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COLLOIDAL CHEMISTRY

HERBERT FREUNDLICH

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THE ELEMENTS OF COLLOIDAL CHEMISTRY

BY

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PREFACE

SUGGESTIONS have reached me from various quarters, that by abbreviation and excision of mathematical deductions and numerical data, my *Kapillarchemie* might become an introduction to the chemistry of colloids for a larger number of students of medicine and technology. Since several books of the kind already exist, I at first viewed this plan with misgivings, but ultimately overcame them, when I realized that the facts and ideas, which to my mind are of special importance to colloidal chemistry, had not yet been presented in simple language. I hope that I have succeeded in doing this in the present book. I desire to thank Professor G. Barger of Edinburgh and Dr. med. R. Stern of Breslau for valuable hints and suggestions, and also Dr. L. Farmer Loeb for reading the proofs.

H. FREUNDLICH

DAHLEM, JANUARY, 1924
KAISER WILHELM INSTITUTE
FOR PHYSICAL CHEMISTRY AND
ELECTROCHEMISTRY

TRANSLATOR'S NOTE

I WAS so impressed by the manuscript of Professor Freundlich's *Grundzüge der Kolloidlehre* that I at once undertook its translation, as a token of my appreciation of the work, in the hope of introducing it to a large number of English-speaking students. Various colleagues in this university have been good enough to discuss with me the rendering of technical terms and Dr. Edgar Stedman has read the proofs and made valuable suggestions, for which my thanks are due.

G. B.

UNIVERSITY OF EDINBURGH

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INTRODUCTION

THE view that matter is built up of individual, minute, sharply defined particles has during recent years met with conspicuous and acknowledged success. It was first successfully applied to gases, of whose properties we can give an excellent representation when we conceive them to be composed of minute particles, the **molecules,** swarming about in rapid motion. In order to give an idea of molecular dimensions, we may recall that the diameter of a hydrogen molecule, regarded as a sphere, must be about 0·2 millionth of a millimetre and that at 0° and 760 mm. 27 trillion[1] molecules are contained in a cubic centimetre of a gas. Quite generally the gram-molecular weight of any substance contains 0·6 quadrillion[1] molecules. We approach somewhat nearer to a realization of these numbers by the following illustrations. The ocean contains something like 1,300 trillion litres, and since a single litre of water consists

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[1] In accordance with a common usage, we mean here by billion 10^{12}, by trillion 10^{18}, by quadrillion 10^{24}. Hence there are about 600,000,000,000,000,000,000,000 molecules in a gram-molecular weight.

of 33 quadrillion molecules, there are many more molecules in a litre of water than litres in the ocean. If we poured a litre of water into the sea, and after complete mixing took another litre of water out, the second litre would still contain 25,000 of the original molecules which we had poured away.

Van't Hoff made a great advance by showing that a substance is present in dilute solution in a condition similar to that of gases. In aqueous solution sugar is therefore divided up into single molecules which move about the liquid without any regularity, and almost independently of one another, like the molecules of a gas. The only difference is, that the sugar molecules are separated from one another by water molecules, whilst a vacuum separates the molecules of a gas. We must at once emphasize that the molecules of a dissolved substance, the **solution molecules,** do not necessarily consist of single molecules of the dissolved substance only; thus in the case of sugar each sugar molecule certainly binds a number (at present unknown) of water molecules.

The molecules consist of **atoms,** the smallest particles into which a chemical element can be subdivided. There are therefore as many kinds of atoms as there are chemical elements. But not even the atoms themselves are uniformly filled by matter, they too have a definite build. Among the various theories of atomic structure, put forward during recent years, that developed by Rutherford and Bohr has met with special success, for it has been of the greatest assistance in interpreting the spectra of the elements, largely on a quantitative basis. According to this theory an atom may be regarded as a diminutive planetary system.

An exceedingly minute, positively charged **nucleus,** with a radius of something like one billionth of a millimetre, is situated in the centre of the atom; round it a definite number of electrons revolve in circular or elliptical orbits. The number of these electrons increases in a definite manner with the atomic weight of the element. The **electrons** are negatively charged particles whose mass is about $\frac{1}{2000}$ of that of a hydrogen atom. They are not only known as structural units of the atom, but also appear in the free state in many natural phenomena: thus cathode rays are streams of rapidly moving electrons.

Gases, liquids, and crystalline solids may be regarded as composed of molecules and atoms. Liquids sensibly resemble gases, in that they too consist of molecules in irregular motion, only their molecules are much more closely crowded than those of a gas. The special peculiarities of the liquid state have hitherto been explained only to a small extent. A very different case is presented by crystalline solids, such as common salt; here the structural units (" bricks ") are not molecules, but atoms with an electrical charge, the so-called **ions.** Each ion occupies a point of a so-called **space-lattice** and executes there an oscillatory movement of small amplitude. We can form an idea of a space-lattice by imagining a large number of uniformly woven nets arranged parallel to each other at regular intervals. At each knot in the network there is an atom, in the case of sodium chloride alternately a sodium ion and a chlorine ion. The distance between two points of the space-lattice in sodium chloride is about 0·3 millionth of a millimetre. The mutual arrangement of the points of the space-lattice varies with the crystal form of the solid.

All the structural units which have so far been considered, viz. molecules, atoms and electrons, are smaller than one millionth of a millimetre ($1\ \mu\mu = 0{\cdot}0000001$ mm.). There are, however, many structures in which we must take larger units into account, and these all belong to the **colloids.** We know there are, for instance, solutions which differ from ordinary ones in that their solute will not pass through parchment paper, collodion, etc. Thus if we place an aqueous solution of sugar or of sodium chloride in a sack of parchment paper, the sugar and the salt gradually pass through the membrane. This is, however, not the case when a solution of gelatine or of starch is similarly treated. We have every reason to assume —and other observations confirm this—that in the latter solutions there are much larger solution aggregates than in those of sugar and of salt. The molecules of these substances pass through the pores of the membrane, whilst the particles present in gelatine and starch solutions are unable to do so. In this way Graham was led in 1861 to differentiate solutions of egg white, gelatine, etc., as **colloidal solutions** or **sols** from the ordinary true solutions of salt and sugar. The term "colloid" is derived from ἡ κόλλα, glue, because this substance gives a typical solution of this kind. The passage of dissolved substances through membranes is called **dialysis.** Colloidal solutions are therefore characterized by the fact that they do not dialyse. Ever since Graham's time dialysis has remained one of the best means of recognizing colloidal solutions as such. If we desire to ascertain whether a solute is in colloidal or in true solution, we place it in a dialyser, such as a sack of parchment paper, hang this in a vessel filled with pure water and test whether or no the dissolved substance appears in the external liquid. If, even after a long time, the solute cannot be demonstrated outside the dialyser, the solution is colloidal. In this way we can for instance readily ascertain that the brown colouring matter of tea is a colloid, for on dialysis it remains inside the dialyser, whilst the sugar with which the tea has been sweetened, passes out.

The question now arises as to the size of the particles of a colloidal solution. The ordinary microscope does not reveal them, even at the highest magnification available. The smallest particles which can be seen in this way have a diameter of about $\frac{1}{2000}$ mm. = 0·5 μ. Colloid particles are therefore still smaller. Siedentopf and Zsigmondy succeeded in 1903 in constructing an apparatus, which in favourable cases allows of the recognition of particles having a diameter of one hundred thousandth of a millimetre. This

ultramicroscope depends on a phenonemon similar to that which renders visible particles of dust, when a powerful sunbeam enters a dark room and is viewed against a black background. In the ultramicroscope a colloidal solution, placed under the objective, is illuminated laterally by a powerful beam of light and care is taken that no portion of this light enters the microscope directly. The particles in the colloidal solution diffract the light which falls on them, just as the much coarser dust particles reflect the sunlight. Some of the light is scattered upwards and enters the microscope, thus rendering the colloidal particles visible. As has been pointed out, the phenomenon is merely similar, not identical in the two cases, for the minute particles present in sols cannot strictly speaking reflect light, as they are too small compared with its wave length; they diffract it, and in this process the incident light is changed in various ways.

With the aid of the ultramicroscope it has been possible to demonstrate in many sols particles having a diameter of 10–500 $\mu\mu$. Not all colloidal solutions can, however, be resolved in this fashion; in some the particles are too small, less than 1 $\mu\mu$; in others the particles are large enough, but their optical properties do not differ sufficiently from those of the surrounding liquid. Thus gold particles in colloidal aqueous solution are very distinct, provided they are sufficiently large, because the optical properties of gold are so very different from those of water. On the other hand the particles of colloidal protein or starch solutions are generally invisible, since the solution molecules here contain so much water, that their optical properties closely resemble those of the surrounding fluid. The ultramicroscope is therefore a powerful aid in the recognition of the colloidal nature of a solution, but we must not infer the absence of colloidal particles from the failure of the ultramicroscope to reveal them.

When Graham first distinguished colloids he believed that, in addition to their incapacity to dialyse, he could ascribe yet another property to colloidal solutions. He was struck by the fact, that when solutions of protein, starch, etc., are evaporated, the solute appears in the form of amorphous masses, jellies or varnish-like pellicles, whereas in the case of true solutions (of salt, sugar, etc.) well-formed crystals generally appear. In Graham's mind the concept non-crystalline, amorphous-solid therefore connoted that of the colloidal state. Now this connotation has been found to be erroneous, or rather, it is found to be inexpedient. The particles of many sols, such as gold sols, which play so important a part in colloidal chemistry, are crystalline, not amorphous. Nowadays we accordingly mean by colloid a certain state of subdivision of matter; structures are termed colloids, when they consist of two or more phases and the structural units of at least one phase have a magnitude of 1–500 $\mu\mu$. It does not matter whether these structural units are excessively large single molecules, or whether they are crystalline particles, amorphous-solid particles, droplets, or gas bubbles, each consisting of many single molecules, although they are themselves minute. It will be remembered, that we mean by a phase a completely homogeneous condition, in which no portion can be distinguished optically from any other. A pure gas, free from dust or mist, is a homogeneous phase; so are also pure liquids, solutions of truly dissolved substances and homogeneous crystals. The concept "colloid" implies nothing whatsoever with regard to the state of aggregation of the particles. A clear glass cannot therefore suitably be called colloidal. It is indeed amorphous-solid, but it is uniform (homogeneous) and therefore not colloidal. Nor do we therefore speak of "colloidal substances" as Graham did. Theoretically any substance can be made to assume the colloidal form, that is to say, it can be subdivided in such a way, that it is not truly dissolved, but has only been subdivided down to particles having a diameter of 1–500 $\mu\mu$.

The more general concept **disperse,** introduced by Wolfgang Ostwald, is often useful in order to characterize the state of subdivision. Structures containing particles of a colloidal size, are **colloidal-disperse**; those which, like milk, contain coarser particles, visible under the ordinary microscope, are termed **coarse-disperse**; true solutions may be called **molecular-disperse.** The peculiarities which characterize the last-named, are not indeed wholly dependent on the molecular-disperse condition. The fact that the solution molecules contain, in addition to the solute molecule, a considerable number of solvent molecules is perhaps of still greater importance. In colloidal solutions we distinguish the **disperse phase,** namely that one, which like starch and gelatine, is subdivided into minute particles ; the surrounding liquid is the **dispersion medium.** The particles of the disperse phase are separated from one another and present convex surfaces to their surroundings. The dispersion medium is continuous and is separated from the disperse phase by concave surfaces. A similar distinction between disperse phase and dispersion medium can be drawn in all colloidal structures.

So far colloidal solutions have only been compared with real ones, and we conceived of them as arising through a continual increase in the size of the solution molecules. But we can approach the subject of colloids from another side. We have only to imagine that the particles of a coarse-disperse emulsion or suspension become so finely subdivided, that they are no longer visible under the ordinary microscope, but only under the ultramicroscope. This process is applied technically, when milk is rendered "homogeneous." The coarse-disperse, microscopically visible globules, with a diameter of about 3 $\mu\mu$, are broken up mechanically to an ultramicroscopic size and are hence rendered colloidal. As we shall see later, there are many processes by means of which we can pass from liquids or from solid substances having a coarse, continuous structure to colloidal solutions. It thus becomes evident, that it is really somewhat arbitrary to fix a superior limit to the colloidal state, above which the particles become microscopically visible. To a large extent coarse-disperse emulsions and suspensions also show the properties characteristic of colloidal solutions, only emulsions and suspensions are generally less stable, because their coarser particles settle more rapidly under the influence of gravity. Incidentally the object of rendering milk homogeneous is to delay the rising of the cream, that is the separation of fat globules. With coarse-disperse structures those properties which are connected with the extent of the interface, naturally become less prominent.

The increase in the total surface, resulting from the continued subdivision of matter, is indeed very important. Let us imagine a cube with an edge of 1 cm. divided into smaller cubes each with an edge of 1 mm., then these 1,000 cubes will have a total surface of 60 square centimetres. If we, however, make the cubes so small that they might be particles of a sol, if we give them for instance an edge of one millionth of a centimetre, one trillion cubes will be formed having a total surface of six million square centimetres, i.e. 600 square metres. Since many colloidal solutions contain one per cent. by volume of colloid we readily understand what enormous interfaces may be present in relatively small quantities of liquid.

At the interfaces between two phases a number of important chemical and physico-chemical processes take place : to investigate them is the task of **capillary** chemistry. Since in colloids the interface is so large, the chemistry of colloids is again and again concerned with capillary-chemical phenomena. It will therefore be convenient to discuss these first with reference to similar, smaller interfaces, directly susceptible of observation and measurement. In the following account a section on capillary chemistry will therefore precede the discussion of colloids.

Capillary chemistry does not, however, comprise the only set of physico-chemical phenomena, of which a knowledge is required for the understanding of the chemistry of colloids. The fact that Graham at first regarded the amorphous-solid state as a real means of differentiating colloids, shows that the state of aggregation of colloidal particles is important. We must therefore decide, how we can distinguish amorphous-solid from crystalline, and in particular we must inquire into the conditions which determine the appearance of a new phase. The preparation of many colloidal solutions consists in the production of colloidal particles in a true solution, in the shape of a difficultly soluble precipitate in a sufficiently fine state of division.

A third set of phenomena is related to those properties which connect colloidal solutions with true ones. We have already pointed out that the molecules of gases or of a dissolved substance are subject to rapid motion, that of heat. Now if we observe the particles of a sol under the ultramicroscope, or the coarser particles of an emulsion under the ordinary microscope, we see that these particles do not remain at rest, but are subject to an incessant, lively, dancing movement, which recalls that of a swarm of gnats. This phenomenon was observed as early as 1827 by the English botanist Robert Brown, in the case of fine powders suspended in water, for instance, granules contained in pollen grains of plants, and after him it is called the Brownian movement. It has been established, that this movement is indeed due to the heat motion of the molecules of the liquid, which collide with individual colloidal particles; the haphazard impacts produce the movement, somewhat as the kicks of football players determine the movements of a football. The phenomena connected with the Brownian movement may also suitably be discussed before we turn our attention to the colloids themselves, especially since the most important laws governing this movement were first discovered by means of coarse emulsions.

In the following survey we will therefore first discuss the physico-chemical foundations of the theory of colloids, indicated above, and then construct on this basis the theory of colloids themselves. Hitherto we have only referred to colloidal solutions or sols as examples of colloidal-disperse structures and to emulsions and suspensions as examples of the coarse-disperse. These are, however, by no means the only ones with which the subject of colloids is concerned. We obtain a survey of the simplest possibilities, when we couple in each case two states of aggregation and remember that either of these may figure both as dispersion medium and as disperse phase. In the following table the first-mentioned state of aggregation will be regarded as the dispersion medium, the second as the disperse phase. We then have :

Gaseous-liquid : Mists
Gaseous-solid : Smokes
Liquid-gaseous : Foams
Liquid-liquid : Emulsions
Liquid-solid : Suspensions
When colloidal-disperse these constitute colloidal solutions, sols or gels.
Solid-gaseous : Solid foams
Solid-liquid : Solid emulsions
Solid-solid : Solid suspensions

It will be seen, that such common formations as mists, smokes and foams belong to the subject of colloids. The gels are also important and comprise not only jellies, but also fibres, membranes, etc. Gels were formerly regarded as solid emulsions, i.e., colloidal-disperse droplets imbedded in a solid framework. More recent investigations have rendered this view improbable ; they are more likely sols, in which solid particles are so abundantly present, that the dispersion medium, the liquid, is reduced to very thin films, which, like a foam, separate the closely packed particles. Solid suspensions are represented by many glasses ; thus for instance the beautiful gold ruby-glass owes its colour to colloidal-disperse gold particles.

It may cause some surprise that in the above manner we pick out for detailed consideration a particular state in the subdivision of matter and a particular range in the size of particles. Nor has this procedure passed without challenge. Nevertheless I regard it as justified, even if it were only on the ground that so very many structures must be accounted colloidal. Without exaggeration it may be said that the vast majority of liquids and solids present in organized nature, belong to the colloids. All body fluids, cell sap, blood, lymph, etc., are colloidal solutions; they contain proteins as well as other substances in a state of colloidal division. All solid substances such as cell-walls, walls of blood vessels, muscle fibres, nerve fibrils, have the character of gels. Hence the chemistry of colloids has also an important bearing on all technical processes concerned with products derived from living matter. In tanning, dyeing, the production of fibres and of rubber, the preparation of food stuffs, etc., colloidal-chemical phenomena have always to be considered. The theory of colloids will not only remain one of the essential foundations of biology and physiology; it will also continue to be of decisive importance to technology.

THE PHYSICO-CHEMICAL FOUNDATIONS OF COLLOIDAL CHEMISTRY

A. CAPILLARY CHEMISTRY

THE subject of capillary chemistry may be divided into natural subdivisions, according to the nature of the interfaces which separate the various possible pairs of phases. We can thus distinguish the following interfaces :

liquid—gaseous
liquid—liquid
solid—gaseous
solid—liquid
solid—solid

For each pair of phases it is especially the **surface tension,** or more generally, the **interfacial tension,** a quantity characteristic of the interface, and its relation to chemical properties, which require discussion. On account of the complete rigidity of the interface between two solids, the section relating to this pair drops out, but in addition to those dealing with the other four pairs of phases, a fifth section will have to be devoted to capillary-electrical phenomena, in which electrical influences are connected with capillary-chemical ones. A sixth section will deal with the thickness of the interfaces.

1.—The Interface between a Liquid and a Gas

THE SURFACE TENSION OF PURE LIQUIDS

In the case of the liquid-gaseous interface, which will be discussed first, we are dealing with surface tension *sensu proprio*. This concept seems at first to present some difficulties to the understanding, and yet the phenomena which suggested it are of common occurrence and easy to observe. Thus small drops of a pure liquid, when not subjected to external influences, tend to assume a completely spherical shape. This is readily seen with drops of mercury, or of water falling on a dry, dusty floor or on a cabbage leaf. If the drops are large, they become flattened by gravity. For the same reason a falling drop of water assumes the well-known pear shape. A different kind of external influence shows itself, when a drop of water is placed on a clean glass plate. The drop does not remain spherical, but spreads and **wetting** occurs, as the result of forces acting between the glass and the water and preventing the assumption of a spherical shape. This wetting is seen very distinctly, when a drop of alcohol is placed on clean glass ;

the alcohol does not remain as a sphere, but at once spreads in a thin layer over the whole plate. On the other hand a dusty surface, or a plant leaf with a waxy coating, cannot be wetted by water, and then the liquid assumes that shape which is not influenced by any external force, namely a spherical one. Now the sphere is characterized by the fact, that *for a given volume it has a minimum surface.* If we were required to give to a fixed quantity of liquid the smallest possible surface, we should have to make it spherical. Since liquids, in the absence of an external force, spontaneously assume a spherical shape, we may conclude that they have inherent in them a tendency to make their surface as small as possible. It is then only a small step to conceive of this tendency as residing in a membrane, which envelops the liquid wherever it is in contact with a gas. The tension of this membrane is then the so-called surface tension of the liquid. The comparison to a stretched indiarubber membrane, which at once suggests itself, may only be instituted with caution : the tension in indiarubber changes with the degree of stretching, but a pure liquid has a constant surface tension at any part of its surface, no matter how large the surface may become.

Now the great variety of shapes which a liquid can assume, whether as drops, as jets or as menisci, can be explained on the assumption, that the liquid tends to acquire a minimum surface in contact with a gas. Interesting experiments, based on familiar phenomena, are described in " Soap-bubbles and the Forces which Mould Them," by C. V. Boys. We mention one example. The hairs of a dry brush, when separated in air, remain so under water, but are drawn together into a bundle with a much smaller surface, as soon as the brush is taken out of the water. The surface tension brings about a minimum interface between water and air.

From the great variety of shapes of a liquid surface there results a correspondingly large variety of methods by which the surface tension may be measured. Thus the latter may be deduced from the shape of jets issuing from a non-circular orifice, from falling drops, from the wave length of ripples produced by a vibrating tuning fork, from the weight and the curvature of a hanging drop, etc. Here we will only deal with two such methods. The heavier the drop which a liquid forms in slowly issuing from a tube, the greater is its surface tension. Since water has a relatively high surface tension, drops of water are larger than those of ether formed under similar conditions, for ether has a lower surface tension. This will readily be understood when we consider, that the drop hanging from the end of the tube is kept attached to the liquid inside by surface tension, whilst gravity tends to tear it off. The larger the surface tension, the larger the drop which can still be retained. The weight of a drop, or the number of drops furnished by a given volume of liquid, is often determined by the **stalagmometer** (Fig. 1) introduced by I. Traube. The liquid is sucked into the pipette-like tube and the number of drops is determined, which flow out between two marks *a* and *b*. The weight of a single drop can be calculated from the volume between the two marks and the density of the liquid. At K a length of capillary is inserted, in order to secure a sufficiently slow formation of drops. If this is not done, the size of the drops not only depends on the surface tension and on gravity, but also on the kinetic energy, with which the liquid issues from the orifice. The stalagmometer is chiefly used for comparative experiments, and is calibrated by means of a liquid of known surface tension.

Another common method of determining surface tension is that of the **capillary rise.** This depends on the readily observable phenomenon, that when a capillary, for instance of glass, dips into a wider vessel, the water attains a much higher level inside the capillary than outside. This phenomenon of course gave the name "capillarity" to the whole subject of surface actions, and thus also led to the term capillary chemistry. In order to understand this ascent of a liquid inside a narrow tube, we must consider the wetting process a little more fully. If a drop of water be placed on a clean glass plate, it spreads and extends to a thin membrane; in that case we speak of **complete wetting.** A droplet of mercury, on the other hand, remains

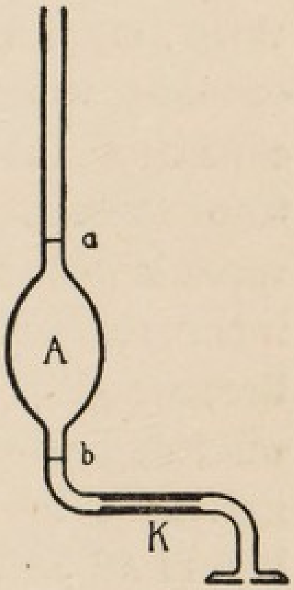


FIG. 1.

spherical and does not spread ; here there is no wetting at all. Other liquids, of an oily nature, form lenticular masses, so that we can speak of a definite angle, the **angle of contact.** This is the angle α in Fig. 2, formed between the liquid-gaseous and the solid-liquid interface. With complete wetting the angle of contact is 0°, without any wetting at all it is 180°. Now when a clean capillary tube is dipped into water, the water spreads over the whole inner surface of the tube, because glass is completely wetted, i.e. over the area indicated in Fig. 3 by the letters ABEF, and over the whole of this area water is therefore in contact with air. Surface tension tends to diminish this considerable surface, but diminution can only take place by the water being drawn into the capillary. If this occurs up to the level GH, the whole surface EFGH is eliminated, and the sensibly smaller surface ABGH remains

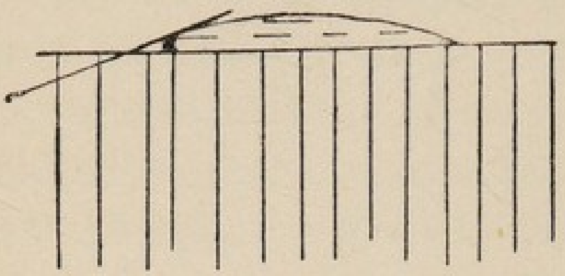


FIG. 2.

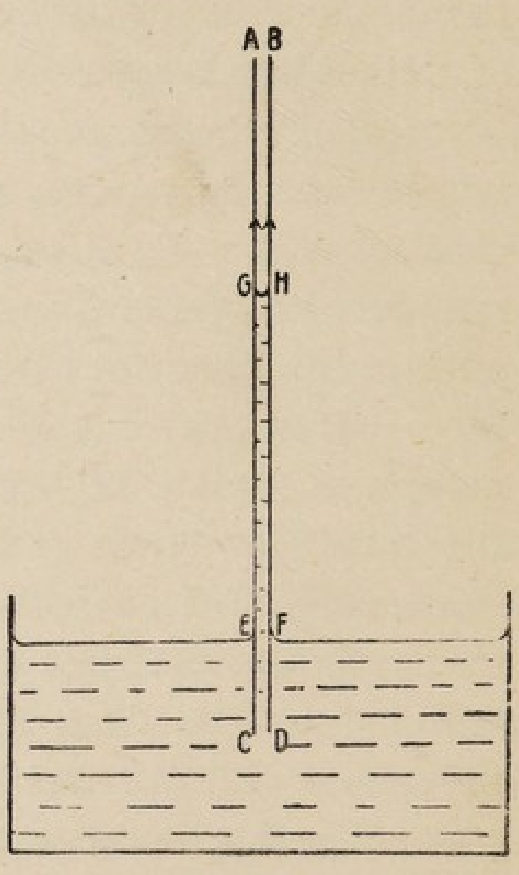


FIG. 3.

as the interface with air. The height to which the liquid ascends is limited by the action of gravity and an equilibrium is reached as soon as the force of surface tension, action upwards in the direction of the arrow, is balanced by the weight of the liquid in the capillary. For the same radius of the capillary the surface tension is proportional to the height of the capillary rise and to the density of the liquid. More exact mathematical considerations lead to a formula, which enables us to calculate the surface tension from the capillary rise.

With a non-wetting liquid, such as mercury, we find in analogous fashion, that the level inside the capillary is depressed below that of the liquid outside. For since mercury does not wet the glass, a layer of air would remain between the liquid and the inner surface of the tube, and to this extent mercury would be in contact with air. Surface tension reduces this air-surface and the mercury is depressed inside the capillary. The above simple conception only applies to completely wetting and to non-wetting liquids. With incomplete wetting, when there is an angle of contact between 0° and 180°, the relationship between capillary rise and surface tension is less simple.

The force, which surface tension exerts on a liquid, is not very large; thus for water at 18° it amounts to 74 mg. over a distance of 1 cm. What this means will be made clearer by imagining, as did Clerk-Maxwell, a frame (Fig. 4) of thin wire, of which the lower bar CD can slide up and down and supports a small scale pan. In this frame we suspend a lamella of water. (It does not affect the argument, that this is difficult to accomplish with pure water; it can readily be done with a lamella of soap solution, in which case the relationship is, however, more complex, since the soap solution is colloidal.) The lamella attempts to contract, and the force which is thus exerted, amounts, if CD be exactly 1 cm. long, to double the surface tension, for this tension acts on the front as well as on the back of the lamella. At 18° we would therefore have to place 2 × 74 = 148 mg. on the scale pan, in order to balance the tendency of the lamella to contract. This train of thought also explains how the diminution of the surface must be regarded as an effect of surface tension. As a rule the surface tension is not expressed in milligrams weight per centimetre, but in so-called absolute units. We must then remember that the weight of 1,000 mg. equals 981 dynes. The table on page 25 gives the surface tension of a few liquids in dynes per centimetre.

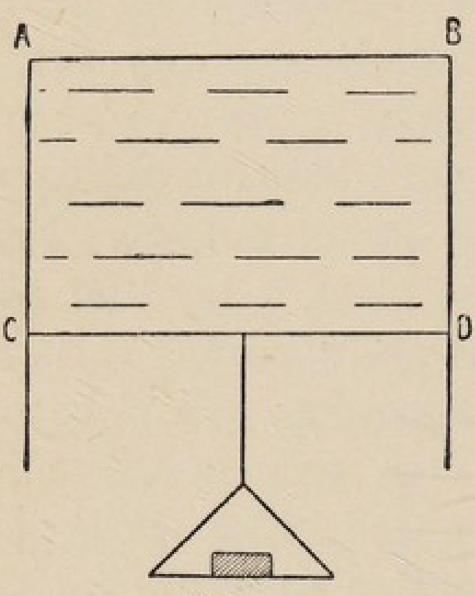


FIG. 4.

In general it may be said that mercury, molten metals and molten salts have a large surface tension; water also has a relatively large one; for organic liquids it is smaller, for liquefied gases still smaller. The surface tension is therefore generally large, when the boiling-point is much above room-temperature, and small in the opposite case.

TABLE I

Surface Tension of Liquids

Liquid.	Temperature.	Surface Tension.
Mercury	15°	436
Water	18°	73
Benzene	20°	28·8
Ethyl alcohol	20°	22·0
Ethyl ether	20°	16·5
Chloroform	20°	26·3
Carbon bisulphide	20°	33·5

The surface tension of pure liquids almost invariably decreases with rise of temperature, but the rate of decrease is by no means the same for all liquids. For water it amounts to about 2 per cent. per degree.

There still remains to be considered a quantity which is closely related to the surface tension, namely the **free surface energy.** Since the surface tension tends to make the surface as small as possible, it is evident, that work will have to be expended in enlarging the surface. We have only to imagine that in the arrangement, shown in Fig. 4, we wish to enlarge the lamella; this will require work, for the tendency of the surface tension to make the lamella smaller will have to be overcome. The amount of work which will have to be expended, is greater, the greater the surface tension and the greater the area by which the lamella is to be increased. It is equal to the surface tension multiplied by this area. This work is simply the free surface energy. Conceptually it is related to surface tension in the same way as work (which is the product of a force and a distance) is related to a force. The free surface energy is a quantity which always tends to assume a minimum value ; for the area of the surface, which increases and decreases with it, also tends towards a minimum as the result of surface tension.

The above consideration of a definite physical quantity and the inquiry into the conditions under which this quantity assumes a minimum (or maximum) value, may appear unfamiliar to some readers ; in theoretical physics, this way of regarding problems has, however, proved very fruitful.

The Surface Tension of Solutions

An examination of the surface tension of solutions leads to their separation into two groups. In some the surface tension differs but little from that of the pure solvent ; generally it is a little higher ; this group comprises the aqueous solutions of salts, particularly of inorganic ones ; further the solutions of many substances in organic solvents, such as benzoic acid, camphor and naphthalene in alcohol or ether. Such solutions are called **capillary-inactive** or **surface-inactive.** The second group, of the **capillary-active** or **surface-active** solutions, is characterized by the fact that the surface tension of the solvent is lowered by the solute, often very strongly even at small concentrations. This group contains almost exclusively aqueous solutions of many organic substances, such as alcohols, aldehydes, fatty acids, acetone, amines, esters. In some cases, such as the solutions of many organic salts, hydroxy-acids, etc., in water, the assignment to either group is somewhat arbitrary. These substances, however, lower the surface tension of water but slightly.

The following important rule applies to the capillary-inactive solutions of inorganic salts in water. As is well known, these salts are largely (probably even wholly) dissociated in solution into cations and anions; in a solution of sodium chloride we have therefore only $Na^{\cdot}$-ions (the cations) and Cl'-ions (the anions). Similarly a lithium chloride solution will contain $Li^{\cdot}$-ions and Cl'-ions. Now it has been found that all lithium salts, no matter from what acids they are derived, increase the surface tension of water more than the corresponding sodium salts and these more than potassium salts. Sulphates, independently of the nature of the cation, increase the surface tension more than chlorides, and these again more than bromides, etc. This behaviour is an **additive** one. The characteristic series of cations and anions so obtained

$$\mathrm{Li} > \mathrm{Na} > \mathrm{K}$$
$$\mathrm{SO_4} > \mathrm{Cl} > \mathrm{Br} > \mathrm{I} > \mathrm{CNS}$$

are called the **lyotropic series.** They play an important part in a large number of other natural phenomena. By lyotropic properties of salts we therefore mean the additive properties expressed by the above series. Probably the lyotropic behaviour is an expression of the affinity of the ions towards water. For it may be taken as certain, that every ion binds a considerable number of water molecules, and is to a certain extent therefore surrounded by an aqueous envelope. Unfortunately we have as yet no reliable means of measuring this power of binding water, the degree of **hydration** of the ions. If we had such means, we should at once be able to elucidate quantitatively a large number of phenomena which at present remain more or less obscure. Such scanty and rather uncertain measurements of the hydration of ions, as have been made, point however to the conclusion, that the $Li^{\cdot}$-ion is more strongly hydrated than the $Na^{\cdot}$-ion, and this more strongly than the $K^{\cdot}$-ion. Among anions the sulphate ion is more strongly hydrated than the Cl'-ion, and this more than the Br'-ion. The lyotropic series therefore also applies to the hydration of the ions.

