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THE CHEMISTRY OF COLLOIDS

THE CHEMISTRY OF COLLOIDS

AND SOME TECHNICAL APPLICATIONS

BY

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PREFACE TO THE FIRST EDITION

It is curious that although colloid chemistry owes its development in no small degree to British investigators, hitherto there has been not only no English text-book on the subject, but no text-book in English available, the foreign works that have been translated dealing with particular aspects of the subject only, or with its bearings on other sciences.

The present book, based on my lectures on Heterogeneous Systems delivered to advanced students in the University of Edinburgh, will, it is hoped, meet the want of a convenient text-book, and at the same time serve as a reference book for workers in other sciences, who are becoming more and more interested in colloids. To increase its usefulness in the latter direction, a section on the applications of colloid chemistry has been added. It makes no claim to be complete or exhaustive; indeed, many important applications are not even mentioned, but it seemed better to deal at some length with a number of selected examples, rather than to give a mere catalogue of the many branches of pure and applied science in which it plays a part. Further, a large amount of experimental data has been included throughout the book, with the idea that this may be of use to those interested in the subject.

The practical instructions for the preparations will, if carefully adhered to, enable any one to prepare sols

whether for purposes of research or of demonstration. In this connexion I desire to express my indebtedness to Svedberg's *Die Methoden zur Herstellung Kolloider Lösungen*, as also generally to Freundlich's *Kapillarchemie* and von Weimarn's *Grundzüge der Dispersoidchemie.*

My thanks are also due to Messrs. Carl Zeiss, who kindly lent the block for Figure 2; to my wife for drawing the remaining figures; and to Mr. J. D. M. Ross, M.A., B.Sc., for valuable assistance in reading the proofs.

W. W. T.

UNIVERSITY OF EDINBURGH.
Jan. 1915.

PREFACE TO THE SECOND EDITION

IN this edition the main features of the book remain unaltered, although a considerable amount of new material has been added. This has only been done, however, where either the new matter was a more convincing illustration of an already established theory, or the new experimental results had led to changes in the previously accepted theory. Opportunity has also been taken of making a few corrections, chiefly concerned with matters of historical accuracy, for which I am indebted to the kindness of friendly critics.

W. W. T.

THE UNIVERSITY, EDINBURGH
July 1921.

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CHEMISTRY OF COLLOIDS

PART I

GENERAL PROPERTIES OF COLLOIDS

CHAPTER I

INTRODUCTION

WHEN Graham, as the result of his epoch-making experiments on colloids, was led to make the well-known statement that "they (crystalloids and colloids) appear like different worlds of matter, and give occasion to a corresponding division of chemical science. The distinction between these kinds of matter is that subsisting between material of a mineral and the material of an organised mass," the science of chemistry was still dominated by the idea of the fundamental difference between inorganic and organic substances. It was natural, therefore, that he should extend this already accepted distinction to the new region of chemistry which he had just discovered.

But, just as the advance of knowledge has removed the distinction in the one case, so too the tendency of recent work has been to bring the other under suspicion. For many years physical chemists have inclined more and more to the view that crystalloids and colloids are not different *kinds* of matter (as Graham considered) but, rather, are different *states* of matter, and that the same

chemical substance may be obtained in the one state or the other by suitable alteration of the conditions under which it is produced.

While this exceedingly important change in our fundamental conception regarding colloids is not due to any one investigation, Paterno's researches, although recently shown by him to be erroneous (p. 289), were the first to indicate that a substance (tannin) may form a sol in one liquid (water), and a true solution in another liquid (acetic acid). Many have contributed to the development of the idea, but it was only recently carried to its logical conclusion by P. P. von Weimarn, who has succeeded in mathematically formulating the main factors which govern the appearance of a substance in either the colloid or the crystalline state; these conclusions he has confirmed in an elaborate series of investigations.

As a result of these investigations we have not only the means afforded of classifying the diverse methods hitherto employed in the preparation of particular colloids, but have indicated in any given case the necessary modifications of the conditions for obtaining a substance in the colloid state. These developments are so recent that they can hardly be said to have been applied in a systematic manner, and yet von Weimarn has already succeeded in obtaining more than 400 substances in the colloid state.

In another direction there have been in recent time very considerable advances: in the development of the connexion between the special properties of the colloid state and capillarity or surface phenomena. Here the question of surface energy is all-important.

As a surface implies heterogeneity, being an interface between two phases, we can at once proceed to classify systems according to the nature of the phases (at least

two in number) which are necessary for the existence of the interface. The special properties ascribable to surface energy only come into prominence when it amounts to a moderately large fraction of the total energy of the system; this is connected with the ratio of the surface to the volume (or mass) of the system, which in turn may be expressed in terms of the "*specific surface.*" The specific surface is the surface divided by the volume. The surface of a cube, the side of which is l, is $6l^2$, and its volume is l^3; the specific surface is $6/l$. Thus a cube of 6 cm. side and the inscribed sphere of 6 cm. diameter have unit specific surface. A large specific surface can only be obtained by the reduction of at least one spatial dimension of one of the phases, hence the name *microchemistry*, suggested by Ostwald, in place of capillary chemistry, the name adopted by Freundlich. Unfortunately, the name has already been misapplied to a special branch of chemical analysis—the analysis of microscopic quantities. What is usually known as colloid chemistry is only a part, though the most important practically, and the most fully developed part, of the general science of microchemistry.

By a systematic application of the two ideas—of heterogeneity involving at least two phases, and of the increase of the specific surface by reduction of one, two, or three spatial dimensions of one of the phases, we arrive at a complete classification of the possible microchemical systems. The phase which is divided into small separate volumes is known as the *disperse phase*, the other is the *dispersion medium;* when the dispersion takes the form of parallel plates, there is no distinction between the two phases. The *dispersity* is the degree to which the reduction of the dimensions of the disperse phase has been carried; it is best expressed numerically in terms of

specific surface, but more frequently in terms of the linear dimensions of the disperse phase, *e.g.* the thickness of films, or the diameter of separate particles.

Diminution of one dimension gives rise to films and bubbles; of two dimensions to threads; and of three dimensions to fine powders, drops, etc. Leaving out of account the two former cases, we have the following classes:—

I. The dispersion medium is a Gas.[1] The disperse phase is

(*a*) liquid, producing cloud or mist;

(*b*) solid, producing dust or smoke.

II. The dispersion medium is a Liquid. The disperse phase is

(*a*) gas, giving rise to foam;

(*b*) liquid, producing emulsions (and gels ?);

(*c*) solid, producing suspensions.

III. The dispersion medium is a Solid. The disperse phase is

(*a*) gas; gas bubbles in a solid produce solid foam or scoriæ;

(*b*) liquid, as in the liquid inclusions in minerals; some gels probably come into this class.

(*c*) solid, producing solid mixtures.

Emulsions and suspensions form by far the most important classes at the present time, comprising as they do what were formerly known as colloids. There is some doubt whether all gels ought not to be regarded as emulsions possessed of considerable rigidity. This question will arise later, and will then be more fully discussed. Solid mixtures have as yet received little theoretical consideration, owing to the difficulties involved. They are,

[1] Since all gases are completely miscible, there is no disperse system consisting of gases alone.

however, of great practical importance, as the mere mention of cements and heterogeneous alloys will indicate. Here, too, the question arises whether, in some of these cases, one at least of the phases may not be liquid rather than solid, and should accordingly be placed among the gels.

Nomenclature.—When the history of the development of colloid chemistry is recalled, it is hardly surprising that there is a certain amount of confusion in respect of nomenclature. To Graham we are indebted for the general term *colloid* in contrast with *crystalloid*. He also distinguished between the two conditions in which the colloids he first investigated, as gelatine and silicic acid, were obtainable, the term *sol* being applied to the form in which the system was apparently liquid, while to the solid, jelly-like form he applied the term *gel*. If one of the components was water, the two forms were a *hydrosol* and a *hydrogel;* if it was alcohol, they were an *alcosol* and *alcogel*, and so on. These terms are still in common use, but are no longer sufficient.

The earlier work was largely done on either naturally occurring colloids, or on others, the discovery of which was more or less in the nature of accident, and which were similar in properties to these natural colloids. These belong to the group II. (*b*) in the above classification (p. 4), consisting of systems of two liquids, and known as emulsions. Now, the colloids of the group II. (*c*), consisting of a solid disperse phase in a liquid dispersion medium, were investigated at a later date, and as they are on the whole of a simpler nature than the emulsion colloids, many of the most important properties of colloids were not found out until comparatively recent times. The terms *sol* and *gel* are frequently applied to them; the former is unobjectionable, not so the latter. It is not desirable to

apply the same terms to processes or states which may be essentially different, though superficially the same.

As already suggested in the above classification, *gels* usually consist of two liquid phases, but may in some cases consist of a solid phase and a liquid phase. In the case of suspension colloids there is little doubt that the sol contains a solid phase and a liquid phase, and this is probably also true of the precipitated colloid, to which the term gel has been applied. It is not impossible that here the two phases may be liquid, but even if it be so, the phenomena are not comparable with those exhibited by the gels proper, and it is better not to extend the name to them.

Starting from the fundamental idea that colloids are heterogeneous systems, one phase of which is liquid, and the other either liquid or solid, we have first of all, when the dispersity is not high, the two classes known as *emulsions* and *suspensions* respectively. As the dispersity increases we have the typical emulsion colloids and suspension colloids, which may conveniently be named *emulsoids* and *suspensoids*, the corresponding general term being *dispersoids*. Some, as P. P. von Weimarn, would still further subdivide the region between this dispersity and the apparent homogeneity of solutions, into *emulsides suspensides*, and *solutides*, the latter merging into true solutions. But these terms have not as yet found common recognition, partly because the phenomena can be adequately described and discussed without them.

The classification of sols into suspensoids and emulsoids, based upon the state of the disperse phase, is not altogether satisfactory, for some systems, in which the disperse phase is undoubtedly liquid, exhibit characteristic properties of suspensoids, while others, in which it may be

solid, are more like the emulsoids. The determining factor seems to be the presence or absence of affinity between the two phases, whether in the form of solubility or chemical combination, the formation of a gel being a significant manifestation of the difference between the two classes. The term *lyophile* has been applied to those systems in which there is marked affinity between the phases, and *lyophobe* to the others. When water is the dispersion medium the terms *hydrophile* and *hydrophobe* are commonly used. Broadly speaking, this classification is the same as into emulsoids and suspensoids.

Lyotrope Series.—Another aspect of the affinity between disperse phase and dispersion medium may be referred to here. There are many striking differences between suspensoids and emulsoids, or better, between lyophobe and lyophile sols, and especially in their behaviour towards chemical reagents. With the former, the effect of the added reagent is produced almost exclusively on the disperse phase, while with the latter, its effect on the dispersion medium is also of importance, and may even overshadow the other, and so become the predominant feature.

It is well to remember at the outset that the ordinary physical properties of a lyophobe sol are very little different from those of the pure dispersion medium, while the converse holds for lyophile sols. Now there is a large number of reactions in solutions which are markedly influenced by the addition of foreign substances, which from their nature seem debarred from taking any chemical part in the reaction. The inference is that their influence on the chemical reaction is an indirect effect, the direct effect being a change in the nature of the solvent, produced by the added substance. This is confirmed by the following facts.

If the reagents are arranged in order of their influence on the reactions, the same sequence is obtained in widely differing reactions. The reaction may be promoted by certain reagents, and hindered by others, in comparison with the reaction in the pure solution. This sequence does not appear to follow any recognisable chemical order, as, *e.g.* valency, atomic weight, etc. In some reactions the order is reversed, but the sequence is still maintained. The order is frequently reversed when the same reaction takes place in acid and alkaline solutions, *i.e.* the substances which favour the reaction in acid solutions hinder it in alkaline solutions, and conversely, the sequence remaining the same in both cases.

