet, if the precipitate is originally formed in the presence of gelatin, there results a colloidal solution of silver bromide, which may be exceedingly fine or grainless, depending on conditions. The latter method is used mainly in preparing photographic "emulsions."

The Lippmann "grainless" emulsion is an illustration of the principle of *plural protection* discovered by J. Alexander [J. Chem. Ind. Eng. 15, 283 (1923)], for in preparing it gelatin is added to both the silver nitrate and the bromide solutions before they are mixed (see p. 43).

As a very fine emulsion is relatively insensitive, it is "ripened" by allowing the silver bromide grains to grow until they are about 0.4 to 10 microns in diameter, the process being facilitated by heat. Certain percentages of chloride and iodide may be used, a small excess of the soluble halide salt aiding in peptizing or stabilizing the precipitate, and keeping its particles within the desired limits which are about 2 to 3 microns in most cases.*

When a sensitive ripened emulsion is exposed to light, some of the silver halide is decomposed, its halogen being probably held by the gelatin,† while the metallic silver forms a colloidal dispersion in the rest of the silver halide, yielding the so-called "photo-halides." These were long supposed to be subhalides (sub-bromide and so on) of silver, but are now recognized as being of the same nature as the "metal fogs" which often appear during the electrolysis of molten salts, and consist of colloidally dispersed metal.

Recently, S. E. Sheppard and his collaborators at the Eastman Kodak Company have shown the im-

* According to Lottermoser the excess of soluble halide gives the particles of silver halide a positive charge, essential to their sensitivity to light.

† Chlorine, bromine and iodine all "tan gelatin"; see Allen's Commercial Organic Analysis, 4th ed., vol. 8, article on Albuminoids or Scleroproteins; also A. C. S. Monograph No. 11, "Glue and Gelatin," by J. Alexander.

portance of traces of impurities in gelatin in forming silver sulphide nuclei, which make the plate or film highly sensitive. They believe that the active material consists of traces of thiocyanates derived from "mustard oils" in the fodder of the cattle from whose skins and bones the gelatin was made. It is said that similar facts were long known to the Lumières in France, but kept as a trade secret.

The particles of silver in the "latent image" are so exceedingly fine that, in time, they apparently recombine again with the halogen, and the latent image fades away. To render it permanent, it must be treated with a "developer," a reducing agent which probably serves the twofold purpose of combining with the halogen and making the extremely fine silver grow into dense visible particles or grains.

The color of emulsions varies greatly with the size of their "grains." Fine blue emulsions are sensitive to red, and even to infra-red rays. Freshly prepared emulsions appear red to transmitted light, but on ripening the color changes to green, the particles increasing from below 0.1 micron to over 0.5 micron. The photo-halides resulting from the action of light on emulsions are also highly colored.

Brewing

In the brewing process it is essential that the starch originally present be converted into sugars which can be fermented, or into very soluble dextrins. In fact both the albumin and the dextrin in beer must be finely enough dispersed to remain clear in solution. Many factors in the brewing process may tend to coagulate the albumin. The influence of solid sur-

faces is seen by changing the inner lining of the fermenting vessel. A certain wort, which showed 0.2450 per cent. of albumin when fermented in a glass or enameled vessel, showed only 0.1925 per cent. in a paraffin-lined vessel, and 0.1750 per cent. in one lined with pitch.

Old-fashioned brew-masters would never use any vessel unless it had first been treated with a decoction of malt kernels and nut leaves, or else with "fassgeläger" (barrel dregs) which acts like the so-called "bierstein," a deposit mainly of organic substances that forms on new surfaces, and prevents them from coagulating albumin.

Fluid surfaces also exercise an effect as may be seen from the fact that in the chemical analysis of beer, such substances as benzol, chloroform and benzin are used to coagulate and shake out the beer colloids.

Gas surfaces are also active. Their formation tends to coagulate the dissolved albumin, and this fact killed the so-called "vacuum fermentation process" designed to recover and use the carbon dioxide liberated on fermentation. Jarring due to transportation or passing railroad trains may have a deleterious effect. A slight trace of acid tends to stabilize the albumin, as do also the tannin and resin from the hops, the dextrins from the mash, and the inorganic colloids of calcium and magnesium. The excellent brewing qualities of the water of the River Trent (England) are in large measure due to the lime content of the water, and patents have been taken out for "Burtonizing" water by the addition of lime salts.

To secure the formation of a lasting foam and a desirable "body" (*Vollmündigkeit*), a proper balance

is necessary between dextrin and albumin. Where beer is served icy cold, the chilling produces cloudiness because of the aggregation or partial coagulation of the albumin. This was cleverly overcome by Wallerstein, who introduced into the beer a proteolytic enzyme (pepsin or papäin) which, by increasing the dispersion of the albumin, prevents clouding.

Isinglass and gelatin are largely used for fining beer and astringent wines. A solution of the fining agent is poured in through the bung and settles down through the cask as a gel which effectually entraps all turbidity-producing particles. The tannin present aids in coagulating the gelatin or isinglass.

Tanning

The skins or hides of animals consist of an organized colloidal jelly, formed of bundles of fine fibrils about one micron in diameter, bound together by cementing substance of similar chemical composition which is largely removed by liming and other treatment preceding the tannage proper. The principal protein of the hide is called collagen (*glue-former*) since from it gelatin and glue may be produced by heating with water. The old processes of bateing, drenching, puering, etc., tended to neutralize the lime and bring the collagen into a flaccid or unswollen condition; in addition, the bacterial enzymes digest off part of the remaining cementing and epidermal substances (elastin) and complete the emulsification of the fat. Synthetic mixtures consisting mainly of ammonium chloride and tryptic ferments (pancretin) are now largely used in place of the foul-smelling bacterial baths which often ate off the grain of the skin.

Much work remains to be done to trace out the action of tanning processes and chemicals on the three colloidal elements in pelt:

1. The primary colloidal particles of the proteins.
2. The secondary colloidal particles of the proteins.
3. The fibrils of collagen (which are about 1 μ in diameter) and other organized structures.

Tanners well know the diversity of effects that may be produced in the finished leather by varying the successive treatments before actual tanning begins; but we cannot reach a scientific understanding of the processes at work until we separate the influence of the several factors on each of the main colloidal elements above referred to.

In vegetable tannage, the prepared hide is placed in an acid tannin solution (tan liquor), whereupon the hide powerfully adsorbs tannin and combines with it to form leather. In alkaline solution both tannin and hide are negatively charged, and no tanning occurs; in fact, leather may be stripped of tannin by alkalis. It is still a moot question whether the combination is chemical or physical, but since the fixation follows an adsorption isotherm and is very variable in percentage, it may be justly termed a colloid combination which partakes of the nature of both, but is chiefly physical rather than chemical—if we use these terms in their established meanings. The positively charged hide and the negatively charged tannin mutually coagulate each other. Neutral gelatin, if practically free from electrolytes, does not precipitate pure tannin, but in acid solution it takes a positive charge and is tanned. The tanning process may be aided by giving the hide a suitable potential, positive in the case of vegetable tannage, negative with chrome.

To prevent the skin from being "case-hardened" by too rapid a deposition of tannin, which would make it act as an ultrafilter and prevent proper tannage of the interior layers, the tanning is usually commenced in very weak or spent liquors, and the skins are moved to baths of progressively increasing strength. Non-tannins seem to play the rôle of protectors to the tannins, and the general rule is that tanning liquors having the highest tanning/non-tannin ratio are the most astringent. The degree of dispersion thus appears to be an important factor; for if highly dispersed, tannin easily enters the tiny interspaces between the fibrils. The efficiency of certain synthetic tanning agents used preliminary to heavy vegetable tannage may be consequent to their protective action, or their ability to enlarge the interspaces by shrinking the fibrils, thus allowing the tannin to enter the hide more rapidly and speed the tannage. [See J. Alexander, J. Am. Leather Chem. Assn., Vol. 18, p. 400, 1923.]

The degree of dispersion of the tannin and the incidental impurities present also influence the intimacy with which the tannin is fixed by the hide. By extraction with organic solvents G. Powarnin (Collegium, 1923, 222–228) obtained the following results from a quebracho tanned leather which showed a cold water extract of 9.54 per cent. by the Koch-Procter method: water-soluble material removed upon Soxhlet extraction by acetone, 12.5 per cent.; by ethyl alcohol, 17.2 per cent.; by methyl alcohol, 22.2 per cent. His tabulated results indicate that for every different tanning material used, part combines chemically and part is adsorbed.

Chrome and alum are believed by H. R. Procter [First Report on Colloid Chemistry, etc., British Assoc. Adv. Science, 1917] to be fixed by the hide in the form of basic salts, so that initially the tannage is largely physical. J. A. Wilson, among others, thinks that a definite chemical combination occurs subsequently. The whole process, however, seems to be a hydrolytic splitting of the salts, accompanied by adsorption (or *sorption*, to use McBain's non-committal expression), of the insoluble basic metallic salt by the hide fiber. The increasing stability of alum-tanned leather upon aging would, then, be due to colloidal syneresis.

Fat tannage, which yields chamois, buckskin, washleather, and the like, is effected by introducing oxidizable oils, usually in the form of a colloidal emulsion, into the skin. The view that fat tannage is due to aldehydes, developed by oxidization of the glycerin in the fats used, seems negatived by the fact that free fatty acids themselves may serve as tanning agents. Apparently the colloidal fat and the hide, being oppositely charged, form an adsorption compound Knapp made a fair grade of leather by simply soaking a flaccid skin in an alcoholic solution of stearic acid.

Paper

The first paper maker was the hornet or wasp, who, by chewing up wood in the presence of his colloidal salivary secretion, imitated on a small scale the action of the "colloid mill." There is no doubt that the prolonged and thorough grinding that paper stock gets in the beater, besides bringing much of it to a swollen or gel-like state, reduces part at least to a

colloidal condition. This colloidal cellulose evidently exerts a powerful cementing action, far above what would be indicated by the small percentage present by weight, resembling in this respect the "ultra-clay" which exerts so great an effect in soils. The formation of a coherent web on the Fourdriner wires thus depends on the greatly extended free surface of the "stuff" or paper stock, and perhaps the addition of a little colloidal cellulose will materially shorten the time in the beater. "Glassine" papers are produced by excessive beating.

In *engine sizing* a colloidal emulsion of rosin in rosin soap is generally added to the beater pulp, and, after being thoroughly mixed in, is precipitated by adding alum or aluminium sulphate. The colloidal rosin and the alumina gel help bind the paper fibers together and to make the paper stronger and resistant to water. Many substitutes for rosin have been used (silicate of soda, glue, and so on) which are added in colloidal solution and subsequently precipitated. To prevent the glue from being largely lost in the back waters, some highly adsorbent filler such as talc or clay must be added to the pulp to adsorb and hold the glue.

Tub sizing of paper involves passing the finished web through a bath of some such colloidal solution as gelatin, glue, starch, and the like, which, on drying, fills the pores and prevents ink from spreading or "bleeding," besides adding to the finish, strength and "handle" of the paper. The nice, crisp crackle of new banknotes and of stocks and bonds is due to a bath of alum and glue.

Bibulous papers, such as *blotting paper and filter paper*, are made without sizing, reliance being placed

for their strength on the binding properties of the colloidal cellulose. Recently rubber latex has been tried as a paper size.

The speed and the degree of drying paper are also factors materially affecting its strength.

Colloidal clays have found several uses in the paper industry. They tend to improve the luster of friction coated papers. Asphalts or tars may be emulsified with water by their aid, and incorporated with the paper pulp in the beater, thus serving both to size and to waterproof the paper. In using resinous woods, the resin often accumulates into small masses or "balls" which stick on the Fourdrinier wire, and cause holes, tears and shut-downs. The addition of colloidal clay to the beater converts the resin into a non-coherent emulsion by coating over the resin particles, and thus eliminates the damage. Old newspapers and magazines may be de-inked by beating and macerating them with a little alkali and colloidal clay, which adsorbs the loosened ink so that the two may be washed away through a special screen. It is estimated that a ton of good standard newspaper can be produced from a ton and a quarter of old newspapers, and by gathering the waste in big cities alone there would be possible an annual saving equal to the cut on 275,000 acres of thickly wooded spruce forest. (Forest Products Laboratory, Madison, Wis.)

Rubber

The milky juice (*latex*) of several kinds of plants yields on coagulation the colloidal gel called rubber. The latices are emulsions containing rubber and resin, stabilized by protective colloids (proteins or peptones)

and the kind of coagulant used depends on the nature of the protector. Thus formaldehyde preserves latices whose protectors are proteins, but coagulates *Kickexia* latex by precipitating the protective peptones.

Vulcanization consists in the combination of sulphur with rubber. The sulphur is at first adsorbed, and upon heating enters into a very close combination with the rubber, which is generally believed to be a true chemical combination.

Fillers increase considerably the strength and wearing power of rubber (in automobile tires, for example) by greatly extending the free internal surface. The rôle of fillers in rubber is similar to what it is in putty, and is therefore intimately bound up with their degree of dispersion. Carbon black, zinc oxide and magnesia are valued in the order given, which represents the relative order of fineness of their particles. An especially fine zinc oxide has recently been produced which is said to give the tread of automobile tires twice the life of those made with ordinary zinc oxide.

Patents have been taken out for incorporating colloidal precipitates in rubber, and even glue jelly is worked into tires to improve their wear by increasing the interior free surface.

Rubber latex is now being largely imported and used for directly impregnating fabrics which are then vulcanized, and also for adding to paper pulp in the beater. Tough, waterproof paper may be thus made.

Wm. B. Pratt has recently patented a process for dispersing commercial rubber (coagulated latex) in water (Italian Pat. 225,949, Dec. 12, 1923). Believing that the original globules in latex maintain

their identity after coagulation and even after vulcanization, he incorporated protective colloids (soaps, glue) with the rubber, or formed them *in situ*, and then gradually worked in water. The rubber may first be swollen with benzol to open it up. As the coagulation of rubber was thought to be irreversible, this is practically unscrambling an egg. (See J. B. Tuttle, India Rubber World, Jan. 1924; Chem. Met. Eng., March 10, 1924.)

CHAPTER XII

PRACTICAL APPLICATIONS (Continued)

FOODS AND THEIR PREPARATION

It is a serious error to judge foods on the basis of a bald chemical or calorific analysis. Fat, protein, carbohydrate and calories alone are not fair criteria of food value; the physical condition of the food and the presence of certain "impurities" now recognized as essential (for example, vitamines) largely affect the usefulness of a food to the organism. The experience of centuries has taught us the value of cooking which hydrolyzes, swells up, or softens many foods and usually destroys the species-specificity of proteins. The Chinese sprout many grains before cooking them. "Light" bread or cake has been leavened by yeast or baking powder until it presents an enormous surface to the digestive juices; as we learn from the Bible, unleavened bread was eaten only in times of stress. Egg-albumen, when cooked, is more slowly absorbed and its coagulum is reduced to its constituent amino-acids which are absorbed as such. Therefore, some persons who have an idiosyncrasy against raw eggs (possibly because of a permeable or ulcerated stomach wall) can eat cooked eggs.

The meats yielded by young animals are more juicy and tender than those obtained from older animals, because the latter consist of tissues which age has hardened by syneresis and dehydration. In cooking meats, the exterior is seared to retain the juices (e.g. pot roast); but in cooking soup it is simmered to extract them. Many foods are highly emulsified (mayonnaise, for example), and this permits their more

ready assimilation. Cream is a natural emulsion of fat in water and *wets* blotting paper; butter is an emulsion of water in fat and *greases* paper. The presence of protective colloids in foods containing milk (ice creams, Bavarian creams and the like) is an aid to their digestibility.

The ancient art of cooking, however, involves psychological factors besides mere digestibility and ease of assimilation; taste, flavor, odor and variety are important.

From time immemorial many colloid chemical principles have been utilized in the kitchen; e.g., the making of Hollandaise sauce, mayonnaise, clarifying coffee by adding egg shells containing some adherent albumen, salting water to "set" eggs in poaching. Agar, an indigestible carbohydrate, forms a hydrous residue stimulating to the intestines.

Oysters, scallops ,etc., are often allowed to "drink" fresh or brackish water, which removes repressing salts and permits swelling or plumping. In making "cream of tomato," it is usual to add some baking soda (bicarbonate)to prevent the acid fruit from coagulating the milk.

Baking

In China, 2000 B. C., the art of baking bread was already an ancient one, and probably developed from the observation that fermentation of the dough by wild yeasts improved the bread. Bread involves a rather complicated colloidal system consisting of starch, gluten, salts, yeast enzymes, and often fat and milk. That the system must contain stabilizing factors is indicated by the fact that almost anyone, working by rule-of-thumb methods, can produce a fair loaf.

Although the temperature of a bread oven usually runs between 200 deg. and 240 deg. C., the interior of the loaf seldom goes over 95 deg. C. Wheat starch is completely gelatinized at 65 deg. C. if sufficient water be present; but as the average dough holds only about 40 per cent. of water, a large part of which is taken up by the gluten, the baked loaf is full of starch granules that have been only partially swollen and gelatinized. According to R. Whymper ("The Conditions That Govern Staleness in Bread," Maclaren & Sons, Ltd., 1919), the gluten acts as a colloidal protector to the starch, maintaining its dispersion and water-holding capacity.

The *velocity* with which a loaf of bread is baked is a more important factor than is generally realized, for there must be a nice coordination between the time and thickness of "crusting" and the speed of "rise" of the loaf, if a satisfactory product is to be had. With too quick an oven, "skinning" is so rapid and tough that the loaf cannot rise properly and is "heavy." With too "slow" an oven, the skin or crust is too weak and the loaf "splits," or overflows. The same applies to baking cakes.

The gluten of wheat flour and like grains is itself a colloidal complex and of variable composition, containing glutenin, gliadin, globulin, albumin and so on in different proportions. The baking properties of flour, that is, its ability to hold water and the leavening bubbles of carbonic acid gas evolved by the yeast, depend mainly on the physical condition of its gluten. This in turn depends on the relative ratio of the several colloids, and especially on the presence of salts which materially affect their solubility and their protective

relation to each other, as is evident from the following:

Gliadin forms an opalescent colloidal solution in distilled water, from which it is precipitated by sodium chloride.

Glutenin is insoluble in water or saline solutions. It dissolves in dilute acids (or alkalis), and is thrown out again upon neutralization.

Globulin and albumin are soluble in sodium chloride solutions.

The various gluten fractions can hardly be said to be definite chemical individuals, and their purification, followed by an investigation of their mutual influence on each other, and also the influence of salts, constitutes a fruitful field for research. It is probable that we shall find here an instance of cumulative protection, where, for example, the protective action of the gliadin on the glutenin is enhanced by the protective action of the globulin and albumin on the gliadin. Salts, by changing the degree of dispersion or solubility of the several fractions, must shift the equilibrium of the complex system. So also does the slight acidity developed by the yeast. Thus, Weyl and Bischoff (Jago, "The Technology of Bread-making") found that flour moistened with a 15 per cent. solution of sodium chloride yielded a dough deficient in tenacity. Flour heated for several hours at 60 deg. C. will not make a dough, probably because one (perhaps more) of its colloids has lost so much water that the constituent particles have approached too close to be separated by water alone. This is similar to the action of gelatin, which loses its solubility upon being heated at 110 deg. C. or above.