The other group, of **capillary-active** solutions, also shows a remarkable regularity. A comparison of the solutions of closely related substances, belonging to a homologous series, like that of the fatty acids, formic, acetic, propionic and butyric, shows that the lowering of surface tension produced by them increases strongly as we ascend the series. Fig. 5 shows this behaviour. Here the concentrations C of the aqueous fatty acid solutions in gram molecules per litre have been plotted as abscissæ against the surface tensions σ as ordinates. It will be seen that formic acid lowers the surface tension of water but slightly, acetic acid about 2 to 3 times as strongly, propionic acid again 2 to 3 times as much. This behaviour has been observed in this series up to undecoic acid, with 11 carbon atoms. A quite similar behaviour, namely a great uniform increase in the lowering of surface tension while ascending a homologous series, has been observed with many other organic substances, such as aldehydes, esters and amines. This regularity is referred to as Traube's

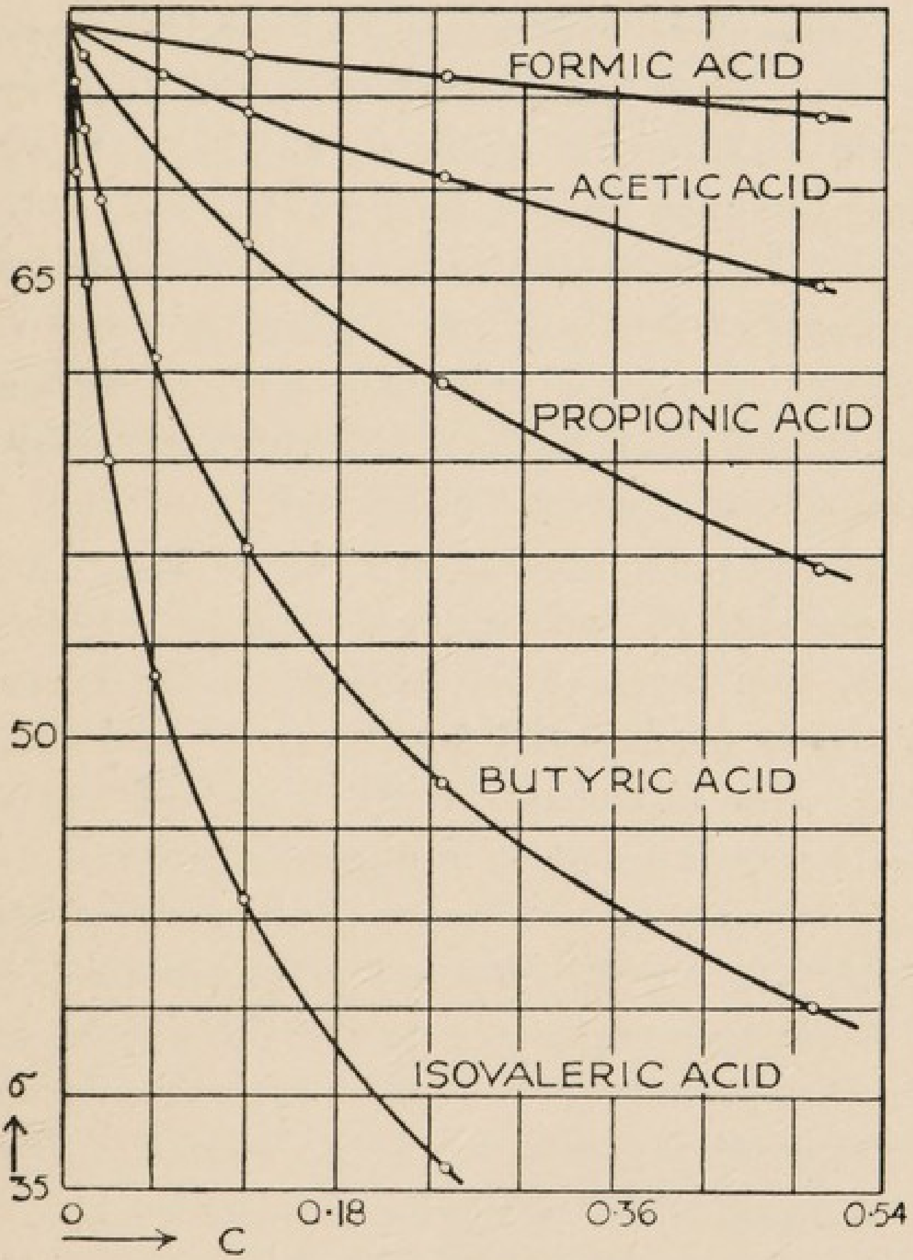


Fig. 5.

rule; its explanation will not be attempted until later (p. 93).

There are quite a number of phenomena in which the marked lowering of the surface tension of water by small quantities of capillary-active substances comes into play. Thus this lowering causes the vigorous movements shown by water on coming into contact with ether vapour; the lowering of the surface tension does not take place uniformly, and so liquid is drawn from places of low surface tension to those with a higher one. A similar local inequality of surface tension is also the cause of the rapid movements shown by particles of camphor on a clean water surface. Movements of the same kind are shown by many surface-active and volatile substances, such as benzoic acid, atropine, fragments of flowers and leaves containing essential oils (chamomile flowers, mint and rosemary leaves). The so-called "tears" formed by strong wines are likewise due to the great change in surface tension, resulting from changes in the concentration of a capillary-active solution. The upper part of the glass, when not quite full, is merely wetted by the liquid. On account of its great surface this wetting layer evaporates rapidly and the alcohol disappears first. A liquid with less alcohol remains behind, which, on account of its greater surface tension, contracts to drops which run down the sides of the glass like tears, while neighbouring portions become wetted again by fresh liquid derived from the main bulk.

Adsorption at Liquid—Gaseous Interfaces

Capillary-active solutions show a property which at first sight may seem rather trivial, yet is of fundamental and general importance. These solutions are apt to froth. The formation of a stable foam is a complicated phenomenon, which can only be discussed more fully later on (p. 195). Here we merely say that a minimum surface tension favours frothing, but the liquid must not be too volatile, nor too mobile. Hence ether and benzene do not froth, although their surface tension is small. Capillary-active aqueous solutions on the other hand do froth, because their surface tension is sufficiently small and the films of liquid which constitute the foam do not evaporate too rapidly, nor collapse too readily. Now if foam be generated on an aqueous solution of amyl alcohol, and then rapidly separated from the bulk of the liquid, and subsequently the amyl alcohol content of both portions be determined, we find that the liquid resulting from the foam is richer in amyl alcohol than the main bulk. Experiments of this kind may be made in a semi-quantitative fashion by letting air bubbles of known size ascend in a capillary-active solution and securing, that the upper part of the liquid, in which they break up, only communicates with the rest through a narrow tube. Any change in concentration, which is thus set up, cannot be abolished by convection or diffusion. Under these conditions we also observe the transference of the dissolved substance by means of the gas bubbles.

This can only be explained on the assumption that the dissolved substance collects on the surface of the bubbles, so that the portion of the liquid which immediately adjoins the bubble contains more of the solute than the rest of the liquid. The theorem, put forward above, that the free surface energy always tends towards a minimum, renders this phenomenon intelligible. For the free surface energy is equal to the product of the surface tension and the area of the surface. In pure liquids only the latter can change, for the former has a definite fixed value at any given temperature. The case of a solution is different, for here not only can the area of the surface change, but also the surface tension, which may increase or decrease through a change in the concentration of the solution. If the surface tension falls with increase in concentration, the free surface energy would become a minimum, if the solute collected on the surface. Its concentration would increase there, and since the surface tension is determined by the concentration in the surface layer, the surface tension, and with it the free surface energy, would decrease. The theorem that the free surface energy tends towards a minimum hence leads to the result, that *a dissolved substance must increase its concentration at the surface, if it lowers the surface tension*; conversely *it must decrease its concentration at the surface, if it raises the surface tension.*

Such an increase in the concentration of a solute at the interface between a liquid and a gas, is an example of **adsorption,** by which we mean the loose fixation of a substance at an interface. The abovementioned theorem, connecting the lowering of surface tension with the increased concentration of a substance on the surface, is termed **Gibbs' adsorption theorem** after the American theorist Willard Gibbs, who first formulated it. We can approximately calculate the quantity adsorbed in the experiment described above, on the bubbling of air through a capillary-active solution. For instance, in the case of a 0·0003 normal solution of nonoic acid in water it amounts to about 0·0001 mg. per square cm. of the surface generated by the gas bubbles. This quantity may appear negligible, but we must remember that, as has already been pointed out, a colloidal-disperse substance may develop a surface of many millions of square centimetres; considerable quantities of substance may therefore be adsorbed in this manner.

We may further point out, that the theorem employed above, according to which the free surface energy tends towards a minimum value, is merely a special case of the more general rule, that the so-called **free energy** always tends to become a minimum. This latter rule in its turn is merely an expression of the so-called second law of thermodynamics, which applies generally to equilibria in all kinds of natural phenomena. Although experiments demonstrating the increase of surface concentration in a capillary-active solution are not very numerous, we may nevertheless depend on them, since such an increased concentration is merely a necessary result of the second law of thermodynamics.

2.—The Interface between Two Liquids

The surface of contact between two partially or wholly immiscible liquids presents phenomena quite similar to those met with in the case of a liquid and a gas. We know that when a small quantity of chloroform or of petrol is shaken with water, the drops of these liquids suspended in the water are spherical, and accordingly the same considerations apply as in the case of the interface between a liquid and a gas. We must therefore postulate an **interfacial tension,** which endeavours to give to the drops of the one liquid a minimum surface. The interfacial tension can thus be measured by the same methods as the surface tension, and the values obtained are of similar magnitude to those found for the surface tension. On the whole they are perhaps somewhat smaller.

We again encounter the antithesis between capillary-active and capillary-inactive solutions, and also Traube's rule, when we examine the interfacial tensions between aqueous solutions of organic substances and liquids which are not completely miscible with them. A complication must, however, be considered, namely the solubility in the second liquid of the substances dissolved in the water. As long as the solute is principally present in the aqueous solution, and thus resembles that at a liquid-gaseous surface, Traube's rule is very evident. But if the solute mostly passes from the water to the other liquid, the lowering of interfacial tension is generally much smaller than we might expect, and Traube's rule scarcely applies, if at all. Thus butyric acid has been found to lower greatly the interfacial tension between water and olive oil, in the same way as it lowers surface tension, but alcohol, which is capillary-active at the interface between water and air, has but a slight effect on the interfacial tension between water and olive oil, since it is soluble in the latter.

The interface between two liquids is likewise subject to Gibbs' adsorption law, and here the experimental verification is somewhat easier than at a liquid-gaseous interface. We can for instance investigate the change in the concentration of a solution, caused by a stream of falling droplets of mercury. We then find, in accordance with Gibbs' law, that those substances are most strongly adsorbed, which most lower the interfacial tension between mercury and water.

The question naturally suggests itself: what is the relation between the surface tensions of two liquids and their interfacial tension? The relationship between these three quantities determines whether one liquid will spread on the surface of another, in experiments analogous to those on wetting. If we for instance place a drop of alcohol on a clean water surface, the alcohol rapidly spreads with a lively movement over the whole surface of the water. The diagrammatic representation in Fig. 6 will explain how this takes place. Let A be the water and B the alcohol. The surface tension of the water acts in the direction PA, that of the alcohol in the direction PB, and the interfacial tension between water and alcohol in the direction PC. Since alcohol is miscible with water in all proportions, we might question whether such an interfacial tension really exists; its existence must, however, be inferred, at least in the first moments of the contact between the two liquids. For a jet of alcohol, issuing from an orifice under water, behaves in the neighbourhood of the orifice exactly like a jet of benzene, which, being not completely miscible with water, certainly has an interfacial tension. Since the interfacial tension between two completely miscible liquids, such as alcohol and water, is in any case small, the larger surface tension of water, acting along PA, will always preponderate over the surface tension of alcohol acting along PB; the liquid at P, and therefore the drop, is drawn out over the water surface. We thus obtain the general result that a liquid, which is completely miscible with water, and has a smaller surface tension than water, must spread over a water surface.

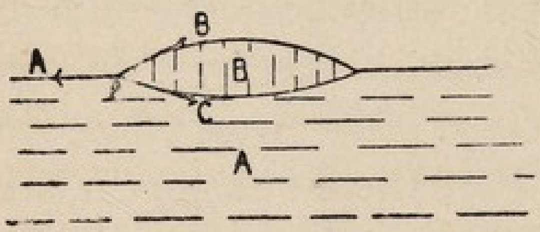


FIG. 6.

The case is not so clear, when the second liquid is incompletely miscible with water and therefore possesses a distinct interfacial tension in contact with the latter. In that case the surface tension of water, acting along PA, may still preponderate over the surface tension B of the second liquid and the interfacial tension, so that the second liquid still spreads over the water, as is the case with ether. If, however, the interfacial tension is large, the case may occur that the tensions along PB and PC together compensate for the tension along PA. The second liquid then remains lying on the surface of the water as a lenticular drop; this happens for instance with pure petroleum. Often especially with oleic acid and impure petroleum, a thin film of the second fluid first spreads on the surface of the water. This so greatly lowers the surface tension of the latter that a further quantity of the second liquid remains in a lenticular form; the diminished surface tension of the water, still acting along PA, now balances the two other tensions. The thin films of petrol, spread on water, cause, as is well known, the beautiful iridescent colours, depending on interference, which may be seen when a motor car has been standing on a wet pavement.

3.—The Interface between a Solid and a Gas

THE SURFACE TENSION OF SOLIDS

It is the mobility of liquids which enables us to recognize and measure their surface tension, but when we come to consider the interfaces of solid substances we encounter quite different conditions. Here the particles suffer mutual displacement with great difficulty, so that we cannot recognize the surface tension directly or measure it. Nevertheless it is found expedient to assume a surface tension of solids against a gaseous space.

This applies in the first place to amorphous-solid substances such as glass, pitch and resin. As will be discussed more fully later, these may be regarded as extremely viscous liquids: their structural units are probably molecules, arranged without any pattern, like those of a liquid, but they can only move extremely slowly with respect to one another. In the long run they do move, however. Thus a long horizontal glass rod, which is only supported at its extremities, sags in the course of time; the contents of a barrel of pitch, as used in road mending, may often be seen to have lost their original shape and to begin to flow when the staves of the barrel have been removed. For the same reason a thread of glass, hanging down vertically, will be lengthened by gravity at a temperature at which glass still behaves like a solid, provided that the thread is long enough and heavy enough. On the other hand, if the thread is not so long, surface tension may preponderate and shorten the thread in order to reduce its surface. Indeed, the surface tension has been deduced from the length at which the thread neither extends nor contracts; thus for lead glass at 500° a value of 70 (measured in dynes per centimetre) has been found for the surface tension, which is therefore of the same order of magnitude as that of liquids.

In the case of crystalline solids a similar comparison with liquids cannot however be instituted. Crystals are built up in a manner quite different from that of liquids, as has already been indicated, and as will be shown more fully later; their structural units are atoms or ions, situated with strict regularity at the points of a space lattice, where they execute small oscillatory movements. We might at first imagine that under these conditions there can be no question of a surface tension, and yet powerful arguments tell in favour of its existence. Their comprehension requires some further explanation.

In dealing with the surface tension of liquids we emphasized that the free surface energy always tends to assume a minimum value. The free surface energy is large, when the surface is large. A dew of very fine droplets accordingly has a larger free surface energy than when these droplets coalesce to a single drop. Hence there must be a tendency in this direction and such droplets are actually known to unite when they come into contact ; this is particularly evident in the case of droplets of mercury, when touching each other, since mercury has a large surface tension. Now, as was pointed out, this principle of the free surface energy is only a particular case of the corresponding principle of the free energy and thus of the second law of thermodynamics. This principle requires that the above tendency of the free energy to assume a minimum value will show itself by any means which is at all possible. When the droplets are not in direct contact, they are nevertheless indirectly connected through their vapour, if they are in the same space and are not separated by a wall. Therefore small droplets will unite to larger ones, even if they are not in direct contact, because the smaller drops evaporate more rapidly than the larger ones. Liquid therefore escapes from the smaller ones as vapour and is condensed on the larger, until in the end all the smaller drops are consumed in this manner. The final state is represented by the same single large drop which would have been formed if the droplets had been placed in direct contact.

This train of thought therefore leads to the result that small drops must have a larger vapour pressure than large ones and that the increase in the vapour pressure is the more considerable, the greater the surface tension of the liquid in question. The convex surface is most strongly curved in the smallest drops; therefore there is an increase in the vapour pressure of a liquid with increased convexity of surface and conversely there is a lowering of vapour pressure, when the surface of the liquid is concave, as for instance in a capillary. The increase in the vapour pressure only becomes appreciable (10–100 per cent. of the ordinary vapour pressure) in the colloidal-disperse region, e.g. with droplets having a radius of 0·00001 cm. or less.

Experiments, devised to demonstrate the increase in the vapour pressure of small droplets, have hitherto been neither numerous nor sufficiently exact. We must remember that such experiments are easily rendered fallacious by slight variations of temperature, so that the liquid simply distils from a warmer to a colder place. Yet we need have no doubt regarding this phenomenon, since it depends on the general applicability of the second law of thermodynamics. Now a phenomenon quite similar to that observed with droplets, is found in a deposit of minute crystals, i.e. they too have a vapour pressure greater than that of large crystals. Thus by passing air through finely powdered *p*-dichloro-benzene a larger vapour pressure was at first observed than afterwards, when all the smallest crystals had evaporated. Similarly it has been shown experimentally that deposits of minute crystals in a vacuum unite in course of time to larger ones. Perhaps, however, these experiments are also invalidated by the temperature not being rigorously uniform and constant. From the higher vapour pressure of smaller crystals we can deduce that they must also have a lower melting-point than larger ones; Tammann and Meissner have actually shown that various solids, when in the form of thin lamellæ (thinner than 0·001 mm.), melt at a lower temperature than when they are in larger fragments.

Just as the increased vapour pressure of minute particles is related to the surface tension of liquids, so we may also connect the phenomena depending on the increased vapour pressure of minute crystals with a surface tension of crystalline solids. We would therefore, on the basis of these observations, postulate such a surface tension for solids.

A few phenomena may still be mentioned which can be explained on this hypothesis. Since surface tension tends to reduce the surface to a minimum, it should also tend to round off the sharp corners and edges of a crystal. Such crystals with rounded edges and corners are actually known. If, for instance, we heat a piece of metal to a high temperature which is still appreciably below the melting-point, surface tension may begin to overcome the rigidity of the individual crystals constituting the metal, the so-called **crystallites,** which then become rounded at the edges and corners. Surface tension is also the cause of **recrystallization,** in which the small crystals unite to larger ones at such temperatures below the melting-point. Probably this phenomenon is similar to the union of minute droplets to larger ones, when in direct contact, for it is unlikely that the formation of larger crystals could be due to the increased vapour pressure of the smaller ones bringing about a distillation; the process takes place far too rapidly to allow of the latter explanation. Further the difference between iron-nickel meteorites and ordinary iron-nickel alloys may be explained on the assumption that the meteorites have been formed from ordinary alloys by such a recrystallization.

THE ADSORPTION OF GASES BY SOLIDS

We have seen, that at the interface between a liquid and a gas the surface tension can easily be measured, but that an adsorption cannot so easily be demonstrated. The interface between a solid and a gas presents the opposite case. As was pointed out in the preceding section, the surface tension of crystalline solids has not yet been measured, although there are good reasons for assuming that such a surface tension actually exists. On the other hand we know many phenomena which must be interpreted as adsorption at a solid-gaseous interface. With solids there is no difficulty in securing a large surface: some can be reduced to an extremely fine powder; others, such as charcoal, are very porous by nature and have a correspondingly large surface. The colloidal-disperse fine structure, characteristic of organized matter, may be preserved by cautious carbonization, and thus we obtain in vegetable and animal charcoals solid substances with an enormous surface. Such charcoals, among which coco-nut charcoal must be specially mentioned, bind gases by loose combination. The gases may readily be removed by evacuation and heating; their fixation has long been known as adsorption.

During recent years adsorption has claimed special attention, since it was extensively applied during the war. The box respirators of gas masks contain as principal constituent granulated charcoal, capable of vigorous and rapid adsorption, which completely retains poison gases, present in the inspired air. The following experiment illustrates the adsorption of gases. A calibrated glass tube, closed at its upper end, is filled with ammonia gas and dips into a trough of mercury. A piece of charcoal is heated to redness, cooled and introduced through the mercury into the tube, so that it floats on the surface of the metal. The volume of the gas rapidly diminishes and the mercury rises in the tube. The ammonia which has disappeared is fixed on the charcoal and can be recovered by exhaustion or by heating. The following experiment is even more striking. A current of coal gas is passed through benzene, so that it becomes saturated with the vapour, and passes on to a burner, where it burns with a luminous, sooty flame. If, however, a layer of adsorption charcoal, only a few centimetres in length, is interposed before the burner, the benzene is adsorbed and the flame becomes non-luminous. The recovery of gaseous benzene and of other organic vapours by means of adsorption on charcoal has recently acquired considerable technical importance.

In these cases a definite **adsorption equilibrium** is established. A given variety of charcoal, at given temperature and pressure, takes up a definite quantity of gas per gram of charcoal. If the pressure be lowered, the charcoal parts with some of this gas ; if the pressure is lower from the beginning, the quantity adsorbed per gram of charcoal is also smaller ; if the pressure be raised, a further quantity of gas is taken up. If we return to the original pressure, we find again the same amount adsorbed as was present originally. By plotting the pressures p (in centimetres of mercury) as abscissæ, and the quantities adsorbed (in cubic centimetres at 0° and 760 mm.) as ordinates, we obtain a curve like that represented in Fig. 7. Such a curve is termed an **adsorption isothermal,** since it represents the behaviour of adsorption at a given temperature. It is characterized by the fact, that the quantity adsorbed does not simply increase proportionally to the gas pressure, but that at low pressures adsorption is relatively much greater than at high ones. The quantity adsorbed does indeed increase with rise of pressure, but much less rapidly at high than at low pressures.

The solid adsorbing substance is called the **adsorbent,** the gas which is adsorbed is termed the **adsorptive,** and

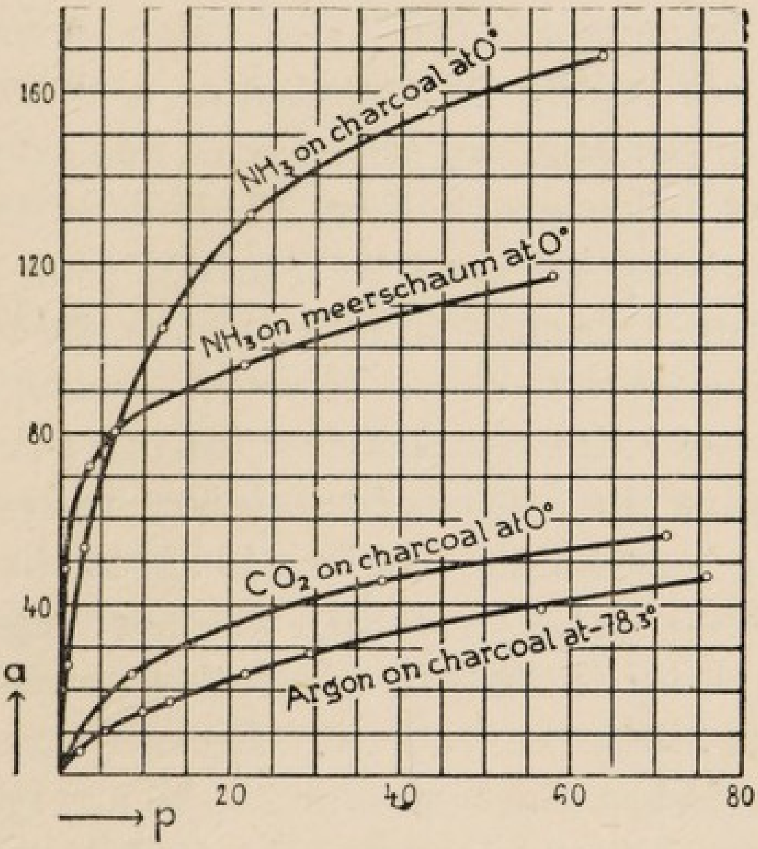


FIG. 7.

the combination of adsorbent and adsorptive is known as the **adsorbate.**

On comparing the adsorption of different gases by one and the same adsorbent, we find that a gas is the more strongly adsorbed, the more readily it is condensable. Difficultly condensable gases, like oxygen and nitrogen, are very slightly adsorbed at room temperature; carbon dioxide, ammonia and ethylene are adsorbed much more strongly. Hydrogen is generally adsorbed more strongly than its slight condensability would suggest, whereas helium and neon are only adsorbed very slightly, in accordance with expectation. Argon resembles nitrogen in adsorbability ; the adsorption isothermal of the former gas is represented in Fig. 7. In any case this loose union of argon with charcoal can hardly be regarded as a chemical combination in the ordinary sense, since no chemical compounds of argon are known. This does not imply, that the adsorption must be regarded as a " physical combination," sharply differentiated from a chemical union. Adsorption does, however, belong to some such class of loose combinations, as are attributed in chemistry to the action of subsidiary valencies.

Nothing very definite can be said about the influence of the adsorbent. Charcoal, whether vegetable or animal, greatly exceeds in adsorptive power all other adsorbents hitherto examined. Recently the dried gel of silicic acid has also been found to be a very powerful adsorbent. Infusorial earth (Kieselguhr), pumice and meerschaum are much weaker. Pretty generally an amorphous substance and minute crystals seem to adsorb weight for weight more powerfully than the finest powder of the same substance, prepared by grinding larger crystals. On account of the technical importance of charcoal as an adsorbent, much attention has been paid to the properties which determine a high adsorptive power. It seems that the cellular structure of the wood must be preserved as far as possible by a gentle treatment during carbonization, so that the original large cellular surface is changed as little as possible and the charcoal does not sinter. We must further ensure that no difficultly volatile tarry substances coat the surface. It is best to carry out the carbonization in such a way that the formation of tar is restricted as much as possible from the outset.

With rise of temperature adsorption always diminishes. In order to obtain considerable adsorption the temperature must therefore be lowered. This is the basis of the use of adsorption to produce a vacuum. The last traces of vapours, such as that of mercury, may be very effectively removed by putting the space to be exhausted into communication with a vessel, cooled in liquid air or hydrogen, and containing a good adsorption charcoal.

The following effect of temperature must also be taken into account. As is well known, there exists for every gas a definite so-called critical temperature, above which the gas cannot be liquefied. At higher temperatures the gas cannot therefore be present in an adsorption layer in the liquid state, but only as condensed gas, whereas below the critical temperature it may also be present in liquid form. If the temperature is sufficiently low, we may therefore assume that every gas will form a thin liquid film in direct contact with the adsorbent.

The second law of thermodynamics, which has repeatedly been referred to, leads to the result, that a process (such as the evaporation of a liquid) which is promoted by rise of temperature, uses up heat, whereas a process, which is checked by such a rise, gives out heat. In accordance with this rule, heat is given out by the adsorption process, because this process is checked by rise of temperature. The evolution of heat may be shown by means of a thermometer immersed in an adsorbent, which is then allowed to take up a gas. This heat of adsorption is responsible for an effect occasionally described: in attempting to measure the body temperature by inserting into the mouth a thermometer bulb wrapped in dry flannel, quite fallacious temperatures up to 44° may be registered, because the flannel adsorbs water vapour and in so doing gives out heat. There is a quantitative connexion between the decrease of adsorption, due to rise of temperature, and the heat of adsorption, so that the latter may be calculated from the decrease in the adsorption.

If an adsorbent is in contact with two gases at the same time, they mutually displace each other. Both gases are adsorbed, but each somewhat less than if it were present by itself. The more strongly adsorbable gas preponderates in the mixture, even if its partial pressure is small. If this were not so, the charcoal of a respirator could not remove small quantities of poison gas, for the air is present in large excess. The more easily condensable poison gas is, however, adsorbed much more strongly than air, even although it only represents a minute fraction of the gases passing through the respirator.

The question now suggests itself, whether the adsorption of a gas may be regarded as a surface condensation in accordance with Gibbs' law already referred to. At present we cannot definitely affirm this, for we have not yet succeeded in measuring the surface tension of solids and its dependence on the gas pressure. Unless this be achieved, we cannot calculate the amount of the adsorption from the surface tension, and test its agreement with the amount observed experimentally. All we can say is that in general the characteristics of gaseous adsorption are not at variance with what might be expected from a surface condensation according to Gibbs. Since we can at present make no progress along these lines, a different conception, due to Haber and Langmuir, has been preferred of recent years. Attention is directed to the attraction which the surface molecules of the adsorbent exert on the gas. Such an attraction may be assumed to exist on the following grounds. As has been pointed out, the ions of a solid crystalline salt ($\mathrm{Na}^{\cdot}$- and Cl'- ions in the case of sodium chloride) are situated at the points of a space lattice. It has further been concluded, that the crystal is held together by the attraction which the ions exert on one another and that this attraction is simply the force which was previously regarded as chemical attraction. Now the ions on the surface of the crystal only adjoin points of the space lattice on one side, towards the interior, thereby differing from the ions inside the crystal, which are surrounded on all sides. The attraction exerted by the surface ions is only balanced towards the interior; a certain residuum extends into the gas space and is responsible for the adsorption. This conception may be extended to all solids, and with its aid the dependence of adsorption on temperature has been successfully calculated from the condensability of the gas.

ADSORPTION CATALYSIS OF GAS REACTIONS

Gaseous adsorption is specially important because of its significance in many gas reactions; at a low temperature nearly all such reactions are influenced by it. If, for example, molecules of methane collide with oxygen molecules in a gas space at ordinary temperature, the number of methane molecules oxidized is altogether negligible, but if the two gases are passed over finely divided platinum, which adsorbs them, a vigorous combustion takes place. This is applied in automatic gas lighters, which contain platinum black. Adsorption catalysis is also used in many technical gas reactions, as in the production of sulphur trioxide according to Knietsch, when sulphur dioxide and oxygen are passed over platinum, or in Haber's synthesis of ammonia, in which hydrogen and nitrogen flow over a finely divided alloy of iron.

The processes with which we are here concerned are very various. Two examples of an acceleration due to adsorption may be considered more fully. In the first place the decomposition of stibine according to the equation:

$$4SbH_3 = 4Sb + 6H_2$$

The liberated antimony forms a mirror on the walls of the reaction vessel. It adsorbs the readily condensable stibine strongly, but the difficultly condensable hydrogen only slightly. The course of the reaction may be interpreted and calculated quantitatively on the assumption, that only those stibine molecules are decomposed, which are adsorbed on the surface of the antimony. The fact that the antimony separates from the very beginning as a mirror on the glass, moreover shows that the reaction takes place preferentially on the surface of the glass.

The conditions of this reaction are specially favourable to acceleration, since the hydrogen formed is but slightly adsorbed and does not, as it were, remain adhering to the surface of the adsorbent, while the other product, solid antimony, actually favours the reaction. In many other reactions the products are, however, strongly adsorbable; they form a surface layer, which checks further catalysis. This occurs, for instance, in the above-mentioned formation of sulphur trioxide from the dioxide and oxygen, according to the equation:

$$2SO_2 + O_2 = 2SO_3$$

Of these gases SO_3 is the most readily condensable and accordingly the most strongly adsorbed; the union of SO_2 and O_2 is indeed accelerated in the adsorption layer, but a layer of SO_3 is soon formed there and checks the access of the other gases to the platinum surface. The velocity of the reaction finally depends on the rate with which the gases diffuse through the thin layer of SO_3. Many other readily condensable gases act like sulphur trioxide, forming adsorption layers on the surface of the adsorbent or changing it by an ordinary chemical reaction. Thus when Knietsch's SO_3 synthesis was applied technically, the elimination of the last traces of arsenic compounds from the reacting gases at first caused difficulties since arsenic checks the reaction to an extraordinary extent, and "poisons" the catalyst.

Among the numerous gas reactions taking place at interfaces, the following further examples may be mentioned: Catalysis of the reaction between oxygen and hydrogen at many surfaces (platinum, quartz, porcelain), the decomposition of nickel carbonyl into nickel and carbon monoxide at nickel surfaces, the decomposition of carbon monoxide into carbon dioxide and carbon at surfaces of nickel and of cobalt, the formation of phosgene from carbon monoxide and chlorine by passing these gases over charcoal. The last named is the technical method for preparing phosgene.

Until recently the strong condensation, to which gases in the adsorption layer are subject, was considered a sufficient explanation of the extraordinary acceleration of gas reactions. A numerical estimate shows, however, that this condensation can hardly account for the phenomenon. We shall rather have to assume with Polanyi that hydrogen, oxygen, nitrogen, etc., dissociate much more strongly in the adsorption layer than in the gas space at the same temperature; it is therefore the larger content of atoms of these gases in the adsorption layer, which may explain the increased reaction velocity at a surface.

4.—The Interface between a Solid and a Liquid

THE INTERFACIAL TENSION OF SOLIDS AGAINST LIQUIDS

Conditions are here again similar to those at the interface between solids and gases. The interfacial tensions and their variations are difficult to determine. On the other hand adsorption is very pronounced and can easily be measured. Nevertheless approximate determinations of the interfacial tension have been possible in a few cases, by means of the following phenomena. Small particles of a solid have a greater solubility than larger crystals of the same substance, just as small particles and droplets have an increased vapour pressure. This increased solubility may be connected quantitatively with the interfacial tension, and its existence may be directly demonstrated. If a saturated gypsum solution be placed in contact with ordinary gypsum crystals, there is of course no change. But if to such a solution extremely minute gypsum crystals be added, having a diameter smaller than 1 μ, some gypsum dissolves, since solubility is increased by extreme disintegration. The process of solution may be recognized by the streaks which appear as the result of the difference in the refractive indices of layers of different concentration; such streaks are often seen when sugar dissolves in water. Since there is a method, the streak method of Töpler, which allows of the detection of exceedingly minute differences in the refractive power and thus of the resulting streaks, it has been found possible to detect also the very slight streaks formed when minute gypsum crystals are dissolved in a saturated solution. Quantitative determinations of this increased solubility of gypsum and barium sulphate as granules of known size, have given for the interfacial tension values of about 1,000 dynes per centimetre, much higher therefore than those known for the surface tension of liquids.

This increased solubility is the cause of the enhanced reactivity often shown by solids, when in a state of very fine division. Laboratory experience shows that if solids are intended to react, they must be carefully powdered. Since in general no increase in solubility is observed until the diameter of the particle falls below 1 μ, the solid must at least be ground to this degree of fineness. This consideration has probably been applied in the so-called leucolith process, recently described; under ordinary conditions anhydrite or anhydrous calcium sulphate reacts with water so slowly, that it does not set to a cement, as does plaster of Paris; by grinding it to an extremely fine powder a useful cement may, however, be obtained.

The very limited possibility of measuring the surface tension of solids and their interfacial tension against liquids, is particularly unfortunate in relation to the elucidation of the **phenomena of wetting.** These have already been briefly alluded to, and will now be considered somewhat more fully. If a drop of a liquid B, represented in Fig. 8, lies on a solid plate A, three forces act at the point P. The surface tension PA of the solid substance A tends to draw the latter in the direction PA, whereas the surface tension PB of the liquid B, and the interfacial tension PC between the solid and the liquid, act in the opposite direction and both attempt to hold the drop together. If the surface tension of the solid largely preponderates over the other two tensions PB and PC, the liquid will be spread over the solid, and complete wetting occurs. Obviously wetting is also favoured, when the tensions PB and PC are as small as possible. Complete wetting therefore often occurs with liquids of small surface tension, such as alcohol and ether. Water, which has a fairly large surface tension, on the other hand does not readily wet a large category of substances, mostly organic, but comprising also many inorganic crystals. Among the most difficult to wet are waxed, polished or smoked metal plates, and many leaves of plants, such as those of *Mimosa* or the cabbage. The extent to which leaves are wetted must be taken into account in the spraying of crops with insecticides. Some solids, such as quartz glass, are readily wetted by water, which fact probably depends on the interfacial tension between these

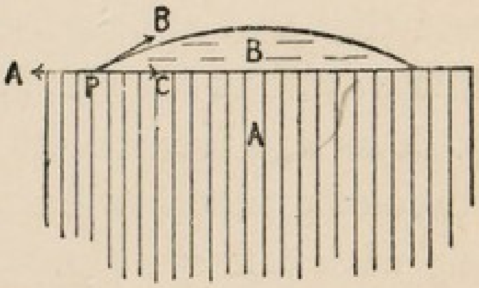


FIG. 8.

solids and water being small; silicates have a pronounced affinity for water.

