II. PHENOMENOLOGY OF LYOPHOBIC SYSTEMS

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§ 1. PREPARATION OF LYOPHOBIC SOLS

By *lyophobic sols* are meant colloidal dispersions of insoluble substances in a liquid medium, usually an aqueous solution. They can be prepared in several different ways. It is very typical for these systems that they can never be prepared by simple contact or slight shaking of macrocrystals of the insoluble substance and the solvent. The roundabout ways by which lyophobic sols can be arrived at may be distinguished according to SVEDBERG [1] into *condensation* methods and *dispersion* methods.

In the dispersion methods larger lumps of the insoluble substance are pulverized by mechanical or other means until colloidal dimensions ($< 1 \mu$) are obtained.

In the condensation methods a molecular (ionic, atomic) distribution of the insoluble substance is prepared first which then by suitable coarsening may give rise to a colloidal dispersion.

It is not always possible to make a sharp distinction between the two different types. The classical method of electric disintegration of metals (see p. 61) for instance probably is at the same time a dispersion and a condensation method. In the electric arc particles of colloidal dimensions are broken away from the electrodes, but at the same time part of the metal vaporizes and then passes the atomar dispersion. Moreover by direct electrolysis ionar dispersion may occur as an intermediate stage.

Usually the condensation methods allow one to reach a finer degree of dispersion than the dispersion methods. It is even not exaggerated to maintain that true lyophobic sols are always prepared by what is, in principle, a condensation method, whereas the true dispersion methods only allow one to prepare fine suspensions with particles not much smaller than 1μ. Nevertheless the old classification of SVEDBERG may still be very useful as a means of cataloguing the different methods of preparation.

In connection with this it may be useful to point out that there is no essential difference between sols and suspensions. The only difference between these two groups is the size of the particles. The boundary between them is chosen in such a way that suspensions do sediment in a reasonable time whereas sols do not.

This may explain why sols and suspensions often have been considered as being qualitatively different. In sols sedimentation is usually taken as a sign of loss of stability (see § 5 c, p. 80), and to the casual observer this might imply that suspensions are never stable in the same sense that sols are. Especially in the treatment of mechanical properties (this chapter § 5g, p. 85 and chapter IX, p. 342) we shall return to the great similarity between sols and suspensions.

[1] T. SVEDBERG, *Herstellung kolloider Lösungen anorganischer Stoffe*, Dresden 1909 (2e Auflage '20); *The Formation of Colloids*, London 1921.

In practical applications, suspensions are by far the more important of the two groups. They occur in the form of paints, lacquers, varnishes, all kinds of ceramic masses, wetted soil etc. The theoretical treatment, however, is much more advanced in the case of sols.

a. Condensation methods

The general feature of all condensation methods is the preparation of a molecularly dispersed supersaturated solution of the substance from which a sol is to be made. The conditions in which this supersaturated solution will lead to a sol, that is to many fine particles and not to a coarsely crystalline precipitate, will be treated in § 2, p. 63.

The means by which the supersaturation is reached depend completely upon the substance to be dispersed. A *sulphur* sol, for instance, may be obtained by dissolving sulphur in alcohol and diluting this solution with water [1] in which sulphur is much less soluble. (Sulphur sol after VON WEIMARN).

In the WILSON cloud chamber a mist is prepared by supersaturating the air with water by means of an adiabatic expansion.

Usually, however, the substance to be dispersed is first molecularly dissolved in a different form and then the supersaturated solution is prepared by chemical reaction.

Sulphur sols can also be prepared in this way, by acidifying a solution of sodium thiosulphate (RAFFO) or by mixing solutions of H_2S and SO_2 (SELMI). ODÉN [2] has treated the properties of these S-sols after RAFFO and SELMI extensively. Both types of sols are therefore often called ODÉN S-sols.

Sols of *noble metals* are usually prepared by reduction of a solution of a metal salt. So gold sols [3] are formed by the reduction of a solution of gold (III) chloride by formaldehyde, by hydrazine, by phosphorus and by other reducing agents, silver sols [4] by reduction of silver oxide suspensions with hydrogen, etc.

Double decomposition is the usual way of forming sols of *insoluble salts*. Silver halides easily give colloidal solutions by mixing of silver nitrate and alkali halide solutions. A sol of arsenic trisulphide is obtained by introducing hydrogen sulphide into a saturated solution of arsenic trioxide.

Sols of oxides and hydroxides are either formed by double decomposition or by simple hydrolysis. A solution of Fe acetate, for instance, gives a beautiful sol of $Fe(OH)_3$ by boiling.

Practically every procedure that is used either analytically or technically to prepare a precipitate may be used to prepare a sol. And it depends solely on the specified conditions of concentrations, mixing proportions, etc. whether or not a stable sol will be obtained. Until a more complete discussion can be given (chapter VIII, § 2, p. 303), a sol will be considered to be stable if the sol particles remain in suspension and do not form rapidly sedimenting aggregates. Now, all hydrophobic sols are very sensitive against electrolytes (see § 5, p. 80) and one of the conditions that must prevail during the preparation is a low electrolyte content. In this respect reactions like:

$$H_2S + SO_2 \rightarrow S + H_2O$$
$$As_2O_3 + H_2S \rightarrow As_2S_3 + H_2O$$
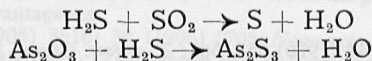
[1] H. FREUNDLICH and P. SCHOLZ, *Kolloidchem. Beihefte*, 16 (1922) 234.
[2] S. ODÉN, Der Kolloide Schwefel, *Nova acta Regiae Soc. Sci. Upsaliensis*, (4) 3 (1913) nr. 4.
[3] R. ZSIGMONDY and P. A. THIESSEN, *Das kolloide Gold*, Leipzig 1925.
[4] V. KOHLSCHÜTTER, *Z. Elektrochem.*, 14 (1908) 49.

have the great advantage that no parasitic electrolytes are formed as for instance in the formation of a silver halide by the reaction:

$$AgNO_3 + KBr \rightarrow AgBr + KNO_3$$

Apart from the condition of low total electrolyte content, it is often found that the presence of small traces of specific electrolytes is necessary to obtain a stable sol. Taking again the case of silver halides a slight excess of either Ag^+ or halide ion is necessary to stabilize the sol formed.

Such stabilizing electrolytes, which in several cases are also capable of redispersing a precipitate to a sol, are called *peptizing electrolytes*.

b. Dispersion methods

The simplest example of dispersion methods is the *mechanical disintegration* of macrophases. It is very extensively used in the preparation of emulsions where, by simple shaking of the two liquid phases, fine dispersions of one liquid in the other may be obtained. Greater forces may be exerted by pressing the two liquids together through a fine capillary or slit or by letting them pass between two rapidly rotating discs, (see Ch. VIII, § 12, Fig. 29 p. 337) which may lead to emulsions with a particle diameter well below 1 μ.

Mechanical disintegration of solids is usually more difficult to perform. On a laboratory scale long grinding in an agate mortar may bring the particle dimensions down to about 1 μ. Ball milling in the long run has the same effect. In so-called *colloid mills* [1] particles are broken in very strong fields of shear, but by all these means real colloidal dimensions ≪ 1 μ are seldom attained, although they certainly are useful in preparing suspensions that do not settle too rapidly. (Settling time of spherical particles of diameter 1 μ and excess density 1 in water amounts to 24 hours for 5 cm). Mechanical disintegration may lead to better results, if the phase to be dispersed is present in the form of conglomerates of very fine particles. In this way clay suspensions may be obtained in which particles (plates) as thin as 50Å with a diameter of less than 1000 Å are present [2].

A method, which is only a dispersion method in its later stages, but which starts as a condensation method is the redispersion (repeptization) of — usually freshly prepared — precipitates. In the preparation of some hydrophobic sols (*e.g.*, V_2O_5) [3] this repeptization is simply obtained by thorough washing of the precipitate (Ch. VIII, § 9, p. 333). In other cases next to the removal of almost all the dissolved salts, addition of traces of peptizing electrolytes is necessary. In this manner a fresh precipitate of silver iodide can be repeptized [4] by washing out and shaking with a dilute solution of an iodide.

The usual preparation of sols of HgS[5] and other sulphides [6] is a precipitation of the sulphide, washing out of the precipitate and peptizing by the introduction of hydrogen sulphide.

[1] H. PLAUSON, *Chem. Ztg.*, 44 (1920) 553, 565; *Z. angew. Chem.*, 34 (1921) 469, 473.
   P. M. TRAVIS, *Mechanochemistry and the colloid mill*, New York 1928.
[2] C. E. MARSHALL, *The colloid chemistry of the silicate minerals*, New York 1949, p. 67 ff.
[3] W. BILTZ, *Ber.*, 37 (1904) 1098.
[4] H. R. KRUYT and M. A. M. KLOMPÉ, *Kolloid-Beihefte*, 54 (1943) 507.
[5] H. FREUNDLICH and H. SCHUCHT, *Z. physik. Chem.*, 85 (1913) 643.
[6] C. WINSSINGER, *Bull. acad. roy. Belg.*, (3) 15 (1888) 390; *Bull. soc. chim. France*, 49 (1888) 452.

Precipitated $Fe(OH)_3$ may be peptized by slight acidification or addition of $FeCl_3$.

A very frequently used dispersion method is electrical disintegration, introduced by BREDIG [1]. An electric arc is maintained under water between two metal electrodes. Clouds of finely dispersed meta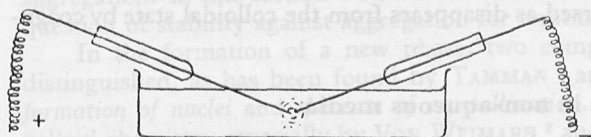l pass then into colloidal solution, and with patience rather concentrated sols may be prepared [2]. Sometimes it is necessary to add traces of electrolytes [3] (for instance an alkali hydroxide) to the water in order to obtain the best results. SVEDBERG [4] made the method more flexible and also

Fig. 1. Preparation of metal sols by electrical disintegration after BREDIG

suitable for preparing sols in non-aqueous media by feeding the arc with high frequency alternating current, which greatly diminishes the decomposition of the liquid. Practically any metal can in this way be dispersed in a liquid with which it does not react chemically, including the alkali metals in liquids like pentane or diethylether.

A comparatively recent dispersion method is the application of *ultrasonic* waves introduced into colloid science by WOOD and LOOMIS [5].

When a system of two liquids is subjected to ultrasonic vibrations, an emulsion is rapidly formed at the interface between the liquids. In the same way a precipitate, in which particles of colloidal dimensions are preformed, is easily redispersed by ultrasound. The direct dispersion of solid matter in a liquid is usually not accomplished by ultrasonic irradiation except when the solid is of very low strength (sulphur, steatite, gypsum, etc.).

A very good general account of the action of ultrasonic waves in preparing and changing colloidal systems has been given by K. SOLLNER [6].

The emulsification of mercury and other molten metals in water or organic liquids depends upon a kind of pumping action of the ultrasonic waves by which the lighter liquid is driven under the heavier one, rises to the surface and in uniting again with the bulk phase disrupts the metal membrane into very small particles.

The mutual emulsification of oils and water seems to depend completely on the phenomenon of cavitation, that is the formation and sudden collapse of gas bubbles at the interface.

The repeptization of precipitates, according to FREUNDLICH and SOLLNER [7] is also caused by cavitation. A peculiar property of ultrasonic waves is that besides their dis-

[1] G. BREDIG, *Z. angew. Chemie*, (1898) 951; *Z. Elektrochemie*, 4 (1898) 514, 547; *Anorganische Fermente*, Leipzig 1901.

[2] For an automatic apparatus see H. R. KRUYT and J. G. VOGEL, *Kolloid-Beihefte*, 52 (1940) 87.

[3] F. EIRICH and WO. PAULI, *Kolloidchem. Beihefte*, 30 (1930) 113.; H. R. KRUYT and J. G. VOGEL, *l.c.*; S. W. PENNYCUICK, *J. Chem. Soc.*, 130 (1927) 2600, found that in the preparation of platinum sols addition of electrolyte was not advantageous.