Among the reactions in which this lyotrope influence has been recognised are the following: the catalysis of esters, the inversion of cane sugar, the setting of gelatine, and the heat-coagulation of albumin. It is very significant that the same sequence is observed in the effect of substances on many of the physical properties of water as compressibility, viscosity, density, surface tension. This it is which points to the lyotrope character of the effect in the chemical reactions, the essential properties of the water, on which its behaviour as a solvent and as a dispersion medium depend, being changed in a definite manner to a fixed extent by these substances. Appended are a few examples of reactions and properties, which will illustrate the lyotrope series. The ions are arranged in order of their effect upon the velocity or the property; thus ions which precede (H_2O) reduce the velocity of reaction or the numerical value of the compressibility, etc., of water, the first mentioned causing the greatest reduction, while those which succeed (H_2O) increase the velocity, etc., the last mentioned having the greatest effect.

1. The Hydrolysis of esters by acids.

Anions: $SO_4 (H_2O)$ Cl < Br.

Kations: (H_2O) Li < Na < K < Rb < Cs.

SO_4 retards the action, the other anions and the kations accelerate it.

2. The Hydrolysis of esters by bases.

Anions: I > NO_3 > Br > Cl > Ā (H_2O) S_2O_3 < SO_4

Kations: Cs > Rb > K > Li (H_2O).

The ions which accelerate the acid hydrolysis retard the basic hydrolysis, and *vice versâ*.

3. The Compressibility of aqueous solutions.

Anions: CO_3 > SO_4 > Cl > Br > NO_3 > I (H_2O).

Kations: Na > K > Li > NH_4 (H_2O).

In all cases the solutions are less compressible than water

4. The Surface Tension of aqueous solutions.

(H_2O) I < NO_3 < Cl < SO_4 < CO_3.

The surface tensions of the solutions are greater than that of water.

5. The Viscosity of aqueous solutions.

Anions: NO_3 > Cl (H_2O) SO_4 [Potassium salts].

Kations: Cs > Rb > K (H_2O) Na < Li [chlorides].

The viscosity of the solutions of KNO_3, KCl, CsCl, RbCl is less than that of water (so called "negative viscosity"), that of the other salts is greater than that of water.

Coagulation, again, is a term which is applied more or less indiscriminately to several phenomena, *e.g.* to the formation of a precipitate in emulsoid sols, as the proteins, especially by the action of heat, and also to the precipitation of suspensoid sols, especially by the addition of electrolytes. As, however, little is known regarding the mechanism of the former type of reaction, this dual use of the term is not of much consequence. But undoubtedly

the latter set of changes are better designated as precipitations.

Sol-gel Transformation.—The ambiguity in the use of the term gel has already been referred to. The reversible transformation of sol $\rightleftharpoons$ gel is a phenomenon, the extreme importance of which is likely to increase, as so many other effects are bound up with it. The nomenclature is admittedly inadequate; verbs to express the processes and names of the processes themselves are much needed. It is now difficult to justify such a statement as "the gel dissolves to a sol," for if the gel dissolved, the result would be a solution, not a sol.

The term gelatinisation is frequently used for the change from sol to gel. It is felt to be too long, for some have reduced it to gelatination, but as gel is the generalised form of gelatine, *gelation* is obviously the most appropriate term, and the corresponding verb is surely *gelate*. The term gelation has been occasionally used.

For the reverse change we are not in so happy a position; *solation* and *solate* are unquestionably the logical antitheses of gelation and gelate, but we already have solute for a thing, and solution for both a thing and a process, and the more recent solvate as an adjective and a noun. Graham introduced the verbs *peklise* and *peptise*, and the corresponding terms *peklisation* and *peptisation* to express these changes, and probably considered the similarity of the two words to express two directly opposed processes to be an advantage, instead of as now the very reverse. At any rate they have not been generally adopted, though curiously the adjective *pektous* is coming into use, especially among biologists, and peptise is also frequently used.

Now the real objection to peptise and peptisation is that they originally were, and still are, strictly applied to

only one of the many methods by which a gel may be transformed into a sol; and it is most undesirable to stamp a general idea with a name which has been and still is properly enough applied to one small part of the idea. There seems no escape from the adoption of the following terms:—

gel, to gelate, gelation,
sol, to solate, solation,

they are unambiguous and brief, are logically connected, and will save an enormous amount of circumlocution.

Degree of Dispersity.—The fundamental idea underlying the chemistry of colloids, and much more, is that of heterogeneity, but between certain well-defined limits. The upper limit has been fairly definitely established, and lies above the limit of microscopic visibility (which may be placed at 10^{-5} cm.). At this dispersity the properties of the substance begin to differ appreciably from the properties of the substance as it ordinarily occurs; at this stage the phenomenon known as Brownian movement, just observable at about 10^{-3} cm., is well developed, and the surface energy is no longer a negligible fraction of the total energy of the system (p. 226). Particles between these limits (10^{-3} cm. and 10^{-5} cm.) are termed *microns* in Zsigmondy's nomenclature.

The lower limit can not be below the dimensions of molecules (about 10^{-8} cm.). Ultramicroscopic heterogeneity has been directly observed at 5×10^{-7} cm., the particles between this and 10^{-5} cm. are termed *submicrons*, and the existence of particles of approximately 10^{-7} cm. diameter has been demonstrated in an indirect manner by Zsigmondy; these are known as *amicrons*. Below this again must lie the apparent homogeneity of true solutions, which, however, must ultimately be regarded as truly heterogeneous.

There is thus unbroken continuity between the coarsest-grained heterogeneity and the apparent homogeneity of the true solutions, and the molecular state in gases.

Historical Note.—Graham is usually regarded as the founder of colloid chemistry, and so in a certain sense he was, but many of the properties on which he based his ideas, and some of the ideas, were already known to his predecessors, as were also many of the ideas which have been put forward since his time.

A glance at the section of the book dealing with methods of preparation will show that metal sols, prepared by reduction of salts, were fairly well known, and several investigators expressed the view that these so-called metal solutions were suspensions and not solutions at all. While the metal sols formed by kathode reduction were generally considered to be hydrides, Ruhland (1815) and Poggendorf (1848) pronounced them to be metals in a very fine state of division. And Berzelius, in his "Lehrbuch" (1844), having described arsenious sulphide sol as obtained by the action of hydrogen sulphide on arsenious oxide solution, says: "For the present this solution is rather to be regarded as a suspension of transparent particles, for arsenious sulphide gradually separates out as a precipitate."[1]

The sulphur sol, formed by the reaction between sulphur dioxide and hydrogen sulphide in water, was discovered by Wackenroder (1846). He states that "if the liquid is frozen and thawed, a great part, but not all, of the suspended sulphur separates out. But it is immediately and completely separated out in large flocks if

[1] "Inzwischen ist diese Lösung wohl mehr als eine Suspension von durchsichtigen Teilchen zu betrachten, denn allmählich scheidet sich das Schwefelarsenik ab und fällt nieder."

a neutral salt of an alkali, as NaCl, is added to the acid liquid."[1]

And Sobrero and Selmi (1850), in an elaborate account of the same sulphur sol, make the following remarks: "If water is added to it, it divides up, forming an emulsion, from which it does not separate out, even on prolonged standing (several months)." . . . "If a little aqueous solution of a neutral potassium or sodium salt is added to the emulsion, sulphur is immediately precipitated, but, singularly, if a sodium salt is used, the sulphur does not lose the property of dividing itself up again in water. All that is necessary is to decant the liquid containing the sodium salt, and to wash the precipitate several times with distilled water; after the second or third washing the sulphur does not settle out, but regenerates the emulsion. If a potassium salt, especially the sulphate has been used, the precipitated sulphur has completely lost the property of emulsifying in water. . . . In spite of repeated washing, it always retains a trace of the potassium sulphate employed for the precipitation. . . ."

"This enormous quantity of sulphur is, one would be inclined to say, dissolved, for it hardly affects the limpidity of the liquid. . . . Sulphur can thus be modified in an extraordinary manner by the substances present at the time of deposition, these adhering obstinately, probably by simple adhesion, and can either acquire the property of emulsifying in water, or assume a state of aggregation which prevents it dividing up in water. It thus appears that sulphur exhibits phenomena analogous

[1] "Lässt man sie gefrieren und wieder aufthauen, so scheidet sich zwar ein grosser Theil, aber nicht aller suspendierter Schwefel ab. Augenblicklich jedoch wird derselbe in grossen Flocken rein abgeschieden, wenn man die stark saure Flussigkeit mit einem neutralen Alkalisalze, vornehmlich mit Kochsalzlösung, vermischt."

to those observed with many other substances, which possess the power of dispersing and dividing themselves in a liqnid, without completely dissolving in it, as *e.g.* soap, starch, and prussian blue, on which one of us (Selmi) has previously made observations similar to those now described. These facts are related to a set of phonomena which M. Selmi has classed together under the name of pseudo-solutions. The number of pseudo-soluble substances seems to be pretty large." [1]

The first observations on the *hydrolysis* of salts

[1] "Si l'on y ajoute de l'eau il s'y divise en formant une émulsion dont il ne se sépare plus, même par un repos très-prolongé (plusieurs mois)." . . . "Si, à l'émulsion de se soufre, on ajoute un peu de solution aqueuse d'un sel neutre de potasse ou de soude, on obtient immédiatement un précipité de soufre, mais (chose singulière) si l'on a employé un sel de soude pour la précipitation, le soufre n'a pas perdu la proprieté de se deviser dans l'eau. Il suffit, pour s'en assurer, de décanter le liquide contenant la sel sodique, et laver le précipité plusieurs fois avec de l'eau distillée; au deuxième ou au troisième lavage, le soufre ne se dépose plus: il régénère l'émulsion. Si, au contraire, on a employé un sel potassique, surtout le sulfate, le soufre précipité a perdu complètement la propriété de s'émulsionner dans l'eau. . . . Malgré les lavages répétés, il retient toujours un peu de sulfafe de potasse employé pour la précipitation." . . .

"Cette énorme quantité de soufre est, on dirait, dissoute, car elle n'altère presque pas la limpidité du liquide. . . . Le soufre peut donc être modifié, dans sa manière d'être, d'une façon toute particulière par la presence des corps au milieu desquels il se dépose, et qui y adhèrent avec opiniâtreté, probablement par simple adhésion, et acquérir tantôt l'émulsion abilité, tantôt un état d'aggregation qui l'empêche de se diviser dans l'eau. Il resulte, en outre, que le soufre émulsionnable présente des phénomènes analogues à ceux qui s'observent dans beaucoup d'autres corps qui jouissent de la propriété de se disperser et se diviser dans un liquide, sans toutefois s'y dissoudre absolument, tels que le savon, l'amidon, et le bleu de Prusse, sur lequel un de nous, M. Selmi, a déjà fait des observations analogues à celles que nous venons d'exposer. Ces faits se rattachent à un ordre de phénomènes que M. Selmi a bien caractérisés, et qu'il a réunis sous le nom de pseudosolutions. Il parait que le nombre des corps pseudosolubles est assez grand." (*Ann. Chim. Phys.*, 1850, [iii.] **28**, 210–215.)

resulting in the formation of sols were made by Gay Lussac (1810) on aluminium acetate. Berzelius[1] then gave a full description of the preparation of β silicic acid by the hydrolysis of silicon sulphide.

"β silicic acid is obtained in its purest form when silicon sulphide is oxidised by water; hydrogen sulphide is evolved as gas, and the β silicic acid dissolves in the water. In a more concentrated state the solution soon turns to a gelatinous mass." Frémy[2] (1853), on the same subject, added little to Berzelius' account; he says: "The hydrated silica remains completely dissolved in the water, and this siliceous water is sometimes extremely stable; if dilute, it can be kept for months without depositing any silica, but it becomes gelatinous and gives up the silica when it is concentrated or boiled, or when a soluble alkaline salt is added to it."