The angle between PB and PC in Fig. 8 is the so-called angle of contact. For those liquids which only wet a solid incompletely, this angle has not such a definite value as we might indeed expect. Its magnitude depends greatly on the previous treatment of the surface, on the duration of contact with the liquid, etc. The cause of this behaviour is unknown. An important factor is certainly that on prolonged contact the liquid penetrates more deeply into the solid, and that this affects the angle of contact. It is only in this way that so-called **halation figures** can be explained, such as are formed on a clean glass plate, to which a trace of grease has been applied locally, e.g. by touching with a finger tip. If we breathe on the plate, the droplets of water on the greasy spot have a quite different appearance from those on the rest of the plate; the greasy glass is wetted incompletely, and on it the drops have irregular, indented contours, whereas the clean portion is either wetted completely or covered by drops with regular borders. That these halation figures may be formed again, even after vigorous cleaning, must be attributed to a deep penetration of the grease into the glass.

A phenomenon, very similar to wetting, is shown in the **displacement** of one liquid from the surface of a solid by a second liquid. We have only to imagine that in Fig. 8 the gas space is occupied by another liquid, and to assume that PA is the interfacial tension of the solid against the first liquid, PB the interfacial tension between the two liquids, and PC the interfacial tension of the solid against the second liquid. All the other conditions remain unaltered. Then there are three possibilities : the first liquid may displace the second, and the latter remains on the surface in the form of lenticular drops, or the second liquid may displace the first and the drop spreads completely over the surface, or finally the second liquid remains lying on the surface with an angle of contact, as is shown in Fig. 8.

Instead of examining these displacement phenomena at a solid surface, we can also test the behaviour of a fine powder, when brought into contact with the two liquids ; in the latter case the final result is the same. If we introduce a little powdered quartz into a stoppered cylinder containing water and supernatant benzene, and shake, the quartz collects in the aqueous layer, because water displaces benzene from the surface of the quartz. On the other hand red oxide of lead collects in the benzene layer, or settles on the benzene-water interface, because benzene in this case either displaces the water, or forms an angle of contact with it. A choice between the two last-named alternatives cannot be made by experiments like the above, but we can decide with some degree of certainty, whether a substance is **hydrophilic,** like quartz, or **hydrophobic,** like red lead.

Wetting and displacement are processes of importance, both in nature and in the arts. This is so in the highest degree with the metallurgical process of **flotation**, which during recent decades has met with wider and wider application. This process depends on the fact that sulphide ores, such as galena, zinc blende and copper pyrites, are much less readily wetted by water than is quartz, and this difference is rendered more pronounced, when they are slightly greasy, or covered with a thin layer of oil. A sulphide ore may therefore be separated from its siliceous gangue by placing the finely powdered ore in water, adding some oil and blowing a powerful current of air through the liquid. The gangue remains in the water, whilst the sulphide ore forms a stable froth which can be scooped off. Often the hydrophily of the gangue does not by itself suffice for the separation, and in the presence of oil the gangue also enters the froth. This may, however, be prevented by the artifice of adding a little acid, which so increases the hydrophily of the gangue, that the latter passes wholly into the water, whilst the hydrophobic properties of the sulphide ores are not sensibly diminished.

Among natural phenomena the ingestion of solids by amœbæ and the formation of the exoskeleton of protozoa is according to Rhumbler largely regulated by displacement processes ; in the latter case he reports the existence of very regular angles of contact.

Adsorption in Solution

The adsorption of dissolved substances closely resembles that of gases ; it has been known for a long time and is easily observed. If for instance we shake blood charcoal with an aqueous solution of methylene blue, the solution at once loses much of its colour. Although in no way colloidal, methylene blue is a dye and at the same time a salt, and since salts show peculiarities with respect to adsorption, it is better to illustrate such adsorption by means of a non-electrolyte. A similar strong decrease in the concentration is observed, when an aqueous solution of amyl alcohol is shaken with charcoal. Acetone in water, or benzoic acid in benzene, behave in the same way. Here also undoubted equilibria are established. The adsorbed substance can be washed out by adding solvent and to a given concentration in the solution there corresponds a definite quantity of the adsorptive on the charcoal, no matter whether the adsorption takes place in dilute solution from the beginning, or whether the dilution is only reached later by adding the solvent. Here also the adsorption isothermal defines the relationship between concentration in the solution and the quantity adsorbed, in much the same way as with gases (see Fig. 9), that is, at small concentrations relatively more is adsorbed than at larger ones. Fig. 9 relates to the adsorption by blood charcoal ; the abscissæ c are concentrations in equivalent weights per litre, the ordinates a the quantities adsorbed in milli-equivalents per gram of charcoal. Here also the equilibrium is as a rule rapidly established, often in a few seconds or minutes, if the adsorbent is not very dense, nor the adsorptive of very high molecular weight, so that diffusion to the interfaces in the interior of the adsorbent is not delayed.

The adsorption isothermal, as represented in Fig. 9, only applies to dilute solutions. At higher concentrations the quantity adsorbed approximates to a certain constant value, the **saturation value,** and at

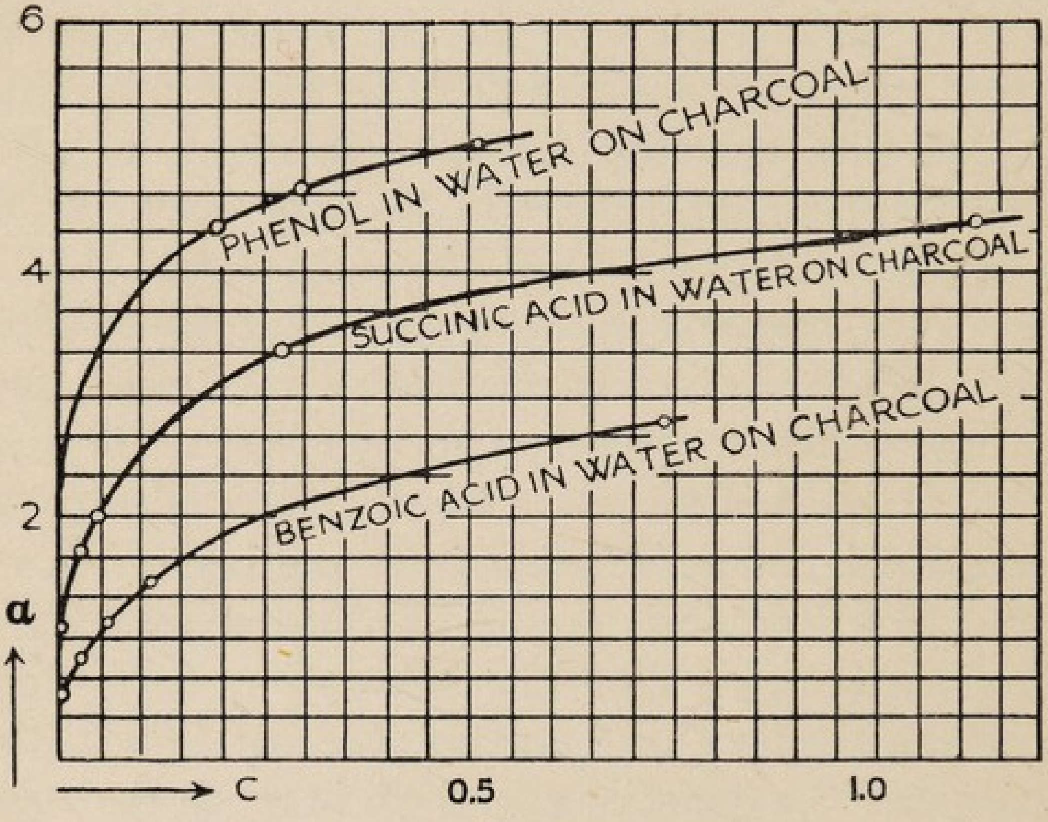


Fig. 9.

extremely high concentrations *a* seems to decrease again. It is only in dilute solutions, that the quantity of substance adsorbed at the interface changes so much more rapidly than the concentration in the solvent, so that the behaviour resembles that of adsorbed gases. At higher concentrations the solvent enters into serious competition with the solute, and since as a rule we can only measure the changes in the concentration of the solute, but are unable to determine the adsorption of the solvent, there is considerable uncertainty concerning the true quantities of the solute and solvent which are adsorbed, and this also renders the course of the adsorption isothermal more complicated at high concentrations.

In the case of adsorption from solution, the connexion with surface-tension phenomena is more clearly noticed than in gaseous adsorption; this is what one would expect, if the former kind of adsorption is a surface condensation, according to Gibbs' law. Thus Traube's rule also applies here. It will be remembered, that in surface-active solutions the lowering of surface tension increases strongly and regularly, when we ascend a homologous series of organic substances (cf. p. 29). From this it can be deduced that the quantity adsorbed on the surface of the liquid must increase in a corresponding manner. In the adsorption of organic substances from aqueous solution we indeed find, that in accordance with Traube's rule, adsorption increases strongly and regularly, when we ascend a homologous series. Fig. 10 illustrates this behaviour by means of the adsorption isothermals of some fatty acids. As before, the abscissæ c represent the concentration of the solution in gram-molecular weights (mols) per litre, and the ordinates a the quantities adsorbed in milligram-molecular weights (millimols) per gram of charcoal.

Just as the surface-activity and the adsorbability resulting therefrom change, so does also the solubility of the members of a homologous series; the solubility decreases in ascending the series, albeit not with the same degree of regularity which characterizes Traube's rule. There is, however, generally some sort of connexion between adsorbability and solubility, in as much as substances which are readily soluble in a given solvent, are but little adsorbed from that solvent by charcoal and other adsorbents, whereas sparingly soluble substances are adsorbed more abundantly. In accordance with this, aromatic substances like phenol, benzoic acid and aniline, are almost always adsorbed from aqueous solutions more strongly than aliphatic substances. The great difference between readily soluble maleic acid and sparingly soluble fumaric acid is also expressed in their adsorbability: fumaric acid is adsorbed much more strongly than its stereo-isomeride.

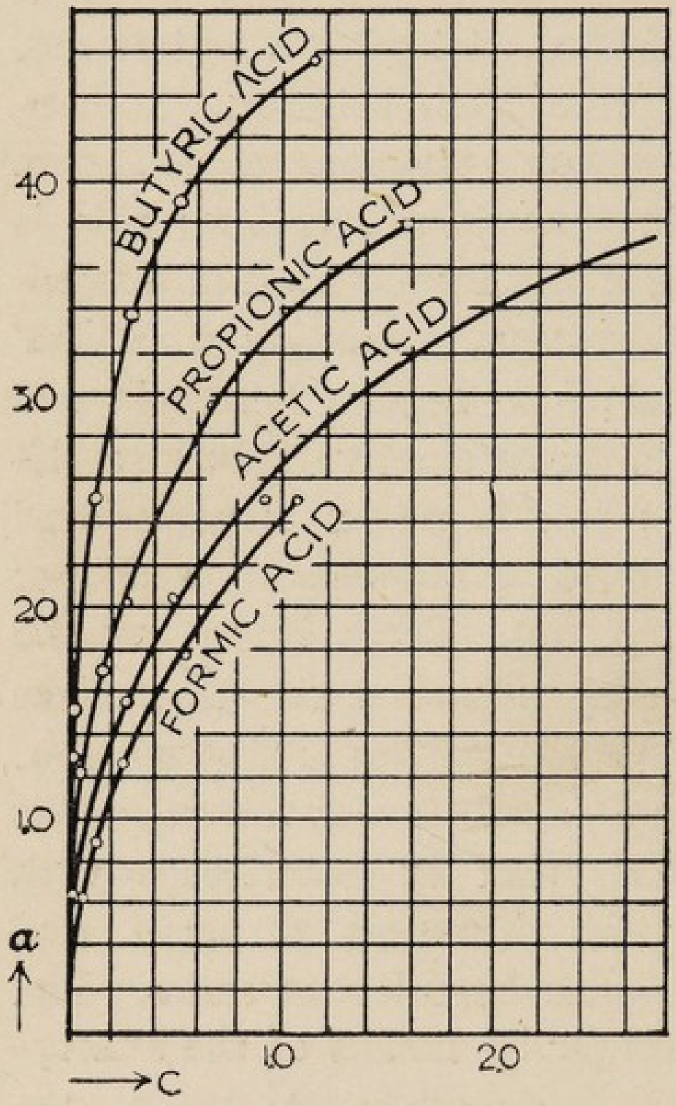


FIG. 10.

The assumption, that adsorption is a surface condensation according to Gibbs, leads to an interpretation (which cannot, however, be succinctly reproduced here) of the fact, that adsorption is usually strong in liquids with a high surface tension, such as water and concentrated sulphuric acid, and is much weaker in organic liquids having a low surface tension. This assumption (of a surface condensation) further accords well with the circumstance, that the order of adsorbability of a series of substances is not greatly affected by substituting one adsorbent for another; it is sensibly independent of the nature of the adsorbent. Thus the order of adsorbability of the series *n*-octyl alcohol $>$ sec.-octyl alcohol $>$ heptyl alcohol $>$ tributyrin $>$ acetone was preserved unchanged in testing three different adsorbents, viz. blood charcoal, talcum and sulphur. Of these three charcoal is by far the most active adsorbent, being 500 times as active as the next one, talcum.

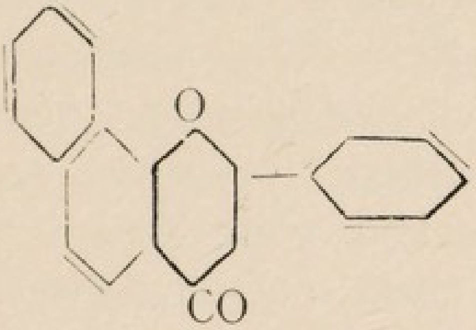
Apart from the phenomena already discussed, adsorption in solution is considered to include a further group having a quite different character. The difference between the two groups becomes particularly evident when we employ as adsorbents substances which may be regarded as difficultly soluble salts (kaolin is an example) and when these adsorbents are allowed to take up electrolytes. Suitable electrolytes, which are strongly adsorbed, are certain dyes, like methylene blue, strongly ionized in aqueous solution and devoid of a colloidal character. Now the adsorption of methylene blue by kaolin differs in various ways from the adsorption of non-ionized or slightly ionized substances by charcoal and analogous adsorbents. One difference is that in the former case only one ion is adsorbed, the dye-stuff cation, whilst the anion (generally a Cl'-ion, since we are mostly concerned with methylene blue chloride) remains behind in the solution in approximately unchanged concentration. Now in solution a definite number of anions must of course correspond to an equivalent number of cations. In place of the adsorbed dye-stuff ion other cations are found in the solution, and these are derived from the adsorbent; in the case of kaolin $Ca^{\cdot\cdot}$-ions are chiefly involved. This kind of adsorption is therefore termed an **exchange adsorption** and is **polar** in character. In contradistinction to it, the adsorption of non-electrolytes described above, will be termed an **apolar** adsorption. The designation "polar" is chosen on account of the electrical antithesis between anion and cation, both of the adsorbent and of the adsorptive. We may imagine the exchange adsorption to take place as follows: the silicate ions of the kaolin constitute a solid framework, because they are, so to speak, difficultly soluble. The cations of the kaolin, especially the Ca''-ions, are mobile, i.e. they can wander out of the surface molecules into the solution, provided that other cations, such as the dye-stuff ions in the above example, can replace them in the silicate framework.

It is possible, that in this exchange adsorption we are simply concerned with the same valency forces as unite the ions of a salt, and that the dye-stuff ions displace the cations of the kaolin, which formed part of the solid surface itself. It is, however, also conceivable that the cations of the kaolin are from the outset not all within the solid framework, but that some are in the adsorption layer; in this case they would still be close to the silicate ions of the solid surface, and in the exchange adsorption, it would be the cations of the adsorption layer, which are replaced by dye-stuff ions. There are, however, various indications, that in exchange adsorption the behaviour of the valency forces is rather different from their behaviour in apolar adsorption. Thus the capacity of an adsorbent for apolar adsorption is largely independent of its capacity for polar adsorption, as revealed by exchange adsorption. The one kind of capacity cannot be deduced from the other. Thus 12 grams of kaolin are equivalent to 1 gram of blood charcoal in respect of the adsorption of methylene blue, whereas even 1,000 grams of kaolin are insufficient to produce the effect of 1 gram of blood charcoal in the adsorption of heptyl alcohol. A similar disparity appears, when we consider the simultaneous adsorption of several adsorptives. In apolar adsorption there is generally a displacement (crowding out), as in the case of the adsorption of a gaseous mixture (see p. 48); the more strongly adsorbable substance largely occupies the surface and the amount of the less adsorbable substance is thereby greatly diminished. Similarly in exchange adsorption one cation can crowd out another, and one anion a second anion. On the other hand the exchange adsorption of an electrolyte is scarcely, if at all, influenced by a non-electrolyte. Cases are moreover known, where an adsorbent apparently adsorbs in both apolar and polar fashion. Thus it has been found in the adsorption of dyes by charcoal, that the quantities of adsorbed anions and cations are not strictly equivalent to each other, that therefore an exchange adsorption has occurred to some extent, although in other cases charcoal is characterized by its apolar behaviour. Probably these two kinds of adsorption do not depend on one and the same interface. The exchange adsorption might well be caused by impurities in the charcoal (such as difficultly soluble phosphates) whilst the apolar adsorption would be due to the carbon itself.

In spite of the differences between polar and apolar adsorption, we must not, however, immediately conclude that they are two essentially different processes. The adsorption isothermal applies also to the taking up of ions in exchange adsorption, and often the capillary-active ions are adsorbed more strongly than the capillary-inactive, which is indeed similar to the behaviour of non-electrolytes.

The influence of temperature on the adsorption from solutions is generally slight. Mostly the adsorption decreases with rise of temperature, although cases of an opposite behaviour are known.

We may now discuss a few specific examples. The well-known blue coloration of starch by iodine partakes so largely of the nature of an adsorption, that the majority of investigators regard it as such. Starch is not the only substance capable of forming with iodine a loose addition compound having a blue colour. There are a large number of organic, and also a few inorganic substances, which do the same. Among the former, xanthone and flavone derivatives may be specially mentioned. Thus α-napthoflavone, of the annexed constitution, is more sensitive to iodine than is starch. The behaviour of many of these substances is so peculiar and throws so much light on the nature of the adsorption process, that we may refer to a few details. The flavone derivatives in question are mostly very little soluble in water. In order to demonstrate their adsorptive power, their alcoholic solution is poured into an excess of an aqueous iodine solution. During the first few moments the alcoholic-aqueous solution may remain supersaturated and then no blue coloration appears. A deep blue coloration may then appear more or less suddenly, and it can be shown that the organic substance has separated in amorphous



form (or in excessively minute crystals). In course of time (after several hours or days) the amorphous (or micro-crystalline) particles are transformed into larger crystals and then generally relinquish their iodine to the solution. We therefore end up with larger colourless crystals suspended in a solution of iodine. Hence the adsorptive power is much greater in the amorphous-solid condition. As long as the organic substance is in true solution, or after it has again separated in larger crystals, its power of adsorption is slight or cannot be demonstrated. Some members of this group, the glucoside saponarin and euxanthic acid, form dilute true solutions in water, which are not coloured blue by iodine, and also more concentrated colloidal ones, which are coloured blue and lose their colour when enough water has been added to make them molecular-disperse.

The adsorbent properties of paper have been investigated in various ways. Paper shows almost exclusively an exchange adsorption, particularly with respect to dyes like methylene blue, the coloured cation of which is retained by the paper. If we let a drop of such a dye solution flow on to filter paper, we obtain a strongly coloured central patch, with a sharp border, surrounded by a colourless zone of pure water. The sharp outline of the coloured patch depends on the shape of the adsorption isothermal (see Fig. 9). The quantity adsorbed does not simply decrease in direct proportion to the falling concentration, but a very dilute solution still corresponds to a considerable quantity of the adsorptive. If this quantity simply decreased in the same ratio as the concentration, we would have a very ill-defined border. The falling concentration at the periphery of the spreading drop would then bring about the adsorption of smaller and smaller quantities of the dye. Actually, however, the absence of proportionality makes a very dilute solution compatible with considerable adsorption. It is on this phenomenon that Goppelsröder has based an analytical procedure for the recognition and separation of substances, so-called **capillary analysis.** If a broad strip of filter paper be suspended with its lower edge in a solution of two dyes, which are not adsorbed with equal readiness, the more strongly adsorbable will be found immediately above the surface of the solution, while the other one will ascend higher. For instance, with a mixture of methylene blue and eosin we find below a blue zone containing a mixture of both dyes, and above a red one of eosin alone. The process is not confined to coloured substances; colourless ones may be separated and recognized in the same manner, if the paper is afterwards treated with reagents which form coloured compounds with the substances to be separated.

A loose union, reminiscent of exchange adsorption, is observed in certain silicates, the naturally occurring zeoliths and the artificial permutites. These, for example, take up $Ca^{\cdot\cdot}$ ions from a solution, and give off $Na^{\cdot}$-ions; the dependence on the concentration is similar to that shown by an adsorption isothermal.

Under certain conditions a sodium permutite may give up almost the whole of its sodium in exchange for another ion, e.g. $Ag^{\cdot}$-ion. The silver has therefore permeated the whole of the permutite structure. Now these silicates are indeed extraordinarily porous and we cannot altogether reject the notion that the silicate ions may form an open and yet solid framework which allows the cations to permeate it thoroughly. For the present it must remain undecided, whether this conception is useful or whether the hypothesis of mixed crystals, hence of a so-called solid solution, will prove more fruitful. The soil has similar properties, i.e. it can bind cations loosely by exchange ; this is attributed to the presence of zeoliths and of humus, which can take up ions in a like manner.

Adsorption is doubtless also important in a number of biological processes. Cell walls may adsorb dissolved substances exactly as other adsorbents do. This has been proved for the fixation of corrosive sublimate by blood corpuscles and for that of phenol and other substances by yeast cells. Probably the first stage in disinfection by substances like corrosive sublimate is simply the adsorption of the antiseptic, which is only later followed by chemical changes. Among the many other intoxication processes, which closely resemble an adsorption, we may refer to the action of veratrine on the cardiac muscle of a marine snail (*Aplysia limacina*), investigated by Straub. All the characteristics of an adsorption are present : the veratrine is taken up rapidly and reversibly ; it can therefore be removed again by washing, and the process may be represented by an ordinary adsorption isothermal.

ADSORPTION CATALYSIS IN SOLUTION

As we have seen, a reaction may be influenced by adsorption at the interface between a solid and a gas; the same phenomenon may take place in solution and present the same diversity.

A very clear illustration is furnished by the decomposition of hydrogen peroxide on the surface of glass wool, in the presence of metallic salts, such as those of copper. The reaction proceeds according to the equation

$$2H_2O_2 = 2H_2O + O_2$$

Glass wool by itself accelerates the reaction, so does a small quantity of copper salt, but if the copper salt and the glass wool act simultaneously, the rate of decomposition of the hydrogen peroxide is about ten times as great as when either agent acts singly. Now the copper is found to undergo adsorption on the glass wool, so that its concentration in the adsorption layer is much greater than in the solution, and consequently the catalytic acceleration, due to it, is also greater, since the reaction takes place almost exclusively on the surface. The rates of decomposition are indeed proportional to the quantities of copper adsorbed.

A close analogy to the decomposition of stibine, described on p. 50, is provided by the decomposition in solution of formic acid, according to the equation

$$HCOOH = H_2 + CO_2$$

which decomposition can be accelerated by finely divided rhodium and particularly by osmium. The analogy extends to the course of the reaction and to its dependence on the concentration. Here also the two products of the reaction (H_2 and CO_2) are difficultly adsorbable, in comparison with the formic acid, and the reaction proceeds as if only those molecules of the acid are decomposed, which undergo adsorption.

The retardation of a reaction in the adsorption layer by other foreign substances was mentioned in reference to gaseous adsorption; it is also found in solution. Thus charcoal accelerates the oxidation of phenylthiocarbamide by free oxygen to sulphur and an unknown sulphur derivative of phenylthiocarbamide, and this reaction is definitely retarded by the products of the reaction. The oxidation of oxalic acid, according to the equation

$$2C_2H_2O_4 + O_2 = 4CO_2 + 2H_2O,$$

is also accelerated by charcoal, and we have here the curious case, that a reacting substance (oxalic acid) retards its own oxidation. The reaction proceeds the more slowly, the more oxalic acid is present in the adsorption layer, doubtless because the oxygen has to diffuse through this layer and does so all the more slowly, the thicker (or denser) the layer is. Foreign organic substances, such as the urethanes, also retard the reaction, and, as might be expected, all the known characteristics of adsorption appear. The adsorbability of the urethanes is known to increase rapidly, as we ascend the homologous series, and to follow Traube's rule. Accordingly ethyl urethane retards several times as strongly as methyl urethane, and propyl urethane excels the ethyl compound in the same ratio. The retardation is doubtless due to the fact that these foreign substances make the access of oxygen even more difficult.

A still deeper insight into the mechanism of such a reaction is afforded by the investigation of the oxidation in aqueous solution of amino-acids, such as cystine, on the surface of charcoal. While neither the original substance nor the reaction products strongly retards the reaction, a number of foreign substances do so powerfully. Among these substances two groups may be distinguished. There are in the first place capillary-active organic substances, which act quite like the urethanes in the previous example. Their retarding action is therefore found to increase like their adsorbability, in accordance with Traube's rule. The action is probably due to these substances displacing the less adsorbable amino-acid from the surface and thus lessening its surface concentration and thereby also the velocity of its oxidation.

There is, however, a second group of substances which retard the reaction about 1,000 times as strongly as the organic substances and yet are not appreciably capillary-active, nor are they strongly adsorbed; hydrocyanic acid is a striking example of this second group. Otto Warburg explains its peculiar action as follows: By no means the whole surface of the charcoal takes part in the reaction, but only certain portions are active, where iron compounds (or compounds of other heavy metals) occur. The importance of iron results from the fact, that all charcoals containing iron accelerate the oxidation of the amino-acids, whilst varieties completely free from iron are not active at all, but become so when a minute quantity of iron has been incorporated in them in a suitable form. The hydrocyanic acid is considered to be loosely bound, especially by the iron compounds, which thus lose their catalytic activity. The interpretation of the behaviour of capillary-active substances, given above, remains unaffected, for when the latter are adsorbed by the charcoal, they cover the whole of the charcoal surface, including the ferrous portions, and displace the amino-acid from them. Charcoal and iron are therefore in the same relation as are glass wool and copper in the previously discussed example of the decomposition of hydrogen peroxide.

These reactions taking place at interfaces are of great biological importance. O. Warburg has shown that the reactions underlying respiration, fermentation and carbon assimilation also take place at surfaces. The proof was partly furnished by the observation that all these processes are retarded by capillary-active substances, which follow Traube's rule. For it is practically certain that these influences only accompany interfacial reactions, and not reactions taking place in true solution. Ferment reactions are doubtless of the same nature, whether the ferment be present in colloidal solution, or whether it be adsorbed at an interface. Many ferment actions, e.g. the decomposition of hydrogen peroxide by catalase, have been found to resemble clearly other reactions which are accelerated by particles in colloidal solution, e.g. the decomposition of hydrogen peroxide by colloidal platinum. This resemblance may be partly explained by the circumstance that interfacial processes are important in both cases.

5.—Capillary-electrical Phenomena

Electrical influences are of considerable importance in the study of colloids, but are here of a quite different kind from those with which electrochemistry has hitherto chiefly concerned itself. We have to consider here the so-called **electrokinetic** processes, which do not appear at all in galvanic cells, and only slightly in electrolysis. These processes may be readily illustrated by the following experiment: Milk is poured into a **U**-tube, as shown in Fig. 11, and, without mixing, a layer of pure water is introduced above the milk into both limbs. Platinum electrodes, E and E′, attached to wires, dip into the water layers. When a potential difference of 100 volts is set up between the electrodes, the border surface separating the milk from the water moves away from the negative electrode in one limb, and towards the positive electrode in the other. The fat globules of the milk therefore migrate with a certain velocity, as the result of the potential difference applied from outside, and they behave as if negatively charged. This phenomenon is called **cataphoresis** and we speak of the **cataphoretic migration velocity** of the globules. In this example the fat globules happen to be liquid, but solid particles, liquid droplets and gas bubbles all behave in the same way; the state of aggregation of the particles is a matter of indifference.

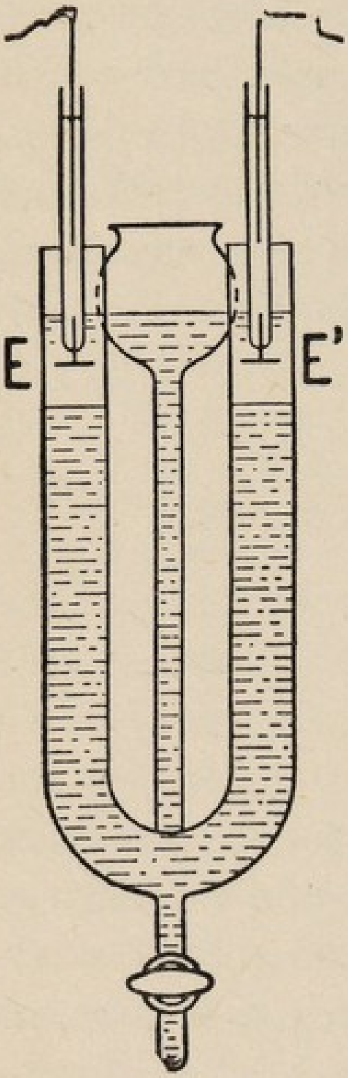


FIG. 11.

In the cataphoresis of solid particles the rigid interface is mobile, the liquid as a whole does not move. The relationship is reversed by the arrangement represented in Fig. 12. D is a porous diaphragm, e.g. an asbestos plug or a gelatin jelly. On either side are electrodes and the vessel K is quite full of water, which rises to a certain height in the capillary R. If a current of about 100 volts or more is passed through, the water moves, as if it were positively charged, i.e. it rises higher in the capillary R. This (inverted cataphoresis) is **electrosmosis**; it will be seen that the walls of the diaphragm pores are fixed, that the liquid can move and that it migrates as the result of an external potential difference.

Whilst in this respect electrosmosis is the reverse of cataphoresis, both phenomena may be reversed in another way. If in the apparatus in Fig. 12 no potential gradient be applied, but the liquid be forced through the diaphragm by means of a pump, an electrometer will indicate a potential difference between the two sides of the diaphragm. Water is charged positively with respect to the material of most diaphragms, and accordingly the electrode, towards which the water is pumped, is charged positively in relation to the other. The potential set up in this manner is called a **stream potential.**

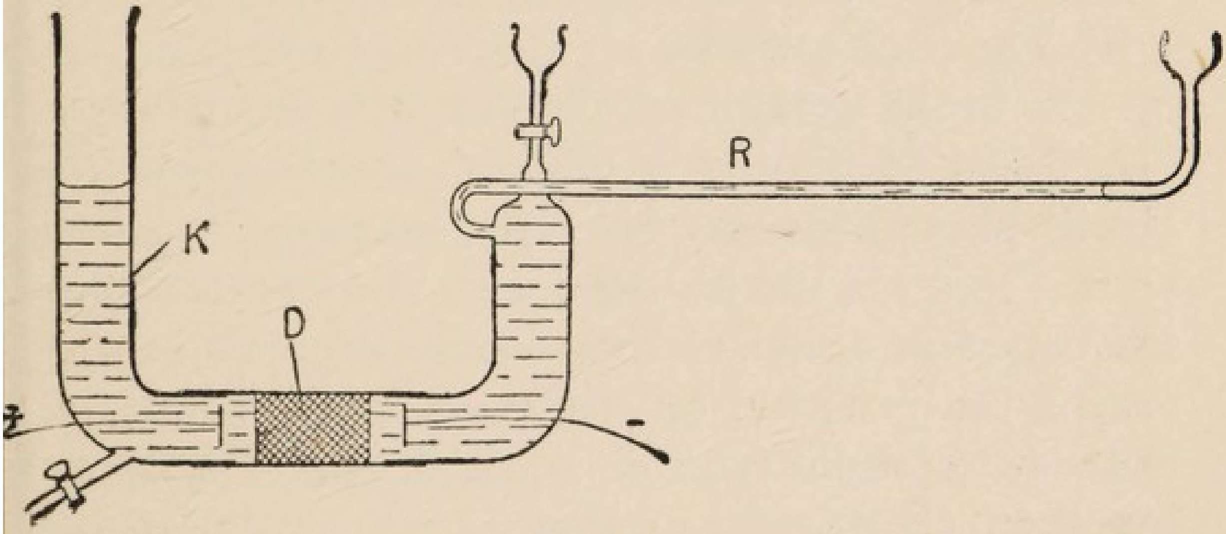


Fig. 12.

The corresponding inversion of cataphoresis is achieved, for instance, when a powder falls through a liquid between two electrodes; the potential difference set up between the latter can then be detected. This is the **potential due to falling particles.**

The following table summarizes the relationship between the four phenomena:

I. A potential difference applied from outside produces a movement:

(*a*) of the liquid relative to a fixed interface: **electrosmosis.**

(*b*) of solid particles relative to the liquid: **cataphoresis.**

II. A movement due to external forces produces a potential difference:

(*a*) The liquid is made to move relatively to the fixed interface: **stream potential.**

(*b*) The solid particles are made to move relatively to the liquid: **potential due to falling particles.**

A theory of the purely physical aspects of electrokinetic phenomena was developed long ago by Helmholtz. It deals, for instance, with the way in which the cataphoretic migration velocity depends on the size of the particles, on the viscosity of the liquid, on the external difference of potential, etc. The theory has been abundantly confirmed; in particular the four above-mentioned phenomena are actually found to be connected quantitatively in the manner required by the description given. Any result obtained, for example, with electrosmosis, may therefore at once be applied to cataphoresis or to stream potentials.