[4] THE SVEDBERG, *Ber.*, 38 (1905) 3616; 39 (1906) 1705; *Nova acta Regiae Soc. Sci. Upsaliensis*, (4) 2 (1907) nr. 1; *Physik. Z.*, 15 (1914) 361; G. BÖRJESON and T. SVEDBERG, *Kolloid-Z.*, 25 (1919) 154; G. BÖRJESON, *Thesis*, Stockholm 1921; E. O. KRAEMER and THE SVEDBERG, *J. Am. Chem. Soc.*, 46 (1924) 1980.

[5] R. W. WOOD and A. L. LOOMIS, *Phil. Mag.*, (7) 4 (1927) 417.

[6] K. SOLLNER, Sonic and ultrasonic waves in colloid chemistry, in JEROME ALEXANDER, *Colloid chemistry, theoretical and applied*, V. New York 1944, p. 337—373, where other literature is cited.

[7] H. FREUNDLICH and K. SOLLNER, *Trans. Faraday Soc.*, 32 (1936) 966.

persing action, they also have a pronounced coagulating action. This coagulation is caused by the accumulation of particles in the nodes, and by the regular movements of the smaller particles with respect to the larger ones (ortho kinetic flocculation, see Ch. VII, § 6, p. 291).

Therefore in a dispersion experiment a stationary state is soon reached in which just as much new material is dispersed as disappears from the colloidal state by coagulation.

c. Sols in non-aqueous media

Most of the methods mentioned in the foregoing subsections, although specialized on the preparation of sols in aqueous medium, can also be applied to non-aqueous solvents. Moreover methods exist by which *aquosols* can be converted into *organosols*.

The mechanical disintegration is a much used technical method of preparing suspensions of finely divided pigments in oils (paints, varnishes). The so-called inversed emulsions (see Ch. VIII, § 12, p. 339) in which drops of water are dispersed through a homogeneous oil-phase are also prepared by mechanical means.

The electrical disintegration of metals in organic media has already been mentioned in the preceding subsection (p. 61).

Double decomposition can in many cases be applied in organic media. A sol of silver iodide in acetone may, for instance, be obtained by simply mixing acetonic solutions of silver nitrate and potassium iodide [1]. The same sol may, however, be obtained more easily and by a method of very general applicability simply by dialyzing an aquosol against the organic medium. By prolonged dialysis the last traces of water may be removed. This method which has been introduced by SCHNEIDER[2], can only be applied to media miscible with water. For immiscible media the dialysis would have to be carried out in steps, first replacing the water by a liquid which is miscible both with water and the final medium.

Shaking out cannot be used to transform an aquosol into an organosol. If an aquosol is shaken with an organic liquid the particles as a rule assemble at the interface because that is their position of minimal free surface energy. Only in very exceptional cases can a distribution of colloidal particles between two liquid layers be observed [3].

In the case of pigments a direct transport of pigment particles from an aqueous phase to an oil phase is often possible and even an advantage. The pigment particles are usually prepared in water in order to obtain a sufficiently finely divided material. Instead of drying the pigment first and then bringing it into contact with an oil, the wet pigment is mixed with oil, and if the interfacial tensions are favourable, the pigment is wetted by the oil, the water being expelled. The condition for success of this "flushing process" [4] is

$$\gamma \text{ solid-water} > \gamma \text{ solid-oil} + \gamma \text{ oil-water}$$

where γ represents the interfacial tensions.

[1] E. L. MACKOR, *private communication.*
[2] E. A. SCHNEIDER, *Ber.,* 25 (1895) 1164.
[3] W. LASH MILLER and R. H. MC PHERSON, *J. Phys. Chem.,* 12 (1908) 706.
[4] E. K. FISHER and D. M. GANS in JEROME ALEXANDER, *Colloid chemistry, theoretical and applied,* VI. New York 1946, p. 322.

§ 2.   BIRTH AND GROWTH OF SOL PARTICLES

Whether or not a stable sol is obtained in a condensation method depends upon two conditions. In the first place the primary particles formed must be of colloidal dimensions, and in the second place these particles must not show any tendency to aggregation. In this section we shall treat exclusively the first condition and leave the question of stability against aggregation for treatment in sections 5 and 6.

In the formation of a new phase, two completely different stages have to be distinguished, as has been found by TAMMAN [1] and his pupils. These stages are *the formation of nuclei* and *the rate of crystallization*. These ideas have been applied to colloid chemistry especially by VON WEIMARN [2] and a good, fairly recent review of our knowledge on phase formation has been given by VOLMER [3]. Very valuable data can also be found in a recent discussion [4] of the Faraday Society.

Nuclei of the new phase can only be originated after a certain degree of super-saturation or supercooling has been reached. The nuclei then grow further by assimilating more material until the supersaturation or supercooling is abolished.

Evidently, a small rate of formation of nuclei and a large rate of crystallization will result in a small number of large particles, whereas a large formation of nuclei and a small rate of crystallization will give rise to many small particles, thus to a colloidal dispersion. Both the formation of nuclei and the rate of crystallization are sensitive to small changes in the composition of the solution, especially to the presence of easily adsorbable substances, and this may partially explain why it is so difficult to get completely reproducible results in the preparation of sols.

In most cases the formation of new nuclei and the further growth of nuclei already existing will occur simultaneously and consequently the particles in a sol are derived from nuclei that have originated at different times. Now the total amount of material accumulated on a nucleus is mainly dependent upon its time of growth and the saturation conditions, but not very much upon its original size. Thus the later formed nuclei will give rise to smaller particles and the first formed nuclei to larger particles, which explains that usually sols are *heterodispersed*. If, however, the formation of nuclei is restricted to a short period at the start of the sol formation, or if spontaneous nucleation is completely prevented and nuclei are added separately, the process of crystallization will lead to substantially isodispersed sols.

a.   Solubility of small particles

Nuclei, and often even colloidal particles, are so small that their thermodynamic properties may differ considerably from those of a corresponding macrophase. A well known example of this behaviour is the increased vapour pressure of small drops as given by the equation of W. THOMSON [5].

$$R T \ln \frac{p_r}{p_\infty} = \frac{2\sigma}{r} V \tag{1}$$

[1] G. TAMMAN, *Kristallisieren und Schmelzen*. Leipzig 1903, p. 131—161.

[2] P. P. VON WEIMARN, *Grundzüge der Dispersoidchemie*, Dresden 1911; *Die Allgemeinheit des Kolloidzustandes*. 2nd ed., Dresden 1925.

[3] M. VOLMER, *Kinetik der Phasenbildung*, Dresden, Leipzig 1939.

[4] Crystal growth, *Disc. Faraday Soc*, 5 (1949).

[5] W. THOMSON, *Phil. Mag.*, (4) 42 (1871) 448.

in which p_r is the vapour pressure of a drop of radius r, p_∞ the vapour pressure over a flat surface, σ the surface tension and V the molecular volume of the liquid.

This relation is easily derived by considering that the amount of work done in bringing dn molecules of the liquid from a large phase bounded by a flat surface to a drop of radius r, is on the one hand equal to $(\mu_r - \mu_\infty)$ dn, in which the μ's are the chemical potentials in the drop and in the macrophase. On the other hand it is equal to the work done in enlarging the surface of the drop, $\sigma\, 2\,\pi\, r\, dr$.

Now $V\, dn = \pi\, r^2 dr$ and thus

$$(\mu_r - \mu_\infty)\ dn = +\frac{2\,\sigma}{r} V\, dn \tag{2}$$

from which (1) immediately follows.

For a liquid like water, p_r is seen to exceed p_∞ considerably when the radius drops below $0.1\ \mu$.

TABLE 1

INFLUENCE OF DROP RADIUS ON VAPOUR PRESSURE OF WATER

drop radius	p_r/p_∞
$1\ \mu$	1.001
$0.1\ \mu$	1.011
$0.01\ \mu$	1.114
$0.001\ \mu$	2.95

The larger chemical potential of the small drops entails not only a larger vapour pressure, but also a larger solubility. Qualitatively eq. (2) may even be applied to small crystals, although, owing to the non-spherical boundary, the derivation and the final equation are slightly different [1].

It is this comparatively large solubility of small particles that can be considered to be the origin of the difficulty with which nuclei of a new phase are formed.

b. Formation of nuclei

As already mentioned the formation of nuclei only starts when a certain degree of supercooling or supersaturation has been reached. The solubility of a nucleus is larger than that of a macrophase and consequently a solution which is only slightly supersaturated in the usual macroscopic sense, would only allow very large nuclei to be stable and grow further, whereas smaller nuclei would not grow but on the contrary dissolve and disappear. Now the spontaneous formation of a large nucleus in which many molecules have to come together and which has a large surface free energy, is a very rare process. When the homogeneous mother phase, however, is more supersaturated, a much smaller nucleus, which has a greater probability of appearing, is already sufficiently stable to grow further and therefore a relatively large supersaturation must exist before spontaneous nucleation may be expected.

It can be shown [2] that the number of nuclei, J, formed per unit volume and unit time, is strongly dependent upon the ratio of the actual concentration c and the saturation concentration c_s. Approximately we have

$$J \sim K_1 \exp\left(-K_2/\ (\ln c/c_s)^2\right) \tag{3}$$

[1] cf. M. VOLMER, Kinetik der Phasenbildung, Dresden, Leipzig 1939, p. 89 ff.

[2] M. VOLMER, Kinetik der Phasenbildung, Dresden, Leipzig 1939, p. 130, 212; M. VOLMER and A.WEBER, Z. physik. Chem., 119 (1926) 277; R. KAISCHEW and I. N. STRANSKI, Z. physik. Chem., B 26 (1934) 317; R. BECKER and W. DÖRING, Ann. Physik, 24 (1935) 719; W. J. DUNNING, Disc. Faraday Soc., 5 (1949) 79.

and consequently the number of nuclei increases both by increasing the concentration or by decreasing the solubility.

It is well known, that very slightly soluble salts (*e.g.* HgS) are usually formed in a very high degree of dispersion. Another nice example is given by K. WOLFF [1], who prepared precipitates of $BaSO_4$ in water-propanol mixtures. In pure water the precipitate is clearly crystalline and sediments rapidly. With increasing amounts of alcohol (the salt concentration remaining constant!) the solubility decreases and the particles remain smaller and sediment more slowly until in the presence of 75% propanol the particles are so small that the solution is practically not turbid. See Fig. 2.
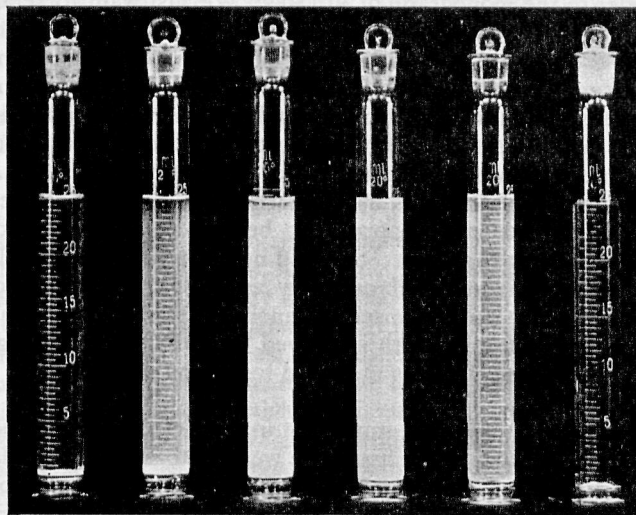
Fig. 2.   Particle size depending upon solubility. Formation of $BaSO_4$ in water (left hand tube) and in propanol-water mixtures of increasing propanol concentrations (left to right). In the right hand tube the particles are too small to give even an appreciable TYNDALL light. Propanol concentrations from left to right 0, 10, 20, 40, 60 and 75%. Picture taken after experiments by H. KOELMANS.

Here we may mention an old rule of VON WEIMARN [2], according to whom colloidal systems of insoluble salts are formed either by the mixing of *very dilute* or by the mixing of *very concentrated* solutions.

Although VON WEIMARN's experiments are not always treated with sufficient criticism, and, in several cases, the coarseness of particles is more connected with the formation of secondary aggregates (flocculation) than with the size of the primary particles, nevertheless the second half of his rule may be explained on the strength of the foregoing theoretical treatment.