The best results with flours are obtained by using water containing small amounts of sodium chloride. Salt, used from time immemorial, besides adding to palatability, enables the gluten to absorb and hold water, an effect shared by chlorides generally. Hard waters, containing sulphates or the like, harden the gluten; whereas, soft alkaline waters disintegrate it and destroy its elasticity. Even distilled water yields a sticky dough.

The importance of water in bread-making is obviously on a par with its importance in brewing, and in both cases the mineral impurities affect the yeast. Alum, calcium sulphate and even sulphate of copper have been used to improve gluten, especially in spoiled flours. Potassium bromate, recently introduced as a "yeast food," also registers its effect on the colloidal condition of the gluten.

While the carbon dioxide formed by the yeast is initially liberated in nearly colloidal dispersion, it soon forms visible bubbles, which, however, must be kept in fine dispersion by the elastic gluten if a loaf of good texture is expected. The addition of a little fat to the dough and the use of, say, half milk and half water, both serve not only to improve the texture of the loaf, but to add materially to its keeping properties. Whymper attributes the keeping properties of the home-made farm loaf to the protective action of fats on the starch—that is, fat tends to prevent *staling* of bread. The casein and salts of the milk also affect the gluten, and the milk fat or other added fat, by going into emulsion, tends to coat over the dough particles and prevent desiccation. Such action of the fat results in *shortening*, the resulting bread, cake or biscuit being flakier and more brittle.

Milk

From a colloid chemical standpoint, the main constituents of milk may be classified as follows:

In crystalloid dispersion:
Salts (e.g., NaCl).
Sugar (lactose).

In colloidal dispersion:
Casein, an unstable or irreversible colloid.
Lactalbumin, a stable, reversible, protective colloid.

In suspension or emulsion: Milk fat.*

Most formulas and recipes for modifying cows' milk for infant feeding and almost all analyses of milk combine the percentages of casein and lactalbumin under the collective title of "total proteids" (in modern form, "total protein"; globulin is also included), thereby obscuring the highly important fact that the lactalbumin stabilizes and protects the casein from coagulation by acid and rennin.

The subjoined table, giving average compositions in per cent., shows how natural milks are influenced by variations in the casein/lactalbumin ratio:

Kind of milk.	Casein.	Lact-al-bumin.	Pro-tective Ratio.	Fat.	Behavior with acid and rennin.
Cow.....	3.02	0.53	0.14	3.64	Readily coagulated into large curds.
Woman .	1.03	1.26	1.13	3.78	Not readily coagulated; forms small curds.
Ass.....	0.67	1.55	2.31	1.64	

It is a striking fact that in the above table the milks are arranged in order of their digestibility by infants,

* It is probable that of some the milk fat is in colloidal dispersion.

which corresponds with their relative degree of colloidal protection. Thus, A. Jacobi ["The Intestinal Diseases of Infancy and Early Childhood," N. Y., 1889] stated that asses' milk has been recognized as a refuge in digestive disorders in which neither mothers' milk nor cows' milk nor mixtures were tolerated.

The addition of protective colloids to cows' milk stabilizes it and makes it behave like mothers' milk, when treated with acid or rennin. In modifying cows' milk for infant feeding, the usual dilution, followed by an adjustment of the fat and lactose ratios, is, of course, necessary. If enough protective colloid be added, coagulation of casein in the stomach may be entirely prevented, or, at least, the coagula kept in a very fine state of subdivision.

Besides stabilizing the casein, protective colloids have a very important effect on the milk fat, on which they exercise an emulsifying and emulsostatic influence. Indirectly their stabilization of the casein is of much greater importance, because insufficiently protected casein in curding, entraps mechanically most of the milk fat, making a fatty, greasy curd which tends to repel the acid gastric juice and pass undissolved or only partially dissolved into the intestine, where its putrefaction causes trouble.

It is probable that the relative percentage of lactalbumin decreases with the period of lactation, so that the milk of a herd is in this respect more uniform than the milk of a single cow. With nervous women, nervous shock probably decreases the amount of albumin secreted, and this would register itself in a digestive upset in the nursling. The protective ratio of any particular mother's milk is an important factor in its usefulness to the infant.

Although their action was not perfectly understood, the most diverse kinds of protective colloids have for years been used in the modification of cows' milk for infants. For over thirty years Jacobi advocated the use of gelatin and gum arabic, and the use of cereal gruels and dextrinized starch is familiar to all. Beer, seaweed (Irish moss) and lichens (Iceland moss) are among the protective colloids used in other lands, and in England especially, sodium citrate is much used, This protective salt, when going into solution, exhibits in the ultramicroscope actively moving ultramicrons, a fact indicative of its colloidal condition.

The action of protective colloids is beautifully illustrated in the ultramicroscope, which enables us to see, in very highly diluted milk, the individual colloidal particles of casein in active motion, and to watch the course of their coagulation by acid or rennin. The casein ultramicrons of cows' milk first form groups of two or three, whose motion is somewhat hampered, and they continue to aggregate into larger and still larger groups whose motion decreases as their size increases, until they finally sink out of solution in coagulated masses. If, however, some gelatin or gum arabic solution be added to the diluted milk before the addition of the acid or rennin, the casein particles continue their active "dance" and do not coagulate. In this connection it is interesting to note that the casein particles of mothers' milk appear to be much smaller than those of cows' milk, probably because of the more highly protective medium in which they are formed and exist. [See J. Alexander, Kolloid-Zeit. 1909, 1910; J. Am. Chem. Soc. 1910, 28, 280; Alexander and Bullowa, Arch. Pediat. 1910; J. Am. Med. Assoc. 1910.]

Since E. Zunz showed that certain albumoses exerted a coagulative rather than a protective action, J. Alexander digested lactalbumin with rennin or rennet, and found that the resulting digestion products no longer acted as protectors in forming and stabilizing colloidal precipitates (for example, AgCl), but actually tended to act as coagulators. He therefore advanced the following simple colloid-chemical explanation of the rennin coagulation of milk [8th Int. Cong. Appl. Chem. 6, 12–14 (1912)]: (1) The enzyme rennin digests the lactalbumin, thereby destroying its protective action; (2) the resulting albumoses are probably coagulators; (3) calcium salts liberated from their adsorption by the lactalbumin and the like also aid in the coagulation.

When cream, or milk, heated to 50 to 60 deg. C. is forced through tiny orifices under great pressures (the pressures used are 200 atmospheres and more, and the fluid is usually spattered against an agate plate), the fat globules are much more finely dispersed, being reduced to about one hundredth their former diameter. As a consequence of the enormous increase in the free or specific surface of the system, the viscosity of such *homogenized milk* is greatly increased. The finely divided fat adsorbs so much lactalbumin (Wiegner estimates that it adsorbs about 25 per cent., as against about 2 percent. in ordinary milk), and is so highly stabilized thereby, that homogenized milk will not yield butter on churning, nor does homogenized cream churn or whip. On the other hand, because of its viscosity, homogenized cream with 17 per cent. butter fat will make as well-bodied an ice cream as an ordinary 25 per cent. cream. In fact cream is now largely kept in cold

storage in the form of sweet butter, which is homogenized with sweet milk in the busy season, yielding cream again.

In *whipped cream* coagulation of the lactalbumin may be a factor too, and with Charlotte Russe and Bavarian creams gelatin is added.

Artificial milks are made by emulsifying vegetable fats or oils with protective colloids or with skim milk. Most of them are deficient in fat-soluble vitamine A.

Ice Cream

One of the essentials in ice cream is that when it is served it shall have a smooth, mellow, velvety texture, and it is a fact amply proved by the experience of practical ice cream manufacturers and housewives, and backed by the authority of even very old cook books and recipes, that ice cream made without the addition of eggs, gelatin, or some similar protective colloid, is gritty, grainy, or sandy, or else soon becomes so on standing. The original standards for ice cream, promulgated under the Food and Drugs act, took no note of these facts, and fell when they were brought out in court during an attempt to justify this standard.

The added protective colloid tends to inhibit the crystallization of the water with the formation of sharp spicules of ice. Furthermore, it also stabilizes the casein, a matter of the highest importance; for as ice cream always contains considerably more fat than milk, the curds formed by unprotected casein would be particularly greasy and hard to digest.

A very misleading impression has been given by some food officials referring to gelatin in ice cream as a "filler," which naturally leads to the idea that it is

an inferior ingredient added in quantity to cheapen the product. But as gelatin is expensive and as only about 0.5 per cent. is used, such a view is erroneous. The food value of gelatin as a protector of the body's nitrogen being generally admitted, and its effect being very beneficial from a digestive point of view, its use in ice cream is necessary, legitimate and scientific.

Confectionery

Originally "gum drops" were made with gum arabic as a protective colloid to prevent the crystallization of the sugar and give the candy a smooth agreeable body. For cheaper grades glucose and soluble starches are now used; for, although the soluble starch is not a powerful protector, it is inexpensive, considerable can be used, and commercial glucose has but slight tendency to crystallize as about half of its dry weight consists of a highly dispersed and protective dextrin. Glucose containing too much dextrose crystallizes on standing.

"Marshmallows" are usually made with gelatin as the emulsifying, body-forming, protective colloid, but albumen and gum are also used.

In molding candies a super-dried starch is used containing only a few per cent. of moisture. Its powerful attraction for moisture tends to keep the candy in shape. Our ordinary fruit jellies and jams contain protective colloids such as pectin, which not only give body, but usually prevent the crystallization of the large quantity of sugar present.

Gelatin and Glue

When bones, hide, or skins are heated with water, especially after a preliminary treatment in lime water

followed by thorough washing, there is formed a solution that gelatinizes when cold. If the raw material is carefully selected and treated, it yields when dried a light colored transparent gelatin; if made without the precautions that should surround a food product, the result is glue.

Since the gelatins from different sources vary considerably in the percentages of amino-acids they yield on hydrolysis, it seems obvious that gelatin is not a definite chemical entity, but is rather an adsorption complex whose structure is at least duplex and is probably even more complicated. The various constituents of the gelatin bear a cumulative protective relation to each other (see p. 62).

Gelatin exhibits its minimum degree of swelling at its iso-electric point, about pH 4.7, and a maximum of swelling at about pH 3, after which more acid causes contraction again. J. Loeb has explained this and many other phenomena exhibited by gelatin on the basis of the Donnan theory of membrane equilibrium, assuming that the gelatin forms salts having a non-diffusible ion (see "Proteins and the Theory of Colloidal Behavior," 1922). The facts are just as well explainable on the basis of a kinetically balanced adsorption, and in view of the variable composition of gelatin, it seems idle to speak of definite salts like "gelatin chloride" or "sodium gelatinate." The presence of small amounts of adsorbed impurities, tenaciously held, exercises a marked effect. For this reason the so-called "water absorption test" for gelatin and glue is uncertain.

Generally speaking, the binding strength of a gelatin or glue is measured by its relative jelly strength

and the viscosity shown by its solution; but the variations in these two factors do not always parallel each other. Heating causes a breakdown of the gelatin into smaller complexes; this lowers viscosity, jelly strength, and binding power, indicative of a drop from the zone of optimum colloidality. On the other hand, as glue solutions cool and the colloid begins to form large aggregates, the adhesiveness also falls off (see p. 17). In choosing a glue or a gelatin for any specific purpose, *all* of its qualities and attributes must be taken into consideration, for foam, grease, color, odor, etc., may be of crucial importance (for further details see Am. Chem. Soc. Monograph "Glue and Gelatin," by J. Alexander).

CHAPTER XIII

PRACTICAL APPLICATIONS (Continued)

GLASSES

While glasses consist of mixtures of silicates containing dissolved or finely dispersed impurities or additions, and while individual silicates may be isolated from glass, the constitution of the glass as a whole is not quite so simple as might be assumed from paper formulas. For it is the physical properties of glass that are the most important, and while these naturally change as the ingredients vary in kind and proportion, still the properties of parts of one and the same batch may differ widely if they are subjected to different heat treatment. Thus *Prince Rupert drops*, made by dropping part of a fluid batch of opal glass into water so that the surface was quickly chilled from 1200 deg. C. down to 20 deg. C., were clear at the exterior, becoming progressively more opalescent toward the center. Slowly cooled drops of the same batch were quite opaque throughout.

The composition of glass is so chosen that the several silicates mutually interfere with each other's crystallization (*cumulative protection*), the result being a colloidal mass in which the tendency toward crystallization may register itself by *devitrification*, a formation of relatively large crystals which render the glass turbid and injure its usual working properties. While many silicates may be cooled quite slowly without crystallizing, the silicates of calcium, magnesium, and aluminum form crystals if not quickly chilled, which is rather difficult to do because silicates in general have high thermal capacity but low radiating capacity.

Tammann (Zeit. Elektrochem. 1904, 10, 502) has pointed out three main factors controlling the behavior of supercooled melts: (1) The specific crystallization capacity (measured by the number of crystallization centers formed in per unit mass per unit time); (2) the speed of crystallization; (3) the variation in viscosity. To these must be added a fourth; mutual or cumulative protection.

Every substance in forming macroscopic crystals must of necessity pass through the colloidal zone, in which surface forces (adsorption, surface tension) exercise a controlling, if transient, influence that may be made permanent if sudden cooling increases the viscosity sufficiently. The adsorption of the various silicates by each other as they reach colloidal dimensions introduces a time-lag which becomes cumulative as the several silicates protect each other, and greater as the viscosity increases. Batches of glass are so mixed as to make this time-lag ample to prevent crystallization at the temperatures and during the times of melting, casting, molding and so on. When glass is cooled from the plastic to the rigid state, as in blowing, drawing, casting, etc., and especially when optical glass is being slowly cooled in melting pots, devitrification may occur through the separation of spherulites or minute crystals finely dispersed throughout the glass. The spherulitic form is usually indicative of crystallization in the presence of a colloid, and the fact that the crystals are by microscopic examination usually found to be tridymite and crystobalite points to the probability that some of the silica dissolves colloidally in the molten silicates. Sulphates, chlorides, an excess of arsenic, and sometimes

fluorine, facilitate devitrification, thus exercising a "salting-out" action.

Practically all transparent colored glasses owe their color to the presence of colloidally dispersed substances, usually metals or their oxides. The gold ruby glasses were carefully investigated by Zsigmondy ["Colloids and the Ultramicroscope" (trans. by J. Alexander), J. Wiley & Sons Co.]. When gold is added to a batch of glass (usually 0.03 to 0.01 per cent. of gold chloride), the melt is colorless and may even remain so on slow cooling unless the batch is regulated to prevent this. All batches, however, if quickly chilled, are colorless and optically clear in the ultramicroscope. The color is developed by reheating the colorless glass to the softening point, whereby the dissolved or crystalloidally dispersed gold begins to separate out upon nuclei ("crystallogens") already formed in the colorless glass.

If the composition and heat treatment of the batch has been such as to yield a large number of small nuclei, the color developed is a bright ruby red; for although each of these amicroscopic particles grows to colloidal dimensions, the available gold is used up before any of them become big enough to render the glass turbid. On the other hand, if a small number of larger nuclei be present in the colorless ruby glass, development leads to a dirty blue or turbid maroon shade because the dissolved gold is deposited in fewer and larger masses.

The subjoined table shows the results of Zsigmondy's ultramicroscopic examination of good and of spoiled ruby glass. Both specimens had been cooled slowly and reheated more rapidly until one

began to melt (hot end) while the other end remained cold (cold end). The fact that the average distance between ultramicrons remained constant in all parts of the specimens proves that reheating formed no new nuclei.

Hot End	Good Ruby Glass	Spoiled Ruby Glass
a	Color intense red. Numerous green ultramicrons, very close together, their brightness diminishing. ↓	Color blue. Ultramicrons fewer, copper-red, further apart.
b		
b′		Color violet. Ultramicrons yellow.
c	Homogeneous green light cone.	Color bright red. Ultramicrons green.
d	Colorless and homogeneous.	Colorless. Few faint specks visible.
Cold End		

Color Red Decreasing ↓↓

Color Decreases ↓

H. F. Bellamy's results (J. Am. Ceramic Soc. 1920) show that the stannic oxide used in gold ruby glass acts as a protector to the gold, keeping the color true and deepening it so that less gold can be used. This recalls the work of Zsigmondy, who, by mixing the hydrosols of gold and stannic acid, synthesized the purple of Cassius (an ammonia-soluble deep red precipitate obtained by mixing solutions of auric chloride and stannous chloride), which Berzelius had regarded as a chemical combination of the tin sesquioxide with purplish oxide of gold.

Most "red" glasses (danger signal lights) are made of selenium glass, which is pale yellow when molten and acquires the ruby tint only on proper heat treatment. If the selenium particles aggregate too

much, the glass becomes an opaque maroon, and finally a muddy orange.

Metals and Alloys

Coarsely crystalline metals are brittle, because they tend to split along the lines of crystal cleavage, and therefore the metallurgist usually aims to produce a fine-grained structure. Among the physical methods used to achieve this end are chilling and rolling, while the chemical methods involve the removal of undesirable constituents (as in the conversion of pig iron into steel), and the addition of desirable constituents (carbon in case hardening, various metals in alloy steels). Thus Pütz found that the predominant effect of vanadium in steel is to decrease the size of the ferrite grains, and make the pearlitic structure fine-grained and homogeneous, yielding a harder steel.

The chief cause of fine-grained structure seems to be the inhibition of crystallization by substances colloidally dispersed in the metal. These may be other metals, such as vanadium, molybdenum, chromium, nickel or tungsten (or their compounds) in alloy steels, compounds such as Fe_3C in ordinary steel, or even the metal itself in the case of pure metals. The last-mentioned phenomenon is consequent on *iso-colloidism* (a colloidal dispersion of the metal in itself as dispersing phase), which may lead to *auto-protection*, the colloidal phase tending to interfere with the crystallization of the rest. Several organic compounds exhibit a similar phenomenon, yielding amorphous gels which gradually become visibly crystalline (see p. 61). It must be remembered that size alone is the criterion of the colloidal condition. As Scherrer has shown with

the X-ray spectrometer, the ultramicrons and even the amicrons in colloidal gold hydrosols consist of tiny crystalline groups; colloidal silicic and stannic acids showed both crystalline and random or haphazard molecular clusters, while gelatin was entirely amorphous.

These experiments give us an inkling as to what occurs during the "heat treatment" and tempering of metals, and it is to be hoped that some technique may be devised that will give us even a clearer insight than does "etching" into the changes that occur in metals in metallurgical operations (heat treatment), use, age, and even "disease" of tin for example.

With metals the crystallization forces are so powerful and act so rapidly, that a coarsely crystalline structure usually results on ordinary slow cooling. To preserve the fine colloidal structure, even in the presence of protectors, drastic chilling or quenching is often necessary.