In Helmholtz's theory an important part is played by the potential difference between the fixed wall and the liquid. In the following discussion this quantity will be termed the **electrokinetic potential difference.** Helmholtz did not further consider the properties of this potential difference, its dependence on dissolved substances, etc. The question arose, however, when Nernst's theory of galvanic cells also postulated a potential difference at every single electrode; the dependence of this potential on dissolved substances is deducible from Nernst's theory with great accuracy.

We might at first be inclined to assume, that the electrokinetic potential difference ζ and Nernst's potential difference at a single electrode of the galvanic cell, which latter potential we will call ε, are identical. This view was often put forward.

Facts were soon discovered, however, which militated against the supposed identity, and when the quantities ζ and ε were then measured at interfaces, as far as possible similar, they turned out to be largely independent of each other. Nernst's potential is mostly determined at metallic electrodes of galvanic cells. We might therefore have attempted, for purposes of comparison, to measure the electrokinetic potential ζ at metallic surfaces, e.g. in the cataphoresis of metallic particles or in electrosmosis through metallic diaphragms. Now Helmholtz's theory of electrokinetic phenomena applies in the first place only to bad conductors; it is not unconditionally applicable to metals. It was therefore desirable to measure the ζ potential at the surface of a bad conductor, such as glass, at which Nernst's potential ε (often called the **phase-limit force**) may also be determined. This can be done by means of the apparatus represented in Fig. 13. A is a very thin glass bulb (having a wall less than 0·1 mm. thick) filled with an electrolyte solution which does not undergo any change, and into it dips a platinum wire, serving as electrode. The bulb A is immersed in a beaker B containing the solution to be investigated. E is a normal electrode, such as is also used in other cases as a standard of reference. (In a galvanic cell we never measure the potential of a single electrode, but always the sum or difference of at least two potentials. Thus if we desire to compare the potentials of a metal in two different solutions, the other electrode of the galvanic cell must remain unaltered; it is the standard of reference.) If we connect the normal electrode with that inside the glass bulb, we measure potential differences, which vary in a quite regular manner when the electrolyte solution in B is varied. The conductivity of the glass is sufficiently large, and the wall of the bulb sufficiently thin, for electricity to pass through the bulb and the platinum wire. The glass bulb therefore behaves like any metallic electrode of a galvanic cell, and thus

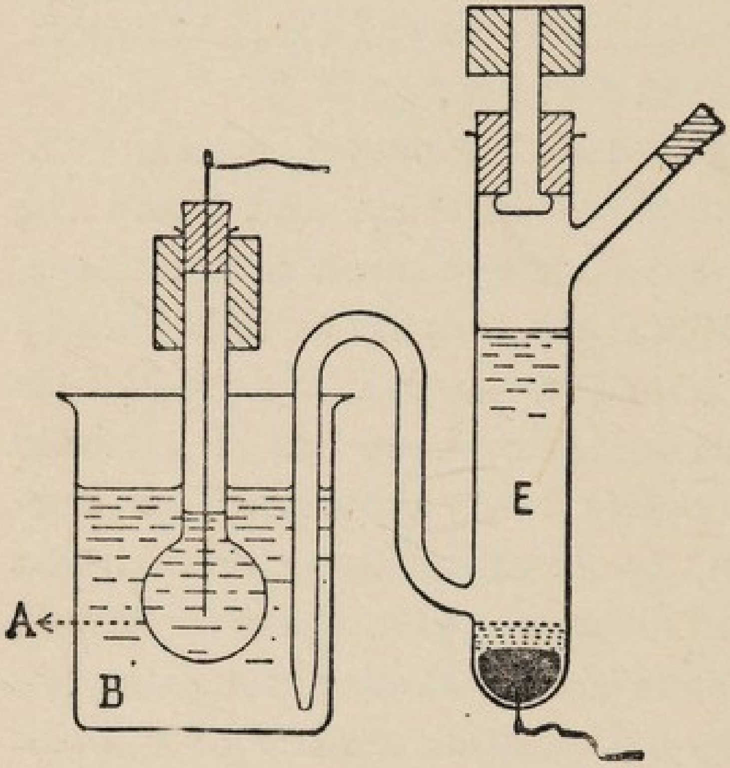


FIG. 13.

the phase-limit force ε of glass against an aqueous solution may be determined.

For purposes of comparison the solutions used in the above experiments were forced through capillaries made of the same kind of glass as the bulb; the resulting stream potentials, and with them the electrokinetic potential differences ζ of the capillary wall, were then determined. It was found that ε and ζ behave quite differently. In the experiments with the glass bulb only acids and bases had a definite effect. Aluminium salts and salts with a strongly adsorbable cation, such as dyes (crystal violet), hardly affected the phase-limit force ε. In the case of the stream potentials the effect of acids and bases was evident, but small compared with that of aluminium salts and dyes; with crystal violet, for instance, the charge on the glass capillary, used for measuring stream potentials, could actually be reversed. Originally negative with respect to pure water, this charge became positive in the presence of the dye.

This behaviour may be interpreted by assuming for the potential at a fixed interface a course represented in Fig. 14. We will suppose that the fixed wall is on the left of A, and the liquid on the right; between A and B is the portion of the liquid which firmly adheres to the wall. The abscissæ x, plotted from A to the right, are the distances from the wall; the ordinates are the potentials at the corresponding distances x. The full curves 1 and 2 represent two possible courses of the potential ε at the wall. We see that we must distinguish two potential differences ; in the first place $\varepsilon_o - \varepsilon_f$, representing the difference between the potential ε_o of the fixed wall itself and the potential ε_f in the interior of the fluid—this difference is Nernst's

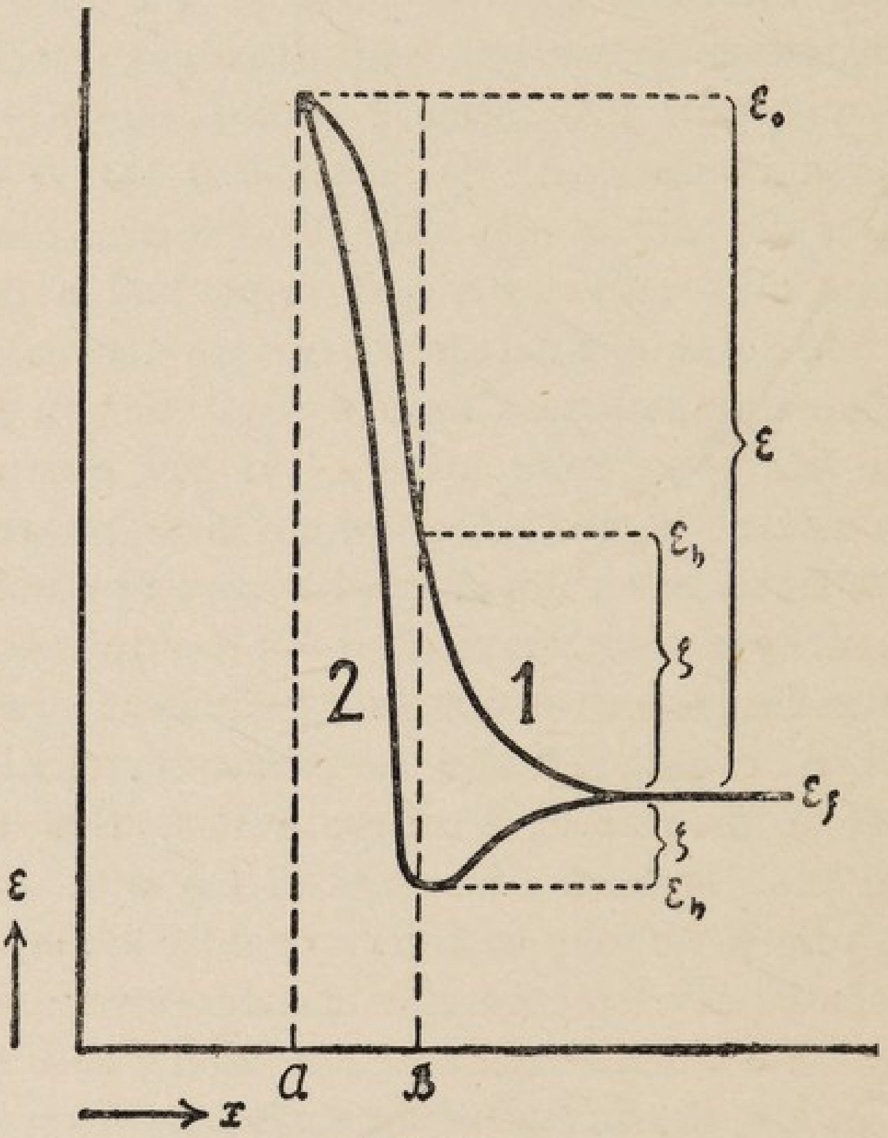


FIG. 14.

potential or the phase-limit force ; in the second place we have $\varepsilon_h - \varepsilon_f$, the difference between the potential ε_h of the layer of liquid adhering to the wall, and the potential ε_f of the interior of the fluid—this difference is the electrokinetic potential ζ. The dotted line passing through B represents the boundary between the layer of fluid adhering to the wall and the interior of the liquid; since the curves 1 and 2, representing the course of the potential, intersect this dotted line in two different places, there are two different values for ε_h and therefore also for ζ. With respect to ε it is evidently important that ions can pass from the interior of the liquid into the wall itself. If, as usual, the electrode consists of a metal, then, as is well known, the ions of this metal are the determining factors, according to Nernst's theory; in the case of a zinc electrode zinc ions pass from it into solution, or dissolved zinc ions are deposited on the electrode as metallic zinc. The fact that with a glass electrode the ε-potential is especially altered by acids and alkalies, is doubtless due to the power of $H^{\cdot}$- and OH'-ions to alter the silicate framework itself; ζ on the other hand will be influenced by any ion whatsoever which is present at the interface, especially in consequence of adsorption. We also see from Fig. 14, how for identical values of ε the potential ζ may be very different, for in the two cases represented ζ has an opposite sign for identical values of ε; this is because in case 2, as a result of the presence of different ions, not occurring in case 1, and of their different adsorbability, the course of the potential is a different one.

The above hypothesis therefore explains why the electrokinetic potential is so largely independent of Nernst's potential, and also that the former, unlike the latter, is greatly influenced by the adsorbability of the ions. Unfortunately we do not know enough about the adsorption of individual ions and the way in which they crowd each other out. We cannot therefore as yet obtain any idea of the actual course of the curves 1 and 2 in any particular case. We merely call attention to a few general results, which will be applied later in our discussion of colloidal solutions. In investigating the effect of increasing concentrations of an electrolyte on the ζ potential of a layer adhering to a wall, it is, as has been pointed out, immaterial whether we employ cataphoresis, or electrosmosis, or stream potentials for this purpose. Whatever the method employed, we find the most effective ion to be the one, which carries a charge opposite to that of the wall layer. In Fig. 15 the abscissæ represent electrolyte concentrations in milligram-molecular weights (millimols) per litre, the ordinates are ζ-potentials, determined from the cataphoretic migration velocities of petroleum droplets in the respective electrolyte solutions.

The droplets—or what matters in cataphoresis, their surface layers—are negatively charged. Hence the ζ-potential in Fig. 15 has been plotted upwards with negative and downwards with positive sign. We now see how in the case of the univalent $K^{\cdot}$-ion, the anion has a distinct effect: the ζ-potential is increased, the charge on the droplets is raised to some extent; the effect is smallest with the univalent Cl'-ion, largest with the quadrivalent $Fe(CN)_6''''$-ion. But with cations of higher valency, the bivalent $Ba^{\cdot\cdot}$-ion, the trivalent

Al$^{\cdot\cdot\cdot}$-ion and the quadrivalent Th$^{\cdot\cdot\cdot\cdot}$-ion, the effect of the anion becomes less prominent owing to a decrease of the ζ-potential; there is a lowering of the charge

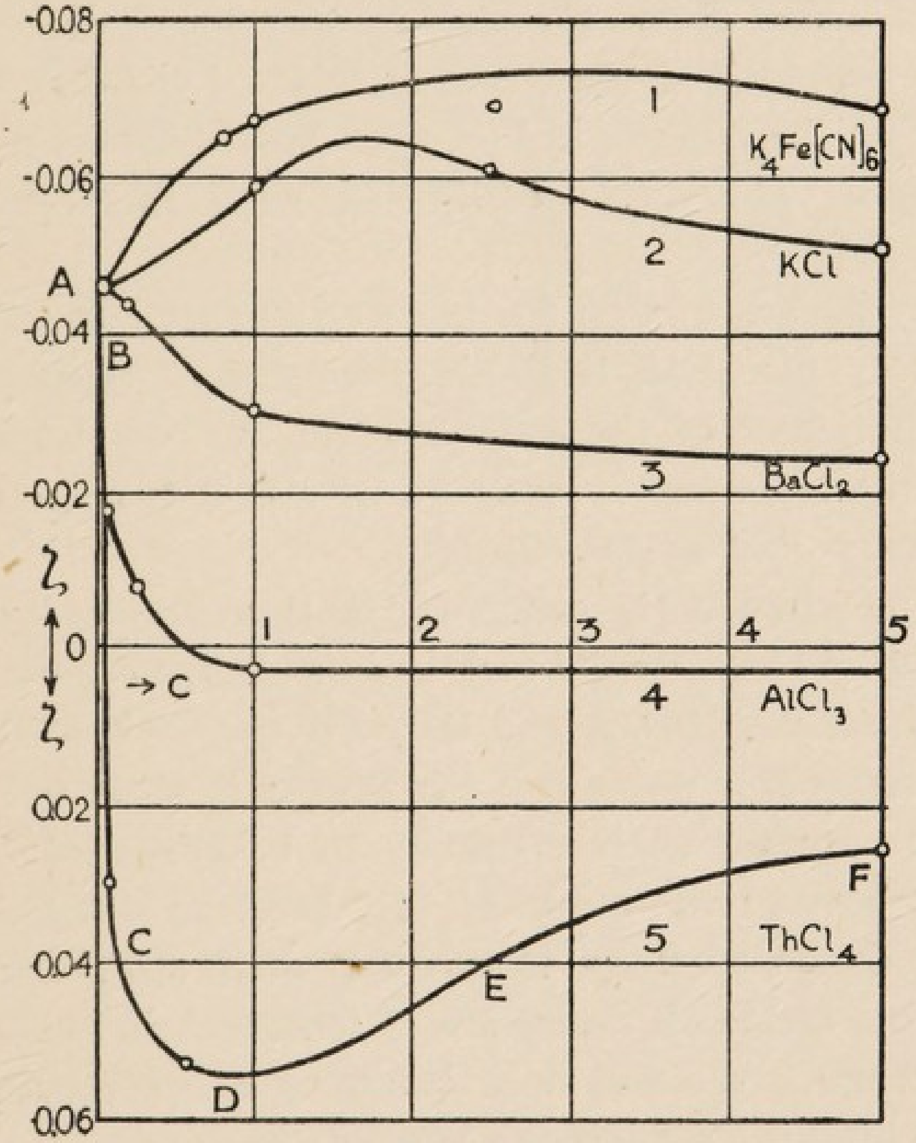


FIG. 15.

and the discharging effect increases quite strikingly with the valency of the cation.

We must add, that valency is not the only factor determining this phenomenon. If we compare the K$^{\cdot}$-ion with organic cations, e.g. with that of aniline or of a dye such as crystal violet, we find that the organic cations lower the ζ-potential much more strongly, and therefore have a greater discharging action, than the $K^{\cdot}$-ion or other univalent inorganic cations. The curve for aniline corresponds more or less to that for $Ba^{\cdot\cdot}$-ions, that for crystal violet roughly to the $Th^{\cdot\cdot\cdot\cdot}$-ion curve in Fig. 15. This stronger action of organic cations is connected with their greater adsorbability.

If on the other hand the layer on the wall is charged positively from the beginning, instead of negatively, it is the effect of the anions which preponderates in much the same way. With them also it is a question of valency and adsorbability.

The electrokinetic potential is therefore primarily affected by those ions, which have a charge opposite to that of the wall layer, and they are the more effective in lowering this potential, the higher is their valency and the greater their tendency to be adsorbed.

It is beyond the scope of this book to discuss the numerous phenomena connected with electrokinetic processes, although many are of technical or biological importance. We will only allude to a few examples. Electrokinetic influences appear in osmosis. The osmosis of solutions of non-electrolytes is the experimental starting-point of the modern theory of solutions, for the fundamental example is the osmotic penetration of water into a cane-sugar solution. The latter is contained in an unglazed earthenware pot, with pores blocked by copper ferrocyanide, a type of cell devised by Pfeffer. This osmosis may be satisfactorily interpreted by means of the osmotic pressure of the sugar solution. The phenomenon becomes much more complicated, if we use electrolytes instead of sugar, and, instead of copper ferrocyanide, membranes of collodion, with or without gelatin.

Unlike Pfeffer's cell, these membranes are not strictly semi-permeable ; in addition to water, they also allow salt to pass. The departure from a regular osmotic behaviour may be of various kinds. With many electrolytes we observe an extraordinary osmosis, which falls off at greater concentrations and begins to increase only at still greater ones as required by the augmented osmotic pressure of the solution. Indeed, electrolytes are known, which from the outset show a **negative osmosis,** that is to say, water does not penetrate into the salt solution, but the salt solution passes out into the water. Recent experiments by Jacques Loeb have definitely established that this behaviour depends on the intervention of an electrosmosis. A potential difference is set up between the two sides of the membrane, the so-called **membrane potential,** and like the external potential difference in electrosmosis, this drives the liquid through the pores of the membrane, provided certain conditions are fulfilled, which allow of the generation of an electric current. Depending on the algebraic sign of the membrane potential, water is driven into the salt solution (osmosis) or salt solution into the water (negative osmosis). Since this varying transport is superimposed on the movement of water due to osmotic pressure, the nett result should show great variety, which is indeed actually observed. Very probably such negative osmosis is important in glandular secretion, in the bleeding of plants, etc.

Technical applications of electrosmosis have been attempted, with some measure of success, by Count Schwerin and the " Elektro-Osmose " company founded by him. Thus peat may be dried by subjecting it between perforated electrodes to an electric current, which drives out the water by electrosmosis, so that it drips out through the holes in the electrode. Again, in order to obtain a high-grade clay, an impure variety is suspended in water, and after allowing the coarser particles to settle, the specially plastic finest particles and the impurities are precipitated by cataphoresis. In electrosmotic tanning the hides are hung between perforated electrodes ; not only is washing accelerated by electrosmosis, but owing to cataphoresis, the tannin also penetrates more rapidly into the hide.

6.—The Properties of Interfacial Layers

Hitherto we have always discussed adsorption layers without considering their thickness, or the question whether any special behaviour should be attributed to the molecules contained in them. Our present knowledge on these points is slight and not well-founded, but slight though it be, it is important for an understanding of surface processes. We may begin by enquiring whether the adsorption layer consists of a single layer of molecules or whether it comprises several such layers. Many investigators are of opinion that generally, if not always, the layer is one molecule thick and that it need not even be continuous, but that the molecules of the adsorbed substance may be distributed at various points, with intervals between them, somewhat as if on a chessboard the black squares only might be occupied by the pieces. A continuous layer might have a thickness of 1 $\mu\mu$ or even less, according to the diameter of the constituent molecules. In contradistinction to this, other investigators believe that the layer consists of two or three, or even of ten to twenty layers of molecules, so that it would have to be 5–10 $\mu\mu$ in thickness.

We cannot here consider the respective merits of these alternative hypotheses and we merely point out that in electrokinetic phenomena more especially, it is difficult to conceive of the adsorption layer as consisting of a single layer, which does not extend into the interior at a greater distance from a solid wall than one molecular diameter. (See Fig. 14.) The adsorption of gases by charcoal and its dependence on temperature may moreover be calculated on simple assumptions, if we suppose the adsorption layer to be several molecules in thickness.

On the other hand it seems pretty definitely established that there are examples of adsorption layers, or quite generally of fluid membranes, which consist of only one layer of molecules. Since these allow various interesting conclusions to be drawn, we will deal with them a little more fully. On p. 36 we discussed the behaviour of two immiscible liquids, and in particular the case in which one liquid spreads completely over the surface of another. If therefore a suitable liquid, e.g. oleic acid, is placed on a clean water surface, it is drawn out to a thin film which covers the water. Now there is a maximum surface, and therefore also a minimum thickness, to which the oily film can be drawn out ; if we try to exceed this maximum surface, the film breaks away. Devaux has carried out measurements of this kind with very simple means. He filled a rectangular photographic dish with water and carefully cleaned the surface of the liquid by drawing a strip of paper across it so as to collect the impurities at one end. Behind this strip, which remained to some extent as a line of demarcation, a clean water surface was formed, on which a minute quantity of oil was placed. The oil spread over the surface, but not over the whole of it, if the quantity of oil was sufficiently minute. The area covered by the oil may be recognized by cautiously dusting with talcum powder. Since the contour of the oil film is not sufficiently regular for purposes of measurement, a second strip of paper is advanced from the side of the clean surface, so that the oily film is confined to a rectangular area between the two strips of paper. If the second strip be moved backwards, the edge of the oil film, recognizable by the talcum dust, detaches itself from the paper, when the latter is in a given position. By moving the paper to and fro several times, this limiting position can be exactly determined, and with it the maximum surface which the oil can cover. From the weight of oil used and its density, the thickness of the film can be calculated.

In this way the thickness of a film of triolein was found to be about 1 $\mu\mu$; this is about the thickness of a single layer of molecules; a substance of high molecular weight, like triolein, has of course molecules of considerable size.

As Langmuir and Harkins have shown, experiments of this kind allow far-reaching conclusions to be drawn with regard to the shape of the molecules. Such speculations may perhaps seem ill-founded, but there is an ever-increasing body of evidence, suggesting that molecules have a definite shape, about which the above considerations may enlighten us. We have already referred in the introduction (p. 3) to the number of molecules present in a given quantity of a substance. A grammolecular weight (885 grams) of triolein contains 0·6 quadrillions of molecules. Since the weight of the triolein placed on the surface is known, the number of molecules can be calculated. Now if the oil film is only one molecule thick and the molecules lie side by side, we obtain the area occupied by each individual when we divide the maximum surface of the film by the number of molecules in it. For triolein this area works out at 1·3 trillionth sq. cm. Quite a number of organic substances have been examined in this way, and a comparison of the results shows the molecules of such different substances as palmitic acid $C_{15}H_{31}.COOH$, stearic acid $C_{17}H_{35}.COOH$, cerotic acid $C_{25}H_{51}.COOH$

and myricyl alcohol $C_{30}H_{61}OH$ to occupy practically the same area in the film. A molecule of tristearin $C_3H_5(C_{18}H_{35}O_2)_3$ occupies almost exactly three times the area of a molecule of stearic acid, and one of triolein three times that of oleic acid.

Now this behaviour may be explained as follows: All the substances referred to are polar in character; at one end they have a group, like -COOH, -OH, or $(\text{-}CO_2)_3C_3H_5$, which is markedly hydrophilic and thus has a great affinity for water; the other end is occupied by alkyl groups, which are hydrophobic and have little affinity for water. It seems plausible to assume, that the affinity for water will affect the orientation of the molecules, in such a way that the hydrophilic groups are turned towards the water and the hydrophobic ones away from it. Now palmitic, stearic and cerotic acids as well as myricyl alcohol, all have the same hydrophobic group pointing upwards, namely a methyl group, and thus the area occupied by these groups is also the same. These polar molecules are to some extent comparable to rods with dissimilar ends, such as pointed lead pencils. They all lie close together in the oily layer and all point a similar end upwards. It is probably more correct to assume, as indicated by other experiments, that the long alkyl chains are folded like a concertina. In tristearin three rodlets are united to a single molecule and three methyl groups point upwards. The area occupied by them is three times as large as that occupied by the single methyl group of stearic acid. The same ratio holds good between triolein and oleic acid, only the area occupied by the latter is larger than that occupied by stearic acid.

We may mention some further conclusions which also seem to be well-founded. It will be remembered, that the lower fatty acids, which are soluble in water, are strongly capillary-active; in accordance with Traube's rule successive members of the homologous series depress the surface tension more than their next lower homologues and are adsorbed on the surface with increasing readiness. (See pp. 29 and 62.) In these dilute solutions the molecules of these fatty acids are probably not arranged at right angles to the surface, as in the oil films discussed above, but probably lie horizontally with their whole length in the surface. It is found that this assumption is quite sufficient to explain the regular increase in capillary activity according to Traube's rule. In cases where this rule holds good, we may therefore assume that the entire molecule lies in the adsorption layer.

Considerations of this kind are also important in connexion with catalysis in an adsorption layer. A reaction between two molecules with polar ends will be accelerated, if the ends, which are required to react, come into contact in the surface. But if this is not the case, if a hydrophobic end is required to react with a hydrophilic one, and the hydrophobic ends of the molecules are directed towards the adsorbent, while the hydrophilic ones point to the water, the reaction is not accelerated by the adsorbent, and may even be retarded by it.

B. THE RATE OF FORMATION OF A NEW PHASE

Many colloidal solutions are prepared by subjecting a dissolved substance to a chemical reaction which results in the separation of a solid. Thus colloidal gold solutions, to which we shall often refer later, are prepared by reducing a gold chloride solution containing potassium carbonate, by means of formaldehyde. In this reaction gold first separates as atoms, which unite to form gold nuclei, and these may then grow to gold crystals. In any case therefore we must distinguish two rates: the rate of reaction which leads to the formation of gold nuclei, **the rate of nuclear formation,** that is the rate at which gold atoms unite to form the smallest gold crystals, and **the rate of crystallization,** at which the gold nuclei grow to larger crystals. Now the rate of nuclear formation and the rate of crystallization have been studied in systems having no direct connexion with colloids. It is therefore convenient to discuss these systems first. A similar consideration applies to the nature of the amorphous-solid state. As was pointed out in the introduction, this state is not characteristic of the colloidal condition as such, but since colloidal particles are often amorphous, an understanding of amorphous solids is desirable for the study of colloids.

RATES OF NUCLEAR FORMATION AND OF CRYSTALLIZATION.

We must first consider the origin of nuclei and their growth in the undercooled melts of pure substances.

These processes do not themselves form part of the subject of colloids, but will serve to illustrate the essential features of the phenomena involved.

Many liquids can readily be cooled below their freezing-point without solidifying; they are then undercooled. If a small crystal of the frozen liquid be then introduced, the whole of the liquid crystallizes from this point. Glazed frost is a phenomenon depending on undercooling. The soil, the pavement, etc., are covered with a film of water, which at first remains undercooled when the temperature falls, and then suddenly crystallizes to a thin coating of ice, as soon as ice nuclei appear. In the case of water the origin of crystal nuclei and the subsequent crystallization cannot be followed very closely, since both processes take place too rapidly, but in a number of organic liquids which freeze at suitable temperatures, these processes proceed sufficiently slowly for convenient study.

We can readily observe in the case of piperine, fused between two glass plates, how on cooling below the melting point, crystal nuclei are formed spontaneously in various places, from which the crystallization proceeds. If we lower the temperature still further, the nuclei at first become more numerous. The number of nuclei formed in unit time represents the **rate of nuclear formation,** and this rate at first increases with falling temperature. Generally it is difficult to determine at low temperatures, because the nuclei grow too slowly. Here Tammann, the principal student of these phenomena, uses the following artifice. He keeps the melt for some time at the temperature at which he desires to measure the rate of nuclear formation, and then raises it to a higher temperature, at which the rate of crystallization is large enough for the nuclei, formed at the lower temperature, to grow rapidly into visible crystals. In this way the rate of nuclear formation was found to increase at first with falling temperature, and then to decrease again. Fig. 16 shows the way in which the rate of nuclear formation depends on the temperature in the case of undercooled piperine. Since this substance melts at 128°, we see that the rate of nuclear formation can only be studied much below the melting point.

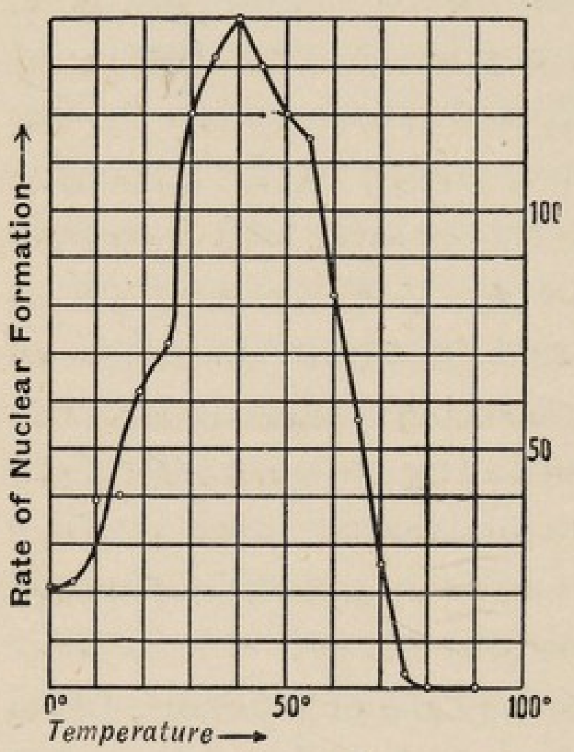


FIG. 16.

It is indeed doubtful whether the phenomena, thus observed, are caused exclusively by the molecules of the undercooled liquid. The rate of nuclear formation is found to be greatly influenced both by dissolved foreign substances, and by undissolved coarser particles; in the case of many liquids there is good reason for believing that the observed rates of nuclear formation primarily depend on the amount and the properties of the dust contaminating the melt. The molecules of the melt are adsorbed on the surface of these dust particles, and are probably orientated in the manner described on p. 92; they thus unite to form a nucleus, provided that the number of the adsorbed molecules is large enough. For this reason caution is necessary in interpreting the course depicted in Fig. 16. The diminished rate of nuclear formation at low temperatures may probably be attributed to the increased viscosity of the melt, which is unfavourable to the union of molecules to nuclei. The increased rate at a somewhat higher temperature is doubtless due to the following: Not all the molecules of the melt are in a condition suitable for nuclear formation; if this were so, every melt would crystallize at once below the freezing point. Only a fraction of the molecules are capable of this, namely those whose heat motion is below the average. Such slowly moving molecules can more readily cohere and form nuclei. If the temperature falls, the heat motion as a whole becomes less and so the fraction of slowly moving molecules, capable of nuclear formation, increases. At still lower temperatures this advantage is wiped out by the increased viscosity.

With respect to crystallization, supersaturated solutions behave in much the same way as undercooled melts. Such solutions are obtained by dissolving the solute at a higher temperature, at which it is more soluble, and then cooling the liquid; as a rule crystallization does not set in at once, but the solution remains supersaturated. The supersaturation may be increased in two ways, either by allowing the temperature of a given solution to fall still further, or by starting from a more concentrated solution, so that at the desired temperature the concentration and the degree of supersaturation are both higher. As in the case of undercooled melts, foreign substances, and particularly dust particles, strongly influence the rate of nuclear formation, so that it is difficult to ascertain its true value, which solely depends on the union of solute molecules to nuclei.

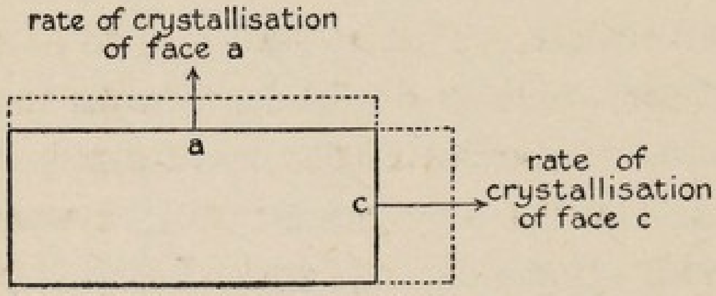


Fig. 17.

When the crystal nuclei have once been formed in an undercooled melt or supersaturated solution, they grow further at various rates by the adhesion of new molecules from the undercooled liquid. This growth rate is called the **rate of crystallization** and differs for different faces of the crystal. Each kind of face has a characteristic rate at which the crystal grows in a direction perpendicular to this face. (See Fig. 17.) This figure further shows that the more slowly growing face always remains the larger, while the most rapidly growing faces are also the smallest. In the case of a needle-shaped crystal the rate of crystallization in a longitudinal direction is much the largest.

The true crystallization rates of the various faces of a crystal are difficult to measure and have therefore rarely been ascertained. Generally investigators have been content to measure a certain average crystallization rate, which is much easier. In undercooled melts this may for instance be done by sucking the melt into a capillary tube provided with a scale and inoculating one end with a crystal. Crystallization then proceeds in the melt, and the demarcation between the crystalline mass and the undercooled liquid is generally so sharp, that the distance traversed during a definite interval of time can readily be observed on the scale. The rate of crystallization may be measured in supersaturated solutions by inoculating with a crystal of the solute, stirring rapidly and observing the fall of concentration by any means which allows of rapid measurement (e.g. by observing the refractive index).

Experiments with supersaturated solutions have shown a specially rapid fall of concentration during the first moments of crystallization, a kind of decrease reminiscent of adsorption ; it seems therefore as if the solute with respect to which the solution is supersaturated, is adsorbed on the surface of its own crystals. According to Volmer there is actually a good deal of evidence in favour of this adsorption and its very great effect on the rate of crystallization. If we watch microscopically the growth of a mercury crystal from supersaturated mercury vapour (below $-39°$), or of a crystal of lead iodide from a supersaturated aqueous solution, we see that crystallization begins at a point of the crystal surface and then extends over the crystal face, forming a layer of uniform thickness. We thus get the impression that the molecules do not directly enter the space lattice from outside, but are present in an adsorption layer on the surface, and are added, as it were laterally, to the crystal nucleus, which has been formed at one point of the adsorption layer. The process of crystallization does not therefore take place in a direction *perpendicular* to the crystal face, but *parallel* to it. The rate of crystallization is definitely fixed by the amount of substance adsorbed on the crystal face and increases with this amount. As yet nothing definite is known about this adsorption at the various crystal faces, but certain plausible assumptions concerning it lead to values for the crystallization velocity of the various faces, which make the formation of needle- and rod-shaped crystals quite comprehensible.