The peptisation of silicic acid gel by alkalies was described by both Berzelius (1833) and by Kühn (1853). The latter[3] also states that "by treating silicic acid jelly with water it is easy to obtain 5 per cent. solutions which

[1] "In ihrem reinsten Zustand bildet sie sich durch Oxydation von Schwefelkiesel auf Kosten von Wasser; es entwickelt sich Schwefelwasserstoff-gas, und die β Kieselsäure löst sich in Wasser auf. In konzentrierterem Zustande gesteht die Lösung bald zu einer gallertartigen Masse." (Berzelius, *Lehrbuch*, 3 auf. 1833.)

[2] "la silice hydratée qui reste entièrement en dissolution dans l'eau. Cette eau siliceuse présente quelquefois une grande stabilité; on peut la conserver pendant des mois entiers lorsq'elle est étendue sans qu'elle laisse déposer de la silice; mais elle devient gélatineuse et abandonne la silice qu'elle tient en dissolution quand on la concentre lorsqu'on la porte à l'ébullition ou qu'on introduit dans la liqueur des sels alcalins solubles." (*Ann. Chim. Phys.*, 1853, [iii] **38**, 312.)

[3] "Die Hauptbedingung zur Darstellung einer solcher Auflösung besteht darin, dass Kieselsäuregallerte, welche dazu dienen soll, in möglichst ausgedehnter Beschaffenheit bereitet und gewissermassen so lange in statu nascendu erhalten wird, bis sie zur Auflösung hinlänglich vorbereitet ist." (*J. pr. Chem.*, 1853, 59, 1.)

are quite stable. The chief condition in making such solutions is to have the silicic acid in as fine a state as possible, and to keep it in statu nascendi until it is being prepared for dissolving up."

The researches of Crum (1853) and of Péan de Saint Gilles (1854) on the hydrolysis of aluminium acetate and ferric acetate come next. In the former case Crum obtained pure aluminium hydroxide sol by heating the dilute solution for ten days in a closed vessel, and boiling off the acetic acid in shallow basins. He failed to do the same with ferric acetate, but Péan de Saint Gilles succeeded in the following year, although he was unable to get rid of all the acetic acid. Both of them carried out precipitation reactions with neutral salts.

Then with Graham's comprehensive researches on dialysis and its application to the purification of sols, and on the preparation of the impure sols by peptisation, by washing out, by double decomposition between salts, and by the action of acids on soluble salts, as silicates, stannates, etc. (1861–1864), we enter on the period when colloid chemistry was recognised as a special branch of science. The historical development of each special department is briefly outlined in the text.

The treatment of the subject falls naturally into three divisions—the general properties of colloids (sols and gels); the methods of preparation, and the factors which govern the production and stability of colloids; the connection between the properties of colloids and surface phenomena, including in particular surface concentration and adsorption in gases and solutions. If justification is needed for dealing with the properties of colloids before detailing the methods of preparation, it may be found in the fact that although obviously colloids were obtained or

prepared before their properties could be ascertained, the latter were earlier made the object of scientific investigation. Thus, while at first the production of a new colloid was of the nature of an accident, their general behaviour was well made out on these natural or accidentally discovered colloids. Not until these general properties had been recognised did it become possible to treat systematically the methods by which colloids might be produced and preserved. This, indeed, has only been done within the last few years by von Weimarn. The order adopted in the text is therefore—

I. The General Properties of Colloids (sols and gels).
II. The Methods of Preparation.
III. Surface Phenomena and Adsorption.
IV. Applications of Colloid Chemistry.

CHAPTER II

GENERAL DIFFERENCES BETWEEN SUSPENSOIDS AND EMULSOIDS

Introduction.—Suspensoids are usually defined as sols in which the disperse phase is solid, while in emulsoids it is liquid, the dispersion medium being in each case liquid. Now this alone will not account for all the divergences between them. It is, indeed, not impossible that in both the disperse phase is liquid. Apart from the theoretical considerations, based on the optical behaviour,[1] which are in favour of spherical particles, there are many facts which point to the same conclusion.

In many of the methods of preparation, there is every scope for Ostwald's "Rule of the appearance of the least stable form." As has been shown time and again, when a *new phase*, which is finally solid, makes its appearance suddenly, whether from vapour or solution, it appears first as a liquid; it may run through many intermediate (labile) forms before reaching its final solid form. Sulphur, for instance, forms globules, which crystallise later. Crystallisation as spherolites is well known. Even in the case of some metals, *e.g.* burnished gold, silver, the surface layer has been found to be of the nature of a liquid film.[2]

The difference must, therefore, be sought elsewhere. Quincke long ago expressed the opinion that what we

[1] Maxwell Garnett, *Phil. Trans.*, 1904, **203**, 385; 1906, **205**, 237.

[2] Beilby, *Proc. Roy. Soc.*, 1903, **72**, 218.

now call emulsoids were two-phase liquids, each of which contained both components. Gelatine sols contain amicrons only at high temperatures, while submicrons appear at lower temperatures; the same occurs with agar sols. Hardy[1] investigated agar, and found that, by pressing out liquid from the gel, two phases were obtained, which contained agar in different amounts, *e.g.*

Agar gel (2·23 per cent. agar).

	Concentration of Agar.	
Temp.	Liquid.	Solid.
36°	0·47	3·2
13°	0·12	4·7
5°	0·09	3·0

Spiro also regarded the "salting out" of albumin as a separation into two liquid layers, each of which contained all three components, but in different proportions.

In suspensoids, on the other hand, we have a disperse phase, solid or liquid, which does not combine with the dispersion medium, and is practically insoluble in it, *e.g.* the metals, sulphur, metallic sulphides, etc. The hydroxides can combine, more or less, with water, and are more like emulsoids in many respects.

Emulsoids may then be regarded as intermediate between suspensoids and solutions, and may in some cases be solutions of substances of high molar weight. Some evidence of this will be found below (see *e.g.* Optical Properties). The behaviour of silicic acid also points in the same direction; when first made by the action of hydrochloric acid on water glass, it is in true solution, as shown by its optical properties and its diffusion. Graham found that 5 per cent. dialysed away in 24 hours, and that no further loss occurred in the next four days.[2]

[1] *Proc. Roy. Soc.*, 1900, **66**, 95.

[2] *Phil. Trans.*, 1861, **151**, 183.

The soluble acid changes with time into a sol, in which Zsigmondy found amicrons only. Even this diffuses to some extent (see below) and has a distinct osmotic pressure; its viscosity, too, increases continuously until gel is formed. Many dyes exhibit similar anomalies; methyl violet diffuses rapidly through parchment paper, but has abnormally high molar weight, and, in the ultramicroscope shows a light cone together with a few submicrons.

Many other instances might be given, in which there are evidences of the existence both of solution and of sol, but one more must suffice. Casein is an acid substance, insoluble in water. It combines with a fixed proportion of alkali, and is then soluble. This solution possesses a good electric conductivity, which changes normally with dilution, but it does not diffuse through parchment paper. Its molar weight, based on its conductivity and its combining weight with sodium hydroxide, is estimated [1] at 5000; a substance with this molar weight should diffuse fairly well (see below).

This fundamental difference between suspensoids and emulsoids finds expression in many of their general properties, and most of all, in those properties which undergo marked changes as the result of solution; such are density, viscosity, and surface tension.

Density.—The density of suspensoids can be calculated by the law of mixtures, as Linder and Picton [2] proved for arsenious sulphide sol.

	Density	
As_2S_3 (per cent.).	Observed.	Calculated.
4·4	1·033810	1·033810
2·2	1·016880	1·016905
1·1	1·008435	1·008440
0·01719	1·000137	1·000134

[1] Sackur, *Zeitsch. physikal. Chem.*, 1902, 41, 672.
[2] *Chem. Soc. Journ.*, 1895, 67, 71.

The densities of emulsoids do not appear to have been determined accurately, but *contraction* occurs when gelatine and starch take up water (*i.e.* the volume of starch + volume of water > volume of sol). When a ferric hydroxide sol is precipitated, there is a slight dilatation,[1] whereas the volume of an arsenious sulphide sol is unchanged.

According to Gayda,[2] the density of albumin is 1·299 ; a volume contraction takes place on solution, and also a slight contraction on dilution of a concentrated solution. Chick and Martin[3] give the density of dry casein as 1·318, the density of a 7·85 per cent. sol is 1·024, which gives 1 39 for dry casein. Similar results were obtained with egg albumin and serum albumin.

Surface Tension.—Linder and Picton found the surface tension of arsenious sulphide sol and ferric hydroxide sol to be the same as that of water, and the same is true for metal sols.

The surface tension of emulsoids is, in many cases, much smaller than that of water. Quincke[4] gives numerous examples; thus, the surface tension of dilute sol of egg-white is 28 per cent., and of gelatine 12 per cent. less than that of water.

In accordance with this difference, suspensoids are not adsorbed, as a rule, while emulsoids usually are. (See Adsorption, Chap. XVI.)

Viscosity.—As the concentration of most suspensoids is small (Zsigmondy's gold sol 0·12 per cent., arsenious sulphide sol 4·4 per cent.; these are maximum concentrations; metal sols are usually below 0·05 per cent.

[1] *Chem. Soc. Journ.*, 1895, **67**, 71.
[2] *Biochem. Zeitsch.*, 1912, **39**, 400.
[3] *Koll. Zeitsch.*, 1913, **12**, 69.
[4] *Wied. Ann.*, 1885, [Iii] **35**, 582.

and the others below 1 per cent.), their viscosity is not likely to differ greatly from that of the dispersion medium. On precipitation, the viscosity is usually found to be *slightly decreased.*

The concentration of emulsoids is not so restricted, and their viscosity is often much greater than that of the medium; it also steadily increases with increase of concentration, as the following figures[1] show:—

Sol	Concentration	t	Viscosity
Gelatine . .	1 %	20°	0·021
„ . .	2 „	„	0·037
Egg-white .	1·6 „	17·5°	0·0115
„ .	2·9 „	„	0·0125
Silicic acid .	0·81 „	20°	0·012
„ .	0·99 „	„	0·016
„ .	1·96 „	„	0·032
„ .	3·67 „	„	0·165

The viscosity of water at 17·5° is 0·0126, and at 20° it is 0·0120. Pauli[2] gives the viscosity of 1 per cent. albumin as 1·068 (water = 1). As both these results for albumin were obtained by the capillary tube method, it is not easy to reconcile the differences found for albumin. The swinging disc method applied to emulsoids is known to yield values which are invariably higher than those by the capillary tube method. The difference may amount to 10 per cent. This and other peculiarities of the results of the swinging disc method are explicable on Quincke's assumption, which Garrett also adopts, of two liquid phases, each containing both components.

Ferric hydroxide sols also give a difference in viscosity, as determined by these methods.

Pauli observed that the viscosity of albumin sols is

[1] Garrett, *Dissertation*, Heidelberg, 1903, p. 51.

[2] *Kolloidchemische Studien am Eiweiss*, 1908, p. 3.

diminished by small amounts of neutral salts (Fig. 1), while it is greatly increased by both acids and alkalies. It is increased 18 per cent. by 0·01n HCl, or by 0·03n.

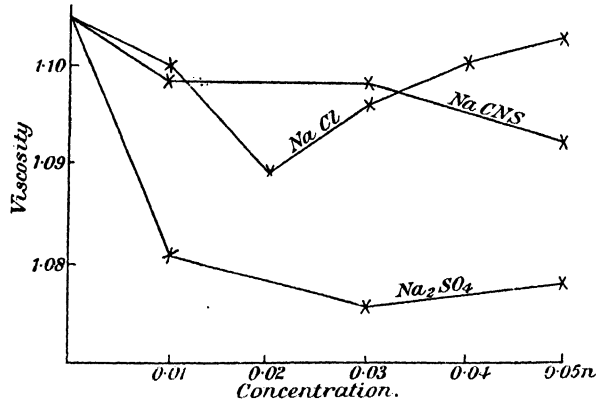


FIG. 1.