The Time Factor

A fact of general importance in nature, having especial application to the phenomena met with in metals and alloys, is that many transformations occur so rapidly as to elude our observation, and compel us to draw upon our imagination to follow what happens between the initial point and the end-point.* By photographs taken thousandths of a second apart,

* T. W. Richards [*Am. Chem. J.*, *26*, 61 (1901)] followed microscopically by instantaneous photography, the separation of crystals from solutions, and reported that the initial growth is much more rapid than subsequent growth. V. Henri applied the "moving picture" camera (cinematograph) to the ultramicroscope, and E. O. Kraemer, National Research Fellow at the University of Wisconsin, is making remarkable films of ultramicroscopic happenings.

Rayleigh showed the curious differences that occur when various liquids are dropped into water.

Iron and Steel

When treated with dilute acid, drastically quenched tool steel does not separate out carbide of iron, but yields instead a complicated mixture of hydrocarbons. This shows that the Fe_3C is in such a fine state of subdivision that upon its decomposition the nascent hydrogen and carbon are within the range of molecular attraction which is of the order of 50 millimicrons; and the Fe_3C is in colloidal state.

Such drastically quenched steel owes its great hardness to its enormous free or specific surface, but it is too brittle to be of practical use, and must therefore have its hardness drawn or reduced. This *tempering process*, as it is called, consists in reheating the steel and keeping it at certain temperatures for various times. As soon as the temperature of the steel permits, the aggregation of the Fe_3C (or cementite, as it is known), which was suspended by the previous chilling, begins anew. Metallurgists recognize the following forms of the iron-iron carbide dispersion:

Iron-Cementite Dispersions.		Nature of Dispersion.	Crystal Structures.
Austenite	Increasing order of size.	"Solid solution"?	Structureless streaks.
Hardenite		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 microscopically resolvable.
Pearlite		Coagulum	Laminated; may segregate into balls.

Hardenite is named from its intense hardness; pearlite from its pearly luster; the rest are named after the metallurgists Roberts-Austen, Martens, Troost and Sorby, respectively.

The Fe_3C in austenite is partly, if not entirely colloidal. Hardenite and martensite represent the hardest dispersions, while troostite, sorbite and pearlite represent a decreasing order of hardness. We have here a typical instance of a zone of maximum colloidality, such as is also met with in the alloy duralumin. (See J. Alexander, J. Am. Chem. Soc. 43, 434 [1921]; Mercia, Waltenberg and Scott, Bull. 150, Bureau of Standards, 1919; Jeffries and Archer [Chem. Met. Eng. 24, 1057, 1921] call it a "critical dispersion.") Mercia and Jeffries and Archer ascribe the hardening of duralumin to the precipitation of colloidal $CuAl_2$, whereas the British National Physical Laboratory believe that Mg_2Si is responsible. Probably both compounds are involved, and we may have here another instance of *cumulative protection*, where a protector is itself protected.

Jeffries and Archer* believe that this phenomenon in steel, an analogue of which occurs in the alloy duralumin, is due to the fact that the hard particles of the dispersed phase act as *keys*, preventing any motion along the cleavage or slip planes as a whole. While this mechanical comparison may appeal to engineers, the action of surface forces, together with the fineness of crystal grain which minimizes the length of the slip planes, is quite sufficient to account for the phenomena observed.

The enormous power of these surface forces is shown by the results of some experiments privately communicated to me by P. Scherrer of Zurich. He coagulated unprotected gold sols with electrolytes, and by X-ray examination found that the tiny ultramicrons (which were about 2 $m\mu$ in diameter and

* *Chem. Met. Eng.*, *24*, 1065 (1922).

showed a crystalline gold space lattice) practically fused together into homogeneous crystals of larger size. Even soft substances, if finely dispersed, will produce great increase in hardness. Thus a few per cent. of oil added to whiting makes a firm putty when ground in with it. And S. U. Pickering * made an extremely stiff mass by emulsifying 99 per cent. of petroleum oil in 1 per cent. of soap water.

The size, shape, initial heating and chilling of the piece of steel, as well as the speed, temperature and time of its reheating or tempering and speed of its second chilling, are all factors controlling the nature of the final dispersion, which is also largely influenced by the chemical composition of steel itself (percentage of the Fe_3C, presence of other metals and of impurities).

As a consequence, the proper tempering of steel requires much experience in the practical control of conditions, otherwise the optimum point is either passed or not reached; and for most uses the optimum dispersion of the cementite lies within or just beyond the colloidal zone. The addition of manganese (m. p. 1225 deg. C.) to steel retards the aggregation of the cementite to such a degree that ordinary slow cooling yields martensite. Steels containing tungsten and other metals of high melting point are known as "high speed" steels because lathe tools made with this highly protected steel maintain their hardness even though brought to a low redness by the high speed of the lathe. Under such circumstances ordinary tool steel at once loses its temper, but the high speed steels are "self-tempering."

The behavior of the iron-carbon alloys is greatly influenced by the allotropic changes of iron.

* *J. Chem. Soc.*, *91*, 2002 (1902).

After "freezing" at about 1505 deg. C., pure iron shows upon further cooling a large evolution of heat at about 900 deg. C. known as thermal arrest point (Ar_3), and a smaller evolution of heat at about 780 deg. (Ar_2). Above 900 deg. the iron exists in the non-magnetic or gamma form,* and below 780 deg. in the magnetic or alpha form, which exhibits a different crystallization from gamma iron. Between these temperatures, Rosenhain believes that the iron exists in a third allotropic form, known as beta iron, which has the crystal form of alpha iron but is non-magnetic like gamma iron. Benedicks, on the other hand, believes that the evolution of heat at 780 deg. does not indicate the change of a beta allotrope into gamma iron, but represents the final disappearance of persistent gamma iron molecular groups from the metal.

These apparently conflicting views can be reconciled by regarding the iron between 900 deg. and 780 deg. C. as an *allocolloid* or *allodispersoid*, the so-called "beta" iron being an alpha-gamma adsorption compound (alpha iron dispersed in gamma iron), whose breaking up into the more completely orientated alpha iron sets free the relatively smaller amount of heat at the point Ar_2. This view accounts for the following facts: (1) Beta iron has the same crystal form as its "predominant partner," alpha iron, but is not magnetic;† (2) gamma iron dissolves carbide, whereas

* A new form, delta iron, is claimed by Honda to exist at higher temperatures.

† Magnetism seems to depend not on chemical composition, but rather on a peculiar regular molecular orientation. The so-called "Hacussler alloys" are magnetic, although their individual constituents are not. According to A. W. Hull [Phys. Rev., 14, 540 (1919)], magnetism depends on the distance between atoms rather than their arrangement. Recently, the concept of "β iron" has been abandoned—see e.g. Colin J. Smithelle, "Impurities in Metals" (1928).

beta iron and alpha iron do not; whatever gamma iron exists in the beta zone is adsorbed by or in some loose kind of combination with the dominant alpha iron, and is not free to exert its solvent action on iron carbide; (3) the increase in strength when alpha iron is transformed into beta iron; as the temperature goes over 780 deg. C., some gamma iron forms, and the resulting alpha-gamma adsorption compound increases the total free surface and strength of the system; (4) the fine acicular structure of beta iron; this is indicative of crystallization in the presence of a colloid.

Steel

The preceding remarks apply to pure iron. With the introduction of carbon, we have to deal with the iron carbide Fe_3C (cementite), and the system is complicated accordingly, dislocating the thermal arrest points.

A *low-carbon steel* (containing, say, 0.2 per cent. of carbon which dissolves in the liquid iron as Fe_3C) when freezing down to 840 deg. C. consists of an apparently homogeneous solid solution or dispersion of cementite in gamma iron. At 840 deg. C. the alpha-gamma dispersion (beta iron) forms (Ar_3), and at 750 deg. C. the residual alpha-gamma adsorption compound decomposes into alpha iron (Ar_2). The steel now consists of alpha iron crystals dispersed in a "solid solution" of iron carbide in gamma iron. With further cooling the quantity of alpha iron crystals increases until at a little below 700 deg. C. the remaining gamma iron-cementite solid solution is transformed into a eutectoid mixture of alpha iron (ferrite) and iron carbide (cementite) with an evolution of heat (Ar_1).

This last transformation seems to be the breaking up of an adsorption compound between gamma iron and iron carbide, the former transforming into alpha iron and the latter being set free to form aggregations of its own. This adsorption compound carries over some of the gamma iron through the so-called "beta" zone to the eutectoid point, where, with increasing carbon content, increasing quantities of heat are evolved. The allotropic transformation of the iron becomes practically negligible when the steel contains above about 0.5 per cent. of carbon (which, however, means about 7.5 per cent. Fe_3C). Steel of eutectoid composition (about 0.9 per cent. Fe, equaling about 13.5 per cent. Fe_3C) exhibits only a single thermal arrest point, at which it glows visibly. This phenomenon, known as *recalescence*, indicates a sudden large release of energy consequent to the breakdown of the extensive metastable system gamma iron-cementite, whereby two delayed transformations occur simultaneously—the iron transforms from gamma into alpha iron (ferrite), and at the same time the released cementite aggregates. The inhibition of the allotropic iron transformation shows that in *eutectoid steel* the large percentage of Fe_3C has carried over practically all the gamma iron in metastable condition to the eutectoid point. The presence of such elements as silicon and manganese perceptibly changes the location of the eutectoid point, illustrative of the easy disturbance of colloidal systems by foreign substances.

The iron carbide (cementite) possesses considerable cohesion and attempts to aggregate against the resistance offered by the now highly viscous iron—an

ideal condition for the development of a colloidal system. The cohesive power of the cementite is so great, however, that in unquenched steels it usually

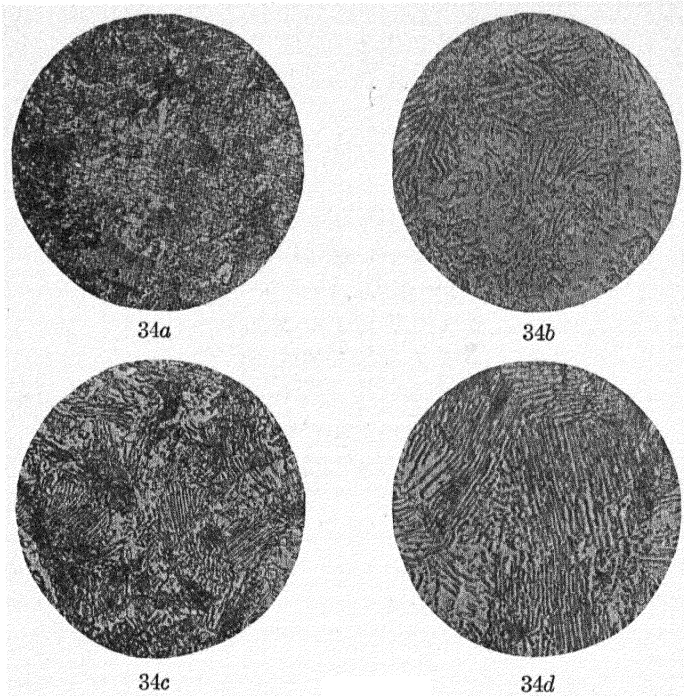


FIG. 2. MICROSTRUCTURE OF 0.85% C. STEEL, HEATED TO 800° AND COOLED AT DIFFERENT RATES. ETCHED IN 5% PICRIC ACID IN ALCOHOL.

Note how the lamellae constituting the pearlite become much thicker and more pronounced as the annealing progressed. The physical properties of the material also changed in corresponding manner.

(*a*) cooled in air—largely sorbite.

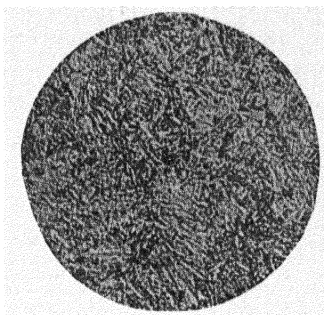
(*b*) cooled in lime—fine lamellar pearlite and some sorbite.

(*c*) cooled in furnace—coarse lamellar pearlite showing some spherodizing.

(*d*) cooled in furnace at much slower rate than (*c*); the pearlite is largely spherodized or "divorced."

(from U. S. Bureau of Standards, Circular 113 (1922))

appears interspersed with alpha iron (ferrite), as fine plates or fibrils, yielding the finely laminated structure known as pearlite because under proper illumination it exhibits the iridescence of mother of pearl. The iridescence is evidence of the fineness of the pearlitic structure, which, like the diatom Pleurosigma, taxes the highest powers of the microscope for its resolution, the lamellæ being often less than 0.2 micron apart.



43*b*

× 500

FIG. 3. VERY FINE MARTENSITE IN 0.46 CARBON STEEL, quenched in water after heating 15 minutes at 850° (1515° F.), just above the A_2 transformation. Etched with 2% alcoholic solution of nitric acid.

Microscopically, eutectoid steel (about 0.9 per cent. C.) when slowly cooled, consists entirely of pearlite, thus corresponding to the pure eutectic of ordinary alloys.* But with very slowly cooled steel, or with steel reheated for a long time at about 900 deg., the cementite tends to form balls or globules, the liberated ferrite at the same time forming larger crystals.

The following table shows the inter-relation of these phenomena:

* As the Greek-derived word indicates, a eutectic is the most easily fusible mixture of two metals or other substances.

CONDITION OF STEEL AT VARIOUS TEMPERATURES

PURE IRON	0.2 PER CENT. STEEL	0.9 PER CENT. STEEL
Gamma iron.....	Gamma iron-cementite solid solution.	This is eutectoid steel. So much cementite is present that no alpha-gamma adsorption is formed, the gamma iron being held in metastable condition by the cementite, down to Ar_1.
900 deg. C. (Ar_3) Gamma iron forms alpha-gamma adsorption compound (beta iron). Largest thermal point.	840 deg. C. (Ar_3) Alpha-gamma compound (beta iron) forms late because of cementite.	
Allocolloidal Zone.	750 deg. C. (Ar_2) Alpha-gamma compound (beta iron) changes to alpha iron.	
780 deg. C. (Ar_2) Alpha-gamma compound (beta iron) decomposes into alpha iron.	700 deg. C. (Ar_1) Gamma iron-cementite "adsorption" compound decomposes, gamma iron changes to alpha iron, and cementite is liberated and aggregates.	700 deg. C. ($Ar_{3,\ 2,\ 1}$) Sudden change of all the iron from gamma to alpha, with liberation of all the cementite.
Alpha iron.	Alpha iron and cementite.	Pearlite.

The following cooling curves taken from Prof. H. C. H. Carpenter [Engineering, 107, 341, 1919] show how with growing carbon content the three thermal arrest points are combined into one in eutectoid steel:

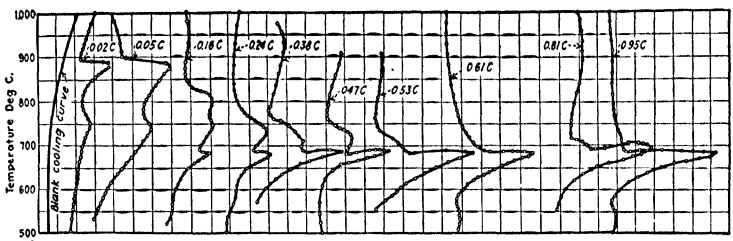


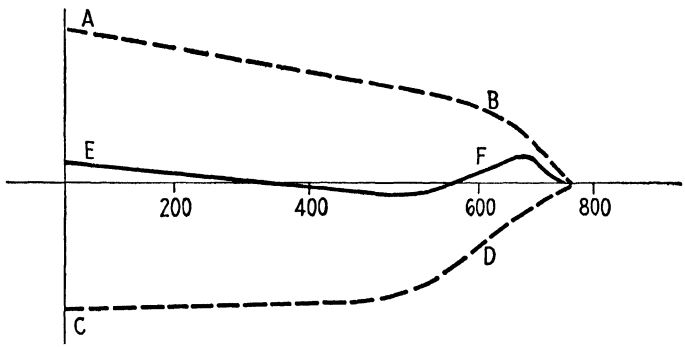
FIG. 4.—Changes in thermal arrest points of steels with increasing carbon content.

Stepped Transformation in Steels

The aggregation of cementite takes time and there is always a time lag in the process. Consequently when carbon steel is rapidly cooled, the A_1 transformation takes place at a lower temperature than when it is slowly cooled. This drop increases with the speed of chilling until it reaches about 600° C., when still more drastic chilling lowers it *discontinuously* to about 300° C. or less.

This *stepped A_1 transformation* as it is known, is beautifully explained by Kôtarô Honda who showed that it is due to the fact that in the inhibited zone the viscosity of the dispersion medium is sufficient to stop the aggregation of the cementite, but that below this zone the aggregation forces of the cementite become so powerful that they then overcome the resistance of the iron, notwithstanding the fact that its viscosity has likewise increased by cooling. The

following curve, taken from Honda's paper shows how two factors operating at various rates over a temperature range, may cause puzzling results, unless their effects can be separately analyzed.



AB = tendency curve; CD = resistance curve; EF = observed resultant.

FIG. 5.—Aggregation-viscosity curves, with resultant showing aggregation inhibited between about 600–300°.

AB is the transforming tendency or aggregating curve, plotted positively; EF is the resultant, which represents the extent to which the tendency is able to establish itself.

Standardized Heat Treatment Terms

A committee appointed by American steel treaters has recommended the following standardization of terms regarding the heat treatment of steel. The relation of many of these terms to what has been stated above is manifest.

1. *Annealing.* Heating above the "critical temperature" followed by a relatively slow rate of cooling.

2. *Loneal.* Heating below the "critical temperature" followed by any rate of cooling.

3. *Normalizing.* Heating above the "critical temperature" followed by an intermediate rate of cooling.

Note.—In good practice the heating is considerably above the "critical temperature."

4. *Spheroidizing.* A long-time heating at or about the "critical temperature" followed by slow cooling throughout the upper part of the cooling range.

Note.—For the purpose of spheroidizing the cementite in high-carbon steels.

5. *Hardening.* Heating above the "critical temperature" followed by a relatively rapid rate of cooling.

6. *Tempering.* Reheating, after hardening, to some temperature below the "critical temperature," followed by any rate of cooling.

7. *Carburizing.* Adding carbon with or without other hardening elements, such as nitrogen, to wrought iron or steel by heating the metal below its melting point in contact with carbonaceous material.

8. *Casehardening.* Carburizing the surface portion of an object and subsequently hardening by suitable heat-treatment.

9. *Cyaniding.* A specific application of carburizing where the object, or a portion of it, is heated and brought into contact with cyanide salt.

By the term "critical temperature" is meant that temperature which is customarily associated with the following phenomena:

(*a*) Hardening when quenched.

(*b*) Loss of magnetism.

(*c*) Absorption of heat.

(*d*) Formation of solid solution.

(*e*) Pronounced refinement of coarse grain upon cooling.

Tin-Lead Alloys

All mixtures of tin (m. p. 232 deg. C.) and lead (m. p. 327 deg. C.) melt below 327 deg. C.; the alloy, 63 per cent. tin and 37 per cent. lead, has the lowest melting point. If the metals are mixed in other than these eutectic proportions, the excess metal tends to crystallize out alone, having the largest possible amount of eutectic, which solidifies later. Microscopic examination shows that the eutectic is not a chemical compound; it is usually laminated and can be brought into relatively coarse dispersion by slow cooling.