In the concentrated solutions the total amount of insoluble substance formed is greater, but the number of nuclei found is more than proportionally larger (eq. 3) and

[1] K. WOLFF, *Dipl. arbeit Technische Hochschule*, Berlin. Cited from M. VOLMER, *l.c.*
[2] P. P. VON WEIMARN, see for instance: *Chem. Revs.*, 2 (1926) 217.

thus the particles formed remain small. In these conditions, however, no sols are formed, because they are flocculated by the presence of the large amounts of accompanying electrolyte. In certain cases, however, the smallness of the particles may be demonstrated by washing the precipitate and peptizing it to a sol.

The fact, that in the very dilute region again sol formation is possible, may be tentatively connected with the presence of extraneous nuclei.

c.   Crystal growth

The process of crystal growth can be most easily investigated when spontaneous nucleation is excluded. For a review of the many beautiful investigations in this field we refer the reader to the monograph of VOLMER[1]. We just want to retain the fact that in solutions the rate of crystallization is sometimes governed by diffusion of the crystallizing substance to the surface of the crystals, although in other cases it may be just the deposition of new molecules on the existing crystal which is rate-determining. In the first mentioned cases the linear growth of a crystal is proportional to the degree of supersaturation $(c-c_s)$ and inversely proportional to the diameter of the crystal. In the second case the linear growth is independent of both these parameters.

In certain well investigated cases [2] of crystal growth, however, the relation between rate of growth and supersaturation appears to be very complicated and many details have still to be cleared up. Moreover, it should not be forgotten, that although results from nucleation research can be immediately applied to the formation of colloids, results on crystal growth lend themselves much less readily to such a transposition. Our best knowledge on crystal growth is derived from the study of the growth of comparatively large crystal faces, whereas in colloid formation only the very first stages of growth are relevant.

The crystal growth is especially important in the preparation of isodispersed sols, a few examples of which exist. In the first place we have to mention the classical method of ZSIGMONDY[3] of preparing isodispersed gold sols. An aurichloric acid solution is reduced in the presence of sufficient nuclei (prepared by reduction of $HAuCl_4$ by P). When the reduction is carried out slowly, spontaneous nucleation can be avoided and all the gold newly reduced is accumulated on the nuclei present and makes them grow. As the time of growth of all the particles has been the same, they have (apart from a small scatter in the size of the primary particles) all the same dimensions.

Similar methods can be applied with various other sols. (Se [4], Ag [5] etc.).

Another beautiful example of isodispersed sols is formed by the sulphur sols prepared by LA MER and BARNES [6]. They mixed very dilute solutions of sodium thiosulphate and hydrochloric acid. During about one hour sulphur was formed as was

[1] M. VOLMER, l.c., p. 64; See also Cyrstal growth, Disc. Faraday Soc., 5 (1949).

[2] C. W. BUNN, Disc. Faraday Soc., 5 (1949) 132; W. F. BERG, Proc. Roy. Soc. (London), A. 164 (1938) 79.

[3] R. ZSIGMONDY, Z. physik. Chem., 56 (1906) 65. See also R. ZSIGMONDY and P. A. THIESSEN, Das kolloide Gold, Leipzig 1925, p. 59 ff.

[4] H. R. KRUYT and A. E. VAN ARKEL, Rec. trav. chim., 39 (1920) 656; 40 (1921) 169; Kolloid-Z., 32 (1923) 29.

[5] R. ZSIGMONDY, Nachr. kg. Ges. Wiss. Göttingen, Math.-physik. Klasse, (1916) 11; J. VOIGT and J. HEUMANN, Z. anorg. Chem., 164 (1927) 409; 169 (1928) 140; 173 (1928) 27.

E. WIEGEL, Kolloidchem. Beihefte, 25 (1927) 176; Kolloid-Z., 47 (1929) 323; 51 (1930) 112; 53 (1930) 96.

[6] V. K. LA MER and M. D. BARNES, J. Colloid Sci., 1 (1946) 71; V. K. LA MER and A. S. KENYON, ibidem., 2 (1947) 257.

indicated by light adsorption, but no nuclei came into existence. When the sulphur concentration had increased to about $5 \cdot 10^{-6}$ molar, suddenly a number of nuclei (about $2 \cdot 10^6$ per cm³) were formed which grew rapidly to a size of about 0.2 μ. Thereafter they increased more slowly in size, remaining extremely isodispersed for times of growth as long as 24 hours. The growth could be stopped at any desired moment by reacting the greater part of the remaining thiosulphate with iodine.

We see again how a rather strong supersaturation is necessary for the formation of nuclei. Nuclei once formed, grow rapidly, thereby diminishing the degree of super-saturation and at the same time their own solubility. In the later stages the slow growth depends upon the continued formation of sulphur by the chemical reaction. REISS and LA MER [1] have shown that the isodispersity could be completely explained by the diffusion of sulphur to the particles.

Analogous techniques have been applied by LA MER and coworkers for the formation of sols [2] of AgCl and BaSO₄ and of isodisperse aerosols [3].

The dimensions of the particles and their isodispersity have been determined by optical methods for which we refer to chapter III, § 2, p. 97.

d. Ageing

Many sols show phenomena of ageing, connected with the lack of stability of small particles and their very large interface. As freshly prepared sols often contain very small particles, these ageing phenomena may be important and usually it is necessary to leave a sol a few days after preparation, before it can be used.

The ageing may proceed by at least three different mechanisms. It may be a partial flocculation, caused by the insufficient repulsion between small particles. [4] It may also be a recrystallization of separate particles without a noticeable change in the number of particles. VERWEY and KRUYT [5] have demonstrated this kind of ageing in freshly prepared silver iodide sols. In later stages, especially at elevated temperature, this same system shows the third kind of ageing, *viz.* a decrease of the number of particles caused by an actual transport of matter from the smaller, more soluble particles to the larger ones.

In a flocculate the large concentration of particles makes the ageing phenomena more pronounced. They can often easily be followed by measuring the decrease of adsorption. [6] (See chapter VII, § 9, p. 300).

KOLTHOFF [7] drew attention to the possibility that in a precipitate particles may be cemented together by bridges which gradually can develop into a complete unification of the particles.

A peculiar aspect of ageing has been stressed by JONKER [8]. When one considers the equilibrium between a small droplet or particle and an infinitely large amount of gas or solution, as we did in § 2 a, p. 63, this equilibrium is always labile. A very small loss

[1] H. REISS and V. K. LA MER, *J. Chem. Phys.*, 18 (1950) 1.

[2] V. K. LA MER and R. H. DINEGAR, *J. Am. Chem. Soc.*, 73 (1951) 380.

[3] D. SINCLAIR and V. K. LA MER, *Chem. Revs*, 44 (1949) 245.

[4] G. H. JONKER, *Thesis*, Utrecht 1943, p. 67; See also chapter VIII, § 2, p. 303; E. J. W. VERWEY and J. TH. G. OVERBEEK, *Theory of the stability of lyophobic colloids*, Amsterdam 1948, p. 171.

[5] E. J. W. VERWEY and H. R. KRUYT, *Z. physik. Chem.*, A 167 (1934) 137.

[6] H. FREUNDLICH and H. SCHUCHT, *Z. physik. Chem.*, 85 (1913) 660; H. FREUNDLICH and E. HASE, *Z. physik. Chem.*, 89 (1915) 417.

[7] See chapter VII, § 9, p. 301 and literature cited there.

[8] G. H. JONKER, *Thesis*, Utrecht 1943, p. 47 ff.

of material by the particle will make it smaller, increase its solubility, and dissolution will continue until the particle has disappeared. On the other hand, a slight increase of the particle will make it less soluble, causing more and more material to accumulate on it. The equilibrium may be changed, however, into a stable one by considering not an infinitely large gas or solution phase, but one of finite, rather small dimensions. In that case a slight loss of material from the particle to the solution phase will result in a higher concentration. This increase of concentration may be larger than the increase in solubility of the particle, thus driving the system back to its original state.

This kind of instability will also be present in dilute sols, but when the sol is more concentrated, it is as if each particle is embedded in a small box, causing the equilibrium to be stable. Consequently, the more concentrated the sol, the smaller its particles may be.

Of course, this instability is especially related to isodispersed sols, and for hetero-dispersed sols the normal growth of the larger particles at the cost of the smaller ones will be the main cause of ageing.

If the ageing is not only based upon the influence of the free surface energy, but is promoted by an allotropic phase change, ageing phenomena may be still more pronoun-ced. A good example is the sol of vanadium pentoxide [1], which, when first formed, contains particles with a true solubility of the order of 1 g/1, whereas on standing, these particles disappear, and are replaced by the characteristic rod-shaped particles, while the solubility decreases to about 0.1 g/1.

§ 3. PURIFICATION OF LYOPHOBIC SOLS

a. Dialysis

Most lyophobic sols contain a larger or smaller amount of contaminations of small molecular weight after the preparation. These can be removed by dialysis, a method of purification and of characterization of colloidal systems, already introduced by GRAHAM [2]. In its simplest form dialysis is effected by placing the sol in a container which has a membrane for bottom. This membrane is permeable to the solvent and the other small molecules present, but imper-meable to the colloidal particles, a kind of semipermeability that is easily realized. The membrane is brought into contact with the pure solvent, which is periodically renewed until no further contamination of the washing liquid occurs.

The choice of the membrane has to be adapted to the system to be dialyzed. For

Fig. 3.   Dialyzer after GRAHAM

most aquosols collodion membranes are very suitable as they can be prepared with practically any conceivable permeability by varying the solvent from which the collo-dion is precipitated, and the drying process.
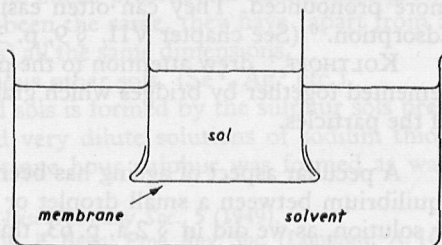
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[1] G. VAN DER LEE, Thesis, Delft 1926.; W. REINDERS and G. VAN DER LEE, Rec. trav. chim., 47 (1928) 198.
[2] TH. GRAHAM, Phil. Trans. Roy. Soc. (London), 151 (1861) 183.

For non-aqueous solvents denitrated collodion or cellophane are in use. They are usually somewhat denser than collodion but especially the easy availability of cellophane makes it a very much used membrane even for dialyzing in aqueous systems.

Pig's bladder and parchment paper are also used as dialyzing membranes. GRAHAM's original experiments were carried out with parchment paper.

As dialyzis is a very slow process — it is based upon diffusion through the membrane — several more refined techniques have been suggested to increase its speed. ZSIGMONDY and HEYER[1] realized a large membrane surface combined with a very thin layer of sol in the star-dialyzer which is represented in Fig. 4.
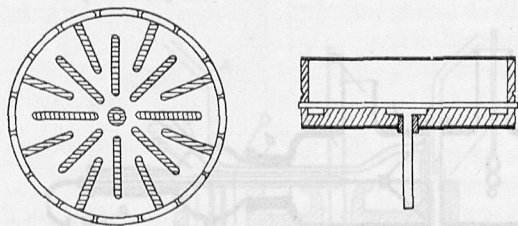
Fig. 4.   Star-dialyzer after ZSIGMONDY and HEYER

Agitation of the sol and the outer liquid and the application of higher temperatures are also helpful, although not all hydrophobic sols can withstand the more elevated temperature, and the membranes may give off unwanted colloidal contaminations. With the easy availability of cellophane or parchment paper tube, (artificial sausage skin), dialysis with a favourable ratio of volume to interface can be very easily performed by partially filling a cellophane tube with sol, closing it on both sides with a piece of — cleaned — string, and placing it in constantly renewed solvent.

b.   Ultrafiltration

The application of pressure to the sol changes the dialysis into *ultrafiltration* (see § 4). It is not a method of purification, but of concentration, forcing the whole intermicellar liquid through the membrane, often even with a certain preference for the solvent. But by diluting the sol with pure solvent after partial ultrafiltration, a purification is obtained.
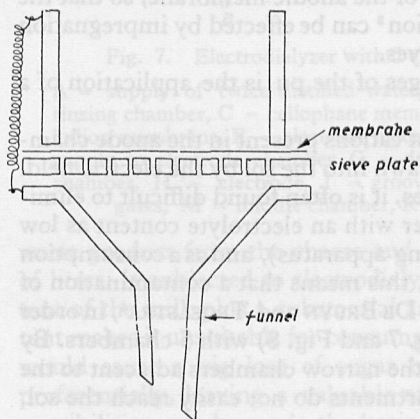
As a membrane cannot withstand large pressures, it has to be supported for ultrafiltration purposes. This is either effected by placing a ready-made flat membrane on a sieve plate (Fig. 5) or by preparing the membrane on a non-glazed porcelain beaker by pouring a collodion solution into the beaker and precipitating the nitrocellulose by evaporation (BECHHOLD filter).