NaOH. The effect of neutral salts is attributed to adsorption, that of acids and alkalies to chemical changes (in the direction of solution).

There are, according to Wo. Ostwald,[1] several other factors affecting the viscosity of emulsoids, *e.g.* dispersity, hydration or solvation of the particles, electric charge, previous thermal or mechanical treatment, addition of small amounts of more viscous sols, and time (p. 121).

Hatschek assumes that part of the dispersion medium is bound by the disperse phase; this leads to $\eta' = \eta(1 + \alpha c + \beta c^n)$. As Wo. Ostwald[1] points out, this is in agreement with the solvation theory, which leads to a similar expression for the osmotic pressure of emulsoid sols.

[1] *Koll. Zeitsch.*, 1919, **24**, 7.

CHAPTER III

DIFFUSION AND DIALYSIS

In the course of his experiments on liquid diffusion, Graham found that solutions could be divided into two classes, according to their rates of diffusion. Salts and crystalline substances generally (*crystalloids*) had diffusion coefficients of the same order, while certain non-crystalline organic substances (*colloids*), as starch, gum, gelatine, etc., and some inorganic substances, diffused at a very slow rate, or not at all. The division was not very rigid, for the rates of diffusion in each class varied within wide limits.

On extending his investigations to the diffusion of solutions into a gelatine gel, he found the two classes were more sharply differentiated, in that the diffusion of crystalloids in the gel was practically the same as in water, whereas that of the colloids was reduced to a very small amount, and in most cases was entirely prevented. Thus, the diffusion of a 10 per cent. solution of sodium chloride into water, and into a 2 per cent. gelatine gel were the same, as the following figures show:—

Number of layer.	Water 7 days at 9°.	2% gelatine 8 days at 10°.
1–2	0·030	0·030
3–4	0·079	0·061
5–6	0·215	0 212
7–8	0·529	0·562
9–10	1·100	1·116
11–12	1·907	2·168
13–14	2·844	2·393
15–16	3·294	3·450

Caramel, on the other hand, had scarcely begun to diffuse into the gelatine at the end of 8 days, so that no similar table for it is possible. Gelatinised starch, gum, and coagulated albumin, also had very little effect on the rate of diffusion of crystalloids.

It will be noticed that the two series of figures are by no means identical, or even parallel, although Graham concluded from them, and from other similar results, that diffusion of crystalloids is not hindered by gels.[1]

In the further modification of the diffusion experiment suggested by these results, the solution is separated from the pure solvent by a thin layer of colloid, such as a sheet of parchment paper or animal membrane. The differences between crystalloids and colloids were again observed, and in a more marked degree. The former readily diffused through such a septum, frequently with undiminished velocity, while the diffusion of the latter, already small, was still further reduced. The connexion between the two phenomena is clearly shown by the figures below, compiled from Graham's results:—

Substance.	Times of equal Diffusion.	Amount dialysed in equal times.
Sodium chloride	1	1·0
Ammonia	0·6	0·85
Alcohol	2	0·47
Glucose	3	0·36
Cane sugar	3	0·47
Gum arabic	7	0·008
Tannin	11	0·015
Albumin	21	0·003
Caramel	42	0·005

This process, which obviously permits of the convenient separation of crystalloids from colloids, is known

[1] Graham, *Experimental Researches*, p. 598.

as *dialysis*. The apparatus employed by Graham consisted of a short, wide glass cylinder, or of a wooden hoop, on which was tied a sheet of bladder, or of parchment paper. The dialyser was floated in a larger vessel containing water, which could be renewed from time to time. This form of dialyser is not at all convenient. The interface, on which the rate of dialysis must depend, is relatively small; again, the solutions to be dialysed, frequently of a very unstable nature, are exposed to atmospheric influences for prolonged periods.

Various practical forms of dialyser are now obtainable. Tubing of parchment paper may be had in any length, and is obtainable from any instrument dealer. It should always be tested for leaks, which can usually be closed up with gelatine, or with white of egg, which is then coagulated by heat. Before use, the tubing should be well purified by soaking it, inside and outside, in many changes of pure water. Inattention to this important detail is accountable for many undesired results, especially in the dialysis of sols which are coagulated by minute traces of certain salts. In the dry state the tubing is liable to crack, and should be well soaked before use. It can then be bent into a U, and placed in a beaker; if the U-tube projects a little above the edge, a slow stream of water can be run through the beaker. With the large surface and the constant renewal of the water, dialysis is rapid. As the ends can be closed with corks, or folded together, the risk of contamination or decomposition is much reduced.

For small quantities of substance, and for substances like albumin, parchment paper thimbles, as made by Schleicher and Schull, are very convenient. They may be mounted in the following way: slip the open end over a carefully fitted glass tube, fixing it by means of a short

piece of good rubber tubing. This joint is quite waterproof, and the rubber does not come in contact with the substance. The tubes are clamped in a beaker, so that the thimble is completely immersed; the water is constantly renewed in the beaker. The whole tube can be sterilised and the glass ends can be plugged with antiseptic cotton wool. With these thimbles the author has dialysed crystallised egg albumin until it was electrolyte-free, without fermentation occurring, even in summer.

Recent investigations have shown that parchment paper is not the most efficient septum. It is slower, and may not only retard the diffusion of the crystalloids, but may also allow the colloid to escape. Collodion films, if suitably prepared, are highly efficient, effecting separations more completely in much less time than does parchment paper. They should be made when required, and can be made of any desired size or shape; the degree of permeability can also be varied to suit given requirements, by a simple alteration in the manipulation. Full instructions and bibliography are to be found in a paper by Bigelow and Gemberling;[1] but the following details will enable anyone to make them.

The collodion solution is made as follows: 75 c.c. of ether are poured over 3 g. of commercial pyroxylin in a corked flask; in 10–15 minutes 25 c.c. of ethyl alcohol are added. The pyroxylin dissolves quickly and completely to a clear liquid, which does not require filtration.

To make a sheet, pour a few c.c. of the solution on a clean, dry glass plate, and spread it by tilting to and fro. Allow the layer to dry until it is gelatinous, and will bear lightly rubbing without wrinkling. Loosen the edges, and peel off. Plunge into water. Larger sheets of uniform

[1] *Amer. Chem. J.*, 1907, **29**, 1576.

thickness can be made by pouring the collodion on to a surface of mercury in a shallow dish.

To make a collodion sac proceed as follows: A small orifice, 1–2 mm. in diameter, is blown in the bottom of a tube of the desired diameter. This hole is closed with one or two layers of collodion, none of which should go inside the tube. This can be done by touching the bottom of the tube with a cork wet with collodion, allowing a portion of the solvent to evaporate, and repeating as often as necessary. The tube is then coated with collodion by rotating it on the surface of the collodion, which is in a tilted vessel. The tube is exposed to air until the coating has "set," and does not stick to the finger; it is then plunged into water, and water is also poured into the tube. If it is immersed too soon, the film is white, opaque, and brittle; if too late, the film cannot be removed without injury. The proper time, between 2–15 minutes, depends mainly on the consistency of the collodion; it is easily found after a few trials. The sac is removed by blowing into the tube and gently pulling the membrane; this forces water through the orifice and between the sac and tube. They can easily be made up to 40 cm. by 2–3 cm.

A very convenient and effective collodion dialyser is obtained by soaking a dried Soxhlet thimble in the above collodion solution, allowing it to set, and plunging it into water. The thimble is cemented to a glass tube by means of collodion, and is then inserted in a glass tube which just admits the thimble. Highly pure water is run in at the bottom of the jacket at a very slow rate, and escapes by a side tube close to the top. Dialysis is very rapid and complete; *e.g.* the electric conductivity of a ferric hydroxide sol, prepared by Kreke's method (p. 199), fell in 2–3 days to a value much lower than any hitherto recorded.

For dialysis to be rapid and at the same time efficient, as also in the case of ultrafiltration, the permeability of the collodion should be adjusted to the particular sol for which it is to be used. In the above process this is attained by varying the time before plunging the film into water. Probably the method of W. Brown [1] is the most satisfactory one yet introduced. So soon as the 4 per cent. (alcohol-ether) collodion film has begun to set (whether formed on a glass tube or impregnated in a filter paper capsule), it is immersed in aqueous alcohol of definite concentration, and left there for some hours. The greater the concentration of alcohol the more permeable is the film. So uniform is the permeability regulated by this means that the alcohol percentage can be used as an index.

The method of preparing ultrafilters described by Wo. Ostwald [2] (p. 58) ought readily to be adaptable to both dialysis and osmotic pressure determinations.

Time of Dialysis in days.	Specific Conductivity ($\kappa \times 10^6$).		
	Gold-beater's skin.	Collodion.	Parchment paper.
0	984	984	984
1	305	416	850
2	81	208	463
4	55	102	256
5	30	85	159
10	23	26	47
12	11	21	43
17	8	11	15
19		11	11

A comparison of the efficiency of collodion, parchment paper, and gold-beater's skin will be found above. The last-named material is the best yet used for dialysis, and parchment paper is the worst, although it still seems to be the one most frequently employed. As a test, a Zsigmondy gold sol was dialysed in three dialysers of identical

[1] *Biochem. J.*, 1915, **9**, 591: 1917, **11**, 40. *See also* Walpole, *ibid.*, 1915, **9**, 284.

[2] *Koll. Zeitsch.*, 1918, **22**, 72; 1918, **23**, 68.

pattern and size, the septa being gold-beater's skin, collodion, and parchment paper. The rate of dialysis was followed by determining the specific conductivity (κ) every 24 hours.

The undoubted superiority of gold-beater's skin is obvious. If a time-conductivity curve is drawn, counting in each case from the conductivity 11, it will be seen that it takes about the same time (6–7 days) in each case to reduce the conductivity from 30 to 11, all the differences occurring in the earlier stages of dialysis.

Membranes made from pure samples of collodion are more durable, and also more permeable, than those made from commercial samples. In any case, the permeability decreases with age, but, as a rule, a film is useful for one to three months.

Dialysis is the basis of one of the general methods of preparing sols. It was also for a long time the generally accepted criterion of a sol, *i.e.* a substance, which to all appearance was in solution, but yet was unable to diffuse through a dialyser, was classed as a colloid, and the apparent solution as a sol.

It should be particularly observed that Graham's results do not show that, as has occasionally been assumed, there is *no* diffusion and dialysis of sols. Though his classification into crystalloids and colloids is based upon the differences between them in this respect, he everywhere gives figures for the dialysis and diffusion of colloids; indeed, in the same paper he states in this very connexion, "in nature there are no abrupt transitions, and distinctions of class are never absolute."

It may have been convenient to disregard the transitions, and to regard colloids as non-diffusible, but recent, more accurate investigation has confirmed the correctness of Graham's view, and his experimental results, qualita-

tively at least. Thus, Linder and Picton[1] found that an arsenious sulphide sol diffused to a considerable extent. After 11 days, the outer vessel contained 0·1185 g. of arsenious sulphide in 350 c.c. of water, and the inner cylinder contained 0·8210 g. in 77 c.c. Further experiments with carefully purified sols gave similar results. Again, in another direction, Bechhold and Ziegler[2] have found that the diffusion of both electrolytes and non-electrolytes is diminished by gels, the effect depending on the concentration of the gel. The addition of various substances to the gel causes further alteration in the rate of diffusion; some, *e.g.* sodium sulphate, reduce the diffusion still further, others, as urea, increase it. As many other properties of gelatine (and other gels) are changed in opposite directions by these substances, this is probably another illustration of this influence (see Lyotrope series, pp. 7 and 125).