But some forces do control the formation of the eutectic. As the fused alloy approaches solidification, lead, having the higher melting point, begins to form molecular groups or tiny crystals ("crystallogens"). This aggregation of lead molecules is opposed by the more fluid tin, thus lowering the freezing point of the mixture. Diminishing thermal agitation finally allows the tin to begin to form groups, and a stage is reached where both metals exist largely in colloidal state.* In this zone a colloidal adsorption compound is formed, the ratio, 63 tin to 37 lead, being consequent on their specific forces; any excess of tin or lead is free to crystallize independently. In the eutectic, the lead by adsorption interferes with the crystallization of the tin to such an extent that, if quickly cooled, the eutectic structure is extremely fine.

As with all colloids, this represents a metastable condition, and if the temperature is kept within limits which permit molecular orientation without disruptive

* All pure metals in solidifying pass through an isocolloidal zone, the narrowness of which is indicated by the sharp peak or cusp in the inverse-rate curve. See W. Rosenhain, "Introduction to Physical Metallurgy, pp. 85–87. D. Van Nostrand Co., N. Y., 1914.

thermal agitation, the eutectic undergoes a gradual syneresis analogous to coagulation or demulsification; a further separation into its constituent phases. The laminated structure, common in eutectics, already represents the aggregation of the preëxisting colloidal dispersion, as has been especialy pointed out in the discussion of pearlite in steel.

Solder, used by plumbers and others, is an alloy consisting of about equal parts of tin and lead. At about 210 deg. C. it begins to extrude crystals of lead into the fluid eutectic cement, rendering it pasty and easy to "wipe," spread or mold into the desired shape. The introduction of the highly crystalline antimony (m. p. 630 deg. C.) into tin-lead alloys results in the early formation of crystals of antimony or of the hard brittle compound Sn-Sb, with the result that the ternary alloy is much harder.

Type metal is one of these ternary alloys whose composition varies with price and service conditions. It is usually chilled quickly, which is conducive to fine structure and hardness. White bearing metals, on the other hand, are usually cast in larger masses and chill more slowly, their composition is chosen to yield hard wear-resisting crystals of Sn-Sb embedded in a colloidal plastic eutectic, which can adapt itself to the bearing's irregularities of shape and pressure.

Zinc-Copper Alloys (Brass)

Brasses containing less than 30 per cent. of zinc, irrespective of their speed of chilling, always consist of a "solid solution" of zinc in copper, known as alpha brass.

This alpha brass is really an adsorption compound between copper and zinc, in which the large

percentage of difficultly fusible copper (m. p. 1083 deg. C.) aggregates so rapidly that even in so-called "quickly cooled" specimens, the zinc (m. p. 419 deg. C.) is for the most part too finely dispersed to be much adsorbed by the copper. Hence the alloy exhibits a dendritic structure showing a copper crystallization as modified by adsorbed zinc, the amount of which increases from the center outward as the copper aggregates and the mother liquor becomes richer in zinc.*

As Rosenhain observes, the percentage of each metal and its state of aggregation are momentarily varying during cooling, and because of the wide disparity between the melting points of the two metals, homogeneity is favored either by extremely rapid quenching from fusion (which tends to prevent the copper from aggregating) or by slow cooling and annealing, which favor the more complete dispersion and adsorption of the zinc (which is segregated by ordinary cooling).

The natural desire to introduce more of the cheaper zinc into brass is limited by the fact that with brasses containing 30 to 37 per cent. of zinc there appears a new, hard, brittle metastable phase, beta brass. Such brasses if quickly cooled are relatively hard and brittle, but if cooled slowly the beta phase disappears. With more than 37 per cent. of zinc, the beta phase is stable at all temperatures down to 470 deg. C. and the slowly cooled alloys exhibit the duplex structure found in *Muntz metal* (approximately 40 per cent. zinc). Carpenter believes that below 470 deg. C. the beta phase decomposes into alpha and gamma phases, and

* Small pieces of alpha brass drastically quenched from fusion in liquid air will probably appear homogeneous in the microscope.

in fact that the beta phase is an almost ultramicroscopic mixture of alpha and gamma brass. (This indicates colloidal dispersion, favorable to hardness.)

Rosenhain [loc. cit., p. 145] says that the gamma brass "is exceedingly hard and brittle and its presence in the alloys renders them useless for any purpose where strength and toughness are required. This is a typical example of a law very widely applicable to alloys, viz., that those phases of a binary system which contain the two elements in anything like equal proportions are hard and brittle, only the alloys near the ends of a series being as a rule sufficiently strong and ductile to be of practical utility. We have already seen that the beta phase is harder and more brittle than the alpha, so much so that the best brasses, in which strength and ductility are of importance, are generally made with a zinc content of approximately 30 per cent., this being the cheapest alloy which does not contain the beta phase."

With solutions, as von Weimarn has shown [Kolloid-Zeit. 3, 282 (1908); ibid. 4, 27 (1909)], medium concentrations are favorable to the development of large crystals, whereas dilute and concentrated solutions both tend to yield colloidal dispersions; and a similar condition appears to exist with mixtures of pure metals. At both ends of the alloy series appear the larger amounts of the so-called "amorphous" phase of the metal, which in most cases is stronger at ordinary temperatures than the crystalline phase. Highly crystalline metal, deficient in the colloidal amorphous phase, is weak because it tends to split along the planes of crystal cleavage. We should therefore expect weakness where the component metals of

a binary alloy are about in equal proportions, for this concentration works against the development of colloidal metal and in favor of the larger, more perfect, but weaker crystals.

Bronze

In their article on "Alloys"* Roberts-Austen and Neville ,in speaking of the copper-tin alloys containing less than 9 per cent. by weight of tin, say that upon quickly chilling small ingots from successively lower temperatures beginning just above the melting point, we thus learn that these alloys (bronzes) "although chemically uniform when solid, are not so when they begin to solidify, but that the liquid deposits crystals richer in copper than itself, and therefore that the residual liquid becomes richer in tin. Consequently, as the final solid is uniform, the crystals formed at first must change in composition at a later stage. We learn also that solid solutions which exist at high temperatures often break up into two materials as they cool. . . ." The work of Beilby on plastic flow and of Benedicks on quick chilling, give an insight into the behavior of metals when stressed, worked and hardened.

Amorphous vs. Colloidal Theory

The amorphous theory of metals, advocated † by Rosenhain [loc. cit., p. 249] among others, stresses particularly the entire absence of regular orientation or crystallization in the so-called "amorphous" phase, in which the molecules are supposed to be in the random, haphazard, and mainly isolated state assumed to exist in liquids. I believe, however, that

* Encyclopedia Britannica, 11th ed., Vol. 1, p. 706.

† Judging from the literature, since this was originally written, Rosenhain has abandoned the amorphous theory.

the amorphous phase consists largely, if not entirely, of molecular groups, many of which may be oriented in the form of ultramicroscopic crystals or crystal fragments; and that its properties are due, *not to the entire lack of orientation* among its particles, but mainly to the fact that *many or most of its molecular groups are of colloidal dimensions.*

In metals the molecules are very close together and have an extremely powerful cohesion and crystallization tendency, so that it does not seem possible that the "amorphous" phase can be composed entirely of isolated atoms, molecules, or even entirely of non-crystalline groups. With the most drastically chilled metal, even allowing for the high viscosity and its rapid increase, it does not appear conceivable that no tiny ultramicroscopic crystals form, or at least that there is no grouping, regular or irregular, of the metal molecules. Even with gold hydrosols, where the dispersing water exercises a restraining influence, the X-ray spectrometer shows that both ultramicroscopic and amicroscopic gold particles are crystalline.

The facts are in harmony with the conception of amorphous metal as an isocolloid—that is, as a dispersion of colloidal crystals, crystal fragments, or non-crystalline groups, forming a solid gel-like mass. The fineness of its particles and the enormous development of free surface found in all colloids are its critical factors.*

* For further discussion of the colloidal state in metals and alloys see J. Alexander [Proc. Am. Inst. Min and Met. Eng., Vol. 63, 1919, and Vol. 64, 1920; Chem. Met. Eng. 1922; First Colloid Symposium Monograph, (Univ. Wisconsin) 1923]. Many of the changes that take place with sulphur are analogous to those that occur in metals. By chilling sulphur heated to 400 deg. C. in liquid air, von Weimarn [Kolloid-Zeit. 6, 250, 1910] obtained a perfectly transparent and ex-

Electro-Deposition of Metals

The powerful effect of protective colloids on depositing metal may be readily shown by dividing a solution of lead acetate between two glasses, to one of which is added some glue solution. Upon immersing a strip of zinc in each glass, the one without the glue gives the usual bright crystalline lead "tree," whereas the other gives a very much inhibited or amorphous looking deposit. A tin "tree" shows similar results, but if some lead acetate be added to the stannous chloride solution, the lead and tin mutually interfere with each other's crystallization. In refining metals electrolytically, new very pure baths usually give coarse-grained brittle anodes, but this effect wears off as "impurities" accumulate or are intentionally added.

In other cases impurities even in minute percentage, are highly injurious. Thus one part of iron in five million may injuriously affect the quality of electro-deposited nickel. In the electro-deposition of zinc, antimony is especially troublesome, even in traces.

A large variety of *addition agents* are used, the essential being that the added substance must be adsorbed by the depositing metal when the latter is in the colloidal zone through which it must necessarily pass. Müller and Bahntje [Zeit. Elektrochem. 1906, 12, 317] found that copper deposited in the presence of colloids to keep it fine grained weighed 0.2 per cent. more than metal deposited without the colloid. They found that gelatin had the most powerful effect,

ceedingly elastic sulphur. Here the rapid cooling results in the temporary preservation of a relatively large percentage of the viscous S_μ dispersed in the more fluid, S_λ, the resulting allocolloid being a sulphur sulphogel or a solid sulphosol.

egg albumen considerably less, and gum and starch but little action. The relative protective efficiency of these colloids parallels their protective action in the case of colloidal gold.

An observation recently made by J. Alexander * is of interest here. Moissan (Comptes rend., **144,** 593, J. S. C. I., 1907, 413) has noted that the addition of a little platinum to metallic mercury causes the latter to "emulsify" in water. Upon making up such an "emulsion," Alexander noticed that the supernatant fluid remained turbid upon standing, and therefore examined the fluid in the ultramicroscope, which revealed the presence of colloidal metallic particles in active motion.

Boiler Scale

When water is purified before injection into the boiler, any precipitate is preferably made as coarse as possible so that it can be readily settled or filtered out. But where the precipitate is formed within the boiler, exactly the opposite result is sought. Most "boiler compounds" contain such soluble colloids as dextrin, tannin and bark extract, and some engineers put potatoes or starch in their boilers together with soda ash.

Any precipitate formed in the presence of these colloids adsorbs them and tends to remain in a finely dispersed non-coherent condition, so that it is readily removed when the boiler is blown down. The formation of hard, crystalline scale is thus prevented.

Cement, Mortar, Plaster

Freshly mixed cement and mortar contain colloidal sols and gels which not only tend to delay or prevent

* J. S. C. I., 1909, **28,** 280.

the crystallization of dissolved substances, but also upon coagulation or setting bind the solid elements of the mixture into a coherent whole.

According to recent investigations [see A. A. Klein and A. J. Phillips, U. S. Bureau of Standards, tech. paper 43 (1914); P. H. Bates and A. A. Klein, tech. paper 78 (1916)], Portland cement contains much tricalcium aluminate ($3CaO.Al_2O_3$), which is responsible for its initial set, but which alone sets rapidly into a brittle crystalline mass. However, the cement contains dicalcium silicate (possibly an adsorption compound between lime and silicic acid), like that described by Le Chatelier [La Silice et les Silicates, 1914] as being formed by adding calcium hydroxide to dilute silicic acid sol,* which hydrates very slowly, forming an amorphous colloidal mass that evidently acts as a protector to the tricalcium aluminate, inhibiting its crystallization. Within about one day the tri-calcium aluminate begins its hydration and crystallization, which lasts about a week, and tends to make the cement weak. For the next three weeks, however, the main change is the progressive hydration of the lime-silica compound, with the development of a large amount of colloidal material which greatly increases the free surface and the strength.

The addition of such salts as calcium sulphate and the like, which are largely used in cement as a retarder, is regarded by W. Michaelis as altering the solubility of the aluminates and silicates, and by Rohland as influencing the coagulation rate of the colloids. Probably both effects co-exist, and there exists in cement a

* From the bulky gelatinous precipitate the lime may be entirely removed by washing.

condition of cumulative colloidal protection analogous to that found in glass, flour and metals.

In the case of plaster of Paris the set may be greatly delayed by glue, gum and protective colloids, and retarders of this kind have been in use for many years. The following table shows the result of adding gelatin to plaster of Paris:

One part water containing gelatin—Per cent.	Time to set in minutes.	Microscopic appearance of slide.
0	40	Characteristic crystals of calcium sulphate.
1/100	50	No crystals, except in a few spots where some colloid-free solution had diffused out.
1/10	260	No crystals.*
1/4	510	No crystals.*
1/2	960	No crystals.*
1	Not set in 48 hr.	No crystals.*
2	Not set in 48 hr.	No crystals.*

* No regular, ordinary crystals, the mass consisting of aborted, modified or sphero-crystals, or of colloidal crystals or other minute unoriented groups, or of a mixture of these.

See article by J. Alexander in J. Soc. Chem. Ind. 1909, on "Colloid Chemistry and Some of its Technical Applications."

CHAPTER XIV

PRACTICAL APPLICATIONS (Continued)

CHEMICAL ANALYSIS *

In gravimetric methods the object of the analyst is to form a non-colloidal precipitate that can be separated on a filter, washed and weighed. Von Weimarn has shown that precipitates formed in very dilute or very concentrated solutions tend to be colloidal, and for this reason the analyst usually chooses solutions of medium concentration, together with an excess of the precipitating reagent as a coagulant, acid in some cases, alkali in others. Adsorption of soluble substances by precipitates is a prolific source of error, which the analyst minimizes by thorough washing and a choice of precipitants, concentrations, and so on. The work of H. J. Weiser [J. Phys. Chem. 1919, et seq.] indicates what large errors may be due to neglect of precautions against adsorption.

Often when analytical methods speak of dissolving a precipitate, it is simply peptized or dispersed into a colloidal solution which passes through the filter paper. Thus the gel of aluminum hydroxide is readily peptized by alkali and that of iron hydroxide by hydrochloric acid.

Sometimes substances are added which inhibit precipitation by producing a colloidal non-filterable sol. Citrates and tartrates are especially apt to do this, and require special analytical treatment. The presence of such salts or of protective colloids (glue,

* This topic has been treated at length by Prof. H. Bassett in 4th Report on Colloids, etc., Brit. Assoc. Adv. Sci. 1922; also his paper in Vol. I of Alexander's "Colloid Chemistry, Theoretical and Applied."

dextrin, organic extractives) in technical products or specimens may lead to grave errors in analysis, so that the analyst should destroy them by oxidation or ignition, or else nullify their effects by a suitable excess of coagulant or precipitant. "Organic matter," as it is vaguely termed, may act: (1) By totally or partially preventing the formation of precipitates; for example, tartrates prevent the precipitation of aluminum, chromic and ferric hydroxides [Yoshimoto, J. Soc. Chem. Ind. 1908, 27, 952]; (2) by preventing the satisfactory filtration of a precipitate when formed [Mooers and Hampton, J. Am. Chem. Soc. 30, 805]; (3) by rendering precipitates difficult to wash and purify [Duclaux, J. Soc. Chem. Ind. 1906, 25, 866].

A few experiments will make this clear. Hydrochloric acid gives with lead acetate solution a heavy coagulated precipitate, but with sodium chloride, a less highly ionized precipitant, only a colloidal precipitate. If some glue solution be first added to the lead acetate, then sodium chloride produces no visible precipitate at all. In testing urine for sugar with Fehling's or Benedict's solution, as Prof. M. H. Fischer has pointed out, the simultaneous presence of albumin (or other protective colloid) is apt to bring down the copper oxide in a yellow colloidal state which, if some of the blue copper remains unreduced, appears as a greenish turbidity. For this reason the urine is boiled and filtered before testing for sugar, to separate out any albumin.

The Wassermann and precipitin tests are best understood on the basis of colloid chemistry—adsorption, peptization, protection or lack of protection, coagulation, and so on. The nomenclature of Ehrlich (com-

plement, middle-piece, end-piece, antigen, and so on), while appealing to the imagination, has no counterpart in the actual facts.

Pharmacy and Therapeutics

Those who laugh at curious Chinese remedies should glance at the illustrated section of the Chinese pharmacopeia, for the pictures of the hundreds of plants, etc., shown there speak in all languages. Recall to the scoffer that for thousands of years, without knowing about "endocrines," Chinese physicians fed sheeps' thyroids to deficient children; to-day we use thyroid extract. Among the materia medica is the toad, distinguishable from the frog by the absence of webbing in its foot. Our own colonists used "toad-skin ointment," and the use of the toad is often referred to in folk-lore. Thus in "As You Like It" Shakespeare says:

> Sweet are the uses of adversity,
> Which, like the toad, ugly and venomous,
> Wears yet a precious jewel in his head.

Comparatively recently, Dr. John Abel showed that the skin of the toad *Bufo* contains adrenalin (an "endocrine" possessing vaso-constrictor, styptic, and blood-pressure raising powers), as well as a substance he termed *bufagin*, which acts on the heart.

The pharmacist and his predecessor, the iatrochemist, have long utilized colloid chemical processes. Mercury is readily brought into the colloidal state by trituration with fats (blue ointment) and was largely used by Paracelsus (1493–1540 [?]), though known long before. Gold was also thought to have great

healing virtues, and its colloidal solutions were known. Eau-de-vie de Danzig seems to be a relic of this practice. It contains gold leaf. Thus Chaucer, in making a sly hit at the physician, says:

> For gold in physic is a cordial;
> Therefore he loved gold in special.

In making emulsions the pharmacist uses gum arabic, Irish moss, tragacanth, and the like. If ferric chloride be added to gum arabic emulsion of codliver oil, it coagulates the gum, and the oil, no longer protected by the emulsostatic action of the gum, promptly separates out. Milk of magnesia may be kept in colloidal state by carbohydrate protectors.

Colloidal silver (collargol, argyrol, and the like) is an excellent germicide in many cases and a preventive of *ophthalmia neonatorum*. Colloidal sulphur, artificially prepared and as ichthyol (a fossil sulphur-containing fish product), is valuable in skin troubles. Colloidal mercury (hygrol, blue ointment, and the like) is largely used. The introduction of gum arabic into the normal saline solution injected intravenously in cases of bleeding and surgical shock has saved many lives. It increases and maintains the blood pressure and viscosity. Ferric salts, especially the chloride which readily hydrolyzes into the hydrate, act as styptics by coagulating the blood colloids. Alum and antipyrine act similarly.

On the other hand, citrates, oxalates, and hirudin (extracted from the head of the leech) tend to inhibit the coagulation of blood.