Fig. 5.   Ultrafiltration funnel.
Left, 'one of three springs, keeping the parts of the ultrafiltration funnel together'.

c.   Electrodialysis

The removal of ionic contaminants from a sol can be enormously accelerated by the application of an electric field. This technique was used for the first time by MORSE and PIERCE[2] for the purification of gelatin, and

[1] R. ZSIGMONDY and R. HEYER, *Z. anorg. Chem.*, 68 (1910) 169.
[2] H. W. MORSE and G. W. PIERCE, *Z. physik. Chem.*, 45 (1903) 606.

has been applied on a larger scale also for lyophilic colloids by DHÉRÉ [1]. PAULI [2], who extended the method to hydrophobic colloids, has designed a type of electrodialyser which is reproduced in Fig. 6. The electrodialysis is especially effective in the end of the dialysis when the concentration gradient and thus the rate of diffusion is small, and high field strengths can be applied in the badly conducting solutions. When the sol still contains much electrolyte, normal dialysis may often be quicker.

One of the difficulties in electrodialysis is the fact that the membranes are usually selectively permeable to the cations. This is because the membranes are negatively charged and thus their pores contain more cations than anions. The transport of electri-
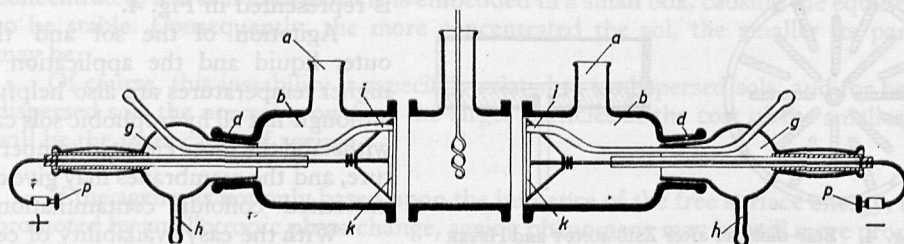
Fig. 6.   Electrodialyzing apparatus after Wo. PAULI.

city across the membranes is therefore preponderantly and sometimes exclusively provided by cations. In an electrodialysis containing such membranes, the cations are removed more rapidly than the anions and, in order to maintain electroneutrality of the solution, the sol becomes acid. For many sols, especially for hydrophilic sols, where the method of electrodialysis is preferably applied, this is undesirable. The effect of acidulation can be suppressed by a suitable positivation of the anodic membrane, so that the anions can leave the cell more easily. This positivation [3] can be effected by impregnation of collodion by suitable proteins, amino acids or dyes.

Another method of avoiding undesirable changes of the pH is the application of a small current density or the use of a diluted sol.

Another danger in electrodialysis is the fact that cations present in the anode chamber or anions present in the cathode chamber are drawn into the sol by the electric field. If these ions are strongly adsorbed to the sol particles, it is often found difficult to eliminate them. As it is difficult to prepare distilled water with an electrolyte content as low as $10^{-6}N$ (metallic contaminations from the distilling apparatus), and as a consumption of 100 l of water to clean 1 l of sol is no exception, this means that a contamination of the sol of the order of 10^{-4} gr eq/l is quite possible. DE BRUYN and TROELSTRA [4], in order to avoid this effect, designed an electrodialyzer (Fig. 7 and Fig. 8) with 5 chambers. By letting the rinsing distilled water first pass through the narrow chambers adjacent to the sol, electrolytes diffusing from the electrode compartments do not easily reach the sol.

[1] CH. DHÉRÉ and M. GORGOLEWSKI, Compt. rend., 150 (1910) 934; Kolloid-Z., 41 (1927) 243, 315.

[2] Wo. PAULI, Biochem. Z., 152 (1924) 355; 187 (1927) 403.

[3] W. G. RUPPEL, Ber. deut. pharm. Ges., 30 (1920) 314; Wo. PAULI, Biochem. Z., 152 (1924) 355, 360; 153 (1924) 253; 156 (1925) 482; H. FREUNDLICH and F. LOEB, ibidem., 150 (1924) 522; R. BRADFIELD, Naturwissenschaften, 16 (1928) 404.

[4] H. DE BRUYN and S. A. TROELSTRA, Kolloid-Z., 84 (1938) 192.

Moreover, the total amount of rinsing liquid may be sensibly decreased. Finally it appears to be possible to prepare distilled water [1] in large quantities containing only between 10^{-8} and 10^{-9} N of contaminants like Cu^{++}, Zn^{++} and Pb^{++}, and by combining these different precautions, electrodialysis may indeed be said to be ideal for rapid and complete cleaning of sols.

Electrodialysis is also applied on a technical scale. As an example we mention a method recently developed in the Netherlands [2] in which whey, a
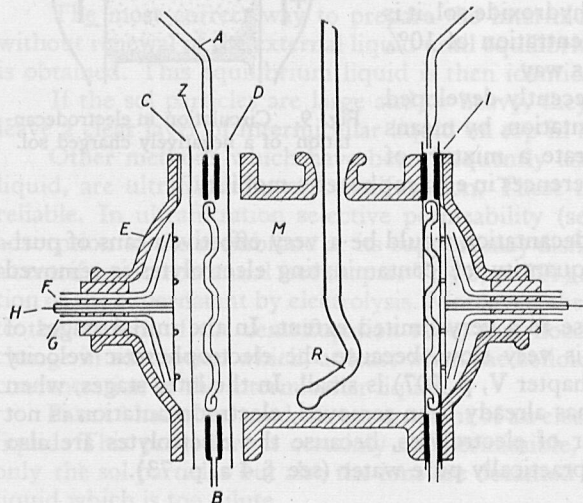
Fig. 7.   Electrodialyzer with 5 chambers

A = supply of twice distilled water, B = drain of rinsing chamber, C = cellophane membrane, D = collodion membrane, E = electrode chamber, F = water supply to electrode chamber, G = drain of electrode chamber, H = electrode, I = groove for escape of gases, M = middle chamber, R = stirrer
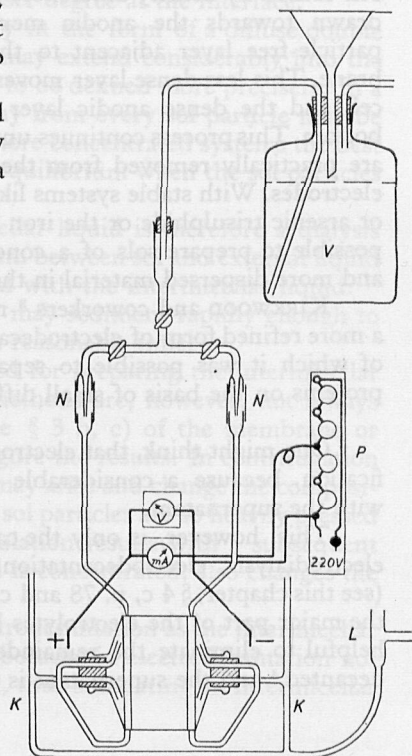
Fig. 8.   Operating scheme of 5 chamber dialyser.

V = stock of twice distilled water
N = drop counters, K = drainage tubes with
L = constant level, P = lamp potentiometers

waste product from the cheese and casein preparation, which is available in millions of litres, is subjected to electrodialysis. Whey still contains nearly the total lactose content of the milk plus a substantial amount of protein, but the relatively high salt content makes it unsuitable for consumption on a large scale even for cattle. Normal dialysis would cause a big loss of sugar but by electrodialysis the salts can be eliminated preferentially, leaving a valuable solution of sugar and proteins, which among other possibilities, can be made the basis of a baby food.

d.   Electrodecantation

The electrodialyzer can also be used for concentrating a sol. By carrying out electrodialysis without agitation in the middle cell, the sol particles accumulate in a relatively

[1] J. A. W. VAN LAAR, Chem. Weekblad, 36 (1939) 611.
[2] Chem. Weekblad, 44 (1948) 343.

thin layer on the bottom of the cell with a colloid-free supernatant. This process of *electrodecantation* which was introduced by PAULI [1], is explained by a circulation in the cell caused by density differences [2]. If the sol particles are negatively charged, they are drawn towards the anodic membrane, leaving a particle-free layer adjacent to the cathodic membrane. This less dense layer moves to the top of the cell and the dense anodic layer sediments to the bottom. This process continues until the sol particles are practically removed from the field between the electrodes. With stable systems like the silver iodide or arsenic trisulphide or the iron hydroxide sol, it is possible to prepare sols of a concentration of 10% and more dispersed material in this way.

KIRKWOOD and coworkers [3] recently developed a more refined form of electrodecantation, by means of which it was possible to separate a mixture of proteins on the basis of small differences in electrophoretic mobility.
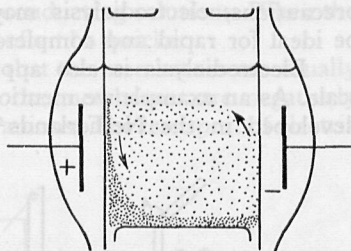

Fig. 9.   Circulation in electrodecantation of a negatively charged sol.

One might think, that electrodecantation would be a very effectivemeans of purification, because a considerable quantity of contaminating electrolytes is removed with the supernatant.

This, however, is only the case to a very limited extent. In the initial stages of electrodialysis, electrodecantation is very slow, because the electrophoretic velocity (see this chapter, § 4 c, p. 78 and chapter V, p. 207) is small. In the later stages, when the major part of the electrolytes has already been removed, electrodecantation is not helpful to eliminate the remainder of electrolytes, because the electrolytes are also decanted [4] and the supernatant is practically pure water (see § 4 a, p. 73).

§ 4.   PROPERTIES OF LYOPHOBIC SOLS

a.   Particles and intermicellar liquid

In a lyophobic sol one distinguishes between the sol particles and the liquid in which they are embedded, called *internal* and *external phase* or *micelles* and *intermicellar liquid* respectively. Moreover, there is the interface between the two phases, on which adsorption phenomena of the utmost importance for the stability of the colloid are present.

Besides the particles themselves, the interface is the most interesting region of a sol. In order to be able to analyze the interface, however, and to understand its behaviour, knowledge of the composition of the intermicellar liquid is indispensable (cf

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[1] Wo. PAULI, *Naturwissenschaften*, 20 (1932) 551.
[2] F. BLANK and E. VALKÓ, *Biochem. Z.*, 195 (1928) 220;
   E. J. W. VERWEY and H. R. KRUYT, *Z. physik. Chem.*, A 167 (1933) 149.
[3] J. G. KIRKWOOD, *J. Chem. Phys.*, 9 (1941) 878;
   L. E. NIELSEN and J. G. KIRKWOOD, *J. Am. Chem. Soc.*, 68 (1946) 181;
   J. R. CANN, J. G. KIRKWOOD, R. A. BROWN and O. J. PLESCIA, *J. Am. Chem. Soc.*, 71 (1949) 1603.
[4] S. A. TROELSTRA, *Thesis*, Utrecht 1941, p. 25.

chapter IV). The intermicellar liquid is of course a saturated solution of the material of the sol particles and further it may contain other electrolytes and non-electrolytes. All these solutes may be adsorbed to a greater or lesser degree at the interface.

Because this adsorption may be present partially in the form of a diffuse double layer (this Ch. § 4 c, p. 78, Ch. IV, p. 115) which may extend considerably into the solution phase, the notion of intermicellar liquid has to be defined more precisely. In a very dilute sol the composition of the liquid far away from every sol particle may be considered to be that of the intermicellar liquid. In more concentrated systems the best definition is the liquid with which the sol can be in equilibrium when the sol particles are prevented from diffusing into it.