Finally, the presence of crystalloids in a sol often has a marked influence on the dialysis of the sol. For instance, a silicic acid sol will diffuse through parchment paper if mixed with sodium chloride. The fairly rapid diffusion of some sols may be due to this influence. The disperse phase will adsorb small amounts of the crystalloids, and their presence may cause diffusion. Linder and Picton noticed that an arsenious sulphide sol, to which a soluble tartrate had been added, diffused appreciably into water, although the particles were so large as to be just visible under the microscope. Or, perhaps, this also may be another instance of lyotrope influences.

The theory of the Brownian movement leaves no room for doubt that sols diffuse, the difference between colloids and crystalloids being one of degree only.

[1] *Chem. Soc. Journ.*, 1892, **61**, 187.
[2] *Zeitsch. physikal. Chem.*, 1906, **56**, 105.

CHAPTER IV

OSMOTIC PRESSURE AND MOLAR WEIGHT

CLOSELY connected with the question of dialysis is that of osmotic pressure, for, as is well known, direct measurement of osmotic pressure depends on the impermeability of the membrane by the solute, while the solvent can freely pass through it. The most important application of the laws of osmotic pressure is to the determination of the molar weight of soluble, non-volatile substances. This was done by van 't Hoff, who proved that the gas laws could be quantitatively applied to *dilute* solutions, osmotic pressure taking the place of gas pressure, and volume of solution the place of gas volume. Thus the formula for calculating molar weights, which was previously limited to gases and volatile substances, was at once extended to all soluble substances.

But before entering into details of the osmotic pressure of sols, and the attempts to deduce the molar weight of colloids from the related methods of depression of freezing point, etc., it is of interest to note that Graham, from purely chemical considerations—for these other methods were not known until twenty years later—had been led to assign high molar weights to colloids. It seems not at all unlikely that this idea, thus early expressed, dominated later research in this direction for many years.

From the fact that sols of ferric hydroxide and aluminium hydroxide, prepared by dialysis of the basic chlorides, could not be entirely freed from chloride, however prolonged the dialysis, Graham[1] concluded that they were compounds of (condensed) bases of very high molar weight, and deduced the chemical equivalent of the base in the usual manner from the ratio of base to acid, which he had found to be approximately constant. After 19

[1] Graham, *Experimental Researches*, pp. 582, 596.

days' dialysis, there was one equivalent of HCl to 30·3 of Fe_2O_3; after 38 days there was one equivalent of HCl to 31·2 of Cr_2O_3; similar ratios were found for other similar sols (see p. 108). Similarly, the gels of silicic acid and stannic acid are dissolved by very small quantities of alkali, *e.g.* 1 part of sodium hydroxide liquefies 200 parts of silicic acid gel, and the acid reaction of 100 parts of the latter is neutralised by 1·85 parts of potassium oxide.

These compounds of acids or bases of high chemical equivalence were distinguished by the prefix "colli" or "co." Graham suggested that "the basis of colloidality may really be this composite character of the molecule."[1]

Osmotic Pressure.—Pfeffer, in his classic researches on osmotic pressure, gave measurements of the pressure of some sols. The values are small in comparison with those for other substances. Thus the pressures of 1 per cent. solutions of the following substances[2] are—

Potassium sulphate .	193	cm. mercury	
„ nitrate . .	178	„	„
Cane sugar	47	„	„
Dextrin	16·5	„	„
Gum arabic	7·2	„	„

That this is a real pressure, in the case of gum at least, is supported by the proportionality between concentration and pressure, as the following figures show:—

c	p	p/c
1	7·2	7·2
18	119·7	6·7
„	120·4	6 9

Whether this is to be ascribed to the colloid itself, or to impurities not completely removed from it, has long been a debatable question. On the one hand, there should be less difficulty in determining the osmotic pressure of sols than of solutions, for it is clear that semi-permeable membranes are much more impermeable by colloids than

[1] Graham, *Experimental Researches*, pp. 582, 596.
[2] *Osmot. Untersuchungen*, Leipzig, 1877.

by electrolytes or ordinary solutes. This difference would lead to dialysis of the impurities, in consequence of which the osmotic pressure would steadily fall during the experiment. Further, a sol prepared in different ways, and possibly containing different impurities, would be expected to have different pressures, according to the nature of the impurities.

This is not at all what is observed. Different preparations of a sol may have different initial osmotic pressures, but they fall to the same final value, which is not zero, but a definite positive value. It is usually small, but is too large to be put down to experimental error. It may be due to a small residue of electrolyte or other active solute which cannot be removed by dialysis, but in this case it must be regarded as something other than an impurity, rather as an essential constituent of the sol (see p. 108).

According to Einstein,[1] the osmotic work varies directly as the *number* of particles, whether ions, molecules, or particles, in unit volume; therefore 6×10^{23} particles (Avogadro's number) in 1000 c.c. of dispersion medium will give an osmotic pressure of a molar solution, *i.e.* of 22·4 atmospheres. Svedberg[2] estimates that to have this osmotic pressure a gold sol, with particles of 1 $\mu\mu$ would contain 50,000 g. of gold in 1000 c.c.; or that a 1 per cent. gold hydrosol, with particles of 1 $\mu\mu$, is a 1/200,000 molar solution, corresponding to an osmotic pressure of 0·00045 atmosphere = 0·34 mm. mercury.

Suspensoids. — Direct measurement of the osmotic pressure of suspensoids gives very variable values, which are always small. The reason for this want of concordance is not very apparent. Perrin's experiments[3] on the arrangement of the particles of a gamboge sol under the action of gravity and its own osmotic pressure, based upon the kinetic theory, afford an estimate of the osmotic pressure, since all the other factors are known. The relation is $\log \frac{n_0}{n} = \frac{1}{k} mgh \left(1 - \frac{1}{\rho}\right)$, where n_0 and n are the

[1] *Ann. Physik*, 1905, [iv.] **17**, 549. [2] *Ber.*, 1914, **47**, 23.
[3] *Compt. Rend.*, 1908, **146**, 967; 1908, **147**, 530.

number of particles in unit volume in the layers at the heights 0 and h, m is the mass and ρ the density of the particles, g is the gravity constant, and k is the osmotic pressure of a single particle in unit volume. The value of k is 43×10^{-15}. On the assumption that this is the same as the pressure exerted by the particle as a gas or solute, $k = \frac{RT}{N}$, N being the number of molecules in a mol (6×10^{23}). If R is calculated from these values, it comes to 2·1 cal. (instead of 1·98 cal.). The molar weight of gamboge calculated from these data is 3×10^9.

If use is made of Thovert's [1] relation, $M \times D^2 = \text{constant}$ (60×10^{-10}), the molar weight of arsenious sulphide calculated from the diffusion constant $0{\cdot}1 \times 10^{-5}$ is over 6000.

Emulsoids.—The molar weight of albumin calculated in the same way from Graham's value of $D = 0{\cdot}07 \times 10^{-5}$ at 13° is 13,000. This molar weight corresponds to an osmotic pressure of about 7 mm. mercury (= 100 mm. water), which ought to be measurable. With the greater diffusion of emulsoids in general, there is also a greater osmotic pressure, and recently direct measurements have been made. The osmometer membrane is usually collodion or parchment paper. Convenient forms of apparatus have been described by Moore and Roaf,[2] Bayliss,[3] and Fouard.[4] The following results may be of use:—

Sol.	Concentration. g. per litre.	Osmotic pressure. mm. mercury.	Molar weight.
Egg albumin [5] . . .	12·5	20	11,000
Gelatine [5]	12·5	6	36,000
Starch iodide [6] . . .	30	15	34,000
Dextrin [7]	10	165	1,000
Gum arabic [7]	10	72	2,400

Probably the best values are obtained from the diffusion-constants and the above relation of Thovert. The

[1] *Compt. Rend.*, 1901, **133**, 1197; 1902, **134**, 507; 1902, **135**, 579.
[2] Moore and Roaf, *Biochem. J.*, 1906, **2**, 34.
[3] Bayliss, *Proc. Roy. Soc.*, 1909, **81B**, 269.
[4] Fouard, *Bull. Soc. Chim.*, 1911, **9**, 637.
[5] Lillie, *Amer. J. Physiol.*, 1907, **20**, 127; see also Moore and Roaf, *Biochem. J.*, 1906, **2**, 34.
[6] Rodewald, *Zeitsch. physikal. Chem.*, 1900, **33**, 586.
[7] Pfeffer, *Osmot. Untersuchungen*, Leipzig, 1877.

diffusion constants of several albumins and enzymes have been accurately determined by Herzog.[1] The results are as follows :—

Substance.	D at 18°.	M.W. $= \frac{59{\cdot}2}{D^2}$
Egg albumin . .	0·059	17,000
Ovomucoid . . .	0·044	30,000
Clupein sulphate .	0·074	11,000
Pepsin	0·070	12,000
Lab	0·066	14,000
Invertin	0·033	54,000
Emulsin	0·036	46,000

The osmotic pressure of emulsoids has been shown by Wo. Ostwald and Mündler[2] to be complicated by the imbibition pressure, the observed pressure being made up of the real osmotic pressure, and that due to combination with the dispersion medium (solvation). The general formula is $P_{obs} = P_0 + P_2 = RTc_1 + Kc_2^n$. In agreement with this, Biltz[3] found that the molar weight of tuch-rot in 0·013 to 0·039 per cent. solution, varied irregularly between 940 and 2200, while the direct osmotic pressure of gelatine varied 10–20 per cent. The molar weight of dyes, dextrin, etc., calculated from the osmotic pressure, systematically increases instead of decreasing, as is the case with sugars, etc. This is ascribed to internal changes of condition, formation of aggregates, *i.e.* decreased dispersity, or to the affinity for water (solvation) being less than the affinity for other particles (aggregation). There may be a minimum value of c/p at moderate concentrations, as in the case of Prussian blue, gum arabic, achroodextrin.

The value of n is usually near 2 ; for various dispersoids it is—

Ferric hydroxide	1·5	Laminaria + H_2O . . .	4·1
Thorium „	2·3	Gelatine + H_2O	3·1
Copper ferrocyanide . .	1·6	Sucrose	1·8–2·3
Congo blue	1·3	Glucose	1·9–2·5
Rubber	2·5–3·3	Lactose	3·0

Freezing Point, Boiling Point, Vapour Pressure.—It is

[1] *Zeitsch. Elektrochem.*, 1907, **13**, 533.
[2] *Koll. Zeitsch.*, 1919, **24**, 7.
[3] *Zeitsch. Physikal. Chem.*, 1911, **77**, 91 ; 1913, **83**, 625 ; 1916, **91**, 705.

quite evident from the above estimates of molar weights, that it is useless to apply the ordinary molar weight methods to sols. Taking the freezing-point method as the most accurate, and the one which gives the largest number to be determined, an osmotic pressure of 9 mm. mercury (= 125 mm. water) corresponds to a freezing-point depression of only 0·001°. Owing to the nature of these emulsoid sols, the experimental error is certainly much larger than in ordinary cases, and, obviously, large concentrations would be necessary to give a readable depression. The question then arises how far such concentrated sols can legitimately be considered to be dilute. The determination of the boiling point or of the vapour pressure of these sols is attended with quite unusual difficulties, the nature of which need not be specified, the more so as no useful estimate of molar weight is afforded by them. In particular solvatised colloids, as starch, gelatine, have abnormally small depressions of freezing point, boiling point, and vapour pressure.