Antiseptics and Bacteriology

Colloid chemical factors largely control the action of *antiseptics*.* To be effective a disinfectant must be adsorbed by the bacteria, and then it coagulates or peptizes their protoplasm, or else flocks them out. Natural antitoxins act similarly. Thus in the Widal test the agglutination of the typhoid germ is observed microscopically. Sodium chloride increases the effectiveness of phenol, an effect analogous to the driving-on action of salts in dyeing. Beyond a certain dose, mercury slays relentlessly. It is fixed by the kidneys and slowly causes an irreversible coagulation of the cell colloids. Lead is likewise irreversibly fixed in the body.

Dilution may remove an antiseptic before its results are irreversible.

Since bacteria are of the order of size of 1 μ, their motion is partially Brownian, though the unequal liberation both of gas and diffusing products is also a factor. As Albert Mary† has shown (Dictionnaire de Biologie Physiciste, 1921) the tuberculosis bacterium (Koch's bacillus) may become toxic by the selective adsorption of substances normally present in small amount in the blood (cholesterin). The extreme sensitiveness of bacteria to minute changes in acidity (pH) shows how intimately their life is controlled by variations in the degree of swelling or dispersion or electrical charge of their constituent colloids.

Rideal attributes the selectiveness of adsorption to the sub-microscopic inhomogeneity of the external

* See H. Bechhold, "Colloids in Biology and Medicine," trans. by J. G. M. Bullowa; E. K. Rideal, 5th Report on Colloids, etc., Brit. Assoc. Adv. Sci. 1923. I. S. Falk, Abstr. Bact., 1923, also Vol. II of Alexander's "Colloid Chemistry, Theoretical and Applied."

† See his paper in Alexander's Colloid Chemistry, Theoretical and Applied, Vol. II (1928).

bacterial surface, which has a checker-work of acid and basic areas. An extension of this idea justifies the now classic statement of Emil Fischer that enzyme and substrate are fitted like lock and key in cases where the enzyme acts (*specific action*).

Biology and Medicine *

The changes which occur in most biological processes are remarkable, not only because of their profound nature, but also because they are produced rapidly, at comparatively low temperatures and in the presence of dilute reagents. With apparent ease the living organism disintegrates proteins, oxidizes carbohydrates and fats and synthesizes substances of great complexity. High temperatures and powerful reagents which would be destructive of life are necessary to bring about changes of this character under ordinary laboratory conditions.

Enzymes

The high efficiency of the biological juices was once thought to be due to a mysterious "vital force," but this idea was disproved by Büchner, who isolated from yeast triturated with sand, a lifeless zymogen or enzyme which had the power of converting sugar into carbon dioxide and alcohol. Enzymes (pepsin, diastase, pancreatin, papain, lipase and the like) are colloidal catalyzers, whose existence seems to depend on the presence of adsorbed protectors; for the more they are purified the more unstable they become. They are coagulated and inactivated by shaking, heating, electrolytes and so on, all of which

* See Vol. II of Alexander's "Colloid Chemistry, Theoretical and Applied," which is devoted to biology and medicine.

cause coagulation of colloidal solutions with a decrease in their free surface and in the activity of their particles. The effective acidity (pH) of the solution in which an enzyme happens to be largely influences its action, probably by regulating its degree of dispersion and electric charge, which in turn affect free surface, adsorbability and kinetic activity.

Enzymes appear to act by forming with the substrate a compound of indefinite and unstable character, probably, as Sir W. M. Bayliss suggests ["The Nature of Enzyme Action"], a colloidal adsorption compound, which breaks down, liberating the enzyme again to continue the action. Croft Hill showed that the action of enzymes may be reversible, but in the organism reversion is prevented by the diffusion, dilution, or peristaltic removal of the products formed. Where increases of concentration occur in cells, tissues or organs, synthetic processes may be induced by enzymes.

Ultramicroscopically, enzymes show a multitude of colloidal particles in very rapid motion. Any substance immersed in such a solution, providing its electric charge or free fields of force permit the close approach or concentration of the enzyme at its surface by adsorptive action, must undergo a terrific bombardment, and it seems likely that enzymes produce their effects by virtue of their specific surface actions (which is influenced by the hydrogen ion concentrations of their solutions) and by the motion of their particles.

To see if this idea could be experimentally verified, J. Alexander followed ultramicroscopically the action of diastase on starch grains and the action of pepsin on coagulated egg albumen.

The diastase ultramicrons, maintaining their active motion, gradually accumulated about the starch granules, which after a time showed a gnawed or ragged margin. The adsorption and motion of only the larger ultramicrons could be followed, but the bright appearance of the field indicated that numerous smaller particles were present, and some of the intermediate size were seen. The albumen specimen was a dilute solution of egg white, heated nearly to boiling. It was opalescent, and showed a field full of bright, rapidly moving ultramicrons which immediately clumped or coagulated into large, motionless masses upon the addition of a droplet of pepsin solution (Fairchild's containing 15 per cent. of alcohol by weight). Upon "activating" the pepsin with a droplet of decinormal hydrochloric acid, the large groups burst into small groups and isolated ultramicrons, which at once resumed their active "dance." Soon, however, the albumen particles began to grow fainter and disappear, the field meanwhile becoming brighter and brighter, indicating that simultaneously smaller ultramicrons or amicrons were being formed. The additon of pepsin to a test tube of the opalescent albumen solution caused it to clear gradually at room temperature.

Cytology

Physiological chemists have made illuminating researches into the chemistry of cell metabolism, and cytologists have, mainly by microscopical methods, accumulated a wealth of interesting albeit confusing facts, the elucidation of which will lead us still nearer to an understanding of the mystery of life processes.

When a germ cell undergoes *mitosis* (or *karyokinesis*

as it is also known), some of the constituents of the nucleus arrange themselves into a long irregularly twisted thread or *spireme* (loose skein), which then becomes more open but shorter (open skein). The open skein splits into short segments, frequently U-shaped, and these divide equally on either side of an equatorial plane which separates the cell into two parts, each of which develops further into a separate cell. The formation of star-like polar centers (*amphiasters*) is one of the many other associated phenomena observed.

Since the substances comprising the skein segment are readily stained by the microscopist's dyes, they are called *chromatin* substances, and the structures are called *chromosomes*. Most heritable characteristics which have been studied are transmitted solely through the chromosomes, which vary both in number and character with different plants and animals.

The problem of investigating the colloid-chemical changes underlying the microscopical picture and accompanying the chemical changes, is a most formidable one; but once it is closely envisaged, some vulnerable points will probably be found. A beginning has already been made by R. Chambers, A. Heilbronn, L. V. Heilbrunn, W. Seifriz and others. The micro-method of Freundlich and Seifriz (Zeit. phys. Chem. *104*, 233–61) (which consists in pulling a tiny [18 $\mu \pm$] particle of nickel through a gel by an electro-magnet of known power) shows that the inner protoplasm of the unfertilized egg of an echinoderm (*Echinarachnius parma*) has about the viscidity of concentrated glycerin, while the peripheral layer has the consistency of a soft gelatin gel [Seifriz, Brit. J. Expt. Biol. *1*, 431–42 (1924)].

At mid-mitosis the cytoplasm about each amphiaster has the consistency of a still plastic gelatin jelly, while the peripheral protoplasm of the egg becomes as viscous as bread-dough. Following the completion of mitosis, the viscosity drops again, in preparation for another division. L. V. Heilbrunn investigated the viscosity of cellular constituents by centrifugal methods [J. Expt. Zool. *30*, 211–37 (1920)].

If in the middle of mitosis (*metaphase*) the egg be subjected to slight pressure, the whole karyokinetic spindle-shaped structure collapses, resembling in this respect (as Seifriz points out) the gel of iron oxide described by Schalek and Szegvary [Kolloid-Z. (1923) *32*, 318–9] and that of metallic cadmium described by T. Svedberg (Rept. Farad. Soc. and Phys. Soc. Lond. on Phys. and Chem. of Colloids, 1921).

Some of the colloid-chemical principles involved in intercellular changes are apparently the following:

Gel formation (pectization)—when the gel forms in certain localities, banded orientation (Liesegang's rings) and differential diffusion may occur in it.

Re-solation (peptization)—this may be consequent upon the action of enzymes released or activated by changes in H-ion concentration, which may follow differential diffusion. These changes in H-ion concentration may also determine viscosity.

Cumulative protection—alteration of one of a connected series of protectors may produce important changes.

Colloidal influence on crystallization tendencies—astral rays seem indicative of this.

Growth

For years it has been taught as an elementary distinction that non-living things grow by *accretion*, while living things grow by *intussusception*. Thus Huxley in his "Anatomy of Invertebrates" (page 10, 1888): "The increase in size, which constitutes growth, is the result of a process of molecular intussusception, and therefore differs altogether from the process of growth by accretion, which may be observed in crystals."

Considering the table of material units shown on pages 14–15, it will be at once evident that intussusception in a body of any upper order of complexity, is resolvable into accretion at the surface of particles of some lower order, while conversely, accretion at the surface of particles grouped to form a mass of a higher order of complexity, results in the growth of this mass by intussusception. All growth is thus, ultimately, accretional.

The fact that structures simulating organic growths can be produced by allowing precipitates to form in colloidal gels has long been known, and many beautiful experiments may be made along these lines.* *Differential diffusion* through semi-permeable membranes, and the resulting osmotic pressure, are large factors in growth, to which must be added the formation of insoluble chemical compounds and, especially in organisms, the manifold effects of colloidal protection, coagulation, peptization, and adsorption.

* See R. E. Liesegang, "Kolloid-chemische Theorie des Lebens"; Stéphane Leduc, "Les Croissance Osmotique et l'Origine des Etres Vivantes"; A. L. Herrera has worked over thirty years on Plasmogeny. There are papers by all these scientists in Alexander's "Colloid Chemistry, Theoretical and Applied."

Thus Wislicenus showed that the *cambial or running sap* of trees in the spring is full of colloidal substances which coagulate irreversibly after their adsorption by the wood cellulose.

The *punctum vegetationis* of plants is usually more acid than the balance of the plant (has a lower pH) and therefore tends to swell more and be more hydrous and tender—e.g. in the case of asparagus.

The colloidal nature of the tissues and enzymes with which food comes in contact directs and regulates the whole process of development. From the same soil we may produce a lily and a beet, a turnip and a rose. From tiny cells almost undistinguishable from each other there develop the most diverse animals; yet compressed within that space are the differences in chemical constitution and colloidal structure that render possible and, in most cases, insure very tenaciously the close resemblance of offspring to parent.

Constructive and destructive processes are going on side by side in the organism, and, as R. S. Lillie puts it [Scientific Monthly, Feb., 1922], visible growth simply represents the accumulated excess of the former over the latter. Broadly, the constructive processes involve the formation of species-specific sols and gels, followed or accompanied by the formation of precipitates in their presence, and then usually by a slow syneresis which produces most of the hardenings of old age. Chemically, there is much similarity, if not sameness, about the structures formed. Thus even cartilage, the precursor of bone, is allied to chitin of insects and the mucus of snails, for all yield chondroitin-sulphuric acid (A. P. Mathews). But, physically, there are enormous differences in form, percentage of composition and function.

Colloidal sols and gels exert a powerful and specific influence on developing structures, as may be seen by allowing different salts and salt mixtures to crystallize in the presence of colloids such as gelatin or gum arabic, and also by allowing precipitates to form by diffusion in various jellies (gelatin, agar and silicic acid). Although the details are of unfathomed complexity, the specificity of organisms and of the fragments, buds, spores or seeds by which they reproduce, is due to specific colloids and to the substances the colloids adsorb or whose formation they direct.*

Some Factors Influencing Development

It is the general rule in biology that descendants resemble parents, and that a parent organism cannot pass on to offspring a factor which the parent did not receive from the germ-plasm of its immediate progenitors. Many apparent exceptions to this general rule have been traced to the existence in the parent gametes of recessive factors, which, while suppressed in the parent, may be liberated again in the offspring. Whether we accept the view of Darwin that large differences can represent the summation of small differences, or the more probable view of Bateson and others, that mutation or variation is a definite physiological event, no satisfactory explanation has been given as to the origin or source of these exceptions to the general rule of resemblance, although they constitute the steps by which evolution haltingly proceeds.

The crying need that we must find a chemical,

* See R. S. Lillie, "Protoplasmic Action and Nervous Action," Univ. of Chicago Press, 1924.

physical or physico-chemical basis for mutation or variation has been voiced by many.* Thus in his address before the British Association for the Advancement of Science (Australia, 1914, reprinted in *Smithsonian Report,* 1915, pp. 359–394), Sir William Bateson says: "Every theory of evolution must be such as to accord with the facts of physics and chemistry, a primary necessity to which our predecessors paid small heed. . . . Of the physics and chemistry of life we know next to nothing. Somehow the characters of living things are bound up in properties of colloids, and are largely determined by the chemical powers of enzymes, but the study of these classes of matter has only just begun. Living things are found by simple experiment to have powers undreamt of, and who knows what may be behind?"

In nature, both animate and inanimate, the following basic factors tend to produce *symmetrical orientation or aggregation:* (1) Crystallization and orientation in surfaces; (2) Diffusion, as in the formation of Liesegang's rings, agate, etc.; (3) Electric or magnetic fields of force; (4) Harmonious vibration as of air, water, etc. We here disregard mere chance and the conscious arrangement by man.

The main factors modifying the crystallization of pure substances are: (1) Concentration; (2) Temperature; (3) Pressure; (4) Agitation; (5) The presence of other substances, especially of colloids, which may profoundly modify crystal forms by protective action; (6) Iso-colloidism. Some substances have the power of interfering with their own crystallization, because a portion, which first reaches the colloidal state, then protects the balance.

* Such an explanation is given at the end of this Chapter (p. 226).

Deviations from normal crystalline forms produced by the presence of colloids are usually symmetrical, but may not appear crystalline. Changes in the nature or degree of dispersion of the colloid, or in its percentage, mixtures of colloids, variations in salt or H-ion concentration* of the solution, must all have an effect on the resultant quasi-crystals. Enzymes may, of course, entirely change the nature of the colloid. The species-specificity of proteins seems to be maintained by degenerating food protein to simpler forms (polypeptids and amino-acids) and then building up the specific proteins from these.

Among the factors influencing diffusion, especially in gels, are the chemical nature and particle size of the gel, and the concentration and nature of the diffusing solution. In his chapter on "Growth, Metamorphoses and Development," Bechhold ("Colloids in Biology and Medicine," trans. by J. G. M. Bullowa, p. 252 *et seq.*, D. Van Nostrand Co., 1920) refers to some of the remarkable diffusion figures and osmotic forms† produced by F. E. Runge and by Stéphane Leduc, some of which resemble algæ, fungi, seaweed, etc., and even show a cellular microstructure. While pointing out the great differences between these formations and the organized structures they simulate, Bechhold says: "The physical forces which produced these inorganic formations are the same as those which produce the growth and configuration of organized material membranes, osmotic pressure, diffusion."

Perhaps the most familiar instance of modified crystallization is to be found in the delicate frost

* NaCl crystallizes in cubes from acid solutions but in octahedra from alkaline solutions.

† A. L. Herrera (Mexico) has devoted many years to these studies.

tracery on window panes, the forms being probably influenced by the glass (itself a colloid) or by substances adsorbed at its surface.* The writer has pointed out the powerful influence exerted by colloids such as gelatin, gum arabic and albumin on crystallization (Kolloid Zeit. *4*, 86, 1909), and R. E. Liesegang, looking at the question from the opposite standpoint, has described the power of crystalloids to give a form to colloidal jellies (Kolloid Zeit. *7*, 96, 1910). It may be said that with different salts or combinations of salts, various colloids or combinations of colloids, and variations in concentrations, temperature and speed of evaporation, will produce characteristic and generally reproducible forms on a microscope slide. A characteristic form of sodium chloride is a four-pointed star with fern-like arms which cross at a slight angle.

A few slides made with solutions of common salts such as NaCl, $MgSO_4$, Na_2SO_4, etc., containing from 0.5 to 50 per cent. of gum arabic or gelatin (figured on the basis of the dry salt), will illustrate what is meant. When a drop of the mixed solution is allowed to dry on the slide without cover glass, changes of concentration and temperature occur, giving a field that changes progressively from rim to center of the drop. A solution of one part sodium chloride, one part sodium carbonate (dry) and one tenth part gum arabic or gelatin in ten parts of water, when dried, shows in some part of the field a "flowering plant,"

* See, e.g., the figures given by Wilson J. Bentley in "Monthly Weather Rev." 1907; also paper by Prof. Howard T. Barnes in Vol. II of Alexander's "Colloid Chemistry, Theoretical and Applied," A pioneer worker was Dr. Wm. A. Ord, whose book, "The Effect of Colloids on Crystalline Form and Cohesion," was published in 1879, too far in advance of its time to be appreciated.

with graceful stems and characteristic four-petaled flowers.

To see that a marked change may be produced by modifying the colloidal state of the protective substance, a slide was made with a solution containing egg albumen as the colloid. The solution was then heated until the albumen began to show a milkiness, another slide was made, and after drying was compared with the first unheated specimen. The difference in crystallization was considerable.

Unusual crystalline forms, such as sphero-crystals and sheaf-like groups which are so often seen in the crystals of substances derived from organisms, are very often consequent upon the protective action of some colloid from which they are not entirely purified. Another curious occurrence must be mentioned here, which may be termed *auto-protection* because it is due to iso-colloidism. Before reaching the ordinary visibly crystalline state, particles of every substance must pass through the colloidal zone, and the particles first reaching that state may interfere with the normal crystallization of the rest. Thus ammonium salts, even without the addition of protective colloids, are prone to assume feathery or fern-like forms. The phenomenon is marked in the oleates and is probably the underlying cause of the formation of myelins, although their formation is fostered by such lipoid protectors as cholesterin. According to J. G. Adami (Harvey Society Lecture, 1906), if certain simple soaps be dissolved by warming on a slide with water and then allowed to cool, they may show upon examination in the polarizing microscope a perfect rain of doubly refracting spherules, which, depending on the

nature of the soap, may last for hours or days or else immediately give place to a brilliant white layer of formed crystalline plates. The fluid crystals of O. Lehmann are probably examples of auto-protection, and W. B. Hardy, E. Hatschek and others have described substances which form unstable gels that soon become crystalline (see p. 45).

The bio-colloids are so readily affected by salts, H-ion concentration (effective reaction), temperature, actinic (sun's rays) and traumatic (shaking, mechanical injury) effects, that it is more surprising that plants and animals should breed true than that they should show variations. Therefore, although individuals may be much affected by such changes during their lives, it is evidently a rare occurrence that these changes are registered in the germ plasm by which alone they may be transmitted to offspring. The specificity of the germ plasm is evidently guarded by many factors, among which seem to be selective adsorption and differential diffusion of dissolved substances through its protecting walls or membranes. Nevertheless unusual influences must occasionally change it materially without destroying it, and along this line experiment may be directed.* It may be that the germ plasm can be affected through the somatoplasm, as well as by direct means. And of all the variations, in nature only the beneficial changes survive.