The most correct way to prepare the intermicellar liquid is therefore a dialysis without renewal of the external liquid until equilibrium between sol and external liquid is obtained. This equilibrium liquid is then identical with the intermicellar liquid.

If the sol particles are large and/or heavy, they may sediment rapidly enough to leave a clear layer of intermicellar liquid on top in a reasonable time.

Other methods which have been frequently used for preparing the intermicellar liquid, are ultrafiltration or centrifugation. These methods are, however, not always reliable. In ultrafiltration selective permeability (see § 3 b, c) of the membrane or adsorption to the membrane or its support may disfigure the results. In centrifugation a centrifugation potential (see chapter V, § 8, p. 221) may arise and change the composition of the supernatant by electrolysis. Moreover, the sol particles are so heavily pressed to the bottom of the centrifugation tube, that flocculation results with a subsequent change in adsorption which, at least when the colloid is concentrated, also changes the concentration of the intermicellar liquid.

PAULI [1] has often used the supernatant of an electrodecantation as the intermicellar liquid. This procedure is certainly not permissible, because in electrodecantation not only the sol particles but also the ions are decanted [2], thus simulating an intermicellar liquid which is too dilute.

b. Dimensions of the particles

In many problems it is necessary to know either the number of particles (flocculation phenomena) or their total surface (double layer problems) or their size and shape (optical properties).

In nearly all problems of this kind it would be an advantage to have *isodispersed* sols at one's disposal (see § 2 c, p. 66). Unfortunately, isodispersed sols are very exceptional and can only be obtained by very special methods of preparation. In practice one has mostly to deal with strongly *heterodispersed* or *polydispersed* sols.

b. 1. *Preparation of isodispersed sols*

There are two different ways of preparing isodispersed systems. The first is sorting out the particles of one size out of a heterodispersed system. The second is preparing the sol in such a way, that all particles grow to exactly the same size. The first way has been followed by PERRIN [3]; in preparing the suspensions of mastix or gamboge on

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[1] *E.g.* Wo. PAULI and E. RUSSER, *Kolloid-Z.*, 58 (1932) 22.
[2] S. A. TROELSTRA, *Thesis*, Utrecht 1941, p. 25.
[3] J. PERRIN, *Les atomes*, Paris 16e mille (1924), p. 135.

which he made his famous investigation of BROWNian motion and related phenomena.

By repeated fractional centrifugation of 1 kg of gamboge it was possible to obtain a few decigrams of spherical particles of uniform diameter (about 0.75 μ).

Needless to say, that this is a very time-consuming method, which moreover can only be successful if the particles are comparatively large (more in the range of suspensions than in that of sols) and are completely repeptizable.

The other method depends on the regular growth by crystallization of pre-existing nuclei and has already been treated in § 2 c, p. 63. With this method isodispersed gold sols [1] have been prepared with diameters varying from 10 m μ to 1 μ, silver sols [2] between 10 m μ and 100 m μ, and selenium sols [3] with particles from about 100 m μ diameter. The method of LA MER [4] for preparing isodispersed sols is not different in principle, although the preparation of nuclei and the further accumulation of material on them is carried out in one process. His investigations include sulphur sols (diameter 0.4 — 1.3 μ), silver chloride and barium sulphate.

b. 2.   *Average size of the particles*

As the limit of resolution of the ordinary *microscope* is of the order of 0.5 μ, direct determination of particle size with the microscope is only possible for lyophobic systems with coarse particles. For normal sols the microscope is useless.

The *electron microscope* with a limit of resolution of the order of a few m μ is a much more suitable instrument, but it has not as yet been frequently used in the field of lyophobic suspensions. One of the difficulties is that suspensions cannot be investigated directly with the electron microscope, but the particles have to be separated from the intermicellar liquid and then it is often not easy to avoid artificial agglomerations.

Reviews on electron microscopic work are given by ANDERSON [5] and by TURKEVITCH and HILLIER [6]. WATSON [7] especially draws attention to difficulties in determining particle sizes.

Electron microscopic pictures of colloidal silver iodide and of colloidal silver are presented in Fig. 10.

As most lyophobic colloids contain crystalline particles, X-ray methods may lead to an estimation of particle dimensions. The *broadening of the X-ray diffraction lines* was used for the first time in the case of colloidal gold by SCHERRER [8], who determined the particle diameter of a nuclear gold sol at about 18 Å. The method has been perfected and applied in several cases also with electron diffraction.

For a more recent discussion of the röntgenographical basis of the method, see BRILL [9] or CLARK [10]. Early applications to colloidal gold, platinum, silver, tin oxide, iron

[1] R. ZSIGMONDY, *l.c.*, p. 66.
[2] R. ZSIGMONDY; J. VOIGT and J. HEUMANN; E. WIEGEL, *l.c.*, p. 66.
[3] H. R. KRUYT and A. E. VAN ARKEL, *l.c.*, p. 66.
[4] V. K. LA MER, *l.c.*, p. 66 and 67.
[5] T. F. ANDERSON, *Advances in colloid science I*, New York 1942, p. 353.
[6] T. TURKEVITCH and J. HILLIER, *Anal. Chem.*, 21 (1949) 475.
[7] J. H. L. WATSON, *Anal. Chem.*, 20 (1948) 576.
[8] P. SCHERRER, *Göttinger Nachrichten*, 1918, p. 98.
    See also R. ZSIGMONDY, *Lehrbuch der Kolloidchemie*, 3rd ed. Leipzig 1920, p. 387.
[9] R. BRILL, *Z. Krist. A.*, 87 (1934) 275; *Kolloid-Z.*, 69 (1934) 301.
[10] G. L. CLARK, *Applied X-rays*, New York, London 1932, p. 336 ff.

oxide, are described by Böhm [1]. A recent example is the investigation of colloidal $Ni(OH)_3$ which crystallizes in small plates [2].

The line broadening is determined by the size of the crystallites and by the degree of perfection of the crystals. So if the particles are composed of more than one crystallite or contain relatively many lattice flaws, this method gives too small an estimate of the particle size.

The *small angle scattering* [3] (See Ch. I, § 4 f. 5 γ, p. 51) around the primary X-ray beam is just of the right order of magnitude to determine particle dimensions. An advan-
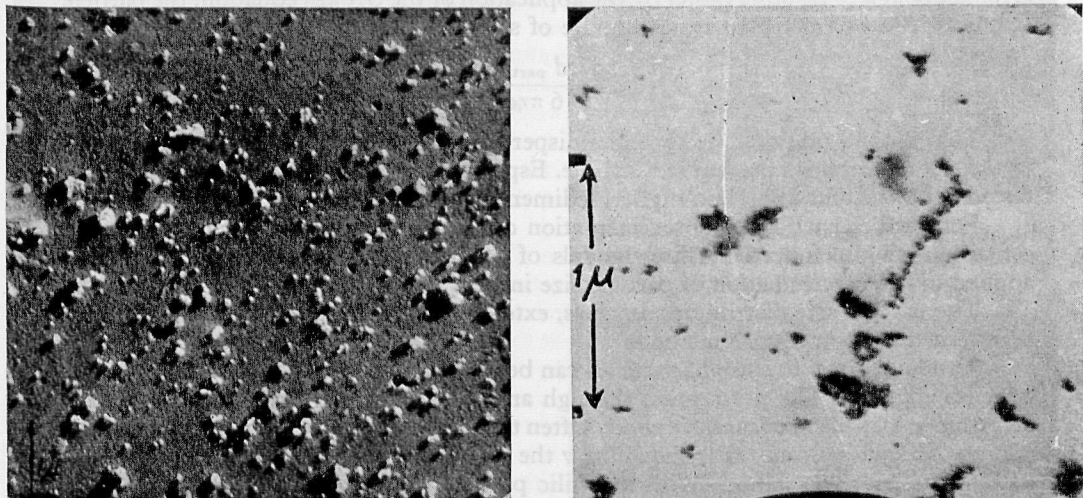
Fig. 10. Electron micrographs of colloidal silver iodide (diameter 100 - 800 Å) and of colloidal silver (diameter of primary particles about 150 Å).

a. Silver iodide, Pt shadowed 10,000 x.   b. Silver   32,000 x.

tage over the broadening of diffraction lines is that the small angle scattering depends primarily on density fluctuations in the sample and thus determines the particle size more exactly than the size of the crystallites.

This method is new, so not many results can be quoted. An interesting comparison has been made by Yudowitch [4], who determined the radius of gold particles by small angle scattering and by direct electron microscopic observation. His results are given in Table 2.

TABLE 2

RADIUS OF GOLD PARTICLES

Electron microscope	Small angle scattering
232 Å ± 13%	237 Å
380 Å ± 16%	387 Å

[1] J. Böhm, *Kolloid-Z.*, 42 (1927) 276.

[2] A. Berger, *Kolloid-Z.*, 103 (1943) 185; 104 (1943) 24.

[3] A. Guinier, *Ann. de Phys.*, 12 (1939) 161; *J. chim. phys.*, 40 (1943) 133; O. Kratky, *Z. Elektrochemie*, 48 (1942) 587; R. Hosemann, *Z. Physik*, 113 (1939) 751; 114 (1939) 133; *Z. Elektrochemie*, 46 (1940) 535.

[4] K. L. Yudowitsch, *J. Appl. Phys.*, 20 (1949) 174.

Applications of the method to amorphous carbon (radii 200—300 Å) are given by WARREN and by HOSEMANN [1], and ELIKN c.s. [2] have determined the very small particle dimensions (32—58 Å) of alumosilicate gels.

A method which has been very frequently used for the determination of particle sizes, is the *counting* of the number of particles in a given volume by means of the *ultramicroscope*. This method is particularly suitable for sols with not too small particles of a substance differing greatly in optical density from the dispersion medium. For details of this method see chapter I, § 4 f. 3, p. 39.

When the particles are large ($> 0.1\ \mu$), *sedimentation* under the influence of gravity is rapid enough to be observable. By the application of the STOKES equation, the particle radius, a, can be calculated from the rate of sedimentation, v.

$$v = \frac{4/3\ \pi a^3\ (d_{\ part} - d_{\ solv})\ g}{6\ \pi \eta a} \tag{4}$$

This method, when applied to heterodispersed systems can give a distribution curve of the sizes of particles present in a sample. Especially in soil science, where one is interested in dimensions of $1\ \mu$ and higher, sedimentation analysis is a frequently used tool [3].

For smaller particles, the sedimentation can be accelerated by the application of centrifugal fields. Indeed the first models of SVEDBERG's ultracentrifuge [4] have been applied to the determination of particle size in gold sols.

The particle size distribution in clays, extending from $2\ \mu - 10\ m\ \mu$ has also been determined by centrifugal methods [5].

A rough idea of the size of particles can be obtained by *ultrafiltration* through suitable membranes. The permeation through an ultrafilter is, however, not exclusively determined by a mechanical sieve effect. Often the influence of the charge of the particles is preponderant. ELFORD [6] has shown how the dimensions of lyophilic particles can be determined by this method. With lyophilic particles, however, charge effects can be suppressed by electrolyte addition which, in the case of lyophobic systems, would result in flocculation.

Finally, various *optical properties* (especially light scattering) are strongly dependent upon particle size. For the application of these methods, see chapter III, § 2, p. 91.

b. 3. *Shape of the particles*

In the foregoing subsection it has been tacitly assumed that the particles are regular in shape (spherical, cubical or the like). In fact of course, they are often more irregular, and especially if their dimensions are much larger in one or two directions than in the other, the rod-shaped or blade-shaped particles give rise to interesting phenomena.

The shape of the particles may be determined by the electron microscope [7][8][9]. See Fig. 11.

In the ultramicroscope, particle shape can be determined in so far as at least one dimension of the particles is larger than the wave-length of light.

[1] B. E. WARREN, *J. Appl. Phys.*, 20 (1949) 96; R. HOSEMANN, *Kolloid-Z.*, 117 (1950) 13—41.
[2] P. B. ELKIN, C. G. SHULL, L. C. ROESS, *Ind. Eng. Chem.*, 37 (1945) 327.
[3] H. GESSNER, *Die Schlammanalyse*, Leipzig 1931.
[4] T. SVEDBERG and H. RINDE, *J. Am. Chem. Soc.*, 46 (1924) 2677.
[5] See for instance C. E. MARSHALL, *The colloid chemistry of silicate minerals*, New York 1949, p. 67.
[6] W. J. ELFORD, *Proc. Roy. Soc.*, 112 B (1933) 405.
[7], [8], [9] see opposite page.