CHAPTER V

OPTICAL PROPERTIES

Macroscopic Observations.—The heterogeneity of a coarse suspension is usually at once apparent to the unaided eye, because of its opaque appearance in transmitted and in reflected light. As the size of the particles decreases, so too do these effects. We thus have all gradations between opacity and absolute transparency, when judged by the naked eye. Frequently, however, the heterogeneity is still observable when a powerful beam of light is sent through the liquid. This was noticed by Faraday[1] to be the case with the gold sols prepared by him. When the sol appears to be quite clear in ordinary light, the appearance, when a concentrated beam of light is sent through it, is similar to fluorescence. It differs from fluorescence in that the light is polarised in its passage through the liquid, which is not the case with fluorescence.

Tyndall Effect.—This phenomenon is usually known as the Tyndall Effect, as Tyndall[2] applied it first with good results in the case of dust and mist in the atmosphere. The light is mainly polarised in a plane normal to the path of the beam, but the amount of polarisation and the angle depend on the size of the particles. The extinction with a crossed Nicol prism is therefore only easily observed when the particles are of approximately

[1] *Phil. Mag.*, 1857, [iv.] **14**, 401, 512.

[2] *Phil. Mag.*, 1869, [iv.] **37**, 384; *Proc. Roy. Soc.*, 1869, **17**, 223.

uniform size, and the corresponding angle sought out. If the particles are below 100 $\mu\mu$ in diameter, the polarisation is complete, and the angle is 90°. The Tyndall Effect is easily seen if a small rectangular slit is placed in the focus of a projecting lantern (arc by preference), and the beam is passed through a sol in a rectangular glass tank. By rotation of a mounted Nicol, such as is used for demonstration purposes in physics, the polarisation is readily detected in a Zsigmondy gold sol, or in a good arsenious sulphide sol. For the reasons given above, the clearer the sol is to the naked eye, the better it is for this purpose. Even if there is not complete extinction, the difference in luminosity as the Nicol is rotated is quite striking. The absence of polarisation in the case of fluorescent solutions (quinine bisulphate, very dilute eosin, or fluorescein) should be shown at the same time.

In the Tyndall Effect we have a powerful means of detecting heterogeneity, where even the best misroscope fails to reveal it. But its delicacy is in actual practice a drawback, for it is a difficult matter to obtain an "*optically void*" liquid. The ordinary processes of purification: filtration, distillation, are quite useless. The only certain way of freeing a liquid from accidental heterogeneous impurities is to produce a (colloid) precipitate in the liquid in a closed vessel; the settling out of the precipitate carries down all the other suspended matter.[1] Zinc hydroxide, ferric hydroxide, aluminium hydroxide, and barium sulphate are among the most efficient precipitates. This action is partly mechanical, partly a mutual precipitation of sols of opposite electric charge (p. 134).

Obviously this makes the application of the Tyndall Effect to the recognition of the heterogeneity of sols a

[1] Spring, *Bull. Acad. Roy. Belg.*, 1899, [iii.] 37, 174.

somewhat doubtful one. Spring's results show that aqueous solutions of salts of the alkalies and alkaline earths are optically clear, but that solutions of salts of aluminium, chromium, iron, copper, mercury, etc., are never so. The explanation is that these salts are hydrolysed, and the product is not a soluble basic salt, as is frequently assumed, but a hydrosol, probably of the basic hydroxide, as the Tyndall Effect disappears when acid is added. Lobry de Bruyn[1] maintains that the Tyndall Effect is produced whenever the molecules of solvent and solute are of markedly different size, in support of which he cites aqueous solutions of cane sugar and raffinose. Although they are usually regarded as crystalloids, the solutions show the Tyndall Effect.

Colour.—The colour of sols is in many cases very striking. Thus Faraday's gold sols varied from blue to a magnificent ruby red; other gold sols range from green to violet, silver sols yellow to green, platinum sols brown to black, arsenious sulphide yellow to orange, antimonious sulphide orange to red. As a rule, however, the colour of sols is bluish-white, *e.g.* sulphur and mastic, just as fine dust and mists in gases are bluish, in agreement with the theory developed by Rayleigh.[2]

Except in the case of dyes, emulsoids also are bluish in colour, *e.g.* starch sol.

The colour of the coloured sols seems to depend to some extent on the dispersity, as well as on the concentration of the disperse phase. The method of reduction, the amount of reducer added, or the rate at which it is added, produce different colours in both gold sols and silver sols. Similar changes can be produced by minute

[1] *Rec. Trav. chim.*, 1900, 19, 251.

[2] *Phil. Mag.*, 1871, [iv.] 41, 107, 274, 447; 1881, [v.] 12, 81; 1899, [v.] 47, 375.

quantities of electrolytes. These changes are usually put down to change in size, and, conversely, conclusions have been drawn as to the dispersity from the colour of the sol. Zsigmondy's investigations do not bear this out, as the following table shows. The sizes were estimated by the ultramicroscopic method (see p. 53).

Colour of Gold sol.	Average size in $\mu\mu$.
Rose	6
Deep red	10, 15, 18, 32
Violet-red	23, 32, 75
Violet	35, 95
Blue-violet	54
Dirty blue	30
Purple-red	38

It must be understood that all these sols were practically as stable as the original sol. They could be filtered, dialysed, and kept for indefinite periods without undergoing any appreciable change. Steubing's researches[1] confirm this result. He suggests that the shape of the particles is different, as the blue colours obtained by adding electrolytes are not the same as the colour of the original blue sols.

But Svedberg's observations[2] on the alkali metal sols in ethyl ether, given below, indicate a displacement of the colour towards the red (greater wave-lengths) with increased size of particles.

Colour of Ether Sols.

Metal.	Small particles.	Large particles.	Colour of metal-vapour.
Li	brown	brown	—
Na	purple-violet	blue	purple
K	blue	blue-green	blue-green
Rb	green-blue	green	green-blue
Cs	blue-green	green-blue	—

[1] *Ann. Physik.*, 1908, [iv.] **26**, 329.

[2] *Methoden z. Herstellung Koll. Lös.*, 1909, p. 481.

In pentane, sodium is reddish-purple, and potassium is blue at —70°, green-blue at higher temperatures. The colour is thus displaced in the same direction (towards the red) by increasing atomic weight.

Microscopic Observations.—As the limit of microscopic visibility is about 10^{-5} cm., a sol whose particles are less than about 0·15 μ will not be recognisable even with the best microscope (magnification 2250). Schulze [1] was unable to detect any particles in arsenious sulphide sol, while Linder and Picton [2] observed them in it, but not in antimonious sulphide sol. Zsigmondy [3] and Bredig [4] were unable to detect particles in their gold sols, even with the highest magnification.

Particles which are small enough to exhibit Brownian movement (10^{-3} cm.) and are yet visible under the microscope (10^{-5} cm.) are termed *microns;* those which fall below this limit are *submicrons.*

The Ultramicroscope.—There is a wide interval between the limit of microscopic visibility (0·15 μ) and molecular dimensions (0·00016 μ, the diameter of a molecule of hydrogen), within which fall the submicron sols and the true solutions, if the latter do not coincide with the lower limit. It is possible to explore this region by the aid of the Tyndall Effect, but, as already explained, it is difficult to apply, owing to its sensitiveness and uncertainty as to the absence of accidental heterogeneity.

The ultramicroscope which renders ultramicroscopic particles visible, gets over this difficulty. Its lower limit, which is fixed by the intensity of the available light, is about 5 $\mu\mu$ (5×10^{-7} cm.), *i.e.* about 0·01 of a wave-length

[1] *J. pr. Chem.*, 1882, [ii.] **25**, 431.
[2] *Chem. Soc. Journ.*, 1892, **61**, 137.
[3] *Zur Erkenntnis d. Kolloide*, p. 79.
[4] *Anorg. Fermente*, p. 27.

of light. This gives the lower limit of size of *submicrons*. Smaller heterogeneous particles, whose existence is inferred on various grounds, are termed *amicrons*.

The principle of the ultramicroscope, on which the various forms of the instrument are based, is as follows: A very thin layer of the sol is illuminated by a beam of light, and as the number of particles illuminated is small the light scattered by each one is not interfered with by that from the others; they are thus seen as coloured discs. To render these discs more readily visible, the field is kept dark, and, since the intensity of the scattered light varies as the intensity of the source of illumination, the latter is made as powerful as possible.

In the Siedentopf and Zsigmondy ultramicroscope the light from an arc lamp (or sunlight from a heliostat) is focussed on an adjustable micrometer slit, by means of which the dimensions of the beam can be varied at will to a known extent. The slit is focussed on a microscope objective, from which the beam passes in a horizontal direction through the observation cell. This was devised by Biltz, and is a rectangular chamber in a glass tube, with quartz glass windows on two adjacent sides, one of which faces the illuminating objective, and the other (upwards) the observing microscope. The illuminated layer is a few thousandths of a millimeter in depth. The light which is not scattered by the particles passes through the cell, and so a dark ground is secured.

The dark field is secured by a simple device in the Cotton and Mouton instrument. In it the beam is not directed horizontally through the cell, but in an oblique upward direction, so that the main beam is totally reflected at the upper cover glass. The drawback to it is that the illuminated layer is not in one plane, and its volume is not known.

The latest form, the cardioid ultramicroscope, deserves notice, owing to its greater simplicity in comparison with the original pattern. An extremely intense illumination of the particles, and a very dark ground are secured by the cardioid condenser, the principle of which is easily seen from Fig. 2. The Biltz chamber is replaced by a special microscope slide of quartz glass. A circular depression is ground in it to a uniform known depth of a few μ, with a deeper channel at the rim. A small drop of the

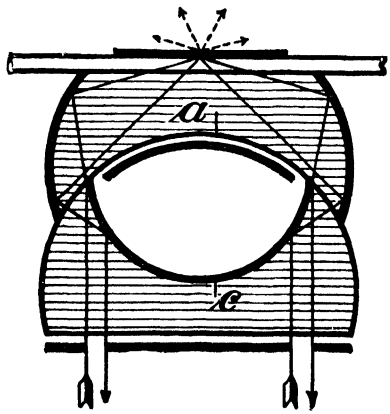


FIG. 2.

sol is placed in this depression, and the quartz cover placed over it. The excess of liquid flows into the channel, and so the illuminated layer of known uniform thickness is obtained. For general purposes of observing and counting the number of submicrons, this cell is most convenient, but for kataphoretic phenomena (*q.v.*) the proximity of the cell walls may be a disadvantage.

There are several forms of dark-ground microscopes, which dispense with the optical bench and horizontal illumination. The illumination is not very intense, and their utility is limited to comparatively large particles.

Ultramicroscopic Observations.—Moderately concentrated sols show as a rule only a brilliant cone of light, which, on dilution of the sol, is either resolved into a number of individual bright particles, or reduced in intensity until it disappears altogether. The former is usually associated with the presence of submicrons, the latter with amicrons. But there seem to be reasons for the belief that submicrons and amicrons are, to some extent and under some conditions, reversibly convertible into each other. The usual method of investigating a sol is to dilute it with an optically void dispersion medium, until the number of submicrons in the field of view can be counted, and to calculate from that the number of particles in the original sol by allowing for the dilution. Some recent work by Coward [1] on this point goes to show that this, in certain cases at least, may not be permissible.

Although emulsoids exhibit the Tyndall Effect, some indeed being opalescent in ordinary light, their ultramicroscopic character is not, as a rule, well defined. It may be, as Zsigmondy suggested, that the visibility of the particles depends on the difference between the refractive index of the disperse phase and medium. In the case of metal sols the difference is very great; it is not large in the case of most emulsoids. It is significant that the basic hydroxide sols are, ultramicroscopically, more like the emulsoids than the suspensoids. Other reasons have already been given for the view that they belong to the emulsoids. The ultramicroscope reveals the presence of a few submicrons with many amicrons. On dilution the light cone is gradually extinguished.

Submicrons have been observed in albumin, gelatine, glycogen, and agar sols. Zsigmondy [2] carefully examined

[1] *Trans. Faraday Soc.*, 1913, **9**, 142.