The influence of foreign substances on the rate of crystallization also falls into line with the above conception. This influence has often been measured, not indeed the influence on the true rate of crystallization of individual faces, but on the average crystallization rate, which, as was pointed out, is relatively easily measured in superfused melts, as well as in supersaturated solutions. In the vast majority of cases the foreign substance lowers the rate of crystallization ; the dependence of the latter on the concentration of the former corresponds completely to the regular behaviour to be expected from adsorption on a crystal face. Indeed, in the crystallization from supersaturated solutions only those dyes retard crystallization, which are visibly adsorbed by the crystals, and therefore stain them. The retardation by strongly adsorbable substances may be so extreme, that crystallization is practically abolished, although the solution is supersaturated with respect to the substance crystallizing out. From what has just been said, it will be quite intelligible, that when the adsorption of a foreign substance lowers the adsorption of the molecules of the substance present in supersaturated solution, the rate of crystallization will also be lowered. It is further clear why the external shape of crystals is often so greatly influenced by the addition of foreign substances. We may find, for instance, that a substance separating from pure solution in crystals of regular habit—cubes or octahedra—may crystallize in long needles in the presence of impurities. The latter may be adsorbed at the different faces to a varying extent, and thereby alter the rate of crystallization unequally, so that the various faces grow at rates very different from those obtaining in pure solution.

The influence of foreign substances on the rate of crystallization must often be taken into account. The careful purification of solutions by means of charcoal, when we desire to obtain crystals from them in preparative chemistry, simply depends on the removal by the charcoal of strongly adsorbable substances, which greatly delay or completely prevent crystallization, even although the solution may be decidedly supersaturated. If we knew more about the influence of foreign substances on the rate of crystallization of individual crystal faces, and how the shape of the crystal is thereby altered, we might perhaps be able to draw conclusions concerning the nature of the solutions, from which naturally occurring crystals originally separated. The crystalline structures of living organisms, such as gall stones, urinary calculi and pearls, show by their very appearance, that they have separated from solutions rich in capillary-active substances; these latter are often colloids, like protein. By lowering the rate of crystallization these substances have caused the concrements to separate in micro-crystalline form, and the capillary-active substances are themselves contained in the concrements, because they collected in the adsorption layer.

The Nature of the Amorphous-Solid State

We have already emphasized in the introduction, that the amorphous-solid condition, often assumed by a substance when it separates from colloidal solution, is not characteristic of the colloidal state, and that the particles of many sols are crystalline. Since the question of the state of aggregation of colloidal particles continually arises, we will here briefly describe the methods which enable us to distinguish the amorphous-solid state from the crystalline. These methods are naturally connected with the behaviour of superfused melts, for a substance may be most readily obtained in the amorphous-solid condition, by very rapidly and strongly cooling its melt, and thus passing as quickly as possible through the region of temperature, in which nuclei are easily formed. The mixture of silicates constituting ordinary glass has such a very slight tendency to crystallize, that we need not take any particular care to avoid the temperature region of rapid nuclear formation and rapid growth of the nuclei. But a glass may be devitrified by heating it long enough to high temperatures, at which crystallization proceeds more quickly. Silicates and borates are by no means peculiar in this respect; many organic substances also form amorphous solids, when their melt is supercooled sufficiently rapidly.

It is not quite easy to decide whether a substance is crystalline or whether it is amorphous-solid. External properties, such as vitreous nature and conchoidal fracture, are not very reliable. Precipitates formed from solutions are apt to show not the slightest indication of crystalline structure, when examined under the microscope, and colloidal solutions may even evaporate to varnish-like pellicles, yet in either case the particles may have a minutely crystalline structure. Now amorphous solids differ from crystals in not showing a definite melting point; they soften on heating and pass into the liquid state gradually, as is familiar in the case of glass. They therefore behave as if they were essentially of the same nature as liquids, only they are extremely viscous, so that their particles lack the mobility of a fluid. The molecules of amorphous solids are arranged, like those of a liquid, in haphazard fashion, and are not distributed with strict regularity in a space lattice, as are the molecules of a crystal. The above criterion of gradual softening is, however, not very definite, and the devitrification (crystallization) of many glasses on heating them is also troublesome. A remarkable difference between the crystalline and the amorphous-solid state is presented by their thermal conductivity, which in crystals rapidly increases at very low temperatures near the absolute zero, but in glasses diminishes in this region and becomes apparently constant near —273°. The utilization of this property is, however, not so simple experimentally, and is particularly difficult in the case of powders.

X-rays on the other hand provide a quite general method for distinguishing crystalline from amorphous solids; it is based on the following considerations. X-rays are light constituted by excessively short waves. The wave-length of visible light varies from 400 to 800 $\mu\mu$, that of X-rays is only about 0·1 $\mu\mu$. When light passes through a fine uniform grating we observe so-called diffraction and interference phenomena: white light is resolved into a spectrum and monochromatic light, e.g. of a sodium flame, shows sharply defined light and dark lines, so-called interference bands. By looking at a source of light through a veil or through the eye-lashes, we can observe spectral colours, due to the same phenomenon, although not in a very pure form. Now von Laue made the far-reaching discovery that the space lattice of a crystal can produce interference of X-rays just as a coarser grating, prepared mechanically, causes interference of visible rays. In order to obtain a readily observable interference, the distance between the rulings on the grating must bear a definite relation to the wave-length of the light. Now the distance between the atoms of a crystal is indeed such, that their arrangement in a space lattice may bring about the interference of X-rays. In contradistinction to the flat gratings, which are used for producing spectra of visible light, the crystal constitutes a spatial grating. The latter may be conceived to arise from a series of gratings or veils which have been arranged behind one another in regular fashion. The space lattice of crystalline substances causes a sharp interference of X-rays, which is wanting in amorphous solids and in liquids, since these have no strictly ordered space lattice.

Debye and Scherrer have described a widely applicable X-ray method, which is also especially suitable for the problems of colloidal chemistry. Fig. 18 represents the apparatus diagrammatically. In the centre is a rod of the finely powdered solid, whose state of aggregation is to be determined. It is surrounded by a photographic film, contained in a lead chamber. The film serves to show the direction of the X-rays after their passage through the solid rod, for these rays cannot of course be seen, although they affect a photographic plate. The X-rays are as far as possible of uniform wave-length (i.e. "monochromatic," like the light from a sodium flame) and they enter through a window in the direction of the arrow. Interference occurs both in the passage and in the reflexion of the rays in the rod, and this interference causes pronounced lines on the film, as indicated in Fig. 18, but only if the particles constituting the rod are crystalline. If they are amorphous, we obtain instead of the sharp lines, a uniform darkening of the film or quite broad bands; the same happens with a liquid. Figures 19 and 20 of Plate I show the contrast between amorphous freshly precipitated beryllium hydroxide and an older specimen which has become crystalline. Good varieties of glass are found to be completely amorphous; their X-ray diagram shows uniform darkening of the film.

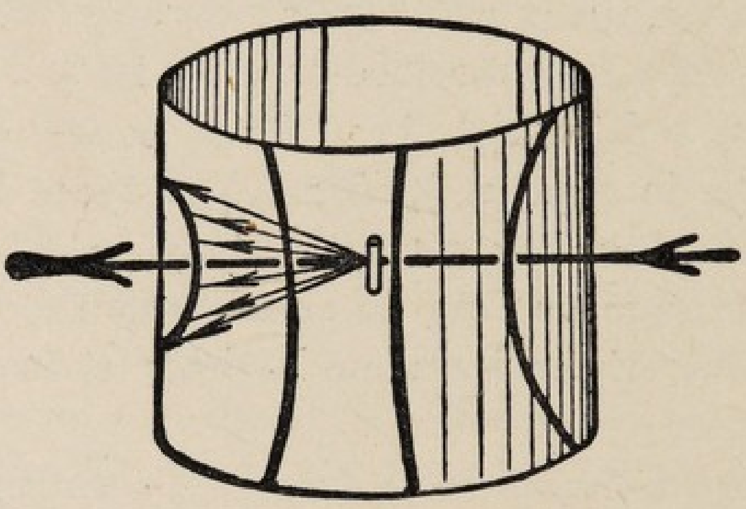


FIG. 18.

The special application of Debye and Scherrer's method to colloidal chemistry will be discussed in

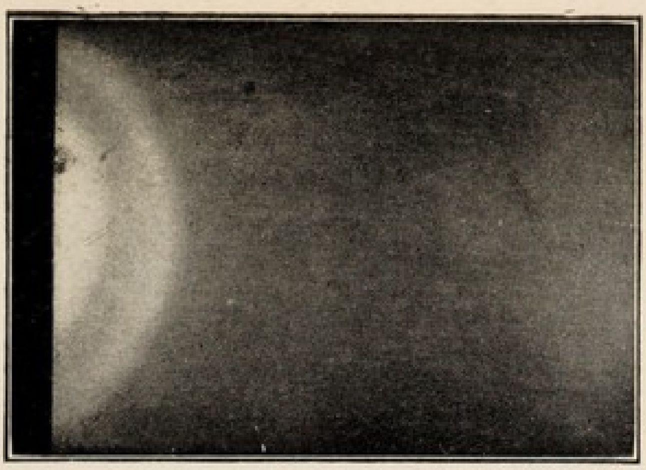


Fig. 19.—Precipitated Beryllium Hydroxide

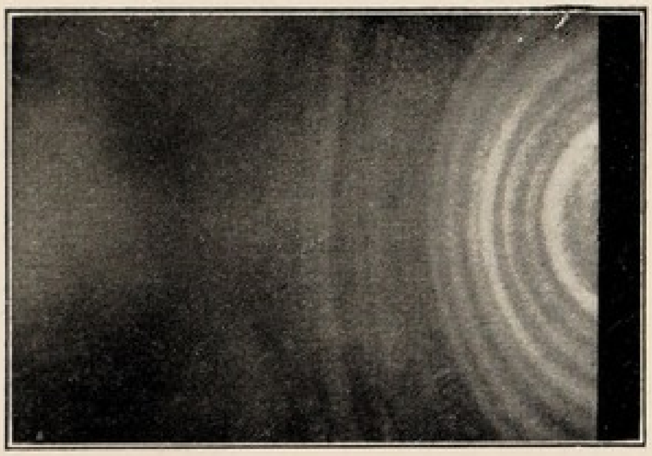


Fig. 20.—Crystalline Beryllium Hydroxide

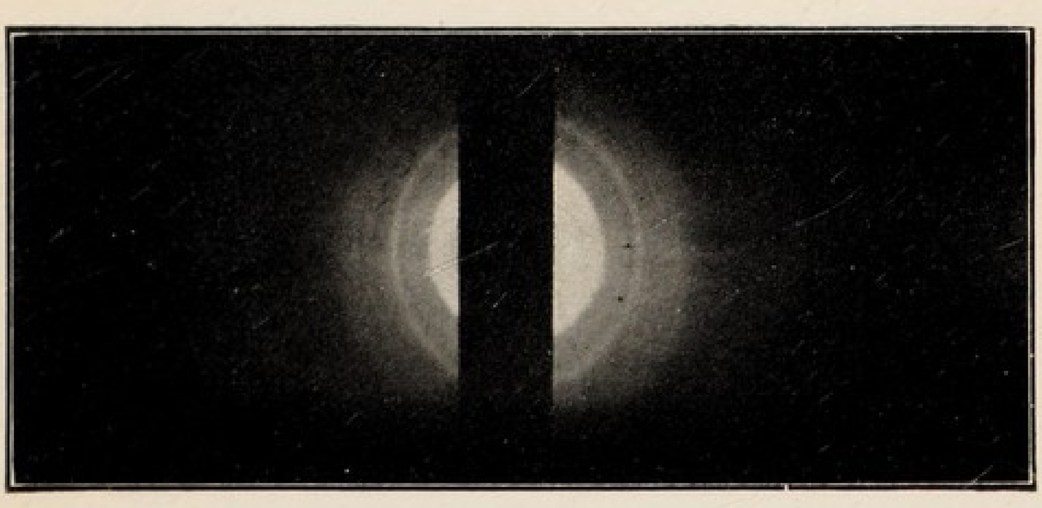


Fig. 28.—Ramie Fibres (Squashed)

greater detail on pp. 133, 183, 184. In any case the X-ray apparatus described is an important requisite in a laboratory devoted to the study of colloids.

C. THE BROWNIAN MOLECULAR MOVEMENT

The importance of the Brownian movement in the study of colloids was already indicated in the introduction. It was discovered by the botanist Robert Brown, in 1827, when studying granules present in the contents of pollen-grains. As was also pointed out in the introduction, the Brownian movement must be regarded as due to the heat motion, and results from impacts of the molecules of the liquid with coarser visible particles. This interpretation of the phenomenon has only become certain during the first years of the present century, although the phenomenon itself had been known for a long time. For many years no special importance was attached to it, evidently because the movement was considered to be the accidental result of external vibrations or of heat currents.

Many investigators were, however, impressed by the incompatibility of such a view with the fact that the Brownian movement takes place quite independently of external influences. It has been observed in a cellar which was so free from vibration that a mercury surface did not show the least disturbance, while the temperature was kept as constant as possible ; not the slightest change in the movement was observable in the course of a year, in a microscopical preparation which was carefully protected against evaporation. Thus Chr. Wiemer was first led in 1863 to assume, that the phenomenon is caused by the blows of molecules of the liquid, which are postulated by the kinetic theory of heat.

To this the following objection has indeed been raised. A single molecular blow would be too weak to cause any visible movement of a particle ; since the blows come quite at random from all sides, they should cancel one another and the suspended particle should remain at rest. As von Smoluchowski has pointed out, this is only true, however, when the interval of time during which the particle is observed may be considered as very long. In a game of chance a stake may be won or lost many times over during a given moderate interval of time. Not until the game has been played for a very long period do losses and gains cancel out completely. On applying the calculus of probabilities to the heat motion of the molecules of a liquid we find that the probable number of molecules, striking the particle in a given direction, is so large, that we may not regard our observations as extending over a very long period, but only over a certain moderately long time. During this time the blows in any particular direction may preponderate so greatly, that we can detect a movement of the particle.

In 1906 Einstein and von Smoluchowski succeeded in basing a theory on this view, first put forward by Chr. Wiemer; the formulæ deduced from the theory are in excellent agreement with experimental data. Einstein and von Smoluchowski started from the idea, that a coarser particle, exposed to the blows of the fluid molecules, would have to behave in just the same way as a large molecule which executes the heat movement spontaneously. Such particles therefore, when their motion makes them strike a wall, exert a pressure which must be equal to the osmotic pressure, that would be exerted by a solution of molecules of similar large size. The laws of van't Hoff, governing the osmotic pressure of dilute solutions, are actually found to hold also for suspensions and emulsions, in the manner which has just been suggested. Without the aid of mathematics it is difficult to explain how these laws were verified in the case of suspensions. We will only remark in general, that the Brownian movement is zig-zag and so irregular that the real velocity of a suspended particle cannot be determined. The movement may, however, be characterized by the so-called **deviation** of the particle. This is simply the length of the straight line joining the initial position to the final position reached in a given time. Fig. 21 represents diagrammatically the trembling haphazard movement of a particle, and every rectilinear portion of a zig-zag line is such a deviation. Now this deviation in its dependence on the viscosity of the fluid, on the radius of the particle, on the temperature, etc., can be shown to behave quantitatively as if the particle moved like a molecule of dissolved substance, obeying van't Hoff's laws for dilute solutions.

We may quote one more among the many deductions of this theory which have been verified. The density of the atmosphere of course decreases as a result of gravity, the higher we ascend. Since a dilute solution behaves exactly like a gas, it is subject

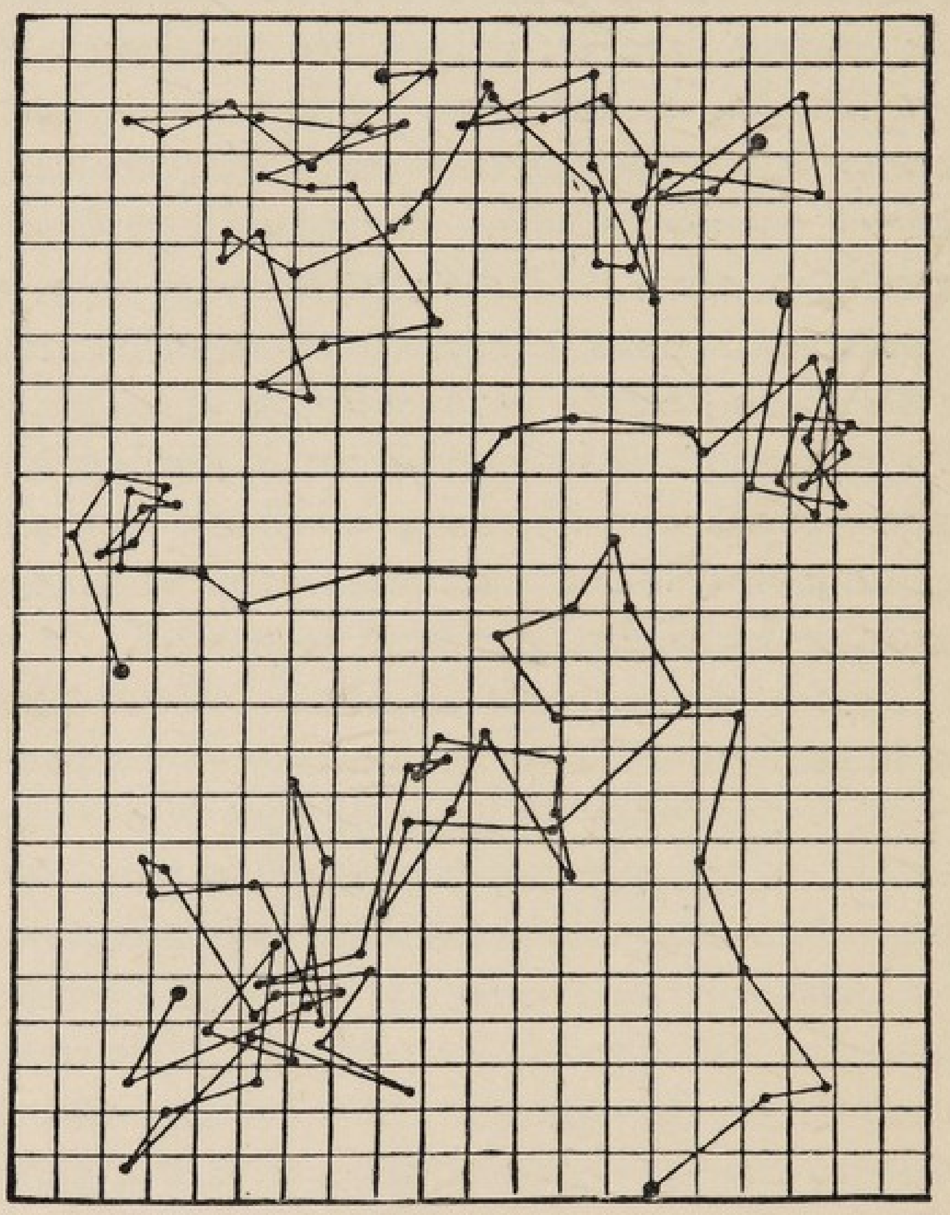


FIG. 21.

to a similar gradation : the concentration of an otherwise uniform solution decreases in its upper layers. With delicate apparatus the decrease in the concentration of an electrolyte solution may even be demonstrated over a difference in level of one metre. The rate of decrease depends on the molecular weight of the solute ; it is most rapid (occurs at the smallest difference of level) when the molecular weight is greatest. In emulsions and suspensions, where, as was explained above, a very large molecular weight must be attributed to the "solute," a decrease in the concentration of suspended particles may already be observed at a vertical distance of a few thousandths of a millimetre. The numbers of particles, determined microscopically at various heights in the liquid, are found to agree quantitatively with the theory of Einstein and von Smoluchowski.

COLLOIDAL-DISPERSE SYSTEMS

A. COLLOIDAL SOLUTIONS, SOLS AND GELS

1.—Sols

General Remarks

AS was explained in the introduction, solutions may be regarded as colloidal, when they contain much larger particles than are present in ordinary true solutions. On the other hand their particles are still too small to be directly visible under the microscope, like those of a coarse emulsion or suspension. The diameters of colloidal particles are comprised between the limits of 1–500 $\mu\mu$. Of course there is no sharp line which separates colloidal solutions from true solutions on the one hand or from coarse suspensions and emulsions on the other. The transitions are quite gradual and continuous. Thus colloidal solutions are known whose particles are smaller than 1 $\mu\mu$, and therefore of a size which is often attained by the solution molecules of true solutions. Moreover many properties of sols are also observed in coarse emulsions and suspensions, only in these the much larger particles usually settle down more rapidly, so that emulsions and suspensions are generally less stable than colloidal solutions.

Although the line of demarcation is not sharp, we have generally no difficulty in deciding whether we are dealing with a colloidal, or with a true solution. **Dialysis,** already employed by Graham, is still one of the best means for this purpose. The solution to be tested is placed in a dialyser—a small sack of parchment paper—and surrounded by pure water, which is renewed from time to time. In the case of a coloured solute we can see directly whether or no it passes through the membrane. A colourless substance must be tested for by a suitable chemical reagent.

The difference between the behaviour of colloidal and of true solutions may be rendered obvious by comparing the dialysis of a strongly coloured true solution, such as potassium permanganate, with a strongly coloured colloidal one, such as a gold sol. In the former case the outer liquid is soon coloured, in the latter case it remains colourless, even after a long time.

There are many colloidal solutions, such as those of soaps and of many dyes, whose solute does indeed pass through the membrane, but much more slowly than in the case of true solutions. We are here concerned with relatively small colloidal particles, which approximate in size to the ordinary solution molecules. Such solutions are often called **half-colloidal** or **semi-colloidal.**

Dialysis is simply a diffusion through a jelly, for as such the dialysing membrane must be regarded. Instead of dialysing we can therefore directly observe the diffusion of the colloidal particles in a jelly. Test tubes are partially filled with a gelatine jelly, on which the solution under investigation is poured. In the case of a coloured solution we can see directly from the penetration of its particles into the jelly, that the solution is a true one. If it is a sol, the dissolved substance does not diffuse at all, or only extremely slowly, but with true solutions the process is rapid. With colourless solutions we can employ the artifice of incorporating in the jelly a substance which gives a characteristic chemical reaction with the diffusing substance.

A further much used means of testing, whether or no a solution is colloidal, is provided by the ultramicroscope. The limits of its application will be discussed later.

A coarse emulsion or suspension is simply recognized as such under the ordinary microscope.

A much more difficult problem than the delimitation of colloidal solutions as a whole is the classification of their many varieties. Fundamentally all classifications are artificial, for every colloidal solution has its own peculiarities determined by the nature of the colloidal particles and of the dispersion medium ; this also applies to true solutions. Nevertheless many colloidal solutions have properties so similar, that they may well be considered and classified together. On the one hand there are those which, like aqueous solutions of starch and of proteins, are clearly more viscous than water and are little sensitive to electrolytes ; even a fairly concentrated solution of sodium chloride or sulphate hardly changes their appearance. This group of sols is often termed **hydrophilic,** because the colloidal solute is evidently related to water; it readily imbibes water and retains it firmly; the colloidal particles contain much water, which may be inferred from the great similarity of their refractive index to that of the dispersion medium. The viscosity of **hydrophobic** sols, on the other hand, differs but little from that of water. These sols are very sensitive to electrolytes; of salts, like sodium chloride or sulphate, a decimolar solution already suffices to precipitate the colloidal particles as flakes, to **coagulate** them. This group includes the colloidal solutions of gold and of many other metals, of the sulphides and of various other substances. It will be seen that these are substances to which we can hardly ascribe any special relationship to water; they are indeed also hydrophobic from the point of view developed on p. 57. Accordingly the colloidal particles of these solutions are not particularly rich in water and their refractive index is usually quite distinct from that of water. An artificial feature of this classification is, however, brought out by a consideration of the sols of ferric and aluminium hydroxides, vanadium pentoxide, etc., which are so sensitive to electrolytes, that in this respect they are absolutely hydrophobic, while on the other hand they are unmistakably related to water, for the refractive power of their particles differs but little from that of water, and the flakes which can be formed from these sols are generally strongly hydrated. Hence the designation hydrophobic does not seem to fit them closely. They are really intermediate between hydrophobic and hydrophilic sols; on account of their sensitiveness to electrolytes we will classify them among the former.

When considering dispersion media, other than water, we may use the expressions **lyophobic** and **lyophilic,** instead of hydrophobic and hydrophilic.

Another method of subdivision is into **suspension colloids** (or **suspensoids**) and **emulsion colloids** (or **emulsoids**). Here the criterion is intended to be the state of aggregation of the disperse phase: if the particles are solid, we have a suspensoid, if they are liquid, we have an emulsoid solution. Now in many cases the state of aggregation of the colloidal particles cannot be determined. This classification is therefore not based directly on a property which can be ascertained experimentally. Many authors are inclined to make the class of suspensoids co-extensive with that of hydrophobic sols, and that of emulsoids with hydrophilic ones. But this is certainly incorrect, for there are sols with liquid particles, such as an extremely fine emulsion of petroleum in water, which behave in a perfectly hydrophobic manner. Conversely there is every reason for assuming, that the particles of many hydrophilic sols are amorphous-solid. Hence if we adhere, as some writers do, to the characteristics, which led to the conception of suspensoid and emulsoid, we may not identify them with the concepts hydrophobic and hydrophilic. If, on the other hand, we follow other writers in giving up the idea which originally led to the differentiation, there is no objection to using the terms suspensoid and emulsoid in the same sense as hydrophobic and hydrophilic. Since however no usage has yet become established which is consistent on this point, we will here only use the expressions hydrophilic and hydrophobic.

A third method of subdivision is into **reversible** (or **resoluble**) sols and **irreversible** (or **irresoluble**) ones. Thus an aqueous sol is resoluble, when after desiccation under certain experimental conditions the residue can be dissolved again to a sol by the addition of water; it is irresoluble when this cannot be done. This method of characterizing sols seems at first sight very clear, but to the author's mind it suffers from the disadvantage that it is not sufficiently general. Thus a concordant classification is not obtained unless the method of evaporation is stated very precisely. Again, a sol which at one time is found to be resoluble, may become irresoluble through the presence of a small quantity of foreign matter, which hardly alters the properties of the sol in any other way. The division between resoluble and irresoluble sols does not coincide with that between hydrophobic and hydrophilic ones. Many hydrophobic sols, such as that of gold, are indeed irresoluble, because their particles are not related to water; but ferric hydroxide for instance, which on account of its sensitiveness to electrolytes, was reckoned above among the hydrophobic sols, is very often found to be resoluble. These three methods of classify-ing sols, into hydrophobic and hydrophilic, into suspensoids and emulsoids, and into irresoluble and resoluble, are therefore not identical. In spite of various objections, we will use in the following pages only the division into hydrophobic and hydrophilic sols.

Preparation and Properties of Some Sols

The method of preparing hydrophilic sols generally presents few peculiarities. A solution of gelatin or of egg white can be prepared in the same way as any true solution ; other hydrophilic sols can easily be prepared from body fluids, such as an albumin solution from blood serum. Hydrophobic sols, on the other hand, are pre-eminently artificial laboratory products, and hence the preparation of a few of the most important will be briefly discussed.

We have already alluded to the fact that the subject of colloids can be approached from two sides. We can either start from true solutions and enlarge their particles by forming a difficultly soluble precipitate, or we can take a liquid or solid in bulk and attempt to divide it up as finely as possible, to " disperse " it. The former is called a **condensation method,** and practically all **gold sols** are made in this manner. The formalin method, which has been studied in special detail by Zsigmondy, may serve as an example. A feebly alkaline solution of a gold salt is prepared by adding to 120 c.c. of very pure water (see p. 121) 2·5 c.c. of a hydrochlorauric acid solution (made by dissolving 6 grm. $HAuCl_4 \cdot 4H_2O$ in one litre of distilled water) and then

3 c.c. of a 0·18 N solution of pure potassium carbonate. As soon as the solution has been heated to boiling, 3–5 c.c. of a dilute formaldehyde solution are added (0·3 c.c. of commercial formalin in 100 c.c. of water). The following reactions then take place:

$$HAuCl_4 + 2K_2CO_3 + H_2O = Au(OH)_3 + 2CO_2 + 4KCl$$
$$2Au(OH)_3 + K_2CO_3 = 2KAuO_2 + 3H_2O + CO_2$$
$$2KAuO_2 + 3CH_2O + K_2CO_3 = 2Au + 3HCOOK + H_2O + KHCO_3$$

The preparation of such a sol is largely determined by the rate of nuclear formation and the rate of crystallization, the most important properties of which have already been discussed on p. 94 *et seq.* From the gold atoms which are formed in the first instance, gold nuclei must result, which then grow out to gold crystals. The production of a colloidal solution is favoured by a high rate of nuclear formation, leading to the rapid production of so many nuclei that in the very dilute solution there is not enough gold available for them to grow to any considerable extent; the particles therefore remain small and within the colloidal-disperse region. On the other hand a high rate of crystallization is unfavourable to the production of a colloidal solution, for it means that the first nuclei formed grow too rapidly to larger crystals, so that a coarse suspension results, instead of a sol. The rates of nuclear formation and of crystallization are greatly influenced by small concentrations of foreign substances, in a manner as yet unknown. It is therefore necessary to follow a reliable recipe as closely as possible. Thus the purity of the water is important; contamination with certain colloids (silicates, ferric oxide, etc.) is particularly harmful, probably because they lower the rate of nuclear formation or coagulate the particles already formed. It is necessary to use water which has been distilled through a silver or quartz condenser. The reducing agent must also be selected with a view to securing a high rate of nuclear formation; this condition is sufficiently satisfied by formaldehyde. An ethereal solution of phosphorus is still better, but hydroxylamine is unsuitable, because with it the rate of nuclear formation becomes too small.

The gold sols prepared in this manner are liquids of a beautiful ruby-red colour, which do not froth and differ but little from water in viscosity, surface tension and other properties. They are markedly hydrophobic, i.e. very sensitive to electrolytes in small concentration; when these are added, the red colour turns to blue and ultimately the gold is precipitated as a bluish-black powder.

Another sol which has been much investigated, is that of **arsenious sulphide.** Analysts are familiar with the observation, that when hydrogen sulphide is passed into a pure aqueous solution of arsenious acid, the arsenious sulphide does not settle readily, but remains suspended in the liquid in a state of fine division. If a colloidal solution with particles of minimum size is desired, we must ensure, that the concentrations of the reacting substances are sufficiently small or that a sufficient number of nuclei are already present. We therefore first add a dilute aqueous solution of hydrogen sulphide to a not too concentrated arsenious acid solution and so produce a large number of nuclei. The reaction is then completed by passing hydrogen sulphide gas. The excess of this gas is removed by bubbling hydrogen through the liquid. This sol is characterized by the fact that in its preparation according to the equation

$$As_2O_3+2H_2S=As_2S_3+3H_2O$$

no electrolyte whatever is formed, which would otherwise have to be removed by dialysis ; hence there is no danger of coagulation. The As_2S_3 sol is a clear pale-yellow liquid, which, if not very concentrated, resembles in colour a solution of potassium chromate.

The sols of the **metallic hydroxides** ($Fe(OH)_3$, $Al(OH)_3$) may often be prepared in a very simple and characteristic manner. Most salts of these hydroxides are so extensively hydrolysed in dilute solution, that on dialysis the acid diffuses away, while a sol remains inside the dialyser. A ferric hydroxide sol may therefore be obtained by dialysing a dilute solution of ferric nitrate, because the latter salt undergoes hydrolytic dissociation according to the equation

$$Fe(NO_3)_3+3H_2O=Fe(OH)_3+3HNO_3$$

A commercial ferric hydroxide sol (*ferrum oxydatum dialysatum*) is prepared in pharmacy by cautiously adding ammonium carbonate solution to a solution of ferric chloride, so long as the precipitated ferric hydroxide still dissolves on shaking, and then dialysing the solution. The salt hydrolysis is therefore increased by suitably reducing the hydrogen ion concentration of the solution.

So far we have been discussing condensation methods. These contrast to some extent with the so-called **peptization** or **dispersion methods.** By peptization we mean the "dissolving" of a coarse precipitate—or of a continuous mass of a solid or liquid—to form a colloidal solution. This often depends on the fact that the precipitate consists in reality of very fine particles, which by suitable treatment can be dispersed in a state of colloidal division. The peptization methods may be illustrated by the preparation of a **vanadium pentoxide sol.** Ammonium vanadate is ground up in a mortar with hydrochloric acid, so that vanadium pentoxide separates in red flakes according to the equation

$$2NH_4VO_3+2HCl=V_2O_5+2NH_4Cl+H_2O$$

The pentoxide is washed on a filter until it begins to run through. It is then placed in a suitable quantity of pure water and shaken, until it has been peptized to a uniform sol of a fine reddish-brown colour.

Metallic sols may further be prepared by the method of electrical disintegration, which was first used in its simplest form by Bredig. An electric arc is produced under water between stout metal wires, so that thick clouds of evaporated and disintegrated metal are formed, composed of particles so minute, that they mostly remain in colloidal solution. It is advisable to make the liquid faintly alkaline, for as we shall see later (p. 148), the hydroxyl ion favours the peptization of substances which tend to assume a negative charge, as most metals do. In this way aqueous sols of platinum, of gold and of silver are readily prepared. Svedberg has elaborated the method and made it more delicate. Instead of a direct current he employs the discharge from an induction coil, and chooses the variables of the discharging circuit—resistance, self-induction, capacity and length of spark—in such a manner, that sparks of minimum duration are formed, which transport a considerable quantity of heat. He could thus actually produce sols of the alkali metals in organic liquids. In this electric disintegration a variety of phenomena seem to occur, but the finest particles (which must be formed in order to get a stable sol) seem to arise chiefly by the evaporation of the strongly heated metal of the electrode.

THE TYNDALL EFFECT AND THE ULTRAMICROSCOPE

Many sols show a peculiar optical behaviour, even without special apparatus; a casual observer might think that they fluoresce. This behaviour is seen very clearly when a powerful beam of light is sent through a sol in a dark room, and the beam is viewed sideways.

Whilst in true solutions, sufficiently free from dust, the path of the beam cannot be recognized, it is very obvious in colloidal solutions. The apparent fluorescence depends on causes and follows laws, different

4000×10^{-10}

4×10^{-7} metre

$= 4 \times 10^{-5}$ cm

$1-120\ \mu\mu$

from those of real fluorescence.[1] These phenomena are called after Tyndall, who first examined them more closely, the **Tyndall effect.**

The sols which have been mentioned so far, have coloured particles and do not show the Tyndall effect in its simplest form. For this purpose it is better to use a colloidal solution or an emulsion with colourless particles, e.g. a mastic emulsion. The latter is prepared by pouring an alcoholic solution of mastic resin into an excess of water. If the somewhat milky liquid be examined for a Tyndall effect in the manner described above, the path of the light, when viewed sideways, is shown by a blue colour. All colloidal solutions with colourless particles show a blue Tyndall light; indeed, this applies to all other colloidal-disperse systems, such as a fine smoke or milk glass, provided the particles are colourless.