Physiology and Pathology

The bio-colloids consist of carbohydrates (starch, cellulose, glycogen), proteins (albumins, globulins,

*Since this was written, mutations have been experimentally produced by X-rays. See concluding section of this Chapter.

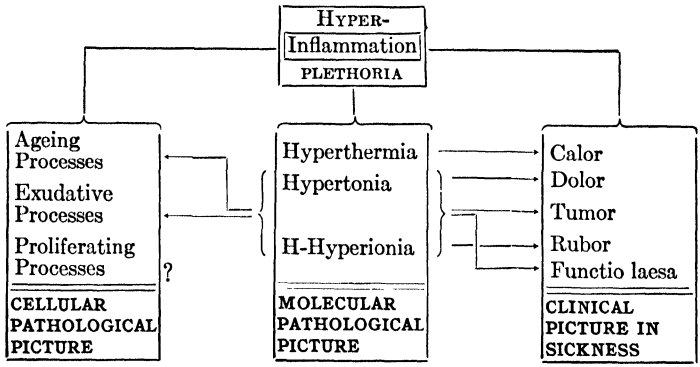
ossein) and lipoids (lecithin, cholesterin, fats and oils). Each tissue has a normal state of swelling or turgor, which is greatly influenced by the effective reaction (acid if pH < 7, alkaline if pH > 7) and by salts. The swelling is least at or near the isoelectric point; its increase by both acids and alkalis soon reaches a maximum, after which it falls again. Neutral salts oppose the action of acids and alkalis, apparently by driving back their ionization, and thus bringing the effective reaction (H-ion concentration, pH value) nearer to the isoelectric point. So sensitive are colloids to minute changes in reaction detectable only potentiometrically or by the use of very delicate indicators, that fibrin will easily distinguish by a big difference in swelling, between conductivity water and ordinary distilled water, which contains CO_2 and has a p_H of about 5.5.

If the *oxidation processes of the body* are normal, the hydrogen in foods is oxidized mainly to water, and the carbon mainly to carbonic acid—a gaseous acid which is exhaled without demanding protein or fixed alkali of the organism for its elimination. Nearly two pounds of caustic soda would be required to neutralize the acid produced daily by the average adult. In cases of pathological oxidation, as in diabetes, dextrose (glucose) accumulates in the blood beyond the normal average of about 1 per cent. (hyperglycemia), exerting a dehydrating or shrinking action on the tissues, while fats are oxidized only partially to the poisonous acetone, diacetic acid, and beta-oxybutyric acid, which may produce "acidosis," really a diminished alkalinity recognizable by the fact that an abnormally large quantity of sodium

bicarbonate is needed to render the urine alkaline. As the body colloids are thus forced nearer to their isoelectric point, their water-holding capacity diminishes, "free" water appears in the blood, and the patient shrinks. In fact, throughout life there is a continual syneresis of the body colloids: compare the chubby hand of an infant with the shrunken hand of an old man.

Local accumulation of acid may cause swelling (*edema*); for example, insect stings which may be simulated by "stinging" gelatin with a needle dipped in acid. If acid accumulates in an organ, having a rigid capsule (eye, kidney), the swelling tends to establish a vicious circle (glaucoma, nephritis) by compressing the blood vessels and cutting down the alkaline blood stream, which is unable to absorb and wash out the acids (mainly CO_2) formed by living protoplasm. The degeneration of the kidney in these circumstances is so typically one of the colloidal swelling and coagulation that the physician judges the condition by the microscopic appearance of the casts (hyaline or granular) sloughed off by the tubules. Certain infections (scarlet fever, for example) produce substances likewise harmful to the kidney tissue. [See "Edema and Nephritis," by M. H. Fischer.]

The relation between the clinical, pathological, and colloid chemical pictures or complexes in inflammation has been diagrammatically illustrated by H. Schade (Münchener med. Wochenschr. 1924, No. 1, p. 1–4) as follows:



Owing to increase in quantity of dissolved substances, the osmotic hypertonia may reach as high as 11 atmospheres, while H-hyperionia may result in a hydrogen ion concentration 50 times normal.*

Capillary Circulation

The remarkable work of A. Krogh and his collaborators† shows that for the most part the capillaries intermittently open and close. They thus act practically as tiny railroad sidings, along which the red blood corpuscles are shoved in single file like tiny trains of freight cars. When the motion stops, oxygen diffuses slowly into the surrounding tissue served by the capillary, while carbon dioxide diffuses about 30 times more rapidly to the red blood corpuscles. When the exchange reaches the proper balance, the capillary opens, and the arterial pressure forces the little freight cars, now loaded with carbonic acid, into the venules, their places being taken by new oxygen-containing corpuscles.

* Note.—This means a pH of between 5 and 6, which is about the acidity of ordinary distilled water not protected from CO_2 absorption.

† See "The Anatomy and Physiology of Capillaries."

Underlying these apparently simple microscopically visible changes are many factors, chief of which seem to be the following:

(1) *Hormonal or Endocrine Control.* The posterior lobe of the pituitary yields to the blood a very potent hormone which exercises capillary control. Krogh thinks it regulates the tone of the tiny Rouget cells which embrace most capillaries; for in the frog, extirpation of this lobe causes an edema which he says is due to the relaxation of the Rouget cells. Krogh estimates that this hormone is effective in less than one part in one hundred million, while Abel has isolated a purified hormone said to be effective one part in 18,750,000,000.

(2) *Nervous Control.* There exists both a psychic nervous control ("blushing," turning pale), and a vasomotor (sub-conscious) control. Light exercises a lasting effect on the reactivity of capillaries to stimuli (work of Finsen).

(3) *Turgidity Control.* A variation in the degree of swelling or turgidity of the tissue colloids comprising the capillary wall or surrounding the capillary, would obviously result in the opening or closing of the capillary and it would seem easy to explain the process by assuming that when the tissues accumulate carbonic acid, they swell and close down on the capillaries, relaxing again as oxygen comes in and carbonic acid diffuses out to the red blood cells. The tissues would thus automatically regulate their supply of blood in accordance with their demands; and in fact Krogh found that in exercising muscle many more and larger capillaries are open than in quiescent muscle. If anything prevents the capillary from

opening again at the proper time, we have a vicious circle—an "acid" capillary surrounded by "acid" tissue—leading to congestion or inflammation.

Krogh states (loc. cit., pp. 131–133) that change in p_H (H-ion concentration) does not seem to be the dominant factor in capillary control but that this control is associated in some way with a lack of oxygen. Krogh however estimates the p_H from the CO_2 tension, a method open to objections because of the many other factors which may influence the H-ion concentration of tissue, e.g. the presence of buffer salts and proteins, and selective diffusion between the plasma and corpuscles. Eliot R. Clark and Eleanor L. Clark [Anatomical Record, Vol. 27, p. 200 (1924)] found capillaries in a tadpole's tail which probably did not lack oxygen because of the thinness of the tissue, but which nevertheless automatically opened and closed, as did also segments of capillaries between Rouget cells.

It seems difficult to determine these microscopic and minute fluctuations in p_H but a technique may yet be developed.* As Krogh says (p. 134), it is "a case for renewed investigation"; but it is hard to forego the belief that *variation in the swelling of tissue*, associated with fluctuation in H-ion concentration and the amount of products of metabolism, is a big factor in the control of capillary circulation.

Psychiatry

The proper functioning of the brain and the nerves depends upon the maintenance of their constituent colloids within certain limits of swelling and disper-

* Prof. Robert Chambers has been able to inject pH indicators into an ameba and even into its nucleus.

sion. As is usual, the word *certain* is used to cloak our ignorance of the exact conditions, for the question is of great and as yet unfathomed complexity.*

Broadly speaking, in most mental disorders there is a preliminary *reversible* stage, which, if not taken in time, may lead to later stages which are partially or totally *irreversible.* As the physico-chemical changes of many of the bio-colloids and proteins (e.g., gelatin and albumin when heated) show first reversible changes which gradually become irreversible as the coagulative or alterative influences persist or increase, it is natural to inquire whether incurable mental disorders may not be consequent upon irreversible changes in some of the brain colloids. When the psychiatrist says that a neurosis has become a psychosis, he is only recognizing a clinical fact without even hinting at the underlying causes.

Since the blood supply throughout the body is subject to nervous and endocrine or hormonal control (see paragraph on Capillary Circulation), and since the endocrine glands (suprarenal, pituitary, thyroid, etc.) may, by nervous stimulation and variation in their blood supply, pour their powerfully acting secretions into the blood stream, it is evident that nervous excitement or shock may affect the whole body most powerfully. Thus Crile bound a rabbit with tape so that it could not move, and allowed a tethered dog to bark at it. The rabbit died of "fright," and its brain showed extreme congestion, probably due to the excessive blood pressure consequent upon activated secretion of adrenalin, etc.,

* Since writing this, a beginning has been made by Prof. S. D. Ludlum. See his paper with Dr. A. E. Taft in Vol. II of Alexander's "Colloid Chemistry, Theoretical and Applied."

without the possibility of any corresponding motor activity to act as a natural relief valve.

Dr. A. J. Justschenko ("The Nature of Mental Diseases," Dresden, 1914) states that the viscosity of the blood is usually increased in dementia præcox, senility, and maniac-depressive insanities, especially during the periods of excitement. Auguste Lumière found that the blood of an epileptic, taken before a seizure and injected into a rabbit, produced epilepsy in the animal. The active part of the serum settled on standing and could also be centrifuged out, indicating that it is a colloidal flocculate of some sort.

Anaphylaxis and Immunity

A. Lumière has also shown that, whereas extremely fine precipitates of inert substances (e.g., barium sulphate) are harmless when injected intravenously when freshly made, if the precipitate is aged it produces serious disturbances whose gravity depends upon the size of the flocculates. The older and more aggregated precipitates cause violent shock and death. Although the organism tends to protect itself against the formation of coarse coagula by the principle of plural colloidal protection (see p. 59), if the protective colloidal chain is attacked and broken, the formation of flocculates of injurious sizes may occur, and as these are selectively adsorbed and block the capillaries in various places, they may cause a whole train of ills, depending on the locus and the degree of action.*

We may understand immunity as due to an antigen which has gradually, by selective adsorption, surrounded itself with a protective colloidal layer of

* It is believed that some bacteria (anthrax) and spirillæ (spirochete pallida) act largely by mechanically obstructing the circulation.

sufficient quantity and quality that it may take up and render harmless a succeeding quantity of antigen, or else insure its agglomeration as a colloidal sol. Thus, the ultramicroscope shows that tetanus toxin and tetanus antitoxin mutually precipitate each other, as do diphtheria toxin and antitoxin. Where the absorbed protective layer is deficient in quantity or quality, we may have a hypersensitization to precipitation, so that a small succeeding dose of antigen produces a coagulation in masses sufficiently large to cause capillary embolism. In this manner we can understand the condition known as anaphylaxis and its occasional consequence, anaphylactic shock.

Healing of Wounds

In general this process depends on the formation of a fluid exudate or transudate (sol) which later sets to a gel, cementing together the severed surfaces and, on desiccation and shrinking, forming scar tissue.

Digestion

Crystalloids, such as sugars and salts, are diffusible through the semipermeable walls of the digestive tube, but fats and most colloidal foods must first be dispersed into a sufficiently fine state. The disintegration of proteins (meat, egg white) and of carbohydrates (starch) is effected through enzymes (pepsin, ptyalin, trypsin); while fats (either directly or after separation of their glycerin) are emulsified by the alkaline pancreatic juice. The presence of protective colloids such as mucin, cholesterin (in bile), and the like may account for some of the divergences between the behavior of natural and artificial digestive juices. Thus, membranes moistened with

cholesterol permit the passage of particles to which they would otherwise be impervious. Indeed since all body fluids contain protective colloids, no chemical action can go on in the organism without being influenced by their presence.

Absorption, Secretion, Excretion

These are largely the results of selective adsorption by, and differential diffusion through, the colloidal tissues and fluids, accompanied by swelling and shrinking. Thus the blood is a circulating colloidal fluid which holds more water when in the "acid" or venous condition than it does when in the more alkaline or arterial condition. Tissues and organs well supplied with venous blood tend to absorb water (intestine); whereas those well supplied with arterial blood tend to give up (secrete, excrete) water (kidney). Since the blood is passing in a continuous stream, the process continues as long as the supply of water permits, or until the blood is in equilibrium with the tissues.

Conditions which decrease the capacity of the blood and tissues to hold water (diuretics, hyperglycemia and acidosis in diabetes) naturally result in the elimination of the excess or "free" water (polyuria, diarrhea).

Minute quantities of acid increase the swelling capacity of colloids, which quickly reaches a maximum; after which increasing acidity causes shrinking. Neutral salts oppose the action of acids apparently by driving back the ionization of the acid and thereby reducing the H-ion concentration which is an important factor, but by no means the only one.

The functioning of organs is largely controlled by nervous influences. Thus, a sudden nervous shock by causing vaso-dilation may send an excessive supply of arterial blood through the mesenteric arteries (in effect an "internal blush"), and cause secretion into the intestine (nervous diarrhea).

Hydrolyzable salts are readily split up upon diffusion through a colloidal gel. Thus, ferric chloride upon diffusion through agar or gelatin gel yields ferric hydroxide which is selectively held back and hydrochloric acid which differentially diffuses ahead. If a little potassium ferrocyanide and alkaline phenolphthalein be added to the colloid gel, the latter will soon be banded in patriotic red, white, and blue (see p. 68). Depending upon the structure of an organ, the location of its cavity, its arteries and veins, and its outlet, it may yield an acid secretion (gastric juice) or or an alkaline secretion (pancreatic juice). Individual substances or mixtures in the blood stream or other body fluids may be selectively separated or concentrated.

An insight into the complexity of these processes may be had by considering the functioning of the kidney. Its Malpighian tufts are plentifully supplied with arterial blood containing "free" water; but since the interior diameter (lumen) of the afferent vessels is less than that of the efferent vessels, a "back pressure" is produced which the heart-throb makes a pulsating pressure, causing the tufts to act as an ultra-filter and pour a copious but very dilute ultra-filtrate of the blood into the convoluted tubules. The tubules, however, have a plentiful supply of venous blood, which is unsaturated with water and reabsorbs

most of it together with some of the substances contained in the preliminary secretion; so that the concentrated excretion (urine) that finally drips into the pelvis of the kidney has in solution many substances

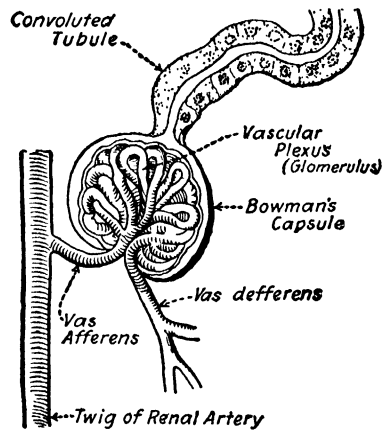


FIG. 6. Glomerular Structure.

found in the blood, but in totally different concentrations. Bechhold estimates that the average of two liters of urine voided daily by a man represents a preliminary secretion of fifty liters, forty-eight being reabsorbed within the kidney itself.

Diagnosis

Among diagnostic methods involving colloid chemical principles may be mentioned the Wassermann, Kahn,* colloidal gold, colloidal mastic,† and formol tests for syphilis, and the Widal test for typhoid. The differentiation between casts and cylindroids, usually

* The Kahn test is replacing the Wassermann. See paper by Prof. R. L. Kahn in Vol. II of Alexander's "Colloid Chemistry, Theoretical and Applied."

† See e.g. Adler and Sinek, Klin. Wochschr. *2*, 2071 (1923).

difficult with the microscope, becomes relatively easy in the ultramicroscope or dark field. (See Alexander and Connolly, Science, July 27, 1923.)

Chemo-Therapy and Colloid-Therapy

We will never understand just how many remedies work until we trace their effects on the body colloids—a most formidable task. Many remedies operative *in vivo* do not work *in vitro*.

All diseases are caused by, or involve, changes in the body colloids which, though delayed by the presence of protective substances, are sometimes irreversible. To cure the disease, we must remove the cause and aid the tissues and body fluids or "*humors*," as they were called, to return to their normal state of dispersion and swelling. Bacteria and other invading organisms, as well as the body tissues, have highly specific adsorptive powers, and the "shot-gun" method of try, miss, and try again is our main reliance in finding something that will kill the germ or disease and spare the patient. Salvarsan was originally known as "606" because that was its number in the long series of compounds Ehrlich was testing against certain resistant organisms. Quinine, long ago known and used by South American savages, is still our specific against malaria.* "Bayer 205," non-operative "in vitro," is said to kill the trypanosomes that cause sleeping sickness.

*Speke and Burton (about 1850) reported that the Congo natives attributed malaria to the mosquito and sleeping sickness. The Zulus called malaria "mosquito sickness." In certain parts of South America the natives go to malaria-infested sections to get relief from syphilis. Recently, this "cure" has been applied; probably the high temperature due to the malarial attack hurts the spirochetes much more than it does the patient.

Many old remedies, relegated to the scrap-heap, had virtues we are beginning to understand, and they are coming into use again. Thus kaolin (clay) is largely being used as a cataplasm and internally as an adsorbent. Some varieties of clay adsorb bacteria and are used therapeutically, e.g. in intestinal diseases like cholera. Charcoal is another colloidal adsorbent in common use; it is sometimes impregnated with drugs which it yields gradually, and it may serve as an antidote by adsorbing strychnine, for example. Freshly precipitated (colloidal) iron hydroxide was introduced by Bunsen as an antidote for arsenic; milk, egg white, and other proteins are used for corrosive sublimate poisoning; gruels or other mucilaginous drinks against aloes, cantharides, and the like. Dusting powders cool by increasing the free evaporative surface of the skin.

Serum-Therapy

Foreign proteins (*antigens*) when introduced into the blood tend to surround themselves by adsorption with a protective film which, after a certain period, acquires in most cases the ability to adsorb, and hence nullify the effects of a subsequent dose of poison, thus conferring *active immunity*. Or the immune serum may be formed in a horse or other animal and injected (*passive immunity*). With some individuals the first doses of antigen accumulate so small a protective layer that the resulting product is *more* readily coagulated. Sensitizations of this kind may cause *anaphylaxis*, asthma, and so on (see p. 218).

Plants

Plant tissues are likewise colloidal gels and sols, and as the sap circulates through them each tissue

selectively adsorbs and elaborates certain constituents. Thus, starch-forming substances are fixed by the roots of the potato and tapioca, by the stem pith of the sago palm and by the seeds of cereals. The stems take up the substances required for upward growth, the roots those for downward growth.

Bio-Electric Currents

Most tissues have a potential against other tissues, the one having the higher solution pressure forming the anode.* That solution pressure is partially dependent on degree of subdivision was shown by Hulett, and is also evident from the fact that strained and unstrained metals have a potential against each other, as do injured and uninjured tissues.