[2] *Zur Erkenntnis d. Kolloide*, p. 174.

a soluble starch sol; a 3 per cent. boiled sol contained amicrons only, but submicrons made their appearance after a time. They disappeared again on heating.

The ultramicroscope does not enable us to ascertain the colour of particles, as will be readily understood from the explanation of the principle of the instrument.

CHAPTER VI

BROWNIAN MOVEMENT [1]

In 1827 R. Brown,[2] the botanist, observed under the microscope that pollen grains, when suspended in water, were not at rest but in constant motion. They oscillated around a mean position, and the movements persisted without apparent diminution for an indefinite period.

This peculiar and characteristic movement appears to take place without exception, when a disperse phase of fairly high dispersity is suspended in a medium which does not unduly impede it. The upper limit of size is not very large, for particles of about 0·01 mm. diameter just show it. At this dispersity the movements are very slow, and the distances travelled are very small; they increase rapidly with increase of dispersity. At very high dispersity (submicrons) the purely oscillatory motion observed by Brown is partially replaced by a continuous irregular motion through the liquid along a series of zig-zag straight lines.

When Zsigmondy first observed this in gold sols by the aid of his newly discovered ultramicroscope, he was so impressed by this difference that he regarded it as something quite different from Brownian movement.[3]

The earlier investigators established the universality of this phenomenon, when a highly disperse phase is

[1] An interesting account of the theory of Brownian movement, and the size of particles (p. 55) will be found in a monograph by Perrin, *Brownian Movement and Molecular Reality*, 1910. *See also Compt. Rend.*, 1911, **152**, 1165, 1380.

[2] *Phil. Mag.*, 1826, **4**, 101; 1829, **6**, 161; *Edin. New Phil. Jour.*, 1828, **5**, 358; 1830, **8**, 41. [3] Zsigmondy, *Zur Erkenntnis d. Kolloide*, p. 107.

suspended in a medium which permits of the motion, *i.e.* whenever a solid, liquid, or gas is highly dispersed in a liquid of not too great viscosity, or when a solid or liquid is dispersed in a gas. The viscosity of the medium has a marked influence, as has also the temperature, increase of temperature increasing the path. In spontaneous suspension the Brownian movement overcomes the action of gravity, since a very fine powder covered with water becomes uniformly distributed through the water in course of time. Small quantities of alum, lime, acids caused the motion to cease in opalescent liquids, the particles clumping together.[1]

Many attempts at explanation were made, usually directed to fixing the cause of the motion on external influences, such as local heating, or absorption of light with one-sided heating, thus inducing convection currents, or impurities causing irregular changes in the surface tension between the particles and the liquid. Wiener,[2] Gouy,[3] and others succeeded in proving that the movement could not be ascribed to external influences. Its persistence in a preparation for years without apparent diminution is irreconcilable with the assumption of accidental or extraneous causes, as is also the reproducibility of the phenomenon, even quantitatively.

Wiener supposed it to be a consequence of the kinetic nature of heat, or, in other words, to be caused by the impacts of the smallest particles or molecules of liquids, which are in constant motion, on the microscopic grains. Similar explanations based on the kinetic theory have been put forward by Gouy,[3] Ramsay,[4] and others.

[1] Schulze, *Pogg. Ann.*, 1867, [ii.] **129**, 366.
[2] *Pogg. Ann.*, 1863, [ii] **118**, 79.
[3] *Physique*, 1888, **7**, 561; *Compt. Rend.*, 1889, **109**, 102.
[4] *Chem. News*, 1892, **65**, 90.

As seen in the ultramicroscope, the motion of submicrons is oscillatory and translatory. The two characteristics of the Brownian movement are (1) the *amplitude* A, and (2) the *period of oscillation* τ. The amplitude is the distance between the extreme and mean positions of the particle, and the oscillation period is the time taken by the particle to make a complete oscillation, *i.e.* to travel from the one extreme position to the other, and back again. The velocity v is then given by

$$v = \frac{4A}{\tau}$$

The amplitude depends in the first instance on the size. This is shown by the following figures given by Zsigmondy [1] for various gold sols.

Diameter (in $\mu\mu$).	Amplitude (in μ).
6	> 10
10	3–4 (also 20)
35	1–7

The relation between velocity and size of particle had been the subject of earlier inquiry. Exner [2] found for a gamboge suspension that, when the diameter varied from 0·4 μ to 1·3 μ, the velocity varied from 3·8 μ to 2·7 μ per second; with a diameter of 3 μ the motion was barely perceptible, and totally ceased when it was 4 μ. The velocities observed by Zsigmondy and Svedberg in metal sols are much greater, over 100 μ per second for particles between 10 $\mu\mu$ and 50 $\mu\mu$.

The only other factor of importance is the *viscosity* of the medium; neither the nature of the particles nor the other properties of the liquid appear to have much effect. This is fully established by Svedberg's extensive researches [3]

[1] Zsigmondy, *Zur Erkenntnis d. Kolloide*, p. 107.
[2] *Ann. Physik.*, 1900, [iv.] **2**, 843.
[3] *Zeitsch. Elektrochem.*, 1906, **12**, 853, 909.

on a series of platinum sols in water and organic liquids, prepared by his method (see p. 221). The sizes were between 40 $\mu\mu$ and 50 $\mu\mu$. An improved method of observation was employed by running the sol at a known slow rate through the observation cell. The particles are then seen as curves of light, the amplitude (A) and wave-length (λ) of which can easily be estimated by means of a micrometer eyepiece. The oscillation period τ is given by $\lambda qt/v$, v being the volume of sol passing across the area under observation, q, in the time t. As stated before, the mean velocity is $4A/\tau$. The following table shows the variation in the amplitude with the viscosity η of the medium.

Medium.	Amplitude. A in μ.	Absolute viscosity. $\eta \times 10^3$.	$A\eta \times 10^3$.
Acetone	3·1	3·2	9·9
Ethyl acetate . .	2·0	4·6	9·2
Amyl acetate . .	1·5	5·9	8·9
Water	1·1	10·2	11
n-Propyl alcohol .	0·7	22·6	16
Isobutyl alcohol .	0·6	39·3	24
Isoamyl alcohol .	very small	43·4	—
Glycerol	0	830	—

The approximate constancy of $A\eta$ shows that the *amplitude for any fixed size of particles is inversely proportional to the viscosity of the dispersion medium.*

The oscillation period, calculated as explained above, increases as the amplitude increases; thus $4A/\tau$ is a constant, and is independent of the nature of the dispersion medium. This is proved by the following figures of Svedberg:

Medium.	A (in μ).	τ (in sec.).	$4A/\tau$.
Acetone . . .	3·1	0·032	390
Ethyl acetate . .	2·0	0·028	290
Amyl acetate . .	1·5	0·026	230
Water	1·1	0·013	340
n-Propyl alcohol.	0·7	0·009	310

Theory of Brownian Movement.—We have already seen that any explanation based on outside sources of energy is untenable. The source of the energy of the movement must be sought within the system: it can only be seated in the particles or in the liquid medium. As far back as 1892, Ramsay[1] explained it by the impacts of the liquid molecules on the particles, *i.e.* the kinetic energy of the molecules of liquid is the source of the kinetic energy of the particles. The modern theories of Einstein[2] and of Smoluchowski[3] are based upon similar considerations. But if we assume, as there are grounds for doing, that there is continuity from coarse heterogeneity, through suspensions and suspensoids, to solutions (and to molecules), and if molecules, whether in a liquid or gas, are possessed of molecular motion, due to their intrinsic energy, it does not seem inconsistent to regard the Brownian movement of the larger particles of sols and suspensions as due to the same cause. That is, the movement of these particles is of the same nature and is due to the same causes as the movement of the liquid or gas molecules of the dispersion medium (which are usually supposed to cause it).

The application of the kinetic theory, however, has taken the line previously indicated, that the motion is caused by the impacts of the molecules on the particles. This at once gives the qualitative connexion between size and velocity; it also follows from it that the velocity of the particles is independent of their chemical nature. The objection that the molecular impacts will be so numerous, and therefore so evenly distributed that they

[1] *Chem. News*, 1892, **65**, 30.

[2] Einstein, *Zeitsch. physikal. Chem.*, 1907, **59**, 451; *Ann. Physik.*, 1905, [iv.] **17**, 549; 1906, **19**, 371; *Zeitsch. Elektrochem.*, 1907, **13**, 41.

[3] Smoluchowski, *Ann. Physik.*, 1906, [iv.] **21**, 756.

will neutralise each other and no motion result, is not valid, for the probability that at any given instant there will be a given excess of impacts in one direction has been shown to be very great. The objection would apply to the system over a long period of time, but the time of observation cannot be so regarded.

It is readily seen, too, that when the particles are very small, as in some of the gold sols, uni-directional impacts will rapidly increase, and the paths will be longer, will indeed become very similar to the paths of the molecules themselves. Thus, as Zsigmondy observed, the oscillatory movements give place to a rapid sequence of zig-zag straight lines.

The equation which Smoluchowski deduced is—

$$4A^2 = \frac{64}{27}\,\tau\,\frac{RT}{3\pi r\eta N}$$

in which A and τ are amplitude and oscillation period, η the viscosity of the medium, r the radius of the particles, and N the number of molecules in 1 gram molecule, R and T are the gas constant and absolute temperature.

Einstein, by different methods, arrived at the same formula, without the numerical factor 64/27. The comparison of the *amplitudes* observed by Svedberg with those calculated from the two formulæ is given below.

	Amplitude (in μ).			
	A_1	A_2	A_3	$\frac{A_1}{A_2}$
	observed	calculated		
Medium	Svedberg	Smoluchowski	Einstein	
Acetone. . . .	3·1	1·1	0·71	2·8
Ethyl acetate . .	2·0	0·68	0·44	3·0
Amyl acetate . .	1·5	0·58	0·38	2·6
Water	1·1	0·31	0·20	3·6
Propyl alcohol .	0·7	0·17	0·11	4·1

As the last column shows, the observed values are all about three times as large as the calculated ones, *i.e.* the formula is correct except for a numerical factor. The same, of course, is true of the other formula, as the two differ only by a numerical factor.

CHAPTER VII

THE SIZE OF PARTICLES AND ULTRAFILTRATION

Size of Particles.—Neither the form nor the size, nor even the colour, of the particles can be directly ascertained by means of the ultramicroscope, for what is observed is a disc of light. As already stated, Bredig [1] fixed the upper limit at 0·14 μ, which is the limit of visibility with the best microscope (mag. 2250). With this magnification he was unable to detect individual particles in his gold sols. The lower limit is fixed by molecular dimensions, which according to the kinetic theory is 0·00016 μ (for hydrogen).

Various estimates of the size, based on the effect of the particles on the passage of light through the sol, have been made, but since the advent of the ultramicroscope, they are of secondary interest.

The Siedentopf and Zsigmondy method [2] of determining the size is as follows:—Chemical analysis of the sol gives the mass m of the disperse phase in unit volume of the sol; the number of particles n in unit volume of the sol is obtained by a direct count of the number of particles in the illuminated volume of the sol in the ultramicroscope. This volume is fixed by the depth of the illuminating beam, and by the area of the field (micrometer squares) in

[1] *Anorg. Fermente*, p. 20.
[2] Zsigmondy, *Zur Erkenntnis d. Kolloide*, p. 93.

which the particles are counted. The volume v of the particle is given by—

$$v = \frac{m}{n\rho}$$

ρ being the density of the particle (the density of the substance in ordinary masses is taken). The linear dimension is calculated from the volume, on the assumption that the particle is a cube or a sphere. The dispersity of a sol is usually expressed in terms of the diameter, obtained in this way. It is better to use the *specific surface* for this purpose (see p. 227).