The phenomenon may be explained as follows. The light passing through the sol cannot, properly speaking, be reflected by the particles; for this they are too small. In order to bring about a true reflexion the reflecting surface must at least have the dimensions of a wavelength, but the colloidal particles are smaller. They do, however, bring about, that a portion of the light is scattered laterally, and in this diffracted portion the

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[1] It was formerly thought that the Tyndall effect could be very simply distinguished from true fluorescence by the fact that the light sent out laterally is polarized in the case of the former, and not in that of the latter phenomenon. Recently, however, the light sent out laterally in true fluorescence has also been found to be partially polarized.

light of short wave-length, namely the blue and the violet, preponderates. Hence the beam of light, when viewed laterally, appears to be blue. If a sufficiently thin layer of such a mastic emulsion be viewed against a white background, it appears yellowish-red, for, as has been pointed out, the blue and violet portions of the light passing through are preferentially diffracted sideways, so that an excess of red and yellow rays are transmitted and make the liquid appear yellowish-red.

The Tyndall effect is simply the so-called primordial phenomenon of Goethe, on which the latter based his theory of colour. He expressed it somewhat as follows : A turbidity seen against a dark background appears blue, against a light background it appears yellowish-red. The physicists of Goethe's time were unable to explain the phenomenon, which was first done by Lord Rayleigh in 1870, in the manner outlined above. No wonder that Goethe placed little confidence in the science of physics, because of its inability to explain so familiar a phenomenon, shown by any milk glass or smoke.

The theory explains a further feature of the Tyndall effect, namely that the light diffracted exactly at right angles to the path of the beam, is completely polarized, i.e. this light vibrates in one plane only, perpendicular to the beam. If we look at the beam from any other direction, not at right angles, then the proportion of polarized light is smaller, diminishing according to a definite law along with the angle which the diffracted light makes with the beam.

If a powerful beam of light, passing through a colloidal solution, is viewed perpendicularly through a suitable microscope, we have the arrangement already referred to as the **ultramicroscope.** We have seen that every individual colloidal particle scatters light sideways. In order to allow this light to be recognized, the particles must not be too closely crowded, for if they are, the light sent out by them overlaps, and we only see a uniformly illuminated field. The colloidal solution must therefore be suitably diluted, and the thickness of the layer under examination must be a small fraction of a millimetre.

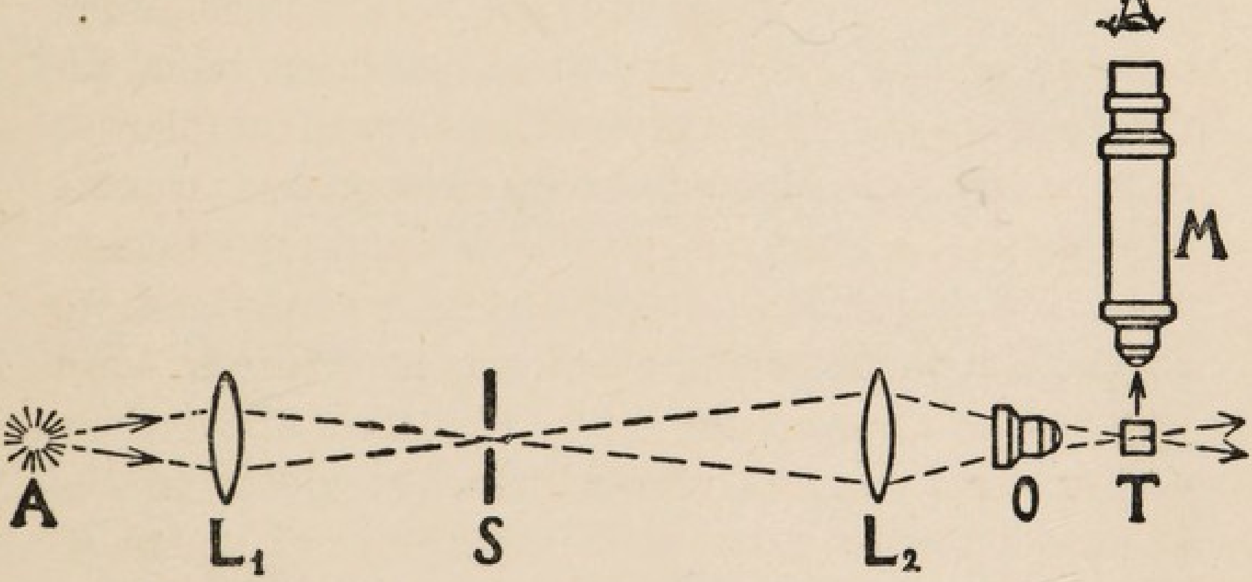

FIG. 22.

Fig. 22 represents the arrangement of the **slit ultramicroscope,** first constructed by Siedentopf and Zsigmondy. A powerful beam of light from the source A, which may be the sun or an electric arc, falls through the lens L_1 on a rectilinear slit S, of which a much reduced image is projected into the inside of the chamber or trough T, by means of a second lens L_2 and an illuminating objective O. The sol is contained in the chamber. The microscope M is so focussed, that the image of the slit comes into the middle of the field of vision. We therefore view an intensely illuminated and very shallow layer in the interior of the colloidal solution. A much used and convenient form of the chamber T was devised by Biltz and is represented in Fig. 23; it allows the liquid to be run in and out with great ease.

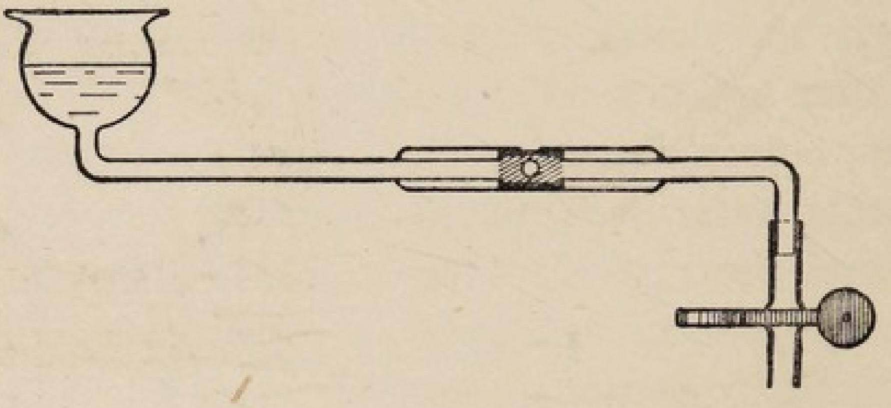

FIG. 23.

Zsigmondy has recently much improved the slit instrument by devising an **immersion ultramicroscope,** in which the illuminating and observing objectives are brought into the closest possible proximity. A chamber of the size used by Biltz is then unnecessary; the liquid is in a small annular container between the two objectives. This arrangement minimizes the loss of light due to absorption in the colloidal solution.

In the ultramicroscopes described so far the light has to be carefully adjusted, in order to get good results. This is not necessary in other instruments, in which a special condenser, simply added to an ordinary microscope, produces dark-ground illumination. Of these instruments we describe only the **cardioid ultramicroscope.** Fig. 24 is a diagrammatic representation of the condenser, which is introduced under the vertical tube of the microscope. Its central portion is impervious to light, which can only enter through an annular space (indicated by dotted lines) and is reflected in such a way, that after leaving the condenser the rays all intersect at one point below the microscope objective. The light emerges at such a small angle to the horizontal, that none enters the microscope directly; it passes through a space (represented in Fig. 24 by the two upper plates) in which the colloidal solution is placed. Usually a quartz chamber is employed, consisting of a slide and a coverslip, 1–2 μ apart. The use of quartz has the advantage that the slide and coverslip can be carefully cleaned by ignition in a flame, for dust particles which are apt to reflect light into the microscope, are very troublesome, and only that light should enter the microscope, which is diffracted sideways from the colloidal particles.

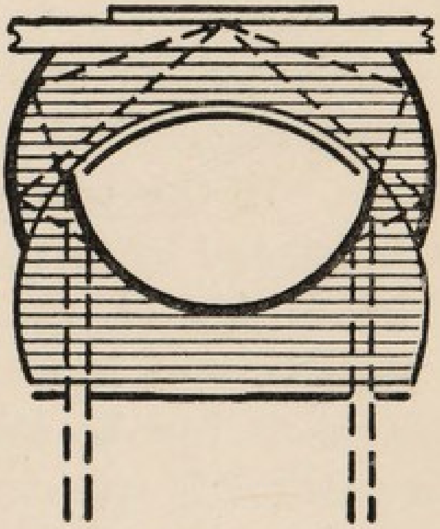

FIG. 24.

SIZE, STATE OF AGGREGATION AND SHAPE OF COLLOIDAL PARTICLES

The size of the particles cannot be directly measured under the ultramicroscope, for of course we only see the light which they scatter, and the theory indicates that the apparent size of the particles depends on the aperture of the microscope. Nevertheless their actual size can be ascertained indirectly, at least under certain simple conditions. If the sol contains particles of one size only, we have merely to find the number in a definite volume of liquid and to determine the total amount of colloidal substance by suitable analytical means. In this way we obtain the total mass of the particles, and by division, the mass of a single particle. A knowledge of the density gives the volume of a particle, and if we know its shape, the required dimensions can be calculated. In the simplest case the particle is spherical and then its radius may be readily calculated.

The lowest limit, at which colloidal particles can be recognized ultramicroscopically, is somewhat indefinite. It does not depend entirely on their size, but also on the difference between the refractive indices of the disperse phase and of the dispersion medium. If this difference is considerable, as in the case of an aqueous gold sol, then particles down to a radius of 5 $\mu\mu$ may still be recognized with sufficiently powerful illumination. Strongly hydrated particles, such as are present in many hydrophilic sols, can only be seen if they are much larger.

Particles which can no longer be resolved under the ultramicroscope, are termed by Zsigmondy **amicrons,** those which are ultramicroscopically visible he calls **submicrons** and the still larger ones, revealed by an ordinary microscope, he terms **microns.** The last-named have a radius of more than 200 $\mu\mu$.

The following table, based on one by Zsigmondy, shows how the various properties change with the size of the particles and indicates where transitions occur.

TABLE 2.

<table>
<tr><td>0·1 μμ</td><td>1 μμ</td><td>10 μμ</td><td>100 μμ</td><td>1 μ</td><td>10 μ</td><td>100 μ</td><td>1 mm</td></tr>
<tr><td colspan="4">Ultramicroscopic region</td><td colspan="4">Microscopic region</td></tr>
<tr><td colspan="5">Particles show Brownian movement</td><td colspan="3">No visible Brownian movement</td></tr>
<tr><td colspan="5">Particles pass through ordinary filter paper</td><td colspan="3">Particles retained by filter paper</td></tr>
<tr><td colspan="5">Particles show increased solubility</td><td colspan="3">Particles have ordinary solubility</td></tr>
<tr><td colspan="2">True solutions</td><td colspan="2">Colloidal solutions</td><td colspan="4">Emulsions and suspensions</td></tr>
<tr><td>0·1 μμ</td><td>1 μμ</td><td>10 μμ</td><td>100 μμ</td><td>1 μ</td><td>10 μ</td><td>100 μ</td><td>1 mm</td></tr>
</table>

An approximate idea of the size of colloidal particles may also be obtained by **ultrafiltration,** a process which consists in forcing the dispersion medium through a suitable filter, by which the colloidal particles are retained. The frame work of the ultrafilter may be filter paper; this is soaked in a solution of collodion in glacial acetic acid and then gelatinized by washing with water. The permeability of the ultrafilter may be diminished by increasing the concentration of the collodion solution; it may be increased by soaking the filters in dilute alcohol. In this way various grades of permeability are obtainable; the filters can be calibrated in respect of the diameter of their pores, by testing them on particles whose size has been ascertained with the ultramicroscope; the filters can then be used to find the size of the particles of other sols. In using this method caution is necessary, because the fineness of the pores is not the only factor which holds back the particles: they are sometimes also held back by adsorption.

Most colloidal solutions contain particles of widely different sizes, including amicrons in particular. They are **multidisperse** (**polydisperse**), and the determination of the size of their particles in the manner outlined above, is therefore not possible. If the particles are so coarse that they settle moderately quickly—if we are therefore really dealing with suspensions—the quantity of particles of various sizes may be determined by measuring their rate of settling, which is connected by certain laws with their size. For this purpose the particles are allowed to settle on a scale-pan suspended in the sol; the change in the weight of the pan is registered automatically.

The preparation of colloidal solutions containing particles of uniform size—so-called **unidisperse** (**monodisperse**) sols—is mostly very difficult, but for gold sols the problem has been largely solved by Zsigmondy. Sols with amicronic gold particles of a fairly uniform size may be obtained by reducing an auric chloride solution containing potassium carbonate by means of an ethereal solution of phosphorus. The particles may be enlarged uniformly by adding this amicronic sol, the so-called inoculation fluid, to another solution of a gold salt, which is undergoing reduction so slowly, that practically no fresh nuclei are formed and that the liberated gold atoms are almost all deposited on the pre-existing nuclei of the inoculation fluid. A solution from which gold is liberated sufficiently slowly, may be prepared by adding a suitably small quantity of formaldehyde to an auric chloride solution containing potassium carbonate. The gold which separates is therefore deposited on the amicrons which have been added, and makes these grow quite uniformly, so that sols, containing exclusively particles of the desired order of magnitude, can be prepared.

As long as the old opinion prevailed, that particles of colloidal solutions are always amorphous, there was a tendency to regard them as spherical in every case. The particles of many sols have however been shown to be crystalline (cf. p. 9), by means of the method of Debye and Scherrer (cf. p. 105). The particles of the sol are collected on an ultrafilter and moulded into a rodlet, which is examined by X-rays in the manner already described. The particles of many sols, such as those of gold, silver, ferric- and aluminium hydroxides, vanadium pentoxide, show more or less intense interference bands and are therefore crystalline. Other particles, of thorium hydroxide, sulphur and selenium sols produce a uniform darkening of the film, and hence are amorphous.

In agreement with this we find that the particles of sols are by no means always spherical, but may have any shape. Thus the particles of aqueous vanadium pentoxide sols, which have been repeatedly referred to, are decidedly rod-shaped. This can be directly deduced from the ultramicroscopic image. These sols are moreover remarkable for a strong **glittering** under the ultramicroscope ; the particles flash into view and then disappear again. This is because the particles are only seen clearly, when their longitudinal axes are perpendicular to the direction of the incident light ; in any other position they are invisible. This rod-like shape of the V_2O_5-particles determines quite a number of other phenomena. Thus the sols show a **fluxional birefringence** (*"stream double refraction"*). A crystal is of course called birefringent, when the light which passes through it in a certain direction, is split into two rays which are polarized in planes at right angles to each other, so that the vibrations of the two rays are at right angles. Such splitting occurs for instance, when a ray of light is suitably directed through a triangular prism, cut from a so-called uni-axial crystal in such a way, that the crystal axis coincides with the longitudinal axis of the prism. Now if we take a glass tube with triangular cross section, allow a V_2O_5-sol to flow through it and cause a ray of light to pass through it in the same way as in a crystal prism, then the light will be split into two rays which are polarized at right angles to each other, exactly as with a crystal. This is, however, only the case as long as the sol continues to flow; when it is at rest, the ray of light remains undivided, as happens in a liquid which is not birefringent. This is only one of the manifestations of fluxional birefringence, which may show itself in a flowing V_2O_5-sol in many other ways. It is due to the fact, that the elongated particles of the V_2O_5-sol, which are originally arranged in haphazard fashion, orientate themselves with their long axes in the direction of the stream lines. The orientation of the particles may be brought about by means other than a flow, namely by a magnetic field or an electric current.

The two rays of light, passing through a crystal and polarized in different planes, may be absorbed to different extents. This leads to the phenomenon of dichroism; the crystal presents a different colour, according to the plane of polarization of the light passing through it. Similarly V_2O_5-sols show a **fluxional dichroism,** which results in the peculiar **streaks** shown by these sols when they are stirred. Then we see, even with the naked eye, a multitude of yellowish, shimmering, silky streaks, like those sometimes seen in a liquid from which crystals are beginning to separate. When the sol has come to rest these streaks disappear again.

A number of sols have properties similar to those of a V_2O_5-sol. Thus under certain conditions the sols of benzopurpurin, cotton yellow and some other dyes may behave in the same way. As an example of sols with leaf-like, instead of rod-shaped particles, we may mention old ferric hydroxide sols.

THE STABILITY OF HYDROPHOBIC SOLS

Our knowledge of the conditions which determine the stability of colloidal solutions is still incomplete. As was pointed out above (p. 116) we can divide sols into two groups according to their stability: the hydrophobic, which are unstable to small concentrations of electrolytes, and the hydrophilic, which are stable. Of course there is no sharp line of demarcation; a number of sols occupy an intermediate position. Pronounced hydrophobic sols are those of gold, silver, platinum and other metals, provided they contain no protective colloids (cf. p. 157); further sulphur sols, prepared by pouring an alcoholic sulphur solution into an excess of water; the sols of arsenic and antimony trisulphides are also strongly hydrophobic. We will first discuss some of the more important peculiarities in the behaviour of these hydrophobic sols towards salts.

On adding an electrolyte solution of suitable concentration to such a sol under the ultramicroscope, we see that the Brownian movement is not primarily affected, but whereas before the addition of the electrolyte a particle, having approached another particle or the wall, did not adhere to it and continued its original motion unchanged, we now find, after adding the electrolyte, that the particle sticks to other particles or to the wall. The individual particles thus unite to larger and larger flakes, whose Brownian movement, on account of increased size, becomes weaker and weaker, and finally the flakes settle down on the bottom of the vessel. This process is called **flocculation** or **coagulation.**

We therefore get the impression that the surface of the particles has been changed by the addition of the electrolyte. Originally the surface was not adhesive, but the electrolyte has made it so. Here the charge on the colloid particle is certainly an important factor and with many sols it is the only one. In discussing electrokinetic processes (p. 76) cataphoresis was described as the migration of the droplets of an emulsion, or of the particles of a suspension, to one of the poles, under the influence of an electrical potential difference, applied from without. Exactly the same is true of the particles of a colloidal solution, which migrate to the positive or negative pole and have therefore respectively a negative or positive charge; hence we speak of negative or positive sols. Those of ferric and aluminium hydroxides, thorium dioxide, etc., are **positive,** those of gold, silver, platinum, sulphur, the sulphides, and vanadium pentoxide are **negative.** The discussion on p. 79 shows that the particles have no simple charge, but carry a so-called electrical double layer, and that the potential difference of the latter, the so-called electrokinetic potential, determines their behaviour. In cataphoresis and in other phenomena they behave, however, as if they had a free charge, which is accordingly referred to as such in this sense, Now there is the following connexion between the stability of the sol and the charge on its particles. As long as the charge is considerable and the particles migrate rapidly in cataphoresis, they do not adhere and the sol is stable. Probably the reason is, that when the particles approach each other closely, their double-layer is changed in such a way, that they repel each other. Now when an electrolyte is added to the sol, the electrokinetic potential difference is decreased in the manner already discussed, and the colloidal particles are therefore discharged. If the potential sinks to a certain small value—complete discharge is unnecessary—the particles show the peculiar behaviour described earlier in this section: they adhere on approaching each other sufficiently closely. This may be explained on the assumption that their mutual repulsion is much decreased, so that the mutual attraction of the particles asserts itself and they stick together. The nature of this attraction is still obscure; perhaps it is of the same kind as that which reveals itself in crystallization and in adsorption.

We can therefore readily understand, that the coagulation of hydrophobic sols by electrolytes is subject to the same influences as were described above (p. 84 *et seq.*) in considering the effect of electrolytes on the electrokinetic potential difference. Since in the latter case the discharge is principally brought about by the oppositely charged ion, we also find a similar preponderant influence of the oppositely charged ions in coagulation: with positive sols the essential factor is the nature of the anion, with negative sols that of the cation. The important features of this nature are the adsorbability and the valency of the ions, as the following tables show. The tabulated numbers are **coagulation values,** being the electrolyte concentrations which produce a degree of change as comparable as circumstances allow. Thus for the red

TABLE 3.

Coagulation values γ of some negative hydrophobic sols. γ in milligrammolecular weights per litre.

Electrolyte.	γ for As_2S_3-Sol.	γ for Au-Sol.	γ for Congo-rubin Sol.
$NaOH$	—	—	about 390
$NaCl$	51	24	105
KCl	49·5	—	96
KNO_3	50	25	102
$\frac{K_2SO_4}{2}$	65·5	23	102
HCl	31	5·5	0·23
Aniline hydrochloride .	2·5	—	0·37
Morphine hydrochloride	0·42	0·54	—
New fuchsine . . .	0·11	0·002	—
$MgCl_2$	0·72	—	1·7
$CaCl_2$	0·65	0·41	—
$SrCl_2$	0·635	—	—
$BaCl_2$	0·69	0·35	—
$UO_2(NO_3)_2$	0·64	2·8	—
$AlCl_3$	0·093	—	0·245
$\frac{Al_2(SO_4)_3}{2}$	0·096	0·009	—
$Ce(NO_3)_3$	0·080	0·003	—

gold sol, which becomes blue on adding electrolytes, that concentration has been selected, which produces the blue colour within a specified time (5 minutes); in the case of the arsenious sulphide sol it is that concentration, which causes the whole of the sulphide to settle down in flakes within two hours.

TABLE 4.

Coagulation values γ of some positive hydrophobic sols. γ in milligrammolecular weights per litre.

Electrolyte.	γ for Fe_2O_3-Sol.	γ for Al_2O_3-Sol.
$NaCl$	9·25	77
KCl	9·0	80
$\frac{BaCl_2}{2}$	9·65	—
KBr	12·5	150
KI	16	about 300
KNO_3	12	—
HCl	> 400	—
$\frac{Ba(OH)_2}{2}$	0·42	—
K-benzoate	—	13
K-salicylate	—	8
K-picrate	—	4
K_2SO_4	0·205	0·28
$MgSO_4$	0·22	—
K_2CrO_4	—	0·60
$K_2Cr_2O_7$	0·195	—
K_2-oxalate	—	0·36
$K_3Fe(CN)_6$	—	0·10
$K_4Fe(CN)_6$	—	0·08

It will be seen that in the case of the arsenious sulphide sol there is very little difference between the values for KCl, KNO_3 and K_2SO_4, while those for KCl, $BaCl_2$ and $AlCl_3$ differ widely; with the positive Fe_2O_3 sol, on the other hand, there is very little difference between NaCl and $BaCl_2$, while KCl and K_2SO_4 show a large difference. The diversity of the values for cations of the same valency, such as $Na^{\cdot}$-, aniline-, morphine- and new fuchsine-ions, depends on the great differences in their adsorbability.

The remarkable quantitative peculiarities of the coagulation values cannot well be explained without mathematical discussion. Here the following indications must suffice: All experimental evidence so far suggests that the same discharging effect is obtained when *equivalent* quantities of the oppositely charged ions are *adsorbed.* The course of the adsorption isothermal (cf. Fig. 9) entails, that among ions of the same valency a much smaller concentration of a readily adsorbed ion is required than of one which is less adsorbable; this brings about a large difference in the coagulation values of ions of different *adsorbability.* In order to explain the influence of valency, it is not necessary to assume, that the ion of higher valency is adsorbed much more strongly; if in *equimolar* concentration it were merely adsorbed as readily as an ion of lower valency, this in itself would bring about, that much less of an ion of higher valency is necessary than of one of lower valency; this again results from the course of the adsorption isothermal.

Perhaps Fig. 25 will make this clearer. Here the adsorption isothermal of cations of various valencies has been represented, for instance $Na^{\cdot}$-, $Ba^{\cdot\cdot}$- and

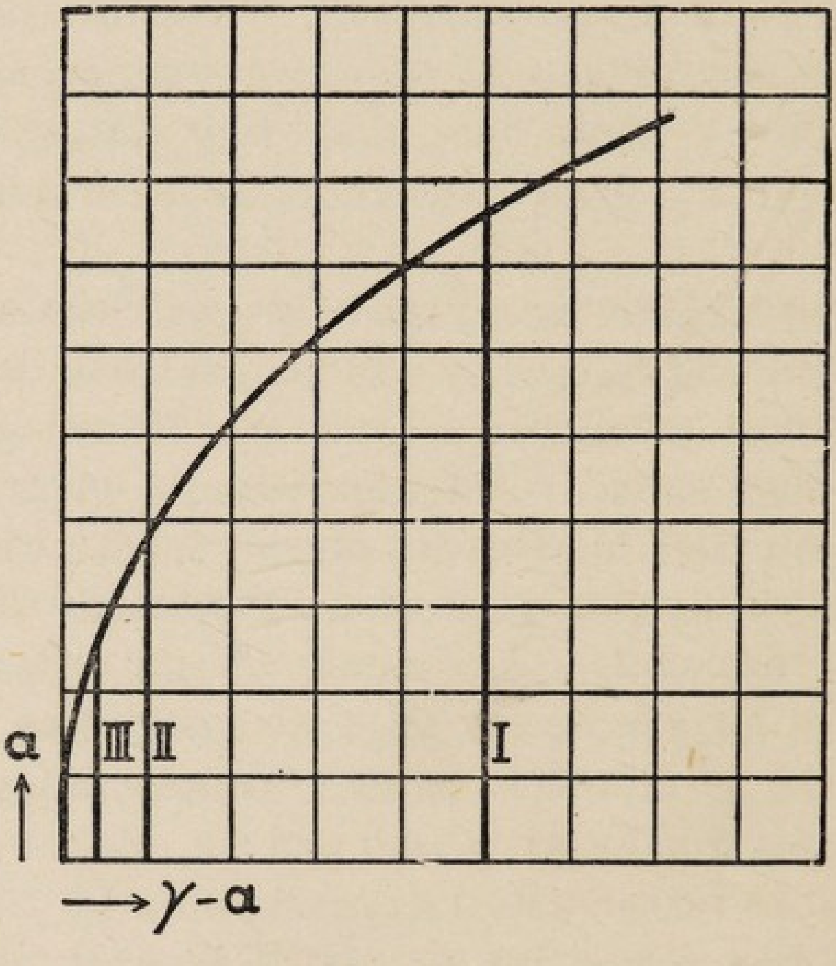

FIG. 25.

$Al^{\cdot\cdot\cdot}$-ions. The ordinates a are the quantities of cation adsorbed by the colloidal particles, the abscissæ $(\gamma - a)$ represent the concentrations of these cations in the solution. We must bear in mind that the coagulation value γ does not take into account, that a certain quantity a of the cation has been adsorbed by the particles from solution and must therefore be subtracted from γ, the total amount added. These concentrations, and the quantities adsorbed, are expressed in grammolecular and milligrammolecular weights respectively. We have therefore assumed that, reckoned thus in *molar weights*, the cations of different valency are adsorbed equally, and therefore the single adsorption isothermal of the figure is assumed to represent the behaviour of all three cations. Now coagulation is brought about by *equivalent* quantities of the adsorbed cations. Therefore, if the amount of univalent cations, which must be adsorbed for purposes of coagulation, be represented by the ordinate I, then the amount of bivalent ions to be adsorbed will be represented by an ordinate II of half this height, and that of trivalent ions by an ordinate III, one third as high as I. It will be seen that the $(\gamma\text{-}a)$ values corresponding to these three ordinates, show a much greater divergency than the ordinates themselves; the γ-values also show correspondingly large differences, which are found to be quantitatively similar to those quoted in tables 3 and 4.

In discussing the effect of electrolytes on the electrokinetic potential difference (p. 84 *et seq.*) it was emphasized, that under certain conditions ions may increase the charge (as well as diminish it). This phenomenon recurs in the coagulation of hydrophobic sols. Thus negative sols are not flocculated by small quantities of alkalies, but become more stable; coagulation does not occur until the concentration of the alkali is very much increased (cf. table 3), when the influence of the cation outweighs that of the OH′-ion. Acids behave in a corresponding manner towards positive sols (cf. table 4). In very small concentrations many other ions charge up, instead of discharging, and this is the reason, why sols are generally not stable, when quite free from electrolytes. Indeed, a small quantity of an electrolyte, the so-called **active electrolyte,** is always necessary, in order that the particles may be provided with a sufficient charge. A colloidal particle may therefore be regarded as a complex, which owes its charge to an ion. The complex need by no means consist of a single constituent, such as pure silver in the case of a silver sol ; we should rather consider that a number of substances make up its constitution. Thus the particles of a silver sol, prepared by reduction with hydrogen, could always be shown to contain Ag_2O. Moreover colloidal particles probably always contain water molecules ; in any case these would be held on the surface of the particles by adsorption. Zsigmondy represents the composition of colloidal particles by enclosing in brackets the constituents which belong to the complex proper. The ion which is in the dispersion medium, and therefore forms the outer stratum of the electrical double layer of the particles, appears outside the brackets. The particles of a silver sol may therefore be represented thus :

$$\boxed{Ag, Ag_2O, H_2O}\,'H^{\cdot}$$

Here the anion, to which the charge on the particle is due, is not known with certainty ; otherwise it would be written at the end of the bracket. The $H^{\cdot}$-ion is pretty certainly the cation of the other stratum of the double layer.

So far we have considered only the preliminary conditions which make the colloidal particles adhere, so as to form larger flakes. Thus we have taken into account some only of the processes, which occur during coagulation. The particles which have been changed by the addition of electrolytes unite to larger flakes at a certain rate, which depends on the degree to which they have been discharged. The simplest case is when the discharge has been complete. They then unite at a rate which can be calculated from their Brownian movement on the basis of the kinetic theory. Since in general two particles collide much more frequently than three or four, the coagulation takes place with a velocity corresponding to a bimolecular reaction, in which two molecules unite to form a chemical compound.

The salient features of the coagulation of hydrophobic sols, for instance the great influence of the valency of either the anion or the cation, extend to many other natural phenomena. Since this influence also occurs in the alteration of the electrokinetic potential difference by electrolytes, we cannot readily decide whether this alteration is the only cause, or whether a coagulation cooperates with it. The following example, in which flocculation doubtless also intervenes, may serve as illustration. The flagella of many bacteria are so slender that they cannot be seen microscopically, unless they are placed in electrolyte solutions, when the slender flagella unite to form thicker tufts. In this phenomenon all the conditions recur which were described for the flocculation of negative sols; the important factor is the valency of the cation.

With those ions which are very strongly adsorbed, or have a high valency, and hence have a powerful discharging effect in small concentration, the following remarkable observations may often be made. Not only are the particles **discharged,** but their charge is **reversed.** Thus a negatively charged gold particle may be converted into a positively charged one by $Th^{\cdot\cdot\cdot\cdot}$-ions or by the cations of a basic dye-stuff. This moreover takes place so rapidly, that in passing through the zero value of the electrokinetic potential no flocculation occurs, but instead a stable positive sol is obtained, containing the particles whose charge has been reversed. Not until a higher concentration of the electrolyte has been added, does coagulation occur, because the positive sol is then flocculated by the anion. If we therefore observe the behaviour of a sol on addition of increasing quantities of such an electrolyte, as in table 5 which represents the action of $FeCl_3$ on a negative Pt-sol, we obtain a so-called **irregular series:** no flocculation at very low concentration; then coagulation through the action of the cation on the negatively charged particles; at still higher concentration reversal of charge, formation of a positive sol, no flocculation; at the highest concentrations again coagulation, this time of positive particles by the anion of the salt.

TABLE 5.

Irregular series.

Ferric chloride solution and platinum sol.

Concentration of the $FeCl_3$ solution (millimolar weights per litre).	Occurrence of Flocculation.	Direction of cataphoretic migration.
0·0208	No flocculation	Migrates towards anode.
0·0417	,,	
0·0557	,,	
0·0833	Complete flocculation	Does not migrate.
0·1633	,,	
0·2222	,,	
0·3333	No flocculation	Migrates towards cathode.
0·5567	,,	
0·8333	,,	
1·633	,,	
3·333	,,	
6·667	,,	
16·33	Complete flocculation	
33·33	,,	
83·33	,,	
163·3	,,	
333·3	,,	
666·7	,,	

The sol with reversed charge behaves exactly like a sol which is positive from the outset.

As was briefly mentioned, the converse of coagulation is **peptization,** the process by which under suitable conditions coagulated flakes may be divided up again into the original colloidal particles. (The term peptization is also employed in the more general sense of dispersing the coarse phase of a liquid or solid into particles of a sol. Here we will restrict its meaning to the disintegration of coagulated flakes.) Peptization may easily be characterized by definite numerical data. It is mostly carried out by washing the coagulated flakes with water, or with a suitable electrolyte solution. The peptization process is influenced by the age of the flakes, by the nature of the electrolyte originally used for coagulation, by the rate of stirring and by other factors, but the following general remarks may be made. It is certain that in the flakes the original particles do not at first fuse with loss of identity, but are separated by thin films of fluid. If the coagulating electrolyte is removed by washing, the particles may under certain conditions resume their original charge without outside interference; they repel each other, and the flakes are broken up into the original fine particles. This succeeds most readily when the distinctive ion of the coagulant is feebly adsorbed or has a low valency, therefore especially with univalent inorganic ions such as $Na^{\cdot}$, $K^{\cdot}$, Cl' and NO_3'; the more strongly the ion is adsorbed and the higher its valency, the more difficult is peptization. Those ions which are capable of increasing the charge on particles, have a pronounced peptic action; hence for negative particles this is so with the OH'-ion (as already mentioned on p. 143), further with the anion of citric acid; the $H^{\cdot}$-ion is especially active in peptizing positive particles.

THE STABILITY OF HYDROPHILIC SOLS

The hydrophilic sols with which we are primarily concerned, are typified by sols of agar and of starch; gelatin and other protein sols will also have to be considered. The latter are markedly amphoteric, i.e. they are capable of forming salts both with acids and with bases, and this often brings about a special behaviour. In contradistinction to the hydrophobic sols, the hydrophilic are often very insensitive to electrolytes, such as the alkali salts of inorganic acids. Quite concentrated solutions of these electrolytes, several times normal, are required to produce any change, and then a separation of the colloidal substance, a so-called salting out, is observed, such as also occurs with true solutions. This separation is determined by anions and by cations, both acting in accordance with their position in the so-called lyotropic series, discussed on p. 27. It was there emphasized, that the lyotropic series is doubtless closely connected with the degree of hydration of the ions. This suggests, that hydration is an important factor in the stability of hydrophilic sols, which suggestion indeed agrees with their behaviour in other respects. The stability of hydrophilic sols depends therefore on conditions, which are similar to those governing the solubility of a truly dissolved substance; for with truly dissolved substances the interaction with the solvent also decides the solubility equilibrium. Although we have as yet no detailed information concerning these hydration equilibria, it is nevertheless probable, that a large water content of the colloidal particles generally enhances the stability of a sol.