The conduction of nervous impulses (pain, sight, hearing) involves chemical changes resulting in electric currents, perhaps due to the liberation of electrons. But though we may trace the chemical or electrical effect on the brain, how this becomes *thought* or *consciousness* is still an impenetrable mystery expressed in the old philosophical circle—"*What is mind?*" "No matter." "*What is matter?*" "Never mind."

When we consider the great variety of bio-colloids and their susceptibility to change under physical and chemical stimuli with resulting changes in their behavior as adsorbents and diffusion media, we can understand why an almost infinite number of reactions may go on within their recesses, as they swing the balance of the law of mass action over particles reduced to a reactive degree of dispersion.

* See work of R. S. Lillie.

Some Physico-Chemical Aspects of Life, Mutation and Evolution *

One of the commonest, most interesting, and yet most inscrutable of natural phenomena is the transfiguration of non-living matter into living matter by growth or reproduction, and the reverse transformation of the living into the non-living by decline and death. The attempt is here made to show that the material mechanism of life and of death is understandable in terms of well known and readily comprehensible physico-chemical concepts. The chemist and the physicist, starting with atoms and electrons, have been working upward into larger and still larger molecules and molecular groups, while biologists have been steadily working downward to smaller and still smaller cellular units. Putting it figuratively, these two groups of scientists have been tunnelling into the mountain of ignorance from opposite directions; they have met in the median zone of colloidal dispersion, and the two bores seem to justify or register perfectly.

Many of the difficulties which confront those who seek to understand the nature of life and life processes, arise from the fact that attention has not been focussed upon vital units sufficiently simple in their nature to be sufficiently comprehended in both structure and behavior. Even the smallest cell or monocellular being is an exceedingly complicated structure composed of many millions of molecules. It presents within its confines and purlieus whole series of simultaneous and interrelated phenomena. We are mentally incapable of envisaging the whole melée at once.

* Based on a paper by J. Alexander and Calvin B. Bridges in Vol. II of Alexander's "Colloid Chemistry, Theoretical and Applied."

If we would form a precise mechanical picture of what occurs in life, we must dissect down through the layered structure of matter, until we reach the simplest unit which can be regarded as living. As the complications of structure fall away, the tiny ultimate vital units indicate that, from their ultra-microscopic domain, they direct and dominate the material changes of life, spinning the thread of life like the Norns of Norse mythology.

Geneticists, cytologists and other biologists all agree that in normal cellular reproduction each chromosome may be seen to double its mass, to move to the equatorial zone of the cell, to divide into two equal parts, each part moving towards one of the two polar bodies at opposite ends of the cell. Thus when the cell divides along the equator, we have two cells, apparently identical, each tending to reproduce itself in like manner. The genetic evidence indicates that the chromosomes, which themselves bulk quite small in a microscopic field, are composed of very large numbers of particulate sub-units (genes or genels), which in size must be of the order of large molecules or small molecular groups; and further, that this same evidence (especially linkage and crossing-over) indicates that each of these chromosomal sub-units actually reproduces itself *next* to itself. Normally, genic reproduction is self-duplication *in situ*.

Since the addition, removal, or modification of these sub-units produces marked and characteristic changes in the cell and in what develops from it, we are justified in regarding them as specific catalytic particles which direct chemical changes within their respective domains, and thus dominate life processes.

It is the genes within the gene-strings or chromosomes, which determine whether a certain cell will develop into a flea, an elephant, or a man.

To epitomize the biological evidence, we have colloidal particles of the order of molecular dimensions, which actually duplicate themselves from what is admittedly non-living matter, and which control and direct the material changes of life. Can we explain such behavior in the light of our present chemical and physical knowledge? It seems to us that this can be done.

Before considering the modern view of catalysis, let us first review some consequences of the structure of matter which make catalysis possible and specific. When electrons and protons combine to form atoms, when atoms combine to form molecules, and when molecules combine to form larger groups, there are always outwardly directed unsatisfied or residual fields of force, which may exert powerful attractions or repulsions on other particles which come within the so-called range of molecular attraction. If we consider a single molecule or a very small molecular group, it is obvious that the residual electrostatic or electromagnetic mosaic presented to the milieu will be highly specific in various directions; that is, the particle or group may exhibit several different kinds of specific action, either separately or simultaneously.

Let us now imagine a simple molecule approaching and fixing itself at the surface of a particle having appropriate opposite charges to those which the simple molecule presents.

As soon as the oppositely charged areas come within their critical range, their mutual neutralization must

cause a reshuffling of all the electronic fields involved, so that the molecule after its fixation will present to the milieu a different configuration from what it presented before fixation. It might now be able, on its own account, to make other attachments previously not possible. The attachment of a second molecule to the first would once more cause a reshuffling of all the electronic fields involved. Now if the bond between the two molecules were to hold, while the bond holding them to the fixation particle were to break, we would have released to the milieu a new duplex molecule, while the fixation surface would be free for renewed action. The subjoined figure (Fig. 7)

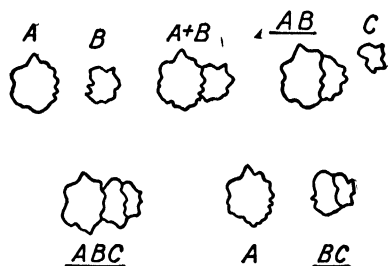


FIG. 7.

shows diagrammatically a synthetic catalysis of this character. It is evident that a reversal of the process would represent an analytic or destructive catalysis.

Suppose now that we have a catalyst particle composed of several simple molecular sub-units, which is on one of its areas conducting a continuous catalysis like those just described. Suppose that at some one of its other areas the catalyst fixes or adsorbs successively the several sub-units of which it is

composed; that because of the order of their fixation or because of subsequent inter or intramolecular changes, these component sub-units form a group identical with the fixation or catalyst group; and suppose lastly that the duplicate particles now separate or are separated. (See Fig. 8.) Each would be

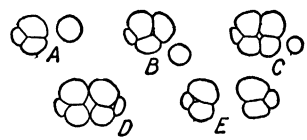


FIG. 8. Diagrammatic representation of a simple type of reproductive catalysis (or autocatalysis).

an exact duplicate of the other in catalytic and in self-duplicating behavior, and our original particle could be properly called an *autocatalytic catalyst.* It would duplicate itself from non-living matter and also would direct and control chemical change; and in these respects as well as in size, it would be identical in the nature of its behavior, with the simple genes we have essayed to explain. It would have to be considered as *living.*

The question naturally arises: Is there in nature, apart from the genes in a gene-string or chromosome, anything resembling our hypothetical free-living, self-reproducing catalyst particle? We believe that in the bacteriophages and the so-called ultrafiltrable viruses we are dealing with living beings (bionts) approaching or actually of this degree of simplicity. It is quite possible, though as yet unproven, that in some cases these ultimate biological units may be molecules, even if large ones.

To those who have brought the experimental proof, it is no longer news that if, prior to the self-duplication of a gene, the gene itself is modified by some non-lethal agent (X-rays, heat, chemical substances or variations in the milieu) the gene or genes thus affected may reproduce steadily true to the modified form; and the cell containing such modified chromosomal material, as well as the clone or living being (biont) formed from it, will show or tend to show the consequences due to the changes in the nature and action of its controlling catalysts, the genes. Thus arise mutations, and thus proceeds evolution; for apart from symbiontic cellular inclusions like chloroplasts, inheritance is carried by the genes or genels in the chromosomes. Strains whose mutations are not disadvantageous or lethal, will survive; if the mutations are advantageous, the strain will tend to dominate.

The cancer cell may be considered as a type of evil mutant, which, being formed or activated in a larger organism, duplicates itself specifically within its host, with destructive consequences. This view harmonizes with the fact that there are several different kinds of cancers, as well as the evidence that a cancer-mutant may be produced or activated by several different types of proximate causes, especially by those which produce gene-mutation—X-rays, heat, and chemical substances (certain tars). Since cancer cells reproduce true to type, even when transplanted, genic changes are evidently involved.

Considering now the bearing of these ideas on the origin of life, the law of probabilities makes it evident that no biont as complicated as even an amoeba or a bacterium could have arisen spontaneously, without

precursors. Much more likely is it that the first living thing was a molecule or simple molecular group exhibiting the directive and self-duplicating power

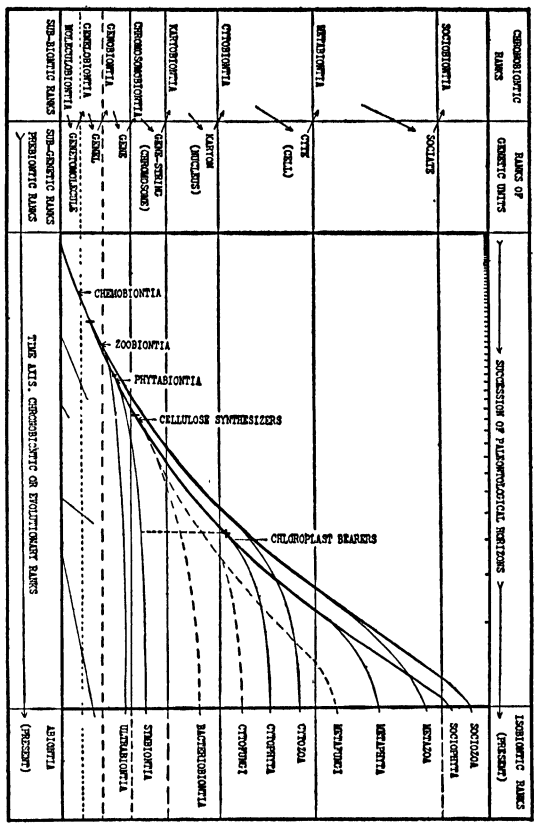


FIG. 9. Diagram of ranks of living units.

shown by genes. Indeed, in this ultramicroscopic zone, spontaneous generation may be continually occurring, without being recognized. The fact that no one has yet produced an autocatalytic catalyst does

not mar the demonstration of their existence. We can no more deny the existence of the genes of a giraffe than we can deny the existence of the giraffe itself.

Diagram (Fig. 9) wherein time is indicated logarithmically, as well as the other figures, are taken from Vol. II of Alexander's "Colloid Chemistry, Theoretical and Applied." It indicates the biological and evolutionary relations above referred to, which are there treated at much greater length.

To attempt to understand the chemistry of the catalytic action and of the autocatalysis of even the simplest ultramicroscopic biont, is in itself a formidable task. But when hundreds and thousands of genes join to form groups, chains or strings, where they and their products can mutually influence each other, the number of permutations and combinations becomes literally numberless. What happens is the result of a multitude of diverse factors and tendencies—*nature is, in fact, a compromise of tendencies.*

Much will be gained if we keep continually before us that all visible living beings exhibit a wheel-within-wheel or box-within-box structure and behavior, and that many facts, some apparently mutually contradictory when seen at different structural levels, may be simultaneously true. The further and deeper we search, the more complicated and wonderful does the whole become. Even though we explore certain areas as best we may, we always find more questions to be answered. *As we extend the frontiers of our knowledge, we likewise extend the frontiers of our ignorance.*

EXPERIMENTAL SUGGESTIONS OR LABORATORY MANUAL

I. Preparation of Colloidal Dispersions

A. Aggregation Methods.

1. Causing aggregation of dissolved substances by decreasing solublity.

(*a*) Tincture of green soap (alcoholic solution) is a clear transparent true solution of potash soap (mainly oleate). Stir a teaspoonful into a glass of water and note that there is at once produced a hazy colloidal solution, whose particles show active Brownian motion in the microscope or ultramicroscope. Evaporate off the water in a double jacketed pot and then note that on adding a glass of water to the residue, it again returns to colloidal solution, showing that the soap is a *reversible colloid.*

(*b*) Try a similar experiment with an alcoholic solution of gum mastic (or shellac). The gum forms a colloidal dispersion when some of its alcoholic solution is dropped into water, but when dried out, will *not* redisperse (*irreversible colloid*).

(*c*) Try a similar experiment with a perfume extract (alcoholic true solution of essential oils). The colloidally dispersed particles of the essential oils are liquid and we get an *emulsion.* On evaporation of the water, the more volatile portions of the oils go off with it; but the residual oil will (in general) not re-emulsify.

2. Causing aggregation of molecularly dispersed substances, by chemical change.

(*a*) Into a cup of *boiling hot* water pour a few drops

of ferric chloride solution (or tincture of chloride of iron, which is an alcoholic solution). The iron salt hydrolyzes, giving a rich brown colloidal solution of ferric hydroxide, and dilute hydrochloric acid. If most of the acid is dialyzed off, the colloidal solution will be quite stable (see U. S. Pharmacopeia for preparation of "ferri hyd. dialysat."). If the acid is allowed to remain, it produces a gradual flocculation of the iron oxid hydrosol. Compare its color with that of the same amount of iron solution mixed into a cup of *cold* water. This hydrosol may be stable though free from detectable traces of chlorine, thus disposing of the fallacious assertion that chlorine or hydrochloric acid are *essential* for its stabilization.*

(*b*) Put a few good sized pinches (say ¼ gram) of ammonium vanadate in a cup and drop on it about 10–12 drops of strong hydrochloric acid. The dark red-brown vanadic acid (V_2O_5) gel that forms is mixed with the ammonian chloride incidently produced. If this latter be dialyzed off (for details see p. 63), the pentoxide will form a dark brown fluid hydrosol, which may be diluted with distilled water without causing coagulation. If the diluted hydrosol be allowed to *age* for a few weeks (in a stoppered bottle to prevent evaporation), it will show, when dilute, a *streaky* appearance on being shaken or stirred. On ageing, rod-shaped aggregates are formed which are

* For details see C. Harvey Sorum, J. Am. Chem. Soc. (1928), *50*, 1263. Freundlich and Wossressensky (Kolloid Z. 1923, *33*, 222) also prepared stable electrolyte-free ferric hydroxide hydrosol by reducing iron carbonyl with hydrogen peroxide. P. A. Thiessen and Otto Koerner (Z. anorg. und allgem. Chemie 1929, *180*, 115) have also produced stable but sensitive electrolyte-free iron oxid hydrosols from iron ethylate.

oriented *at random* when the fluid is at rest, but which point in the direction of flow when the liquid moves, just as logs floating in a stream tend to point end-on to the current, though in a still lake they would point any which way. The phenomenon is known as *thixotropy* or *thixotropism* (Freundlich).

(*c*) Make a little gold chloride as follows: (1) Dissolve a little of the metal off from an old piece of gold jewelry by attaching it to a cotton thread and dipping it for a while into aqua regia (3 parts strong hydrochloric acid, 1 part strong nitric acid). (2) Put a strip of zinc in the metal solution; the dissolved gold *and* copper will precipitate out on the zinc as a black "mud." (3) Dissolve the copper from this mud with dilute sulphuric acid, which will leave the gold. (4) Dissolve the remaining black gold "mud" (after washing it) in as little aqua regia as possible, allow to evaporate to dryness, and dissolve in distilled water. This should give a bright yellow solution of chloride of gold, $AuCl_3$.

Let us now treat the chloride of gold so as to separate the chlorine from the gold. The liberated gold will *tend* to aggregate into particles large enough to settle out again as a black mud. We oppose this tendency either by using high dilution, by avoiding the presence of coagulating electrolytes, or by employing protective colloids.

Faraday's method. Stir 10–20 drops of the gold chloride solution into a carefully cleansed cup of distilled water, and then add about 10 drops of a solution of yellow phosphorus in ether.* A brownish

* This is poisonous and dangerous to unskilled persons. If necessary, have some experienced person do it for you.

or orange tint should slowly develop, gradually becoming ruby-red as the gold particles become larger. If the water is not sufficiently pure, further aggregation may occur, the solution becoming purplish, then blue or blackish, and depositing its gold. If a stable red hydrosol is not obtained, repeat the experiment, adding a little gelatin or gum arabic solution *before* adding the phosphorus.

Zsigmondy's method. To the diluted gold solution, add a drop or two of potassium carbonate solution. Then add a few drops of formaldehyde to reduce the gold, having first warmed the gold solution. If a protector is needed, use gum arabic, as formaldehyde combines with gelatin.

Wo. Ostwald's method. Warm the gold solution and add a few drops of a solution of tannic acid, which not only reduces the gold, but also serves as a protective colloid. If no tannic acid is available, a little may be dissolved out of a piece of *washed* sole leather by ammonia, and the ammonia boiled off.

B. Dispersion Methods.

1. *Mechanical.* Put a small lump of clay in a mortar; add enough water to make a thin cream, and grind, and *grind, and grind.* It will greatly help to add a little gelatin, gum arabic, or tannic acid dissolved in *weak* ammonia. Mix the thoroughly ground mass into a quart of distilled water, and allow to stand a few days. Depending on circumstances, more or less of the clay will still be afloat as a colloidal suspension, the balance having settled out.

2. *Deflocculation.* Put about ¼ teaspoonful of lamp black (or carbon black) into a warm ½% soap

solution and shake well. The carbon particles should be separated and form a stable black dispersion. Try the same experiment, using zinc oxide and 1% gelatin solution.

3. *Emulsions.* Make mayonnaise according to any of the good cook book recipes. Or shake up a teaspoonful of olive oil in a warm ½% soap solution.

4. *Spontaneous dispersion.* ("Natural" colloids.)

(*a*) Stir gum arabic in cold water; a colloidal solution results.

(*b*) Soak a bit of gelatin or glue in cold water until it is soft (powdered gelatin softens immediately). Then warm. A colloidal solution is obtained, which will set to a jelly if sufficiently concentrated.

(*c*) Stir a little starch in cold water and note that it quickly settles out on standing. Stir it up again and heat to burst the starch grains; a paste or sol results, depending on concentration. Or the starch may be made to burst by stirring in some 10% lye solution. If the dissolved starch be boiled with hydrochloric acid, it is slowly converted into non-colloidal sugar, thus passing downward through the three stages: (1) suspension, (2) colloidal dispersion, (3) crystalloidal dispersion or true solution.

(*d*) Milk contains salts and sugar in crystalloidal solution; casein etc. in colloidal dispersion; and fat in emulsion. The cream layer that rises consists of a dispersion of fat in an aqueous medium, and will *wet* blotting paper. When beaten to butter, we get a dispersion of water in fat, which *greases* blotting paper. Put some butter in a frying pan and fry out the water from it—note how it splutters until all the water is gone.

II. Optical Effects

Faraday-Tyndall effect.—Add a little of any of the colloidal solutions made as per I, to a glass of distilled water, put the glass in a darkened room or in front of a black cloth, and then allow a narrow beam of sun-light (or bright electric light) from a small hole or slit in a piece of metal or cardboard, to pass through the glass. Examine the beam, looking at right-angles to its course. The beam becomes visible because the tiny particles in it diffract or scatter the passing light.

Similarly, a searchlight cuts a "path" through hazy or foggy air at night, and in a sunbeam, especially against a dark background, we see the otherwise invisible motes. A magic lantern or projector shows the same phenomenon; tobacco smoke, mica dust, or other fine powders may be used to make the air hazy. Apply the light beam to the aged vanadium pentoxide sol (page 235) and note the peculiar silky streaked effect of thixotropism.