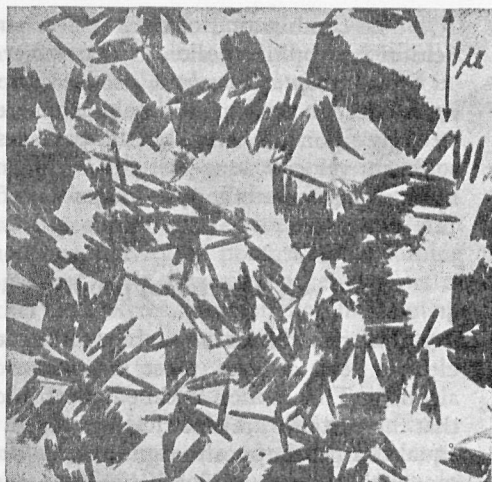Fig. 11a.   Vanadium pentoxide-sol   2500 x.

Fig. 11b.   Iron hydroxide particles prepared by hydrolysis of Fe Cl$_3$. Notice the strong tendency to form oriented aggregates.   15,000 x.
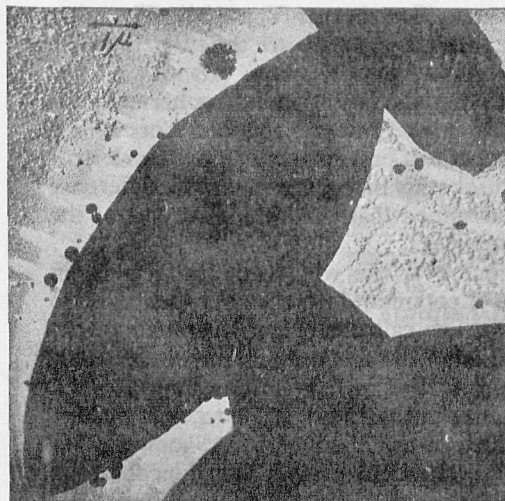

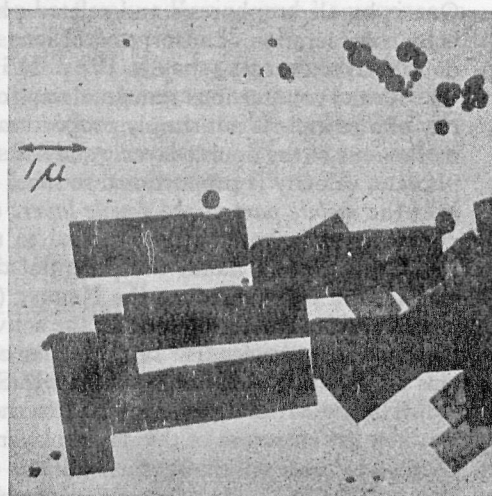Fig. 11c.   Tungsten oxide particles, fresh, Cr-shadowed, angle < 15°. 7,000 x.

Fig. 11d.   Tungsten oxide particles, aged, Cr-shadowed, angle < 15°. 8500 x.

Fig. 11*.   Electron micrographs of rod-shaped (V$_2$O$_5$, diameter < 0.02 μ, length several μ and FeOOH, 0.05 μ x 0.04 μ) and blade-shaped (WO$_3$, 10 μ x 4 μ x 0.1 μ and 2 μ x 0.8 μ x 0.04 μ) particles.

[7] J. TURKEVITCH and J. HILLIER, *Anal. Chem.*, 21 (1949) 475.

[8] W. FEITKNECHT, R. SIGNER, and A. BERGEN, *Kolloid-Z.*, 101 (1942) 12.

[9] T. F. ANDERSON, *Advances in colloid science I*, New York 1942, p. 384.

The combination of rates of *sedimentation* and of *diffusion*, very important in the field of hydrophilic colloids [1], has never been applied to lyophobic systems.

Several *optical methods*, particularly streaming double refraction, double refraction in an electric or magnetic field, and special properties of the scattered light depend strongly upon the shape of the particles. For instance, in a laminar field of flow of sufficient velocity, long particles are arranged with their long sides parallel to the stream lines, which makes the system double refracting. These methods are treated in chapter III, § 3, p. 108.

c. Electrical properties of hydrophobic systems

The particles of lyophobic sols move along the lines of force when subjected to an electric field, at least, those in aqueous and in polar organic media like ketones and alcohols. This motion is called *electrophoresis*. The existence of electrophoresis proves that the particles are electrically charged. As the sol as a whole is electrically neutral, an equal charge of opposite sign must be present in the intermicellar liquid, and in consequence of the attraction between charges of opposite sign, charge and counter charge remain in each other's neighbourhood.

So each particle is surrounded by an *electrical double layer*. Information on the constitution of this double layer can be obtained in two fundamentally different ways. One is by electrophoresis and related phenomena. (See chapter V, p. 194). The other is by consideration of adsorption of ions at the interface, as they are the carriers of the double layer charges (chapter IV, p. 115).

As the counter ions remain always close to the interface, the electrophoretic velocity of a particle is not simply proportional to its charge, but it is retained more or less by the ions of the double layer. Analysis shows that to a first approximation the electrophoretic velocity is proportional to the ζ-*potential*, this being the potential difference over the *mobile part of the double layer*. (It is assumed that the innermost part of the double layer is immovably attached to the particle).

On the other hand, the potential difference over the whole double layer is, in equilibrium cases, equal to the NERNST (or ε —) potential difference between the two phases and is thus determined by the activity of the so-called *potential-determining ions* [2] (Ag^+ for Ag particles, H^+ or OH^-, for oxides and hydroxides and also for noble metals (gas electrodes), Ba^{++} or SO_4^{--} for $BaSO_4$ etc.).

Theoretical investigations lead to the conclusion that there is a far going analogy between the structure of the double layer and that of the DEBYE-HÜCKEL ionic atmospheres. In fact, considerations [3] of this kind on the double layer are older than the DEBYE-HÜCKEL theory of strong electrolytes.

The counter ions are subjected to two influences. In the first place, by their irregular BROWNian motion they tend to diffuse away from the interface. On the other hand they are attracted to the interface by the COULOMB forces. These two opposed influences lead to a distribution equilibrium, characterized by a certain mean distance between the counter ions and the surface of the particle. This distribution is very sensi-

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[1] See T. SVEDBERG and K. O. PEDERSEN, *Die Ultrazentrifuge*, Leipzig 1940.

[2] E. LANGE, *Handbuch der Experimentalphysik*, XII, 2 (1933), 265, Akadem. Verlagsgesellschaft, Leipzig.

[3] G. GOUY, *J. physique*, (4) 9 (1910) 457; *Ann. d. phys.*, (9) 7 (1917) 129; D. L. CHAPMAN, *Phil. Mag.*, (6) 25 (1913) 475.
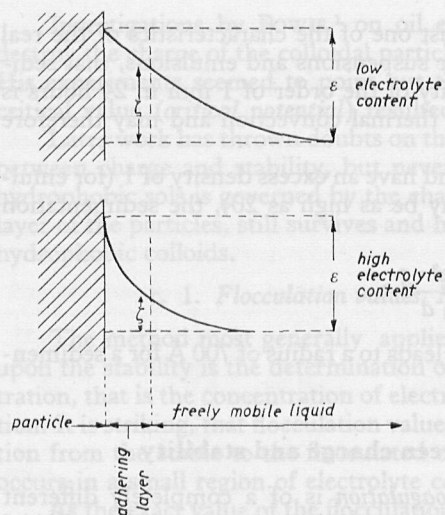
Fig. 12.   Illustrating the influence of electro-
lytes on the structure of the double layer and
on the ζ-potential.

tive to the concentration and valency of
the electrolytes present in the intermicellar
liquid and this explains the pronounced in-
fluence of added electrolytes on the electro-
phoretic velocity.

Fig. 12 gives a schematic representation
of the distribution of the electrical poten-
tial in the double layer for two cases with
the same activity of potential-determining
ions, but with different concentrations of
other electrolytes. It is seen that the ζ-poten-
tial is much lower for the higher electrolyte
content.

Electrophoresis is applied among other
things in the process of electrodeposition
(chapter V, § 10, p. 234), in which colloidal
particles (often in an organic medium) are
drawn by an electric field to one of the
electrodes and, under suitable conditions,
form a firmly adhering and homogeneous
deposit on it.

A property of the electrical double layer which is of very great practical impor-
tance, is the possibility of exchange of ions in the outer layer against other ions present
in the intermicellar liquid. This process of ion exchange that can be studied in a very
pure form in colloids (chapter IV, § 9, p. 175) finds applications on a very large scale in
nature, in the ionic balance of the soil, and in industry (see chapter IV, § 9 d, p. 183).

§ 5.   STABILITY OF LYOPHOBIC SOLS [1]

a.   Lack of stability in the thermodynamic sense

Although in certain cases lyophobic sols may seem to be stable for an indefinite
time, they are never really stable in the strict thermodynamic sense of the word. The
large interface, present in these systems, represents a large amount of free energy which
by recrystallization (coarsening) tends to reach a lower value and which is only at a mini-
mum when all the sol particles have united to one large crystal or one large liquid mass.
In many experiments this lack of stability, however, does not play a significant role.
Only with sol particles that are comparatively soluble (*e.g.* AgCl), this kind of coarse-
ning may play a part.

b.   Sedimentation and creaming

As the sol or emulsion particles usually have a density different from that of the
dispersion medium, they will tend to accumulate under the influence of gravity either
at the bottom or at the surface of the sol. These sedimentation effects are greatly depen-

[1] Most of the subjects treated in this section find a much more elaborate treatment in the chapters
VI, VII, VIII and IX.

dent upon the degree of dispersion and it is just one of the characteristics of the real colloidal systems, as compared with the coarser suspensions and emulsions, that sedimentation is negligible. A sedimentation velocity of the order of 1 mm in 24 hours is usually sufficiently counteracted by accidental thermal convection and may therefore be considered negligible.

Assuming that the particles are spherical and have an excess density of 1 (for emulsions it is usually smaller, for metal sols it may be as high as 20), the sedimentation velocity is given by STOKES' equation

$$v = \frac{4/3 \, \pi \, a^3 \cdot g}{6 \, \pi \, \eta \, a}$$

which for water at room temperature ($\eta = 0.01$) leads to a radius of 700 Å for a sedimentation velocity of 1 mm/day.

c. Flocculation. Relation between charge and stability

The loss of stability by *flocculation* or *coagulation* is of a completely different character. Here we are dealing with an irreversible sticking together of the colloidal particles in the form of loose and irregular clusters, in which the original particles can still be recognized; nevertheless it is impossible to disintegrate them to any great extent.

Flocculation is usually brought about by the addition of electrolytes to a sol. In § 4 c, p. 78, it has been mentioned that the electric properties (charge, electrophoresis) of sol particles are strongly dependent upon the electrolyte content of the intermicellar liquid, and now we find the same for the stability. It is therefore obvious to look for a direct relation between charge and stability.

That such a relation exists has already been stated by HARDY[1] in 1900 and by BURTON[2] in 1906. HARDY studied the properties of egg-albumin, which had been denatured by heat treatment and had lost its solubility. His systems may thus be truly regarded as hydrophobic colloids. HARDY found that, when the denaturing is carried out either in acid or in alkaline solutions, a stable sol results which is positively (acid) or negatively (alkaline) charged; but when the denaturing is carried out in or near the *isoelectric point*, where the egg-albumin is uncharged, a mass of flocs results.

BURTON compared the influence of aluminium salts on the electrophoresis and on the stability of a gold sol. From Table 3 it is clear, that the more highly the sol particles are charged, the greater is their stability and especially at zero charge the sol is immediately transformed into a flocculate.

TABLE 3

$Al^{+++}\mu$ eq/l	Electrophoretic velocity in μ cm/V sec	Stability
0	3.30 (towards anode)	Indefinitely stable
21	1.71 („ „)	Flocculated after 4 hours
—	0	Flocculates spontaneously
42	0.17 (towards cathode)	Flocculated after 4 hours
70	1.35 („ „)	Not yet completely flocculated after 4 days

[1] W. D. HARDY, *Z. physik. Chem.*, 33 (1900) 385.
[2] E. F. BURTON, *Phil. Mag.*, (6) 11 (1906) 425; 12 (1906) 472; 17 (1909) 583.