The stability does not, however, depend on this water content alone. Perhaps electrical influences, which were described in the previous section in explanation of the behaviour of hydrophobic sols, are also of importance to hydrophilic ones, together with the influence of hydration. In the case of agar sols it has actually been possible to separate the contribution, which the electrical charge makes towards the stability, from that due to hydration. Kruyt succeeded in discharging the particles by addition of an electrolyte and then obtained sols which retained a certain stability as the result of the water content of the particles, but were flocculated by dehydrating agents, such as alcohol. If, on the other hand, alcohol was added to an agar sol free from electrolytes, the stability due to hydration was abolished, and only the stability resulting from the electrical charge remained. Thus the sol became practically hydrophobic and was flocculated by electrolytes in accordance with the rules of coagulation.

A further circumstance affecting the stability of hydrophilic sols is that in most cases their particles are appreciably smaller than those of hydrophobic ones. Whereas in the latter sols the diffusion of the particles can hardly be demonstrated directly, it is so considerable in many hydrophilic ones, that the rate of diffusion of their particles can be measured in the ordinary way. If for instance a layer of pure water is poured on a protein solution, the protein is found after some time to have diffused into the water. The molecular weight of the substance in colloidal solution may be deduced from its rate of diffusion ; for egg albumin a value of about 50,000 is found by this method, so that the radius of a spherical particle of this protein works out at about $3\mu\mu$.

In other cases it was found possible to ascertain the osmotic pressure of a colloidal solution directly. With true solutions this is of course measured with the aid of an osmotic cell, a vessel closed by a membrane which is impervious to the solute. It contains the solution and is immersed in another vessel filled with the pure solvent. In the case of most substances in true solution it is difficult to find good semipermeable membranes, although a membrane of copper ferrocyanide happens to be suitable for sugar solutions. The osmotic pressure of colloidal solutions may be measured in the same way and here there are plenty of membranes possessing the required property of semipermeability. All the membranes ordinarily used in dialysis (p. 114), such as parchment and pig's bladder, are available for this purpose. Nevertheless reliable measurements of the osmotic pressure have only been possible in few cases, more especially because the contamination of colloidal solutions by truly dissolved substances causes serious error, and may produce a considerable osmotic pressure, masking the smaller one of the colloidal particles themselves

Among the more reliable measurements are those on hæmoglobin ; here aqueous solutions gave a molecular weight of about 15,000, in agreement with the equivalent weight deduced from the iron content ; if the particles were spherical, they would have a radius of $2\mu\mu$, which once more is a very small value.

The small size of the colloidal particles of hydrophilic sols probably brings about that they are taken up by charcoal, kaolin, and other adsorbents in the same way as truly dissolved substances, in complete accordance with the rules of adsorption. Willstätter has recently utilized this fact for purifying ferments by fractional adsorption ; ferment solutions are essentially hydrophilic sols. The separation of substances by adsorption constitutes a very gentle treatment, particularly suitable for the purification of substances which, like the ferments, are so very sensitive.

In general therefore the hydrophilic colloids are more closely related to true solutions than are the hydrophobic. Among the hydrophilic, with soaps and many dyes, doubt may arise whether they are colloidal at all ; these, as we have already seen, are called **semi-colloids.** They actually dialyze through membranes, but very slowly ; they have molecular weights of not much over 4,000, at which value the colloidal properties begin to show themselves. In these semi-colloidal solutions we can distinguish, as in true solutions, between non-dissociated and dissociated particles ; the former are here colloidal, the latter are ionized into **colloidal ions** and true ions. By colloidal ions we mean electrically charged particles which are relatively small and therefore often present in considerable concentration ; they make an appreciable contribution to the conductivity, lowering of vapour pressure, etc., and their concentration can therefore be determined by the methods in use for ordinary ions. In this way it has been possible to determine the proportion of colloidally and truly dissolved constituents of soap solutions, their content of true ions and of colloidal ions. Among many other solutions, which doubtless resemble soap solutions in this respect, those of salvarsan may be mentioned ; here the cation is colloidal, with soaps it is the anion.

Markedly amphoteric colloids, like gelatin and the proteins generally, show many peculiarities. They form both colloidal cations and colloidal anions, the former chiefly in solutions containing excess of hydrogen ions, the latter in those containing hydroxyl ions in excess. If an electric current is passed through the solution of such a substance, the colloid migrates to the negative electrode in acid and to the positive in alkaline solution. In the neighbourhood of the neutral point the migration is less definite and the hydrogen ion concentration at which there is no migration at all, is called the **iso-electric point,** and is characteristic of the particular colloid. At this point the sol contains the minimum quantity of colloidal ions and the colloid is composed practically entirely of neutral protein particles. The iso-electric point is distinguished by other features; it represents the condition of minimum stability of the sol, in which it is most readily flocculated. This does not simply depend on the fact that hydrophilic sols, like hydrophobic, are least stable, when they have been most fully discharged (cf. p. 138), for doubtless the influence of hydration is here even more important. All the experimental evidence points to the colloidal ions being much more strongly hydrated than the neutral protein-particles. Since hydration generally increases the stability, it is evident, that sols are least stable at their iso-electric point. At this point the viscosity is also a minimum, since the strongly hydrated colloidal ions materially increase the viscosity of the solution, and are here present in minimum amount.

In connexion with the above we must consider a phenomenon, important in many respects, and termed Donnan's **membrane equilibrium.** It may be observed with special ease in solutions of colloidal ions, although the conditions determining it are present in almost all colloidal solutions. In a solution of Congo red, the anion is colloidal and does not diffuse through a collodion membrane, whilst the $Na^{\cdot}$ cation passes through. Now if an osmotic cell contains Congo red and another salt, like sodium chloride, having the same cation, this salt does not distribute itself uniformly between the liquids inside and outside the cell and quite independently of the Congo red, as one might expect offhand. On the contrary, the second law of thermodynamics leads to the conclusion, that when the concentration of sodium chloride is small, Congo red hinders the entrance of the salt into the cell; more of it remains outside the cell than inside it. If the Congo red solution is dialyzed against pure water, we even see that the outside liquid becomes alkaline, whilst the dye solution becomes darker and turbid, as a result of the formation of the dye acid. This once more depends on the fact that the $Na^{\cdot}$-ion passes through the membrane, that of Congo red does not. In order that the $Na^{\cdot}$-ions may have an equivalent amount of anions, hydrolysis occurs; OH'-ions also pass through the membrane, whilst an equivalent quantity of $H^{\cdot}$-ions are formed in the solution of the dye. Donnan's membrane equilibrium probably determines the distribution of many ions between the various structures of the organism.

THE MUTUAL INTERACTION OF DIFFERENT SOLS

It is now fully recognized, that colloids are of decisive importance in many biological and technical phenomena; yet the application of colloidal chemistry to these subjects often presents considerable difficulty. One of the chief reasons for this is, that both in nature and in the arts we are hardly ever concerned with structures containing a single variety of colloidal particle, but mostly with two or more varieties, and that the interaction between the colloidal particles of different kind presents many problems, as yet unsolved.

The interaction between two hydrophobic sols is the least complicated case. As a rule these do not coagulate each other, unless their particles are oppositely charged. In order to obtain complete flocculation, the quantities of the two kinds of particles must be in a definite ratio, depending on the magnitudes of their respective charges. If this ratio is not maintained, if one or other kind of particle is present in excess, we do not observe any coagulation, or at most a slight turbidity, and the resulting sol has practically the properties of the variety present in excess. In this way we can for instance obtain a positive sol, by rapidly adding an excess of a positive sol to a negative one. This behaviour is therefore very similar to that found in the coagulation by strongly adsorbable ions, or by ions of high valency (cf. p. 146); there also a reversal of charge readily occurs, leading to an irregular series. The similarity is not merely formal, and depends on the fact, that the interaction of positive and negative particles is subject to conditions, similar to those under which a particle takes up ions of opposite charge.

Two hydrophobic sols with similarly charged particles generally do not affect each other. The properties of the mixture are such as might be expected from the proportion between the quantities of its two constituents. There are, however, remarkable exceptions to this behaviour. Thus pronounced changes have been observed on mixing a negative sulphur or arsenious sulphide sol with a negative silver sol. There is a characteristic change of colour and sometimes flocculation actually occurs; all this can only be explained on the assumption, that similarly charged particles have here also united to larger complexes. Probably it is the chemical affinity between the Ag atoms contained in the one kind of particle, and the S atoms in the other, which has made this possible, in spite of the charge on both particles being negative.

The interaction of hydrophobic with hydrophilic sols is still more complicated. We might expect in the first place, that a hydrophilic sol is capable of imparting to a hydrophobic sol its own considerable stability towards electrolytes. This is actually the case. If, for instance, gelatin be added to a gold sol (such as is obtained by the reduction of an $AuCl_3$ solution by means of formaldehyde, cf. p. 120), concentrations as low as 0·005 or 0·01 mg. in 10 c.c. of solution will be sufficient to prevent the change of colour from red to blue on the addition of 200 millimolar sodium chloride solution ; without gelatin a content of 20 millimols per litre is enough to bring about this colour change within 5 minutes. Zsigmondy has termed this effect of hydrophilic on hydrophobic colloids a **protective action** and the quantity of the hydrophilic colloid, which under certain conditions protects 10 c.c. of the gold sol, he calls the **gold number** of the sol. Gold sols are of course not the only ones to be thus changed by hydrophilic ones. All hydrophobic sols which have been tested in this respect, are influenced in similar fashion. In most cases gelatin is specially active ; proteins are generally less effective and gum arabic, dextrin, etc., are still less so.

The protective action is undoubtedly due, at least in part, to the adsorption of the hydrophilic colloid by the particles of the hydrophobic sol, so that the latter are entirely enveloped and acquire the properties of hydrophilic particles. An adsorption of gelatin by gold has been directly demonstrated. We do not know, however, what properties are responsible for the greater protective action of some hydrophilic colloids, as compared with others. It does not seem to be merely a question of adsorbability, but rather of the uniformity, closeness and solidity of the envelope, which the hydrophilic colloid forms round the hydrophobic particles.

This protective action has been applied in many ways. Thus the gold number serves to characterize and distinguish hydrophilic sols. We may recall the remarkable clinical observation that in certain diseases the cerebro-spinal fluid coagulates gold sols, whilst the normal fluid leaves them unaffected. The colloidal solutions of metals, e.g. of silver, which are used in therapeutics for various objects, are practically all protected by small quantities of hydrophilic colloids. Often fission products of proteins are used for this purpose; thus the salts of lysalbic and of protalbic acids are particularly active. Unprotected silver sols would be liable to be precipitated by the electrolytes of serum and other body fluids.

Some hydrophilic colloids, like saponin, protect hydrophobic sols at all concentrations, but many others only do so when their particles are present in sufficient excess, compared with the particles of the hydrophobic colloid. If the hydrophilic colloid is present in smaller amount, we strangely enough do not observe any protective action, but the very opposite: the hydrophilic colloid flocculates the hydrophobic one or at any rate it favours the flocculation of the latter by electrolytes, that is, in the presence of (these insufficient quantities of) the hydrophilic colloid a smaller concentration of a given electrolyte is required for coagulation than if the hydrophilic colloid is absent. The following will serve as an illustration. When a ferric hydroxide sol, and a solution of serum albumin, both as free as possible from electrolytes, are mixed, a clear, stable sol is obtained. The mixture is, however, far more sensitive to electrolytes than the pure ferric hydroxide sol after corresponding dilution with water; its coagulation value for sodium chloride is for instance 1·2 milligrammolecular weights per litre, whilst that of the pure sol is 37 milligram-molecular weights. This phenomenon is termed **sensitization.**[1] Gelatin is remarkable in having in small concentrations a sensitizing action on many hydrophobic sols, such as neutral and acid sols of gold and of silver, and sols of many hydroxides; in larger concentrations gelatin protects them. It is therefore incorrect to describe a colloid simply as protective; according to its concentration and the

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[1] This concept must be sharply distinguished from the specific, purely biological action, which serologists call sensitization.

nature of the hydrophobic sol it may either protect or it may sensitize.

No general explanation of sensitization has yet been given. In many cases the determining factor would appear to be the presence in the hydrophilic sols of colloidal ions (cf. p. 153), and their flocculating action on the particles of the hydrophobic sol, similar to the action of oppositely charged ions in general. It would therefore be a question of discharge by colloidal ions which bear a charge opposite to that of the colloidal particles of the hydrophobic sol. In the above-mentioned example of the interaction between sols of ferric hydroxide and serum albumin the anions present in the latter solution would discharge the ferric hydroxide particles to such an extent, that the further discharge, required for flocculation, would be brought about by a smaller concentration of electrolytes than without the addition of the hydrophilic colloid. Cases are known, however, in which this explanation seems to be inadequate. Thus tannin sensitizes both positive and negative sols of dye stuffs, and there is no reason for assuming, that a tannin solution contains both colloidal anions and colloidal cations. Here we are evidently not concerned with a discharging effect, but there is much that tells in favour of the state of hydration of the colloidal particles having been altered by the tannin, so that the stability of the dyestuff sol would have been diminished in much the same way as was described above (p. 150) in discussing the stability of hydrophilic agar sols; the stability of these dye-stuff sols would therefore really depend in part on the state of hydration of their particles.

Sensitization, like protective action, is susceptible of wide application. Since hydrophilic sols are apt to differ greatly in their capacity to sensitize, they may often be characterized in this manner. Thus the colloids of beer wort have been differentiated by this action, and by comparing them with colloids prepared from malt, it has been ascertained, that it is the gum of barley which has a decisive effect on the power of the wort to form a stable foam. It is further remarkable that a distinct difference is alleged to exist between the paraglobulins of normal and of pathological sera (e.g. in diphtheria and in tetanus) with respect to the power of sensitizing a ferric hydroxide sol. If this result were to be confirmed, we should here have a case, in which sensitization reveals differences between sera, which can otherwise only be distinguished by biological means. Further the Wassermann reaction, and that of Sachs-Georgi, may amount to a sensitization, as was recently rendered probable by R. Stern. It seems very likely that luetic serum contains a substance, which favours the coagulation of the so-called extract-lipoids in a similar way to the above-mentioned action of tannin on the sols of dyes, without the colloidal particles necessarily being completely discharged. This substance is always associated with the euglobulin; it might also be, that in luetic serum a modification of the euglobulins has brought about a stronger sensitizing action. In the Wassermann reaction the same change in the luetic serum reveals itself by a greater adsorption of the complement, as a result of the formation of complexes from the extract-lipoid and the luetic euglobulin.

A further example of sensitization is provided by so-called agglutination. Many bacterial cultures, when suspended in water containing formaldehyde, yield a suspension which is markedly hydrophilic in character and is not flocculated by salts of the alkali or alkaline earth metals. Now typhoid (and other) bacilli may be changed into agglutinin-bacilli by inoculating an animal with the organism in question, and then treating the bacilli with the serum. This serum of the inoculated animal contains a substance termed agglutinin, which is taken up by the bacteria as if by adsorption, and renders the bacterial suspension hydrophobic. It is now precipitated by salts of the alkali metals, and of the alkaline earths, showing the same regularities of behaviour as have been described for the flocculation of negative sols. Table 6 shows the coagulation values of a suspension of typhoid bacilli, of typhoid agglutinin-bacilli and, for purposes of comparison, of an arsenious sulphide sol.

The agglutinin, which is probably present in colloidal form, has therefore had a sensitizing action on the bacilli. It should, however, be borne in mind that in one respect this agglutination differs greatly from the sensitizing actions discussed hitherto. It is extremely specific : typhoid bacilli are therefore only acted on by an agglutinin produced by inoculation

TABLE 6.

Comparison of the coagulation of typhoid agglutinin bacilli with that of untreated typhoid bacilli, and of an arsenious-sulphide sol.

Electrolyte.	γ of untreated typhoid bacilli.	γ of typhoid agglutinin bacilli.	γ of A_2S_3 Sol.
NaCl	No coagulation	25	51
$NaNO_3$	—	25	—
$\frac{Na_2SO_4}{2}$	—	55	—
KOH	No coagulation	No coagulation	—
HCl	0·5	1	31
HCOOH	1·0	1	—
$AgNO_3$	25	1	—
$MgSO_4$	No coagulation	1·3	0·81
$CaCl_2$	"	2·3	0·65
$BaCl_2$	"	2·5	0·69
$Ni(NO_3)_2$	—	1·3	—
$HgCl_2$	1·3	0·25	—
$\frac{Al_2(SO_4)_3}{2}$	0·08	0·08	0·096
$\frac{Fe_2(SO_4)_3}{2}$	0·2	0·04	—

with typhoid, and not by inoculation with any other organism. It may be that a definite steric structure of the bacterial surface and of the agglutinin is required, in order that the agglutinin may fix itself on the bacterial surface so as to give to the latter a more hydrophobic character. In this connexion we may recall the special orientation of adsorbed molecules, which Langmuir has so successfully invoked in explanation of many phenomena (cf. p. 91). A steric structure of this kind might explain the great specificity of agglutination.

PEPTIZATION BY HYDROPHILIC SOLS

Many hydrophilic sols, especially semi-colloidal ones like soap solutions, have the power of emulsifying liquids, and of producing a suspension from solid substances. Although this power is connected with the protective action of the sols, it is undoubtedly distinct from it. As is well known, a pure oil, shaken up with water, yields a quite unstable emulsion, whilst a stable one is obtained, when the water contains a little soap, or when it is slightly alkaline, and the oil contains free fatty acid, so that a soap film can be formed at the interface between the oil and the water. The great activity of soap is shown by the following experiment: Oil is allowed to flow from a dropping-pipette, the nozzle of which dips below the surface of water, and the number of drops is counted which is furnished by a given volume of oil. Thus in one experiment 55 drops were obtained, both in pure water and in a slightly alkaline solution; no larger number were obtained with acid olive oil flowing into pure water. But when the acid oil flowed into alkaline water the number of drops rose to 331.

As with protective action, so also here the important factor is the adsorption of the hydrophilic colloid on the surface of the liquid to be emulsified, or on that of the solid to be suspended. But here, as in protective action, the adsorption is not the only factor, for apparently those colloids which are most strongly adsorbed, are by no means the most active, and undoubtedly other factors, as yet unknown, also play a part. A noteworthy feature is the power of forming solid or viscous envelopes at the interface, for an emulsion may also be stabilized by the addition of a suitable fine powder (such as soot and zinc hydroxide), if the solid powder forms a more or less continuous film at the interface. The hydrophilic colloid or the emulsifying powder is called the **emulgent.**

When two liquids are emulsified together, the question keeps arising : which liquid is the disperse phase, which the dispersion medium ? When one liquid is in considerable excess it necessarily becomes the dispersion medium. But there is a fairly wide region of volume proportions, in which both water and the organic liquid (oil) may become the dispersion medium, according to the nature of the emulgent. The envelope formed by the latter presents its convex side to the dispersion medium, and the larger of the two interfaces formed by the emulgent envelope will necessarily be on the side of that liquid, which most tends to have its interface increased by the emulgent. Hence the larger interface will for instance face the liquid in which the emulgent turgesces (swells), or by which the emulgent is readily wetted. For this reason hydrophilic emulgents, such as gelatin, gum, and alkali soaps, tend to make the water into the dispersion medium, whilst hydrophobic emulgents, such as resin soaps and the soaps of multivalent metals, favour an organic liquid as the dispersion medium (cf. Fig. 26).

Further that liquid, which has the greater solvent power for the emulgent, also tends to become the dispersion medium, for then the droplets of the disperse phase can build up their protective envelope from a relatively large store of the emulgent, whereas they are less favourably situated if they have to rely on their own small store. The charge on the emulgent envelope also has some influence. A negative charge, which may be caused by OH′-ions, or by anions of high valency, favours water as the dispersion medium; a positive charge, resulting from cations of high valency or from cations of the heavy metals, favours the organic liquid.

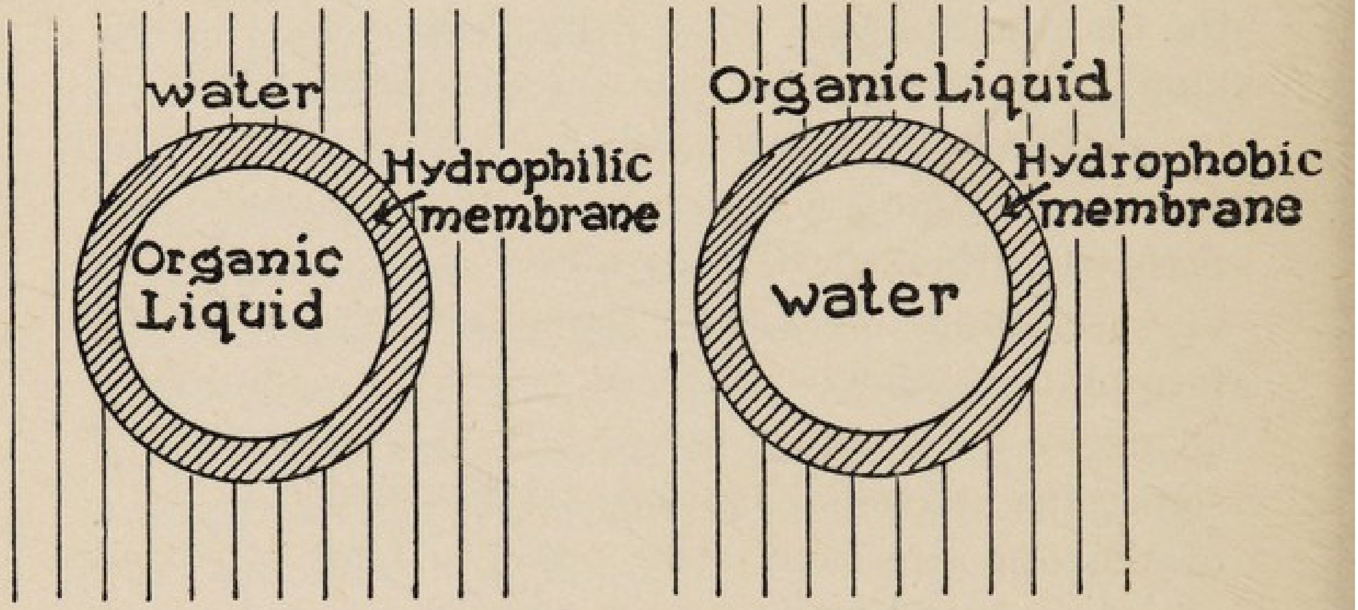

FIG. 26.

As will be seen from the nature of the emulgents referred to, there is a distinct possibility that when the amounts of the two liquids are in a suitable proportion, an oil-water emulsion may be converted into a water-oil emulsion. (The first-named word always indicates the disperse phase.) Thus an oil-water emulsion, prepared with alkali soap, may be changed to a water-oil emulsion by the addition of calcium- or zinc salts. These form calcium- or zinc soaps, which so strongly favour the oil as dispersion medium, that the one kind of emulsion finally turns into the other kind. The transformation is most readily detected by means of the electrical conductivity, which is greatly decreased by it. Such transformations are perhaps of biological importance. It is possible, as Clowes assumes, that the semipermeable protoplasmic membrane resembles such an emulsion, and that a change in the concentration of salts in the cell converts something resembling an oil-water emulsion into one of the opposite kind; this might determine certain changes observed in the permeability of the protoplasmic membrane, which are difficult to explain in any other way.

The emulsifying action of hydrophilic sols is important in other respects. The **detergent action** of soaps in washing depends essentially on the emulsification of greasy matter, which is thereby removed from the surface. The production of **clay casts** depends on the same principle. By stirring with alkali, clay and kaolin, which contain humus-like substances, are converted into a liquid sludge, which can be poured into moulds of plaster of Paris. The peptizing influence of the humic acid salts formed by the alkali results in the larger flakes of clay being disintegrated into their finest constituent particles, thus producing a fluid sludge.

2.—Gels

THE GENERAL PROPERTIES OF GELS

At the present time the class of gels cannot be sharply delimited. The concept suggests in the first place jellies like those of gelatin and silicic acid, and so forth, and in the second place also structures like wool and cotton fibres, which are capable of taking up reversibly considerable quantities of water. The slightly hydrated flakes resulting from the coagulation of metal sols, sulphide sols and such like, will not be regarded as gels. For these flakes we propose to use, where necessary, the term **coagulum,** while we classify all jellies among the gels. It is, however, still uncertain whether all the structures classified above as gels, are really similar in character, and whether we shall not be forced at a later stage to draw some essential distinctions between them.

Gels are often formed from sols, in many cases by **coagulation.** Thus an Al_2O_3 sol sets to a gel on the addition of electrolytes, and the process follows closely the laws which govern the coagulation of hydrophobic sols (cf. p. 138 *et seq.*). The formation of a silicic acid gel from the corresponding sol also has the character of a coagulation, but it resembles more closely the coagulation of a hydrophilic sol. These two processes are irreversible; it is impossible to reproduce the sol simply by warming, or by washing away the electrolyte. On the other hand the formation of gelatin-, agar-, and soap gels is reversible: sufficiently concentrated colloidal solutions of these substances are sols above a certain temperature, and set to gels on cooling; on warming these gels liquefy again and the transformation can be repeated any number of times, if we neglect accessory factors and the chemical changes, which may occasionally affect these substances. This process is called a **sol-gel-transformation (gelation),** and should be sharply distinguished from a coagulation.

In all these cases the gel is formed from a sol, and as was explained in the previous section, sols must in general be regarded as two-phase systems. Since during the conversion of a sol into a gel nothing occurs which might suggest the disappearance of the diphasic character, we are also obliged to regard gels as two-phase systems. Under suitable conditions ultramicroscopic examination leads to the same result; if we observe the setting of a silicic acid-, gelatin- or agar sol, we see (provided the sol is not too concentrated) a swarm of submicrons which at first are in lively Brownian movement. Individual particles undergo appreciable changes of position in the field of view, as is indeed also the case with sols. When gelation proceeds this translatory movement changes to an oscillatory one, in which the mean position of each particle remains fixed. This oscillatory movement becomes weaker and weaker, until finally it escapes detection. The flakes of the resulting gel, however, emit a bright Tyndall light under the ultramicroscope, and thus show that they consist of submicrons and amicrons. The above applies to gels formed from dilute sols. Those formed from more concentrated ones are often quite incapable of ultramicroscopic resolution, for two reasons. In the first place the sols of silicic acid, gelatin and agar, which here come into question, often have strongly hydrated particles, whose index of refraction does not differ sufficiently from that of the dispersion medium (cf. p. 130). In the second place the submicronic or amicronic particles of concentrated sols are generally only separated by amicronic liquid films having a thickness of 3–5 $\mu\mu$, and such a structure is not resolvable under the ultramicroscope.

We have therefore some difficulty in directly demonstrating the diphasic nature of a gel, and hence some investigators prefer to regard the gels as one-phase systems. They assume that in a gelatin gel the individual particles are large molecules and that the water is, as it were, present in solid solution. Still other investigators lay stress on the fact, that a gel not only has a polyphasic character, recognizable under the ultramicroscope, but also a coarser heterogeneity already visible under the ordinary microscope. A heterogeneity of this kind was observed by Bütschli, especially on allowing a silicic acid gel to dry, when interstices, originally containing water or a solution, become filled with air. He therefore concluded that a gel has an alveolar or honeycomb structure, and that membranes, themselves consisting of submicrons and amicrons, surround cells filled with a liquid, or (in the desiccated gel) with air. According to Zsigmondy's experiments it is pretty certain that this microscopically visible polyphasic character has nothing to do with the actual structure of the gel, but that it is due to gas bubbles. Although a framework of closed honeycomb cells is extremely unlikely in most gels, it is quite possible that there are often or always filaments or films composed of connected colloidal particles, and that these are of great significance in determining the elasticity and other mechanical properties of the gel.

The statements on p. 130 concerning the size, shape and state of aggregation of the particles of a sol, also apply to the particles of a gel. Already quite a number of cases are known, in which the particles of a gel are rodlike, and hence probably consist of minute crystals. This is so for instance with the gels of soaps, of some urates and of many salts of the more complex alkaloids like quinine, eucupine, and ergotoxine. These alkaloidal salts separate from supersaturated solution as gels, and may on prolonged keeping be converted into larger crystals, which separate from the saturated solution. Such gels with crystalline particles show characteristic double refraction and dichroism, as was described for sols on p. 134 *et seq*.

The interconversion of sol and gel is always a gradual, continuous process. On cooling there is never a definite "freezing point," nor is there a definite "melting point" on warming, no matter what criterion be adopted. By rapidly cooling a sol it may often be kept fluid for some time at a temperature, at which the gel is the stable condition ; the sol then only sets gradually on prolonged keeping. It has been shown for soap gels—and the same doubtless applies to many other gels—that at one and the same temperature there is in many respects no demonstrable difference between the sol and the gel ; this applies to vapour pressure, electrical conductivity and other properties. It is only by its much greater solidity and elasticity, that the gel differs from the sol.

We must not infer, however, that in contradistinction to gels, sols are quite inelastic. Those sols which are capable of setting, do indeed have a certain elasticity, although a much smaller one than the gels to which they set. This may be shown by observing the movement of a magnetic particle under the microscope. A minute fragment[1] of a magnetic metal, such as nickel, is placed in a sol under the microscope, and we observe how the particle is attracted by the pole of an electro-magnet. If the current be switched off, so that the attraction ceases, the particle does not remain at the spot to which it had moved, but recoils, sometimes even regaining its original position. This

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[1] Unless the fragment is microscopic, it settles down too rapidly in the liquid, and is useless.

elasticity can be demonstrated in many sols (e.g. of sodium stearate and of gelatin) at concentrations so low, that the sol is only slightly more viscous than water. Highly viscous liquids, like glycerin or a concentrated sugar solution, do not show any trace of this elasticity. With gels the same experiments are possible, but of course the elasticity is here much greater; a much larger force is required to give the same displacement to the nickel particle. Since so many sols are elastic, their viscosity cannot be measured with the ordinary apparatus; the rate at which a sol flows from a capillary tube depends not only on its viscosity, but also on its elasticity.

By means of these experiments with magnetic particles it is possible to measure not only the elasticity, but also the elasticity limit, i.e. the limit to which the particle can be attracted without disruption of the sol or gel; if this limit be surpassed the particle no longer springs back to its original position. This is the only indication that the elasticity limit has been exceeded; the disruption itself is not directly observable. Experiments of this kind yielded the important result that the elasticity limit is especially high in "soft" gels, that is in those which are as it were intermediate between sols and gels; the more dilute sols and the more concentrated gels both have a lower limit of elasticity. In the region of the high elasticity limit gels are apparently specially capable of being drawn out to filaments.

In addition to the gelation of a sol as a whole, and to the separation of gel flakes, there is another way in which a gel can be formed from a sol. Very often thin pellicles of a gel are formed on the surface of colloidal or semi-colloidal solutions. The skin which is formed on the surface of boiled milk, is a well-known example. It is evident that this skin originates at the interface between liquid and air, for it can be lifted off without wetting the finger tips. Such pellicles are formed on the surface of many solutions of soaps, proteins, peptones and dyes. They may be considered to originate as follows: The colloidal particles are first adsorbed on the surface, and becoming closely crowded, they are coagulated or undergo a sol-gel transformation, so that finally a pellicle of the gel is formed. Proteins apparently undergo chemical change in these skins, and are denaturated, so that they are no longer soluble in water. For this reason it is possible to remove protein from a solution by mere shaking, when care is taken to remove the foam each time it is formed, for every bubble of the foam is surrounded by a surface layer of protein, which has become insoluble. The production of foam implies the formation of an extensive surface, containing an abundance of protein, which is removed along with the foam. Such films are formed not only on the interface between liquids and gases, but also on that between two liquids. Therefore they doubtless play an important part in the processes of cell division.

TURGESCENCE AND DETURGESCENCE[1]

Gels may be divided into two groups, with reference to their power of imbibing a liquid and giving it up again ; those which can be made to swell, the **turgescible** gels, and those which do not swell, the **non-turgescible.** An aqueous gelatin gel may serve as an example of the former class. On desiccation it loses water uniformly without the formation of vacuoles and finally the well-known horny gelatin plate is left. If the dry plate is immersed, water is taken up again uniformly, the total volume increases and finally we obtain a hydrated gelatin gel practically identical with the original. The term **turgescence** will be confined to this kind of volume change, due to the imbibition of liquid, and **deturgescence** will be restricted to the converse phenomenon, the giving up of water. Other turgescible gels are those of agar with water, and of rubber with benzene, toluene or chloroform.

An example of a **non-turgescible** gel is furnished by silicic acid. When the gel is first formed from the sol, it contains so much water, that its volume decreases

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[1] A determined attempt should be made to fill a gap in English scientific terminology by inventing equivalents for the German *quellen* and its derivatives. This can be done by anglicizing the Latin *turgesco,* and using "turgesce" transitively for *quellen.* Turgescence and turgescible already exist in English and other derivatives can readily be formed. In deference to custom I have not entirely abandoned the rather unsatisfactory term "swelling."—G. B.

somewhat on drying. Beyond a certain definite point this no longer occurs, the external volume is preserved and the further removal of water results in the interstices of the gel becoming filled with air or with water vapour. At first the gel is vitreous and semi-transparent, for its particles and the intervening pores are all amicronic or submicronic, and when this is so, we can indeed observe the Tyndall phenomenon, but no opacity. On further desiccation the gel assumes a white, chalky appearance. It is then permeated by microscopically visible gas bubbles, and the reflexion of light from their surfaces makes the gel white and opaque, for the same reason that fine glass-powder is white and opaque. The gas bubbles are so large that each contains a considerable number of colloidal particles and of pores. On still further desiccation the gel once more becomes vitreous and semi-transparent ; the gas bubbles have disappeared, the pores are uniformly filled with air, and the small quantity of water still retained, envelops the colloidal particles as an adsorption layer. The optical conditions are therefore the same as at the beginning, except that the pores are now filled with air, instead of with water. Since they are amicronic, or anyhow of a fine submicronic character, the gel is again transparent.