Note the color changes evinced as substances change in degree of dispersity—gold passes from bright yellow, through orange, ruby red, purple and violet, to black, as the particles grow larger. Very fine particles tend to scatter the shortest waves of light (blue); therefore very dilute milk, looks "blue." The longer red waves are not so readily scattered. Therefore sunset colors generally transmitted are reds, oranges, and yellows (the blue being scattered out); and red danger lights are visible further in hazy air than blue lights.

III. Diffusion, Dialysis, Filtration, Ultrafiltration

Diffusion.—Put drops of various colloidal solutions, and also of red ink (eosine) and violet ink (methyl violet) on a piece of clean white blotting paper, and see that in some cases the dispersed material will diffuse to the outside of the drop with the water, which, as a rule, soon outruns the colloid material, and makes a colorless "water" ring beyond it. With ferric hydroxide sol and India ink, the colloid material hardly diffuses at all, and the clear water ring is larger. Try solutions of various Easter egg, and other "dyes." Also milk and cream.

Mix several different dyes, or mix dyes with ultramarine blue and India ink, and then drop the mixtures on a clean white blotter. Note that some dispersed substances diffuse further and faster than others, thus causing separation by *differential diffusion.*

Patriotic Test-tube.—Make the patriotic test-tube experiment described on page 68. The phenolphthalein may be obtained from the druggist, or from any of the common laxatives which contain it.

However, a good substitute indicator can be made from ordinary red-cabbage, by boiling some leaves to extract the purplish coloring matter. Vinegar (acid) turns it bright red; lye (alkali) turns it bright blue; and ammonia turns it green. If the agar solution be made up with red-cabbage water, the whole tube will, originally, be purplish, and the acid band will show red instead of white, the Prussian blue band being the top one, as before, but slightly modified in shade by the cabbage-water color.

Dialysis.—Dialyzing thimbles may be bought, or

may be made thus: pour some collodion into a large test-tube or a small flask or glass, roll it about so as to cover the entire interior and pour off the excess. After allowing the collodion to "set" for say half a minute, carefully pour in cold water, and when the collodion film has become tough, remove it from the glass. Introducing a little water between the glass and the film, at the mouth of the vessel, is a great help.

Put a mixture of gum arabic and salt solution in the dialyzing thimble, close its neck with a rubber band, and then hang it into running water, or into water which is frequently changed. Taste will readily show that the salt passes through into the outer water, while the gum which remains behind, becomes less salty. To prove that the gum is mostly left behind, evaporate the contents of the thimble and recover the gum.

Another simple way to make an efficient dialyzer is to place a folded filter paper in a funnel (the filter paper should project above the edge of the funnel), pour collodion into the filter paper so as to coat it thoroughly, drain off the excess collodion, and then allow water to flow upward through the funnel tube from a rubber hose attached to the cold water tap. When the collodion film has set, wet its upper surface with cold water, and drain off. Then place the mixture to be dialyzed in the filter paper, and open the tap slightly, so that a continuous supply of fresh cold water flows up through the funnel tube and laves the under side of the collodionized filter paper.

Colloids may be freed from diffusible impurities (salts, acids, alkalies etc.) by dialysis. Often some of the colloid itself is lost, for many colloids diffuse

perceptibly. The more concentrated the collodion solution, the "tighter" or more resistant to diffusion the dialyzer will be.

Instead of using collodion, a warm weak (½ to 2%) gelatin solution may be poured into the filter paper in the funnel, the excess drained off and replaced by a 5% solution of formalin. Let this soak in for about 1 hour to harden the gelatin and render it partially insoluble.*

Filtration.—Add hydrochloric acid to a solution of silver nitrate. Note that the white precipitate of silver chloride readily settles out on standing, and will not pass through an ordinary filter paper. Repeat the experiment, adding some gelatin or gum arabic solution to the silver nitrate *before* addition of the acid. Note that the precipitate of silver chloride does not settle out and will readily pass through the same kind of filter paper.

Ultrafiltration.—Where diaphragms are sufficiently close or "tight" to prevent, largely or completely, the passage of a certain colloid by filtration, the fluid medium and even the colloid itself may be *forced* through by application of pressure. Generally, simple apparatus is not possible; but the principle may be demonstrated by attaching *one end* of a rubber balloon with double outlets (e.g., obtained from a toy "bagpipes") to a dialyzing thimble; and blowing the balloon up, securing *the other end* to maintain the pressure. A glass tube over which has been slipped a piece of rubber tubing, makes a good connection between the balloon and the thimble, and can be tied air-tight.

* Formalin (40% formaldehyde) is poisonous, and will harden the skin.

IV. Surface Tension, Viscosity, Swelling

Surface Tension.—(1) Dip a brush with long, soft hairs (camels' hair brush) into water and note that the hairs tend to float free of each other. Now withdraw the brush, and notice that the drawing together of the water-films between the hairs, pulls the hairs tightly together (W. D. Harkins).

(2) Float a small drop of fat, butter, or olive oil on the surface of hot water. The surface tension of the droplet tends to form a sphere, but this is flattened out by gravity into a lens-shaped drop. (A mercury droplet on a glass plate is nearly spherical, owing to the high surface tension of mercury.)

Now add to the water some lye solution (caustic soda), and note that the fat droplet breaks up into a fine emulsion. The main factor here is the formation of some *soap*, by the action of the alkali on the fat or on its free fatty acid (usually present); and this soap *lowers* the surface tension at the interface between the fat and the water (F. G. Donnan). Emulsification can, therefore, also be produced by adding a little strong soap solution, instead of adding the lye. Slight agitation may be essential to effect emulsification.

Spreading.—Dust a little talcum or other light powder on the surface of a glass *full* of water, and touch the corner of a bit of soap into the center of the surface of the water. The soap instantly spreads over the water as a superficial film, and drives the floating powder to the rim of the glass. Oleic acid and camphor will act in the same manner as does the soap. These surface films are only *a few*, and often only *one* molecule deep. If enough of the film-forming mole-

cules are present and they are long and *polar* (i.e., show greater attraction to air at one end and to water at the other), the molecules may pack together like logs floating end up. With fewer molecules, they may float lengthwise in the water and may leave bare gaps. Make experiments using large vessels (dish-pans, etc.) and smaller and smaller amounts of soap, camphor, etc. The area over which they spread is shown by the talc, and can be measured and compared with the amount of spreading agent used (I. Langmuir).

Soak some match-sticks or toothpicks in soap solution and then dry them out. On floating the soaped sticks on water, note how they float *apart.* Now add some acid (vinegar, hydrochloric acid) and see how the sticks approach and cling together.

Surface Orientation of Molecules.—Put a piece of pure stearic acid (or other pure solid fatty acid) about the size of a pea, on the surface of a cup of *hot* water. The fatty acid should melt to form a lens-shaped drop, which solidifies again as the water cools. When the fatty acid is thoroughly hard, remove it and dry carefully without disturbing the surface—or allow it to stand in a cool place until it drys spontaneously.

Note that the bottom of the lens which has solidified *in contact with water,* can be wet by water; whereas the upper surface of the lens, which has solidified *in contact with air,* repels water. The "oily" ends of the molecules of fatty acid are directed outward in the upper surface, whereas the "water-loving" or hydrophile ends are directed outward in the bottom surface of the lens of fatty acid (Devaux).

Capillary Rise.—If a clean glass tube with a very small, hair-like (capillary) bore is dipped into clean

water, the water rises in the tube, due to the surface attraction between the glass and the water (*wetting*). The *height* to which the water rises, depends upon the *strength* of its film at the glass surface, that is, upon its surface tension, because gravity tends to drag the water down, and the strength of the film must just balance the gravitational pull on the column of water.

A bit of broken thermometer tube, open at both ends is good to use, as it is graduated, and you can see the effect of adding soap, lye, acid, etc. to the water. See how far alcohol will rise. A medicine dropper with a long thin point and the rubber bulb removed, will show capillary rise to a slight extent.

Staglomometer or "*Drop-measurer.*"—Use an ordinary medicine dropper or a pipette, and count *how many drops* you get from the *same volume* of different liquids; e.g., alcohol, having a lower surface tension, gives *more drops* than water, because the drops tear loose more readily, despite the fact that water has a much greater weight for the same volume of drop. Try pure water and then soap-water. Soap lowers the surface tension of water against air, and we get more drops.

Viscosity.—Soak the *same* amount of gelatin in *different* amounts of cold water, and when softened, dissolve by warming. Note how much "thicker" or viscous the more concentrated solutions are than the more dilute ones. Watch the solutions as they cool, and note how the viscosity of each solution increases as it cools, and finally jells if the solution is sufficiently concentrated (over about 1–2%).

Make 5% and 50% solutions of gum arabic by prolonged soaking and stirring of the gum in cold

water. Compare the viscosities of these solutions, cold and hot. Evidently, viscosity is increased by concentration and low temperature, both of which tend to increase molecular aggregation and thus increase the *internal friction*, which is responsible for viscosity. (If particles get too large, however, viscosity again falls—see p. 72.)

Zone of Maximum Colloidality.—Mix about 2 parts by weight of starch into 100 parts of *cold* water (say a teaspoonful of starch to a large cup of water). Note that the viscosity of the *suspension* is not appreciably different from that of water.

Now, while stirring steadily, pour in some 10% lye solution, until the mixture begins to thicken and get clear. Cease adding lye and stir steadily until the thick mass becomes smooth and clear. Note how the viscosity increases as the lye bursts the starch grains and makes of them a *colloidal dispersion*. On prolonged stirring, the paste will get somewhat thinner.

Then add *enough* strong * hydrochloric acid to neutralize the alkaline lye; this may be gauged by the paste becoming white and opaque. Add a little more acid to be sure that the mixture is well on the acid side, and then boil. On boiling, the acid hydrolyzes the starch into much more finely dispersed dextrins and sugars. Note how the viscosity falls as dispersion proceeds towards true or crystalloid dispersion. We have therefore run the gamut of viscosity thus:

Low Viscosity	High Viscosity	Low Viscosity
Suspension of starch (coarse dispersion).	Colloidal dispersion of starch (intermediate).	Crystalloidal (sugar) and fine colloidal (dextrin) dispersion of split-up starch.

* If weak acid be used, the paste is thinned by the contained water.

Obviously, *somewhere* in the colloidal range, there must be a *zone* (or point) where the viscosity is a maximum. This may be observed by careful watching.

Swelling.—Break up a *sheet* of gelatin into several pieces, which will have the same initial thickness. Immerse one piece of each of the following: distilled water; tap water; ½% hydrochloric acid; 5% hydrochloric acid; ½% hydrochloric acid + ordinary salt (about 5%); ½% lye solution. Allow to stand over night.

Note that the gelatin swells more in weak acid and in weak alkali than in pure water. Salts and stronger acid depress the swelling.

Fibrin is much more sensitive than gelatin in this respect, and shows marked swelling differences with small differences in the composition of the water bath—e.g., it swells much more in ordinary distilled water (which has a pH of about 5.5 due to absorption of atmospheric carbonic acid) than in *freshly* distilled water (pH about 7).

V. Adsorption

Liquid Solid.—(1) Wash some bits of white woolen cloth (flannel) or yarn thoroughly with soap and warm water, and rinse well. Then drop them into a warm dilute solution of green (malachite green) or violet (methyl violet) ink, and note that much of the color, *but not all,* is taken up by the wool, which becomes *dyed.* Try the same experiment with white washed silk. A *dilute* solution of any basic aniline dye (silk or wool dyes) may be used. Dyeing takes *time;* therefore early removal from the dye bath gives a lighter shade.

Dyes may generally be abstracted from their solutions by charcoal, which, when washed, will not give up the color to water, but will give it up to alcohol. This solvent also "strips" many colors from silk or from glass or porcelain. Observe the effect of *very small* * additions of acid (hydrochloric) and alkali (lye) on the adsorption of the dye by wool, silk, or charcoal.

(2) Cut up a thoroughly "dirty" dust rag, after having shaken out all loose dust, and place pieces in (*a*) plain water, (*b*) vinegar-water, (*c*) ammonia or borax water, (*d*) soap-water. Note how the soap and the alkalies free the firmly held "adsorbed" dirt from the fabric. Heat helps the process.

Obviously, adsorption is a reversible process, and therefore tends to reach an equilibrium; so that while *more* dye may be adsorbed from a strong solution than from a weaker one, a *larger percentage* of dye is adsorbed from the weaker solution.

Liquid/Liquid.—Shake a little lamp black or carbon black (soot will serve) with a mixture of water and carbon tetrachloride (Carbona will do). Note that the carbon remains with the heavy bottom layer of tetrachloride when the two immiscible liquids separate. On the other hand, if we use clay instead of lamp black, the clay will remain with the water. With a mixture of clay and lamp black, we may effect a separation of the two. Observe the effect of the mixed solvents on powdered galena (lead sulphide), flowers of sulphur, and copper sulphide, and then read the section on "Flotation" (p. 110).

* Stronger lye will dissolve wool and silk, but not cotton. Therefore if an "all wool" cloth leaves a residual lot of fiber in strong lye, we suspect the seller of error.

Liquid/Gas.—(1) Mix some soap powder or soap into hot water, and beat up a good "suds." Skim off these "suds," and repeat the operation again and again. Finally, no more suds will form, because the soap is selectively adsorbed at the air/water interface of the suds bubbles, and is thus gradually removed.

(2) Hold a poker or other bit of soft iron pointing north and south, with an inclination or "dip" that will direct it toward the earth's magnetic pole (about 45° dip in temperate latitudes). Then hit it sharply several times with a hammer (this tends to make the poker, temporarily at least, magnetic). Now rub *one end* of a thin sewing needle from the *center* of the poker to one end of the poker, repeating this about a dozen times (this tends to magnetize the sewing needle).

Next coat the needle with a thin film of vaseline or grease—enough may generally be secured by wiping the finger alongside the nose—and carefully *float* the needle on a full glass or cup of cold water. The surface tension between the water, the air, and the adsorbed film of grease is sufficient to make the needle float. If the magnetization has been successful (as is generally the case), the needle will slowly point north and south, thus serving as a *household compass.* It may be made to follow any nearby piece of iron, just like a compass-needle (R. Ogden Doremus).

Colloidal Protection.—Make the experiments with silver nitrate as explained on page 58, and see the effects of ordinary and of double colloidal protection.

Use distilled water, as most tap waters contain some chlorides.

VI. Electric Properties

Electrophoresis.—Join a strip or rod of clean zinc to a strip or rod of clean copper by a bit of copper wire in tight electric connection. Immerse this "electric couple" in various colloidal solutions, preferably faintly acid ones, and see if there is not an accumulation of the dispersed material at either "pole." Positively charged particles go to the copper; negatively charged ones to the zinc.

Any small dry cell may be employed to supply a potential (current)—e.g., a radio C battery.

Precipitation of Oppositely Charged Colloids.—The dispersed particles in ferric hydroxid sol (colloidal iron oxide) are positively charged, while those in gum mastic sol (see p. 70) or in gum arabic solution are negatively charged. Therefore colloidal iron oxide will precipitate mastic sol, and *vice versa.* The iron sol will also precipitate gum arabic solution, *unless too much gum is added all at once;* for the excess of gum then acts as a colloidal protector towards the newly forming precipitate, and keeps it in colloidal state, thus preventing it from settling out.

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GLOSSARY

For the convenience of the reader, most of the less common terms employed by colloid chemists are here collected and briefly defined.

absorption—passage of a liquid into a solid or a gel by the action of capillarity; e.g., water by a sponge, ink by blotting paper.

adsorption—binding of a finely divided substance (a gas, liquid or colloidal dispersion) to an interface.

allocolloid—one allotrope colloidally dispersed in another, e.g., as with sulphur.

amicron—a particle invisible in the ultramicroscope, usually less than about 5 $\mu\mu$ in diameter.

colloid—any substance when dispersed into particles whose sizes may vary between the approximate limits 5 $m\mu$ and 100 $m\mu$. The individual particles may be tiny crystals, or haphazard, random or amorphous groups; or mixtures of the two may coexist. Fineness of dispersion is the critical factor, but the effects of dispersion extend beyond the limits stated.

deflocculation—dispersion of aggregates or flocculates.

emulsion—a fine dispersion of one liquid in another. The dispersed particles may or may not be of colloidal size; if not they usually form a cream layer on standing long enough.

emulsoid—a colloid dispersion in which both phases are a liquid.

gel—an aggregation of colloidal particles into practically non-motile larger groups. Internal readjustment may cause syneresis (q.v.).

hydrophile—literally "water-loving"; applied to colloids which tend to remain dispersed, hold water or remain in solution (see lyophile).

hydrophobe—literally "water-hating"; applied to colloids which tend to aggregate and shed water, or fall out of solution (see lyophobe).

hysteresis—time-lag in the aggregation of colloidal particles.

interface—the surface between two phases.

irreversible—a colloidal dispersion that will not redisperse after desiccation at ordinary temperatures.

isocolloid—a substance colloidally dispersed in itself, e.g., as colloidal ice in water.

Liesegang's rings—bands or rings usually regularly or rhythmically placed, which form when precipitates are produced by diffusion in jellies or similar structures.

lyophile—literally "solution-loving"; same as hydrophile, but also applicable to dispersion media other than water.

lyophobe—literally "solution-hating"; same as hydrophobe, but also applicable to dispersion media other than water.

micron (μ)— $\frac{1}{1{,}000}$ mm.

milli-micron ($m\mu$)— $\frac{1}{1{,}000}\ \mu = \frac{1}{1{,}000{,}000}$ mm. = 10 Å.

orientation—disposition in space or on a surface, relative to certain points, lines or surfaces. Opposed to molecular chaos.

pectization—gelatinization; an aggregation of colloidal particles into masses of sufficient size to be substantially devoid of Brownian motion, the resulting mass forming a flocculent precipitate; gel, or jelly, according to conditions.

peptization—the reversal of pectization; the dispersion of a solid colloid by an enzyme (e.g., pepsin, whence the term) or by simple action of a dispersing agent (e.g., of $FeCl_3$ gel by traces of HCl, SiO_2 gel by traces of NaOH), or by heat (gelatin).

protection—inhibition of aggregation.

protector—a substance, usually a reversible colloid, which prevents or tends to prevent the aggregation of colloidal particles.

reversible—a reversible colloid is one that redissolves after desiccation at ordinary temperatures.

sol—a colloidal dispersion whose particles have sufficient Brownian motion to keep them in solution. The dispersing medium is often employed as a prefix: e.g.,

hydrosol = in water
sulphosol = " H_2SO_4
alcosol = " C_2H_5OH
aerosol = " air
pyrosol = " a melt (glass, metal, etc.).

specific surface—external, free, or rind surface per unit wt.

submicron—ultramicron.

suspensoid—a colloid in which the dispersed phase is a solid.

syneresis—aggregation of particles in a gel, with incidental liberation of liquid.

ultrafiltration—filtration (usually under pressure) through very close pored gels or jelly septa.

ultramicron—a sub-microscopic particle visible in an ultramicroscope.

ultramicroscope—a compound microscope having a dark field and means of intense illumination of the object to be examined by a beam of light preferably at right angles to the optical axis of the microscope. Particles are thus seen by the light they diffract.

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