Investigations by POWIS [1] on oil emulsions showed that it is not necessary to destroy the charge of the colloidal particles completely in order to obtain a flocculation. His experiments seemed to point out that a lowering of the ζ-potential to a certain critical value (*critical potential*) resulted in flocculation.

Later work has thrown doubts on these all too simple interpretations of the relation between charge and stability, but nevertheless the general idea, that the stability of hydrophobic sols is governed by the charge or more generally, by the electrical double layer of the particles, still survives and has lost nothing of its importance in the field of hydrophobic colloids.

c. 1. *Flocculation values. Rule of* SCHULZE *and* HARDY

The method most generally applied in investigating the influence of electrolytes upon the stability is the determination of the flocculation value or flocculation concentration, that is the concentration of electrolyte just sufficient to bring the sol to flocculation. It is striking, that flocculation values can be determined rather sharply. The transition from the stable to the flocculated condition, although in principle a gradual one, occurs in a small region of electrolyte concentrations.

As the exact value of the flocculation value is dependent upon details in the performance of the experiment, it is customary to normalize circumstances at least in one and the same investigation. The specific choice of the circumstances often depends upon the properties of the sol. We shall give a few examples.

A *gold sol*, which is beautifully red when stable, turns blue at a certain degree of flocculation. The usual determination of flocculation values with gold uses this property and determines the concentration of electrolyte at which, five minutes after mixing, the first hint of blue colour is noticed or the last hint of red colour has disappeared.

Flocculation values of *arsenic trisulphide sols* are determined by mixing sol and electrolyte, waiting for two hours, agitating the mixture, waiting for another half hour and taking as flocculation value that concentration of electrolyte for which the supernatant is just clear and colourless.

As it is always necessary to wait for some time before a flocculation experiment can be judged, it is hardly possible to carry it out in the form of a titration. The normal experimental set-up is making a *flocculation series*, in which the sol is mixed with electrolyte solutions of increasing concentrations in a series of test tubes. After a specified time (see above) one judges which tube corresponds most accurately to the flocculation conditions. If necessary a second and a third series with smaller concentration differences between the tubes is employed.

The most remarkable thing about the flocculation values is that they are strongly dependent upon the valency of the electrolyte, more specifically upon the valency of the ions that are charged oppositely to the sol. Moreover, flocculation values are practically independent of the specific character of the ions and only slightly dependent upon the concentration and even the nature of the sol.

For monovalent counter ions ("gegen" ions) the flocculation values range between 25 and 150 millimols/1; for divalent ions from 0.5—2 millimols/1; for trivalent ions of the order of 0.01—0.1 millimols/1.

This regularity is known as the rule of SCHULZE [2] and HARDY [3] and is illustrated in

[1] F. POWIS, *Z. physik. Chem.*, 89 (1915) 186.
[2] H. SCHULZE, *J. prakt. Chem.*, (2) 25 (1882) 431; 27 (1883) 320.
[3] W. B. HARDY, *Proc. Roy. Soc. London*, 66 (1900) 110; *Z. physik. Chem.*, 33 (1900) 385.

Table 4, whereas larger tables are given in chapter VIII, § 3, p. 307. An influence of electrolytes according to the rule of SCHULZE and HARDY is not only found in flocculation values, but also very clearly in electrokinetic phenomena and generally in all phenomena, where the electrical double layer plays an outstanding role.

TABLE 4

FLOCCULATION VALUES IN MILLIMOLS PER LITRE

valency of counter ions	Sol of As_2S_3 [1]		Sol of Au [2]		Sol of $Fe(OH)_3$ [3]	
	negatively charged		negatively charged		positively charged	
mono-valent	LiCl	58	*½ K₂SO₄ 23*		NaCl	9.25
	NaCl	51	NaCl	24	½BaCl₂	9.65
	KNO₃	50	KNO₃	*23 25*	KNO₃	12
di-valent	MgCl₂	0.72	CaCl₂	0.41	K₂SO₄	0.205
	MgSO₄	0.81	BaCl₂	0.35	MgSO₄	0.22
	ZnCl₂	0.69			K₂Cr₂O₇	0.195
tri-valent	AlCl₃	0.093				
	½(Al)₂(SO₄)₃	0.096	½(Al)₂(SO₄)₃	0.009		
	Ce(NO₃)₃	0.080	Ce(NO₃)₃	0.003		

Exceptions to the rule of SCHULZE and HARDY occur when the counter ions are of a kind to be specifically adsorbed (large organic ions) or to react chemically with the ions building up the double layer.

A very good example of this last behaviour is given by the SnO_2 sol [4] in which the SnO_2 had been peptized by potassium hydroxide. Whereas the flocculation values of different alkali salts are normal, salts or acids that can form insoluble stannates (or SnO_2 itself), all flocculate at a concentration equivalent to the added KOH, that is to the peptizing stannate.

TABLE 5

FLOCCULATION VALUE OF SnO_2 IN MILLI EQUIVALENTS PER LITRE

	molar ratio SnO_2/KOH				
	2	10	25	50	100
Na Cl	180	170	34	26	14
Na NO₃	190	150	30	28	14
Na₂SO₄	180	170	32	28	14
Na H Citrate	230	200	40	52	50
H Cl	33	7	2.5	1.35	0.7
Ca Cl₂	33	7.5	2.2	1.35	0.7
Ba Cl₂	35	6.5	2.2	1.30	0.7
Al Cl₃	33	7	2.5	1.35	0.7
Al (NO₃)₃	33	7.5	2.4	1.40	0.7
Ag NO₃	—	—	2.5	1.80	0.9

[1] H. FREUNDLICH, Z. physik. Chem., 44 (1903) 129; 73 (1910) 385.
[2] H. FREUNDLICH and G. VON ELISSAFOFF, Z. physik. Chem., 79 (1912) 385; H. MORAWITZ, Kolloidchem. Beihefte, 1 (1910) 301.
[3] H. FREUNDLICH, Z. physik. Chem., 44 (1903) 151.
[4] E. HEINZ, Thesis, Göttingen 1914; R. ZSIGMONDY, Z. anorg. Chem., 89 (1914) 210.

This equivalent flocculation is also encountered in silver halide sols, peptized by halide ions which are flocculated by equivalent amounts of silver ions; or in $Fe(OH)_3$ sols, peptized with HCl which are flocculated by NaOH. In these last two cases a more than equivalent addition of the flocculating electrolyte leads to a second region of stability, where the charge of the sol proves to be inverted in sign.

At still higher electrolyte concentration the second region of stability is closed by a new flocculation value. This phenomenon is called an *irregular series* or *double flocculation*. It may be graphically represented as in Fig. 13, where the regions of stability and the charge of the sol are given in a schematic way in one figure.
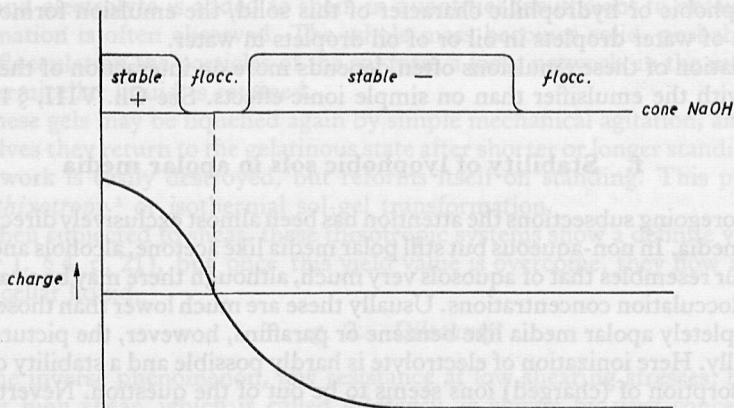

Fig. 13.   Irregular series of $Fe(OH)_3$ sol with NaOH.

d.   Mutual influence of sols

When two hydrophobic sols of the same charge that do not react chemically with each other are mixed, the resulting system is a stable sol containing two different kinds of particles. The behaviour of such a system is more or less the average between the two original sols.

If, however, one sol is positively charged and the other negatively, they flocculate each other, at least if the mixing proportions are not too extreme. This mutual flocculation is easily understood, as the particles attract each other strongly and form conglomerates which have only a very small charge or no charge at all.

When a hydrophilic sol is added to a hydrophobic one, usually a phenomenon called *protective action* makes its appearance. It is as if the hydrophobic particles are surrounded by the hydrophilic ones and thus acquire the lack of sensitivity against electrolytes, which is a typical property of hydrophilic systems. In certain conditions very small quantities of hydrophilic sols may make the hydrophobic sols *more* sensitive against flocculation. For details see Ch. VIII, § 4, p. 317.

e.   Stability of emulsions

Although the behaviour of *dilute* emulsions of oil in water is to a great extent similar to that of other hydrophobic sols and some of the more important early experi-

ments on hydrophobic colloids have been carried out with emulsions [1], the more *concentrated* emulsions seem to be dependent partly upon other mechanisms for their stability, and their flocculation does not simply follow the rules of SCHULZE and HARDY. These concentrated emulsions can only be prepared in the presence of emulsifiers which may be of two different types. An emulsifier is either a soap or soaplike substance which evidently is adsorbed at the interface between the two liquids and so protects the small drops, which have been formed by shaking or other agitation, against coalescence. Or an emulsifier may have the character of a finely divided solid, which, owing to its wetting properties, is preferentially adsorbed at the interface. Depending again on the more hydrophobic or hydrophilic character of this solid, the emulsion formed may be an emulsion of water droplets in oil or of oil droplets in water.

Flocculation of these emulsions often depends more on interaction of the flocculating agent with the emulsifier than on simple ionic effects. See Ch. VIII, § 12, p. 338.

f.   Stability of lyophobic sols in apolar media

In the foregoing subsections the attention has been almost exclusively directed to sols in aqueous media. In non-aqueous but still polar media like acetone, alcohols and the like, the behaviour resembles that of aquosols very much, although there may be a rather large shift in the flocculation concentrations. Usually these are much lower than those in water.

In completely apolar media like benzene or paraffins, however, the picture changes fundamentally. Here ionization of electrolyte is hardly possible and a stability connected with the adsorption of (charged) ions seems to be out of the question. Nevertheless, in such media stable sols exist. We have already drawn attention to some metal sols prepared by SVEDBERG (§ 1, p. 61). Moreover, most paints and varnishes belong to this category and also many emulsions of water in oil.

In these media one certainly can distinguish stable and flocculated systems, but the actual mechanism of stabilization and of flocculation is still far from clear. It seems that systems consisting of particles and a single component oil phase are never stable. Addition of a more or less polar component in small quantities is necessary to obtain stability. This added component (the "stabilizer") is adsorbed at the interphase and stabilization and adsorption run parallel [2].

Various detergents may act as stabilizers, *e.g.* oleic acid, fatty acids and their heavy metal salts, long chain sulphates and sulphonates, derivatives of polyethylene oxide etc.

The addition of a third phase, *e.g.* water, decreases the stability [3], because the free surface energy between the oil phase and the water can be greatly diminished by coagulation (see Ch. IX, § 5, p. 357).

A survey on the various aspects of the dispersion of pigments in oils is given by FISHER and GANS[4] and by APPEL [5].

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[1] R. ELLIS, *Z. physik. Chem.*, 78 (1911) 321; 80 (1912) 597; 89 (1915) 145; F. POWIS, *Z. physik. Chem.*, 89 (1915) 91.

[2] See *e.g.* D. HARKINS and D. M. GANS, *J. Phys. Chem.*, 36 (1932) 86.; P. KHOMIKOSŮKU and P. REHBINDER, *C. R. de l'Ac. des Sc. de l'U.R.S.S.*, 18 (1938) 575; V. R. DAMERELL and A. URBANIC, *J. Phys. Chem.*, 48 (1944) 125.

[3] W. D. HARKINS and D. M. GANS, *l.c.*; H. R. KRUYT and F. G. VAN SELMS, *Rec. trav. chim.*, 62 (1943) 407, 415.