The intermediate range of hydration, in which the gel appears chalky, is termed the **region of inversion.** The process of desiccation may be studied quantitatively, by measuring the vapour pressure of the liquid contained in the gel. For this purpose the gel is placed in a desiccator containing dilute sulphuric acid of known vapour pressure, and the water content is determined, which the gel assumes in equilibrium with this pressure of aqueous vapour; it may take months before a state of equilibrium is reached. The results of such experiments have led to the following conclusions: small quantities of water are held by adsorption on the colloidal particles; the rest fills the pores of the gel, which pores are capillaries having a radius of 1–3 $\mu\mu$. Since in such very narrow capillaries the surface of the liquid is strongly concave, the vapour pressure is much smaller than that on a plane surface at the same temperature. We may recall the increase and decrease of vapour pressure at convex and concave surfaces respectively (cf. p. 40).

A silicic acid gel of this kind may be made to imbibe other liquids, organic or inorganic, and on this the technical application of similar gels is based. Dynamite is an example of this application; nitroglycerine, imbibed by infusorial earth, is much less dangerous and more easily handled than in the liquid condition. Even if it undergoes decomposition locally, the heat given out does not raise the temperature sufficiently to cause an explosion, for the extensive surface of the colloidal particles absorbs much heat, and hence has a strong cooling effect. The great lowering of vapour pressure in such gels may occasionally be put to technical use. Thus a pungent and caustic liquid like bromine may be manipulated much more readily for disinfection and other purposes, if it is imbibed by infusorial earth ; this is so-called " solid " bromine.

In turgescible gels we must consider more particularly the **turgidity pressure.** The tendency of a dry, turgescible gel to take up water is so great, that considerable pressures, acting on the gel, may be overcome and conversely, a high pressure is required to squeeze water out of the gel. Fig. 27 represents an apparatus by means of which small turgidity pressures (of a few atmospheres) may be measured. Q is a disc of the gel, for instance dry gelatin or india-rubber. It lies in a glass tube G and rests on the bottom of a porous cell T, which is immersed in the liquid having a turgescent action. The tube G and a portion of the calibrated capillary K are completely filled with mercury. K is joined to a cylinder of compressed gas, by means of which a known pressure can be exerted on the turgescent gel. The displacement of the mercury meniscus in the capillary indicates the amount of liquid taken up by the gel, and so the connexion between the turgidity pressure and the degree of turgescence (amount of swelling) may be studied.

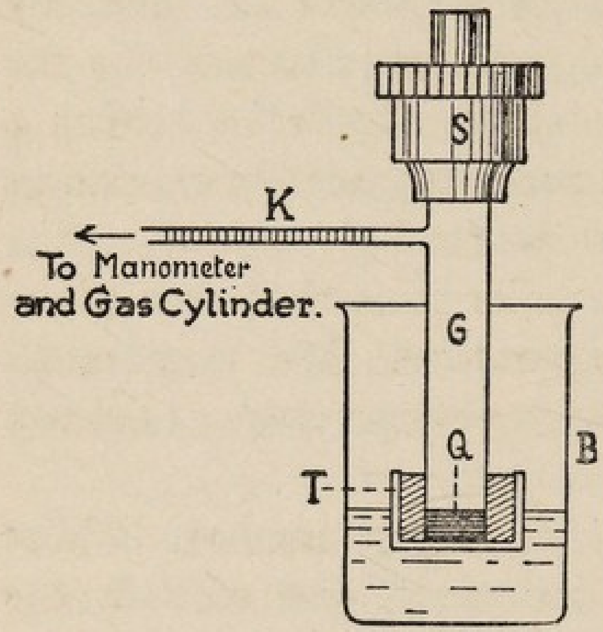


FIG. 27.

In this way the turgidity of gelatin in water and of rubber in many organic fluids have been measured. The turgidity pressure increases very rapidly when the amount of fluid contained in the gel is small. Pressures of many thousands of atmospheres must be applied, in order to squeeze more fluid out of a gel, which is already fairly dry, and conversely enormous pressures may be overcome, when a very dry gel is allowed to turgesce. This was utilized by the ancients. Rocks can be split asunder by driving very dry wood into existing crevices, and then making the wood swell with a little water.

In turgescence there is a considerable evolution of heat, the **heat of turgescence,** which is especially large for the initial small quantities of water imbibed by a gel.

The nature of turgescence is still in dispute. Katz, who has studied the phenomenon most closely during recent years, considers it a process of solid solution; thus in a gelatin gel water would be present in a state of molecular division between the molecules of gelatin. The similarity of the vapour pressure curves, when a turgescible gel and when concentrated sulphuric acid take up water, is indeed very striking, as Katz has rightly emphasized. On the other hand there is much justification in regarding a turgescible gel as a two-phase system in which the fluid has insinuated itself between the colloidal particles; the imbibition would accordingly resemble an adsorption. There is indeed a distinct difference from ordinary adsorption, in so far as in the latter the interface of the adsorbent is not altered in extent, nor are the parts of the adsorbent interface appreciably displaced or rearranged. In turgescence, on the other hand, we must assume that the colloidal particles of the gel become disunited and that new interfaces are generated, or that the particles become separated by adsorption layers of increasing thickness, without the gel losing its cohesion.

Turgescence is extremely important in many biological processes. There is every reason for assuming that muscles are to a large extent turgidity motors, and that the movements of plants are due to turgescence and deturgescence. Bütschli and Spek have pointed out that the turgescence of two firmly united gel plates of different turgescibility may result in the formation of the pouches, which occur in the development of living beings, as for instance in the gastrula invagination. Indeed, the turgidity of living structures seems to have a definite influence in the formation of species. Thus Tower found in the case of certain beetles belonging to the genus *Leptinotarsa* which are related to the Colorado beetle, and inhabit dry districts of Mexico, that the crossing of related species resulted in quite different progeny, depending on whether the parent species did or did not live under the same conditions of moisture. Yet another biological application results from the following consideration. Just as the freezing point of a solution is lower than that of the pure solvent, so the liquid imbibed in a gel has a much lower freezing point than the free liquid.

At low degrees of turgidity, and therefore at turgidity pressures of a few thousand atmospheres, the freezing point may be lowered by 100° or more. This circumstance is certainly important in determining the resistance to very low temperatures of organisms containing very little water, such as bacteria and spores.

Now the process of turgescence in organized beings does not as a rule take place in pure water, but in aqueous solutions of electrolytes and of other substances. Our knowledge of turgescence and of turgidity pressure in such solutions is by no means as extensive as we might wish. Present experience seems to indicate that in the turgescence of proteins the influence of $H^{\cdot}$- and OH'-ions preponderates over that of all others and that both these ions greatly favour turgescence.

These facts suggested to M. H. Fischer an explanation of the origin of œdema in kidney- and heart disease. He imagined that the connective tissue becomes acid and that its increased $H^{\cdot}$-ion concentration produces turgescence resulting in œdema. This theory is untenable. It was found that in the diseases in question the connective tissue does not become acid at all, and further, that in this particular tissue an increased $H^{\cdot}$-ion concentration does not lead to turgescence, but to deturgescence. Nevertheless turgescence remains important for the explanation of many processes taking place in connective tissue. Here we can only refer to the antagonism which exists according to Schade between the ground substance of the connective tissue and the parenchyma cells imbedded in it. Influences which favour the turgescence of the connective tissue, are adverse to the taking up of water by the parenchyma cells, and the converse also holds good. Thus for instance an increased $H^{\cdot}$-ion concentration has a deturgescent effect on the connective tissue, whilst the capacity of the cells for taking up water is increased; an increased OH'-ion concentration has the opposite effect. In normal connective tissue there is therefore a certain turgidity balance.

THE ADSORPTION BY GELS. DYEING AND TANNING

The colloidal particles of gels adsorb gases and dissolved substances according to the rules previously referred to (pp. 42, 58). Charcoal, which served as the principal example of an adsorbent, is indeed simply a non-turgescible gel; for instance, it largely resembles a silicic acid gel (p. 176) in its power of taking up water. We may mention that in particular the adsorption of gases by a silicic acid gel has been investigated and was found to obey the well-known rules. The adsorption of substances of high molecular weight and of colloids from solution is influenced by the following circumstance: The pores of the gel may be so fine, that the large molecules or the colloidal particles cannot penetrate into the interior of the gel; they remain on the surface and are there adsorbed. Thus the particles of a silver sol merely cover the surface of a silicic acid gel and form a silver mirror; something similar is observed in the adsorption by a silicic acid gel of colloidal solutions of ferric hydroxide, benzopurpurin and casein.

The adsorption by gels is important in dyeing, tanning and related processes. Cotton-, silk-, and wool fibres are distinctly gel-like in character. In any case they are able to increase their water-content continuously and reversibly, as in turgescence, and therefore with a change in volume; they also bind gases and dissolved substances as if by adsorption. Any attempt to explain dyeing processes is inadequate, which bases itself exclusively on a single aspect of the phenomena (whether wholly on adsorption or wholly on chemical combination), and neglects the great variation in the properties of fibres and of dye-stuff solutions. To illustrate the dyeing process we may consider more closely the dyeing of cotton by so-called substantive dyes like Congo-red and benzopurpurin. These colouring matters of course dye cotton without a mordant, while many other dyes, such as those of the triphenylmethane group, require that the cotton should first be mordanted in a suitable manner. Cotton, like most other cellulose fibres, has a decidedly crystalline structure; examined by the method of Debye and Scherrer, it yields sharp lines (cf. Fig. 28 of the plate opposite p. 106). Cotton further resembles many crystalline adsorbents, in not adsorbing very strongly. Its chemical constitution makes an exchange adsorption (cf. p. 64) improbable. The solutions of the substantive dyes are colloidal; these substances must be reckoned among the semi-colloids, since their molecular weight is not large. They are adsorbed by cotton in accordance with the ordinary adsorption isothermal. Microscopic and ultramicroscopic investigation of the dyed fibre indeed shows, that the dye is chiefly present on the surface, and has not penetrated to any considerable depth. The important factor is, that the dye has been coagulated on the surface; the dye bath of course contains salts in suitable concentration, which serve to secure this coagulation. Their concentration has to be selected in such a way, that coagulation only occurs on the surface of the fibre, where the amount of dye has been increased as the result of adsorption, and not in the bulk of the dye-stuff solution, for in the latter case dyeing would be adversely affected. Hence there is an optimum content of electrolyte, above and below which less good results are obtained. That it is really a question of coagulation results from the fact that in comparing different electrolytes, the nature and the valency of the cation are found to have a predominant effect, exactly as in the coagulation of negative sols (p. 139); the colloidal solutions of these substantive dyes are indeed negative.

Of other fibres, silk, examined by the method of Debye and Scherrer, is found to be crystalline, and wool amorphous. Both adsorb distinctly more strongly than cotton, especially also substances in true solution, not only azo-dyes and triphenylmethane dyes, some of which are entirely in true solution, but also alkaloids and their salts, mercuric chloride, etc. Silk and wool further have a marked tendency for exchange adsorption, which is in accordance with their chemical constitution ; as proteins they have a salt-like character, and it is quite possible for the ion of a dye-stuff salt to be exchanged for an ion of the fibre. Most probably the first stage of every dyeing process is an adsorption. This is followed later by another process, perhaps a purely chemical one, such as salt formation with the fibre or a chemical change of the dye in the adsorption layer, which second process makes the coloration into a true dyeing process. Examples are known in which these two successive stages can be clearly distinguished. Thus freshly precipitated flakes of aluminium hydroxide adsorb the blue acid of Congo-red, when they are shaken with the colloidal solution of this dye ; the blue flakes gradually become red, especially on warming, as the result of the formation of a red aluminium salt of the Congo acid.

A similar succession of processes is found in **tanning.** The hide is an amorphous adsorbent, the solution of tannic acid (and of many other vegetable tanning agents) is semi-colloidal. The tannin is in the first instance taken up by hide powder according to an ordinary adsorption isothermal, but the adsorption compound so formed from hide and tannin, has not yet the properties of leather. It only acquires these gradually, becomes brown, no longer gives off tannin on washing, and becomes more resistant to dilute alkali. The adsorption is followed by another process, a chemical action or a coagulation, by means of which the adsorption compound acquires the properties of leather.

DIFFUSION IN GELS. LIESEGANG STRATIFICATIONS

Gels combine in a remarkable manner the properties of liquids with those of solid substances. The similarity to liquids shows itself *inter alia* by the fact that dissolved substances of not too large molecular weight diffuse in a dilute gel quite as rapidly as in a pure liquid. Common salt or urea diffuse in gels containing a few per cent. of gelatin or agar exactly as fast as in water. In concentrated gels, however, the diffusion of substances of high molecular weight is retarded, in comparison with their diffusion in pure liquids. The similarity to solids shows itself in the great elasticity of gels, mentioned above, and further particularly in the absence of convection currents, which are also absent from solids, but occur inside a liquid. The capillaries of a gel, in which the liquid is contained, are narrow, and a large part of the liquid is held as an adsorption layer, so that liquid currents are excluded.

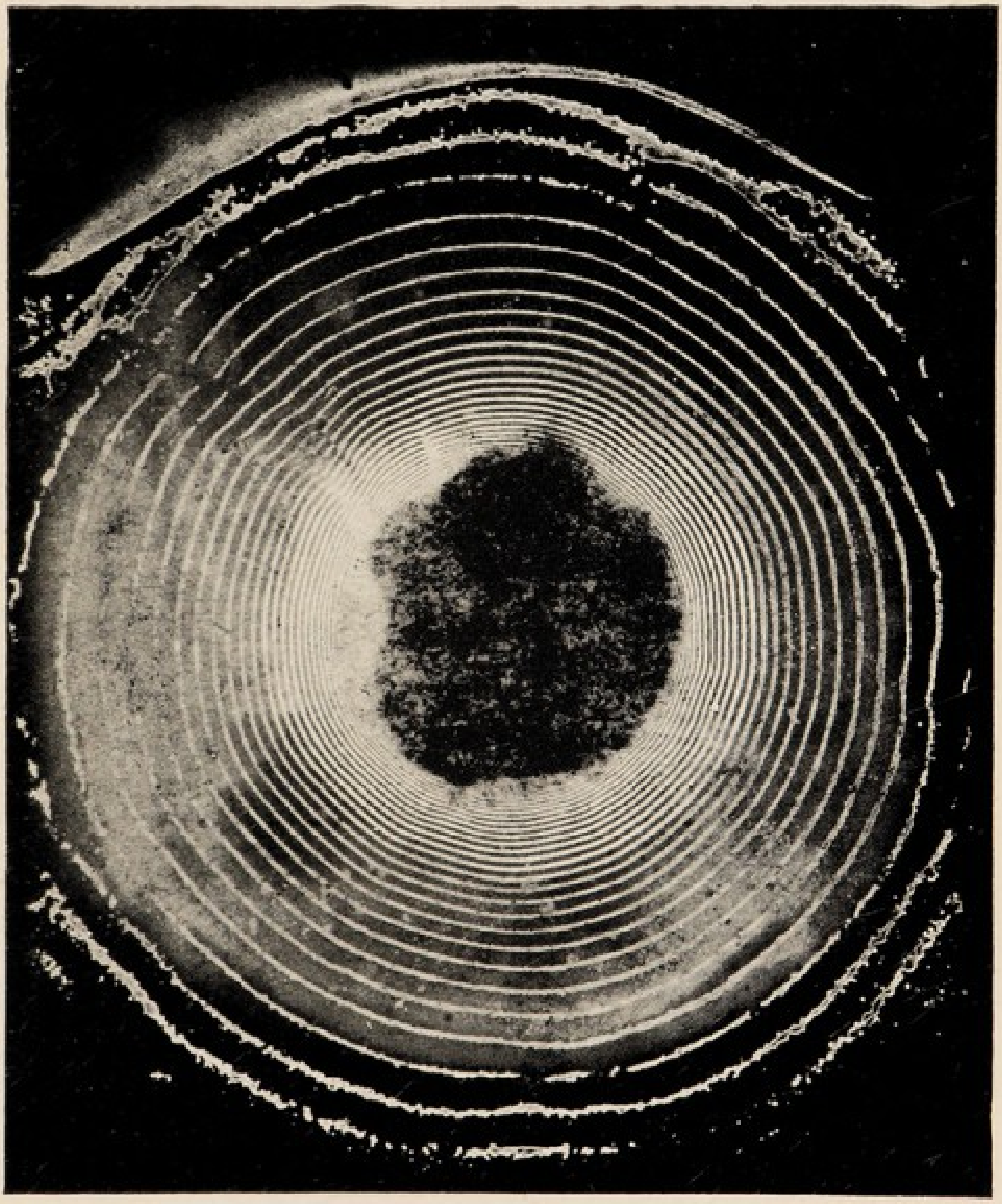
This combination of properties, which are elsewhere only encountered separately, results in the fact, that quite peculiar and characteristic processes may take place in gels. On account of the relatively rapid diffusion, chemical interaction may take place in a gel as it does in a liquid. This chemical change might also be observed in solids, if it were not that the extremely slow diffusion in the latter generally prevents the detection of such interaction. Thus it is possible under suitable conditions to produce large and well-formed crystals in a gel, when in a liquid only a microcrystalline powder is formed. The conditions are most favourable to the formation of large crystals, when a crystal nucleus can grow as freely as possible in a solution which is not too highly supersaturated. In a free liquid the corresponding conditions are not good ; any nucleus, which may be formed, falls to the bottom as the result of gravity and is thus removed from the uniform conditions obtaining in the interior of the liquid. There is further the possibility that several nuclei may unite, which likewise is unfavourable to regular growth. In a gel, on the other hand, a nucleus once formed adheres by adsorption to a portion of the gel framework and grows out uniformly, because the substance present in supersaturated solution only reaches the nucleus by diffusion. Hatschek was able to grow gold crystals up to 2 mm. in size, by allowing a suitable reducing agent, such as oxalic acid, to diffuse into a silicic acid gel containing auric chloride. Under other conditions of concentration gold leaflets, which are united together, may also be formed on the surface of the gel. All these structures (crystals, leaflets, etc.) closely resemble the metallic gold which has separated in nature. There is every reason to believe that the natural forms of gold have also been produced by the penetration of a reducing agent into an auriferous silica gel.

A further example of this kind is supplied by the **Liesegang stratifications,** which occur most readily in gels. If two solutions, capable of forming a difficultly soluble precipitate, are allowed to interact inside a gel, the precipitate is not always formed uniformly throughout the gel, but is often deposited in layers. These are repeated in regular fashion and are separated by intervals almost free from the precipitate. Liesegang stratifications have been examined most closely in the case of silver chromate. They may be prepared by allowing a sol containing 2–3 per cent. of gelatin and about 0·1 per cent. of potassium dichromate, to set on a glass plate; a drop of concentrated silver nitrate solution (50 per cent.) is then placed on the plate. The following reaction takes place:

$$K_2Cr_2O_7 + 4AgNO_3 + H_2O = 2Ag_2CrO_4 + 2KNO_3 + 2HNO_3$$

and the silver chromate separates in concentric bands, as represented in the frontispiece.

An explanation first suggested by Ostwald and later modified somewhat, has proved correct. The principal factor is the rate of nuclear formation, the most important properties of which were discussed on p. 95 *et seq*. It is of special significance to the present case, that this rate increases so rapidly with increasing supersaturation. At a low supersaturation the rate of



Liesegang Stratifications

nuclear formation is low, and few nuclei separate ; at a high supersaturation many nuclei are formed. When the silver nitrate solution penetrates into the gel containing the dichromate, the supersaturation in the foremost layer of the advancing silver nitrate solution is so small, that practically no nuclei are formed. A little further back the supersaturation is, however, already so large, that abundant nuclei result. These rapidly grow to crystals by the deposition on them of silver chromate molecules, with regard to which the solution is supersaturated. The silver chromate molecules come not only from the region with abundant nuclei, but also from the zone in front, out of which silver chromate diffuses backwards to the nuclei. In this way there is formed in front of the zone of precipitation a region in which supersaturation is almost completely abolished, and in which no potassium dichromate remains. The concentrated silver nitrate solution now diffuses rapidly through this region, until in a region lying further forward and containing more potassium dichromate, an abundant formation of nuclei and precipitation once more occurs, whilst in the intervening space a few crystals at most are formed. Hence a ring of precipitate is always formed there, where the rate of nuclear formation reaches a sufficiently high value in consequence of a sufficiently high degree of supersaturation.

The Liesegang stratifications are very dependent on the nature of the gel and of the precipitate formed in it ; this has been advanced as an objection to the theory just outlined, which does not predict this dependence. In many gels the rings are readily formed, in others not at all or imperfectly, and the nature of the precipitate also greatly affects the ease with which stratifications are formed. These differences, however, become intelligible, if we consider that the substance present in supersaturated solution is adsorbed by the colloidal particles, and that this adsorption greatly influences the nature and the rate of nuclear formation. Microscopic observation seems to indicate, that the nuclei actually adhere to the colloidal particles of the gel and remain immobile, wherever they arise.

If the above theory of the Liesegang stratifications is correct, the gel *qua* colloidal-disperse structure is not an essential requirement for the phenomenon. The only thing which matters is that a chemical reaction should take place in a liquid, undisturbed by currents. Thus it is actually possible to produce these stratifications in the narrow spaces formed by pressing a cover-slip on a microscope slide.

The importance of Liesegang stratifications in nature cannot be doubted. Thus the bands in agate are essentially of the same kind. Yet caution is necessary, when we desire to explain any banded vegetable or animal structure in this manner, for such banding may arise in a variety of other ways. Thus the patterns on butterfly wings must not be explained in this way, for they are already present in relief on the wings of the pupa, before the pigment has developed.

The formation of folds and furrows, constituting the relief pattern, is therefore due to conditions of growth, and later the existing pattern is merely rendered more striking by the deposition of colouring matter.

B. COLLOIDAL-DISPERSE STRUCTURES OF A DIFFERENT KIND

1.—Mists and Smokes

Mists and smokes are colloidal-disperse structures in which the dispersion medium is gaseous, while the disperse phase consists of droplets (in the case of a mist) or of solid particles (in the case of a smoke). Just as coarse emulsions and suspensions are closely analogous to sols, so there is no need to separate off the smokes and mists containing microscopically visible particles from those consisting of particles of colloidal size ; the coarser structures are merely less stable, as a rule. Many other statements concerning sols are also applicable to smokes and mists. The latter arise either by condensation or by dispersion processes : either the disperse phase may separate from a supersaturated vapour, or a liquid or solid substance may be " atomized." The particles show a lively Brownian movement, more lively than in a sol, since the viscosity of a gaseous dispersion medium is of course less than that of a liquid one. The Tyndall effect is well marked and the ultramicroscope can be employed with success.

One of the chief differences from sols is found in the electrical behaviour, at least in comparison with those sols, which have water as the dispersion medium. In water the number of ions is so large, that electric double layers, described on p. 138, are formed, and that we are unable to observe the taking up or giving off of single electrical charges by a particle. In a gas space the initial number of ions is small. If a mist or a smoke is generated in it, the particles are either uncharged or only charged to a slight extent, whether positively or negatively. The charge of individual particles may be altered by a definite, small amount, if we ensure that new carriers of electrical charges reach the particles and unite with them. In order to bring this about, we must increase the number of carriers of electricity in the gas space, the so-called gas ions, which can be done most conveniently by exposing the gas to radiation, for instance to X-rays. The gas is then ionized, that is, a large number of gas ions are formed. This phenomenon is very important, for by its aid it has been possible to measure the charge of an electron, i.e. the smallest quantity of electricity capable of existence. The number of such charges on a single mist- or smoke particle may be ascertained by observing ultramicroscopically how rapidly the particle moves upwards or downwards between two oppositely charged plates.

The particles of coarse mists and smokes are deposited under the influence of gravity. Here the other influences, such as that due to the electrical charge, become negligible, but in colloidal-disperse mists and smokes they play a real part. They have not yet been studied sufficiently closely, however, to allow of brief description. There is a further complication in the case of mists, since they may disappear, not only by the increase and consequent settling of their particles, but also by complete evaporation; thus an aqueous mist may disappear in a sufficiently dry space. If for any reason evaporation is prevented, the remarkable case occurs, of a mist persisting in dry air. This is the cause of the extraordinary stability of the notorious London fogs. Their droplets are coated with soot and with films of oily liquids, resulting from imperfect combustion of coal; this envelope prevents evaporation to such an extent, that the fog persists in a space which a hygrometer shows to be sensibly dry.

The above example sufficiently illustrates the important part which the stability of mists and smokes may play in meteorology; the technical importance of this factor is also becoming more and more evident. In the Cottrell process mist and smoke particles are precipitated in large flakes at the surface of high tension electrodes (charged to about 100,000 volts). The process not only serves to remove smoke particles from furnace gases and so to combat the smoke nuisance, but also to collect technical reaction products, which, like sulphuric acid, are generated in the form of a mist. Another phenomenon of technical importance is the explosion of combustible dust, such as flour or coal dust. These dusts have been found to acquire considerable electrical charges, which may lead to discharge by sparks; in this way the finest colloidal particles are burnt, and the resulting flame may bring about the combustion of the whole cloud, provided the latter is thick enough, for the flame of each particle has to be communicated to neighbouring ones. The adsorption of oxygen by the finest dust particles seems also to be an essential feature of these explosions.

2.—Foams

In the simplest case foams are disperse structures, consisting of a liquid dispersion medium and a gaseous disperse phase. Whilst in most other colloidal structures the particles of the disperse phase are of colloidal minuteness, this is by no means essential, or even usual, in the case of foams: the gas bubbles of a foam are generally macroscopic or at least microscopic. On the other hand the dispersion medium is often of colloidal fineness, that is, the gas bubbles are separated from one another by liquid films, having a thickness of only a few $\mu\mu$. Hence in a foam the surface of the liquid has been enormously extended, which is in opposition to the tendency of the surface tension to make the liquid surface a minimum (cf. p. 20). For this reason a liquid, which is to furnish a stable foam, must fulfil a number of special conditions. In the first place the surface tension of the liquid must be small, for otherwise its tendency to reduce the surface would be too powerful. Pure liquids with a low surface tension, like ether and benzene, are, however, by no means specially inclined to foam. The reason is that at room temperature these liquids are all rather near to their boiling points ; they therefore have a high vapour pressure and films, composed of such liquids, evaporate too rapidly. A second condition for the production of stable foams is therefore that the vapour pressure should be small, as well as the surface tension. These conditions are fulfilled by aqueous solutions of capillary-active substances (e.g. of amyl alcohol), and especially by solutions of many colloids and semi-colloids, like soaps, saponins, and proteins. In protein solutions a third influence plays a part, for they all have the property, referred to on p. 174, of forming solid pellicles on their surface. These pellicles retard evaporation and surround the liquid lamellæ with a framework, in the narrow lumen of which the liquid can only flow down very slowly. The quantity of liquid flowing through a capillary of course decreases extremely rapidly, when the bore is reduced. Since the rate of flow also depends on the viscosity of the liquid, it is evident that a certain degree of viscosity favours the stability of foams.

Quite a number of conditions must therefore be satisfied, in order that a liquid may be capable of furnishing a strong and persistent foam. In the case of wort, the infusion of malt, before it is fermented to beer, two kinds of influences can be distinguished. In the first place there are substances, like albumoses, which cause strong frothing any how; but the froth produced by them is not very persistent. The stability of the froth of beer is primarily due to the gum of barley, which increases the viscosity of the liquid.

Definitely ultramicroscopic particles, such as are present in the above-mentioned gel-pellicles of soaps, saponins, etc., are not absolutely necessary for increasing the stability of the foam. This may also be done by much coarser microscopic or macroscopic solid particles, which remain on the surface, because they are only wetted with difficulty. The coarser particles also act by forming a framework, so that extremely fine channels are formed, through which the liquid only flows down very slowly. Such foams, rendered stable by coarser powders, play a part in the flotation process for separating ores, described on p. 58. The present discussion will show that the factors which stabilize foams are very similar to those which render emulsions stable (cf. p. 164 *et seq.*). In emulsions stability is also promoted by soaps, saponins and other semi-colloids, forming solid pellicles, and by powders adhering to the interface. The cause is also the same in both cases, namely the support of the large interface of the foam or emulsion by a solid or viscous framework.

The stable foams of soap solutions have been investigated in special detail, and also the properties of a single lamella of a soap solution, which properties may be observed by blowing soap bubbles with sufficient care. If such a lamella is made thinner and thinner, the following changes are observed: At first the lamella is colourless, then brilliant colours appear, which are due to the interference between the light reflected from the two surfaces of the lamella. Reference has already been made (pp. 37 and 105) to the formation of such interference colours by diffraction from a grating, or by thin oil films. On still further reducing the thickness of the soap lamella, remarkable black patches are formed, which represent the thinnest films of soap solution, capable of existence. The thickness of these films is of the order of 5 to 15 $\mu\mu$. The black patches border on a much thicker lamella, so that at the boundary there is quite a sudden change of thickness. Within the black patches black lamellæ of varying thickness may be distinguished, which also pass into each other discontinuously. Probably these black patches consist exclusively of the viscous surface layer, which on other grounds must be assumed to exist on the surface of soap solutions (cf. p. 174), and since these layers consist of only a few strata of molecules, there is the possibility of the existence of black patches of varying thickness, each composed of a different number of molecular strata. The relatively high stability of these extremely thin films probably depends on the fact that soap sols and soap gels contain pre-eminently filamentous particles (cf. p. 171). These filaments are only a few molecules in thickness, but very long, and form a strong felt work in the gel films, giving support to the extremely thin lamellæ.

3.—Disperse Structures having a Solid Dispersion Medium or having more than Two Phases

Among colloidal-disperse structures with a solid dispersion medium certain glasses deserve further consideration. **Gold ruby-glass** is not only one of the oldest technical colloidal products, first prepared by Kunkel more than 200 years ago, but also figures prominently in the history of colloidal chemistry. It was one of the first cases in which Siedentopf and Zsigmondy proved the existence of colloidal particles by means of their ultramicroscope. Gold ruby-glass is prepared by dissolving a little gold salt in melted lead- or baryta- glass; on rapid cooling a colourless glass is obtained, which probably does not contain gold in chemical combination, but in supersaturated true solution. On heating once more to a high temperature, the supersaturation is abolished and the gold separates in the glass in a state of colloidal dispersion. Under the ultramicroscope the appearance is very similar to that of a gold sol, except that the particles remain motionless in the glass, and show no Brownian movement. If the glass be heated too strongly or too long, its colour changes to blue and brown, the gold particles are coagulated, and become coarser, if the glass is sufficiently fluid; thus the same colour changes occur which have been described for the coagulation of a gold sol (p. 121). Besides the gold ruby-glass, other ruby glasses may be prepared in similar fashion with silver, copper, selenium, etc. With copper distinct varieties with particles of various sizes are manufactured: the red ruby-glass proper, with ultramicroscopic particles, the opaque copper-coloured hæmatinon with microscopically visible particles, and Aventurine glass, which contains copper spangles visible to the naked eye.

A further group of similar structures is represented by the so-called **coloured salts,** which owe their colour to metals present in a state of fine division. Thus if a carefully dried crystal of sodium chloride be heated in sodium vapour at a temperature somewhat below the boiling point of the metal, it is coloured yellow or sometimes brown and green. Similar colours are produced when a crystal is exposed to X-rays, cathode rays or the radiation from radio-active substances, which decompose the salt with separation of the metal. Under the ultramicroscope these coloured salts show particles, quite similar to those in ruby glasses, and hence there is every reason to conclude that they contain colloidal-disperse metal. Coloured rock salt also occurs in nature; it is generally blue, but other colours, such as violet, green and yellow may occur. The behaviour of these natural coloured salts is so similar to that of the artificial ones, both under the ultramicroscope and in other respects, that the natural colours are probably also due to colloidal-disperse metal, set free by radio-active substances in the neighbourhood.

This group of structures also comprises the important **photohalides.** This name is applied to silver halides, containing silver in a state of colloidal division, in allusion to the fact, that they are especially formed from silver halides by exposure to light ; this exposure brings about a partial reduction to silver, which first separates in a colloidal-disperse condition with the unchanged halide as dispersion medium. The photohalides are variously coloured yellow, purple or violet, according to their content of free silver and the shape of the silver particles. The substance constituting the latent image of an undeveloped photographic plate is without much doubt simply a photohalide of such low silver content, that it cannot be recognized by its colour ; the silver particles are nevertheless able to act as nuclei for the deposition of further quantities of silver, formed by the reducing action of the developer.

We will mention only two of the remarkable properties, which distinguish photohalides, and particularly photochlorides, that is, colloidal solutions of silver in silver chloride. In the first place they have the property of **colour adaptation.** If a photochloride is exposed to coloured light, it acquires to a large extent the colour of the particular light, with which it has been illuminated ; a kind of colour photography is achieved in this way. The blue and red colours especially are reproduced with some approach to accuracy. A still more surprising phenomenon is the **photodichroism** of photochlorides, discovered by Weigert. If these substances are exposed to plane polarized light, a red spot is produced. This, viewed through a Nicol prism, is found to be dichroitic; it is brightest when the plane of polarization of the light, originally used for illumination, coincides with that of the light by which the spot is viewed through the Nicol prism. It would take us too far to explain, how according to Weigert photodichroism and other related phenomena are connected with the colour adaptation of photochlorides, and how this group of phenomena is the basis, not only of the numerous examples of colour adaptation in nature, but also of the action of light on the retina of the eye.

It will be evident from what has just been said about photohalides, that the chemistry of photography is very largely based on applications of colloidal chemistry. Indeed, the photographic plate turns out to be a specially complicated colloidal structure, in which no less than four phases must be distinguished! In addition to the gelatin, and the aqueous solution in which it swelled, there is the photobromide, itself consisting of silver bromide and free silver. This large number of phases, capable of colloidal-chemical (and chemical) interaction in various ways, makes it so difficult to explain the processes occurring in a photographic plate. A large number of structures, important alike in nature and in the arts, present the same difficulty. Thus wood contains, apart from the turgidity water, both cellulose and lignin; starch contains amylose and amylopectin; in bread we must distinguish colloidal particles, as well as the coarser ones of crust and crumb, in which the starch grains are moreover embedded in a matrix of coagulated protein. A similar polyphasic character must be assigned to almost all natural membranes and fibres. At present the elucidation of the varied behaviour of such complex structures presents great difficulties, rarely overcome. Not until this has been achieved, however, will it be possible to treat many technical and biological problems successfully from the standpoint of colloidal chemistry. The investigation of these polyphasic structures is essentially the task of the colloidal chemistry of the future.

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