[4] E. K. FISHER and D. M. GANS, Dispersions of finely divided solids in liquid media, in JEROME ALEXANDER, *Colloid chemistry, theoretical and applied* VI, New York, 1946, 286—327.

[5] F. APPEL, *Peintures, pigments et vernis*, 22 (1946) 277, 318, 387.

g.   Mechanical properties of lyophobic systems

g. 1.   *Gel formation*

In most cases hydrophobic sols are NEWTONian liquids, with a viscosity only slightly deviating from that of the dispersion medium. In the flocculated state more or less clear indications of non-NEWTONian behaviour, especially the presence of a yield value, may be detected. This is most evident for sols containing blade-shaped or rod-shaped particles like iron oxide or vanadium pentoxide. When these sols are not too dilute and electrolyte is added to them in quantities insufficient to obtain flocculation, *gel* formation is often observed. The whole mass becomes solid, probably because by partial flocculation the particles of the sol form a loose network, in the meshes of which the intermicellar liquid is retained.

These gels may be liquefied again by simple mechanical agitation, and when left to themselves they return to the gelatinous state after shorter or longer standing. Evidently, the network is easily destroyed, but reforms itself on standing. This phenomenon is called *thixotropy* [1] or isothermal sol-gel transformation.

When subjected to shear, these thixotropic systems show a definite yield value (see chapter I, § 4, p. 21), but once this yield value is overcome, they flow as easily as the intermicellar liquid.

g. 2.   *Dilatancy*

The inverse phenomenon, low resistance at low shearing stresses, but high resistance at high shear, which is called *dilatancy*, is shown by very concentrated stable suspensions [2]. In these suspensions there is no permanent contact between the particles, and consequently they can easily make the motions necessary to obey small shearing stresses. If, however, the motion tends to become more rapid, the very high concentration (*e.g.* 50% by volume) of these systems makes it impossible for the particles to retain a close packing. But a less dense packing can only be obtained by sucking liquid into the mass of particles, and the extra energy required for this process strongly reduces the mobility of the system. Moreover, when the dense suspension is not submerged in a large mass of liquid, so that no extra liquid is available to enter between the particles, any quick motion draws the liquid away from the surface of the system and leaves many capillaries between the particles half filled, thus creating a large capillary pressure which counteracts the motion.

g. 3.   *Sedimentation volume*

The above-mentioned phenomena, especially the flow character of a sediment, may be used to distinguish between "flocculated" and "stable" suspensions, in cases where the particles are so large that they sediment very quickly and thus make a normal determination of flocculation impossible.

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[1] See H. FREUNDLICH, *Thixotropy*, Paris 1935.
   The name thixotropy was proposed by PÉTERFI, *Arch. f. Enwicklungsmech. d. Organism.*, 112 (1927) 689.
   [2] E. J. W. VERWEY and J. H. DE BOER, *Rec. trav. chim.*, 57 (1938) 383; H. FREUNDLICH and H. L. RÖDER, *Trans. Faraday Soc.*, 34 (1938) 308.
   H. L. RÖDER, *Thesis*, Utrecht 1939; H. R. KRUYT and F. G. VAN SELMS, *Rec. trav. chim.*, 62 (1943) 407, 415.

Another very good indication in that case is the sedimentation volume, which is small in the case of a stable suspension (the particles roll over one another until the densest packing is obtained), but larger for a flocculated one (the particles remain in the position, in which they were when they touched for the first time).

§ 6. THEORETICAL CONSIDERATIONS ON STABILITY AND FLOCCULATION

The large interfacial free energy is a cause of the instability of all lyophobic systems, but the rate at which equilibrium is approached may be so extremely small, that it can be neglected in many cases.

If we do so and see therefore the colloidal particles as constant data in our problem, we remark that evidently a number of colloidal particles embedded in a liquid, may occur in two different states: the stable state, in which the particles are more or less evenly distributed and the flocculated one in which the particles form large and difficultly reversible clusters. Evidently in the flocculated state the particles attract each other, and in the stable state there is a repulsion between them.

a. Repulsion

From the data cited in § 5 c, p. 80 it is clear that the repulsion is related to the charge of the particles as manifested in electrophoresis. This charge arises from the adsorption of ions (or electrons) and it is obvious to assume that the *peptizing* ions (§ 1, p. 60) which appear to be indispensable for stability, are the carriers of the charge. Peptizing ions always show a close relation to the material of the particles, they "fit into its lattice" and it is just this fitting into the lattice which makes these ions the *potential-determining ions* (§ 4 c, p. 78), which determine the potential difference over the electrical double layer in accordance with the NERNST equation.

In the case of silver bromide in contact with an aqueous solution, the NERNST equation is

$$\psi_{AgBr} - \psi_{H_2O} = \text{Const} + \frac{RT}{F} \ln a_{Ag} = \text{Const}' - \frac{RT}{F} \ln a_{Br} \qquad (5)$$

Thus with excess silver ions in the solution the silver bromide is positively charged and with excess bromine ions it is negatively charged. Somewhere between (not necessarily at the point of equivalence. See chapter IV, § 6, p. 159) the silver bromide is uncharged; the concentrations of Ag^+ or Br^- ions for which this is the case are called the *zero point of charge*.

The existence of a zero point of charge explains the possibility of reversal of charge and the phenomenon of the irregular series (§ 5 c, p. 83).

Nevertheless we know that not only the peptizing electrolytes, but all other electrolytes as well influence the stability of a colloidal solution. The question is, how can they influence the repulsion between particles when the potential difference between the two phases is fixed by the presence of potential-determining ions. We have mentio-

ned in § 4 c that the extension of the electrical double layer is very much dependent upon the electrolyte content of the solution. By addition of electrolytes, the double layer is compressed and as the double layer screens the field of the particle charge, a compression means that the repulsion between two particles is only active at shorter distances.

Generally speaking, one can say that the repulsion between two particles is greater, the greater the potential between particle and solution, and that it reaches further the more dilute the solution.

As sols are coagulated by finite (and even rather small) amounts of electrolyte, there is certainly a repulsion left at the flocculation value, although it may not reach further than *e.g.* 10 or 20 Å (see chapters IV and VI).

Flocculation can consequently only be understood if the range of the attractive force is also at least of this order of magnitude.

b.   Attraction

As flocculation is a generally occurring process, it is necessary to look for a very general type of force to explain the attraction.

KALLMANN and WILLSTÄTTER [1] were the first to draw attention to the possibility that the LONDON-VAN DER WAALS — forces could be responsible for attraction. Ordinarily these forces are thought to have only a very short range *e.g.* of 1 Å. It can however be easily shown that the range of these LONDON-forces between larger particles is of the order of the particle radius. Thus we have here a force, uniting the three requirements following from experimental data, *viz.*, it is not very specific, its range may be of the order of 10 or 100 Å and it is always attractive. It must be left to a closer investigation to see whether its quantitative properties are of the right order of magnitude. (For more details see chapter VI, § 9, p. 264 and chapter VIII, § 3, p. 306).

c.   Potential curves

HAMAKER [2] has introduced a very useful method of getting a survey of the interaction between sol particles and thus of obtaining an impression on the stability of the corresponding sol. This method consists of drawing potential curves, representing the potential energy as a function of the distance between two colloidal particles.

The repulsion will then be given by a curve as represented in Fig. 14 and the attraction by one as represented in Fig. 15. The combination of the two curves may in principle lead to different kinds of curves, from which a few examples are sketched in Figs. 16 and 17. For stability of a sol it will be necessary that a maximum of sufficient height ($\gg$ kT) exists in the potential curve (*e.g.* Fig. 17, curves 1, 2, 3 and 4).

The further working out of these curves will be given in chapter VI and we shall see there that the curves represented in Fig. 17 correspond to the actual situation.

The flocculation by addition of electrolyte is now explained by the shorter range of the repulsion curve, which depresses the maximum, till at the flocculation value it is too small to prevent coagulation.

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[1] H. KALLMANN and M. WILLSTÄTTER, *Die Naturwissenschaften*, 20 (1932) 952.
[2] H. C. HAMAKER, *Rec. trav. chim.*, 55 (1936) 1015; 56 (1937) 3, 727.

d. Particular cases

There are some cases, especially the suspensions in apolar media and probably emulsions of water in typical apolar oils, where the above given explanation of the repul-
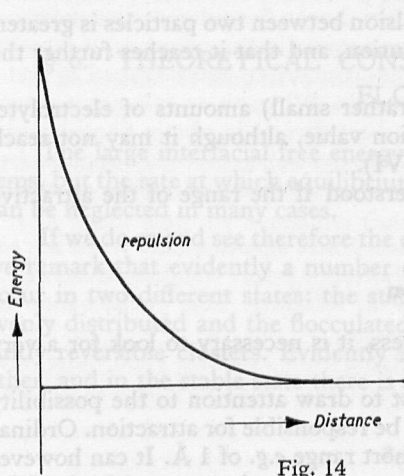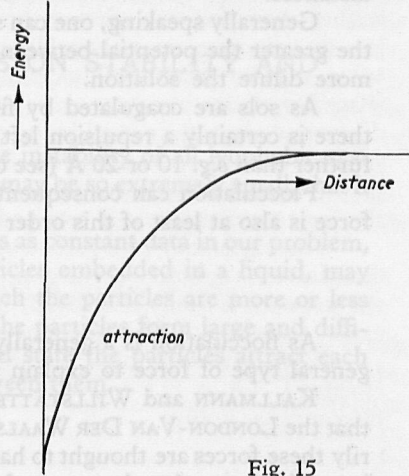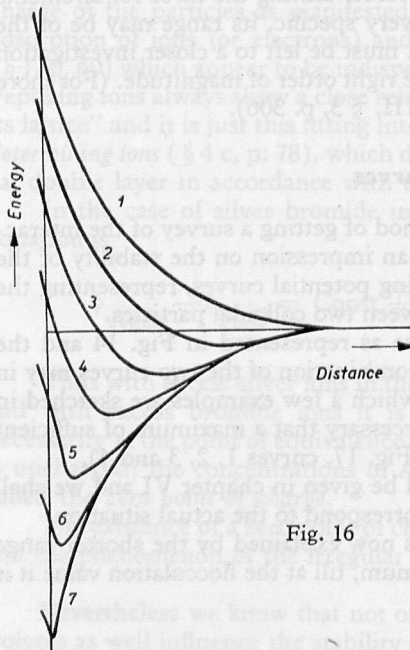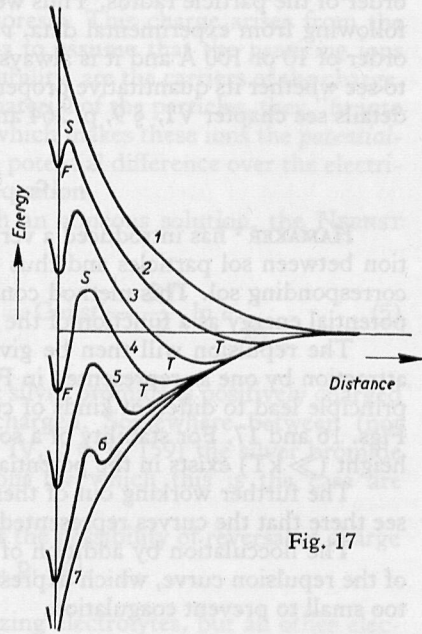

Fig. 14

Fig. 15

Fig. 16

Fig. 17

Fig. 14—17. Examples of potential curves representing the energy of interaction between colloidal particles.

sion is hardly tenable, because in the nearly complete absence of ionization a double layer of sufficient strength cannot be present.

As one must assume that attraction in these cases is not much lower than in aqueous media, and stable systems may exist, another cause for the repulsion must be present. Because this kind of suspension is only stable if certain, usually long chain, compounds like soaps, phosphatides, polyethylene oxide derivatives are present at the interface, the repulsion must somehow be connected with these adsorbed layers. This repulsion might well be of an entropic instead of an energetic nature [1], but little theoretical work on these systems has as yet been published.

[1] M. VAN DER WAARDEN, *J. Colloid Sci.*, 5 (1950) 317; 6 (1951) 443.
E. L. MACKOR, *J. Colloid Sci.*, 6 (1951) 492.