If the Brownian movement is rapid, it is easier to estimate the average distance between the particles than to count their number. The number can easily be calculated from this distance.

Observations on many sols lead to the conclusion that the size is not even approximately constant for a particular substance; it ranges between 6 $\mu\mu$ and 250 $\mu\mu$, according to the method of preparation or subsequent treatment. Even larger particles are found along with submicrons, and frequently there are a few submicrons, and a large number of amicrons, which are less than 6 $\mu\mu$. That these are still *sols*, and not *solutions*, is inferred from the fact that they can be "developed."[1] Thus a mixture of gold salt and reducing agent is more rapidly reduced if an amicron gold sol is added to it. Addition of such a gold sol will even accelerate the reduction of an alkaline silver solution by formalin. By repeated application of this process, in which the amicrons increase in size owing to the further deposition of gold on them, Zsigmondy succeeded in preparing a series of gold sols with particles of any desired size.

[1] Zsigmondy, *Zeitsch. physikal. Chem.* 1906, 56, 63; Lottermoser, *ibid.* 77.

From their ultramicroscopic character, *emulsoids* seem to consist mainly of amicrons, unless, as is not altogether improbable, the disperse phase is not present in isolated particles, but in a more or less continuous net-work; or, owing to the smaller differences in refractive index of the disperse phase and the medium, it may be impossible to detect emulsoid particles so easily as suspensoids. On the other hand, emulsoids exhibit more of the general properties of solutions, which is consistent with the smaller size of the particles in emulsoid sols.

An interesting resumé of the methods of estimating the size of particles in a sol is given by Henri.[1] The ultramicroscopic method is very uncertain, for frequently the chemical nature of the particles is not known: a certain amount of a metal may be in form of oxide, and may even be in solution, or it may be hydrated, any one of which renders the calculation erroneous.

The methods which connect the size of the particle with other properties of the sol are—

(1) The determination of the density of dispersion at different heights (Perrin)—

$$\log \frac{n_0}{n} = (\rho - \rho_1)\frac{h \cdot r^3 \cdot 10^{17}}{9}$$

n_0, n = number of particles in equal volumes at heights o and h.

ρ, ρ_1 = density of dispersion medium and disperse phase.

r = radius of the particles.

(2) The relation between Brownian movement and size of particle (Einstein)—

$$r = \frac{RT}{N}\frac{t}{3\pi\eta l^2} = 3{\cdot}7 \times 10^{-13}\frac{t}{l^2}$$

l being the displacement in time t

[1] *Koll. Zeitsch.*, 1913, **12**, 246.

(3) The velocity of sedimentation—

$$r^2 = \frac{9}{2}\frac{\eta}{2(\rho - \rho_1)g}v$$

v being the velocity. For gold hydrosols the equation becomes $r^2 = 2{\cdot}5 \times 10^{-6}v$.

It is only applicable when the dispersity is low, for if $r = 10\ \mu\mu$ the time to fall 0·1 mm. is 7 hours.

(4) From diffusion (Sutherland)—

$$\delta = \frac{RT}{n} \cdot \frac{1 + A\frac{a}{r}}{6\pi\eta r}$$

A is a constant = 0·815, and a the mean path of a molecule of the dispersion medium (a/r vanishes if the radius is great in comparison with the mean path); at ordinary temperature the formula is—

$$\delta = 1{\cdot}58 \times 10^{-8}\frac{1}{r}(\text{cm}^2,\ 24\ \text{hours}).$$

It is only applicable to highly disperse sols, *e.g.* if $r = 1\ \mu\mu$, $\delta = 0{\cdot}158$ (cm.^{2}, 24 hours), while for urea it is 0·97 (cm.^{2}, day).

(5) Intensity of scattered light (Rayleigh)—

$$c = \frac{An\gamma^6}{\lambda^4}$$

c is the intensity of the scattered light.

A is a factor depending on the refractive indices of the liquid and the disperse phase, on the intensity of the incident rays, and the angle at which the scattered light is observed.

n is the number of particles.

λ is the wave-length of the scattered light.

(6) There is a close connexion between the size of particles and the light absorption by the sol (Garnett,

Wood, Svedberg), but so far it is only of use in determining changes in size.

Ultrafiltration.—Many sols can be filtered through filter paper without appreciable change. Small quantities may be adsorbed to begin with, but beyond that no further loss is experienced. Emulsoids often filter very slowly, owing to their great viscosity.

Linder and Picton [1] tried the filtration of arsenious sulphide sols through porous earthenware, and found that the size of particles varied in different samples. They recognised four kinds of sols: α, visible in the microscope; β, showed Tyndall Effect; γ, retained by a porous plate; and δ, filtered unchanged through a porous plate. Barus [2] made an estimate of the size of the particles in a silver sol by filtration through porous plates. He tried plates of gradated porosity, and calculated the size of pore of the plate which just permitted filtration to take place. He arrived at a size of 36 $\mu\mu$ for one silver sol. By using a colloid membrane as a filter it is possible to concentrate sols, or to separate a mixture of colloid and crystalloid. For this purpose Martin [3] used a Chamberland candle impregnated with gelatine. A pressure of 30 atmospheres was necessary.

Later, Bechhold [4] elaborated the method, and applied it in several useful directions. He made a graduated series of filters by impregnating a support of filter paper, fabric, or wire gauze, with gelatinous colloids of varying concentration. Collodion in acetic acid, and gelatine in water, are the most suitable substances; the filter is subsequently treated chemically: the collodion

[1] *Chem. Soc. Jour.*, 1892, **61**, 148. [2] *Sill. Jour.*, 1895, **48**, 51.
[3] *Jour. Physiol.*, 1896, **20**, 364.
[4] *Vortr.* 78 *Vers. d. Naturf. u. Aerzte*, 1906; *Vortr.* 14 *Vers. Bunsen-Ges.*, 1907; *Zeitsch. physikal. Chem.*, 1907, **60**, 257; 1908, **64**, 328.

dipped into water to render it porous ; the gelatine treated with formaldehyde to harden it (see also p. 27). The filters are standardised with a haemoglobin sol.

According to Wo. Ostwald[1] an efficient ultra-filter can be prepared easily as follows:—Take an ordinary round filter paper, of ordinary rough paper, fold smoothly, fit it in a very clean funnel, fill it to the edge with 2 per cent. collodion solution, wait until it runs through the paper, pour out, rotate to dry the surface (5–10 minutes), and place in distilled water. After some hours it can be taken from the funnel; clean the funnel, and replace the filter with suction. Use with an india-rubber stopper in an ordinary filter flask and a pump. Test with dilute night-blue or congo-red. Such a filter filters with great rapidity, up to 200 c.c. of night-blue per minute.

Or the filter paper is moistened with water, a 4 per cent. collodion poured in and spread over by turning the funnel round, and then poured out. The milky suspension of collodion in water is drained off, the filter allowed to dry for 5–10 minutes, and a second layer of collodion is poured in and allowed to dry on the surface. The filter is then removed from the funnel and soaked in water. By this means filtration takes place with great rapidity, 3–6 c.c. per minute without suction, and 30–70 c.c. per minute with a water-pump; also large quantities of sol can be filtered without serious falling off in the rate.

These filters can be used to separate the colloid from the dispersion medium, as in arsenious sulphide sol or ferric hydroxide sol, or to concentrate albumin and similar emulsoids, the filtrate containing no emulsoid. They can also be employed to free sols from soluble

[1] *Koll. Zeitsch.*, 1918, **23**, 68, 143.

filtrable impurities, the process being similar to purification by dialysis. Another important application of ultrafiltration is in the preparation of graduated series of sols, the sizes being regulated by filtration through a series of graduated filters.

The approximate size of particles in sols can also be ascertained by finding which of a series of filters will just allow the particles to pass into the filtrate. The sizes obtained in this way agree on the whole with the ultramicroscope results. Bechhold gives the following series in the order of diminishing size :—

Prussian blue, Bredig's platinum, ferric hydroxide, casein, arsenious sulphide, gold (Zsigmondy's 40 $\mu\mu$), gelatine, bismuth hydroxide, gold (Zsigmondy's amicrons 1–4 $\mu\mu$), haemoglobin, Paal's silver, serum albumin, [diphtheria toxin], collargol, haematin, protalbumoses, silicic acid, deuteroalbumoses, dextrin.

It must be remembered that this process of ultrafiltration is a complex one, as ordinary filtration, dialysis, and adsorption can all play a part in it. Even with filter paper, and still more with porous plate, adsorption and precipitation may and do take place. This is especially the case with positive hydrosols. They cannot be filtered even through filter paper without partial retention of the colloid by the filter. The reason is that the paper becomes negatively charged in contact with water (p. 68), and at the entrance to each pore a corresponding quantity of positive colloid is precipitated (p. 134).

Malarski[1] has recently shown that the electric charge of a positive sol is diminished or even changed in sign by repeated filtration through filter paper. The same holds for negative sols to which positive ions or sols have been added. Glass wool, purified sand, purified cotton wool,

[1] *Koll. Zeitsch.*, 1918, **23**, 113.

all of which are negative to pure water, give similar results. For example, a ferric hydroxide sol became negative after three filtrations, the negative charge increasing with two further filtrations. The reversed sols thus obtained show the same reactions—as to mutual precipitation and reversal—as other sols of the same sign; *e.g.* when the above negative sol was added to the original positive sol, the migration to the kathode was gradually reduced to zero, and was finally reversed. The following table illustrates both these effects:—

$Fe(OH)_3$ Hydrosol

$V = 6{\cdot}3$; $a = 0{\cdot}8$ cm.; $S = 78\ \mu$

Number of Filtrations.	Migration Velocity $v \times 10^5$.	Drops of $Fe(OH)_3$ sol to 10 c.c.	Migration Velocity $v \times 10^5$.
0	+ 18·6	0	+ 18·6
1	+ 13·4	4	+ 12·3
2	+ 6·2	6	+ 6·0
3	− 6·6	8	0·0
4	− 19·0	12	− 6·0
5	− 19·7	30	− 14·3

The effect of adding various ions, $H^{\cdot}$, OH', or $Al^{\cdot\cdot\cdot}$, etc, on the sol, or on the filter paper, is in accordance with Perrin's electro-osmose results (p. 68). Similar results were obtained with silver sols which had been made positive by the addition of aluminium salt or of ferric hydroxide sol.

CHAPTER VIII

ELECTRICAL PROPERTIES

IN no other branch of the subject is it more necessary to keep in mind the two points of view, viz. the facts, and the theories which have been advanced to *explain* the facts. As regards the former, there is no longer any serious question, since the main phenomena have been established in a satisfactory manner. When we come to the origin of the electrical charge of colloids we are confronted by one of the most difficult problems, a complete solution of which is still awaited, and which, when found, will prove an invaluable aid towards the elucidation of the whole subject.

The phenomena will be described first, and then the principal hypotheses which have been advanced will be discussed in detail.

The electric conductivity of sols will be taken first, and then migration in an electric field.

ELECTRIC CONDUCTIVITY

Suspensoids.—The electric conductivity of suspensoids is very small, so little removed from that of the dispersion medium that the question arises whether this small conductivity is not due to the small quantities of (adsorbed) electrolytes, which, as has already been pointed out, are impossible to remove, at least by washing or dialysis.

The following data[1] will give an idea of the electric conductivity of several typical sols.

Sol.	Specific conductivity (κ) in mhos. Sol.	Medium.
Au (Bredig) . .	$1{\cdot}14 \times 10^{-6}$ to $1{\cdot}6$ „	$0{\cdot}81 \times 10^{-6}$
Au (Zsigmondy)	$7{\cdot}9$ „	$1{\cdot}2$ „
Pt (Bredig) . .	$2{\cdot}9$ „	$1{\cdot}1$ „
Au (Blake) . .	$12{\cdot}7$ „	$1{\cdot}5$ „
$Fe(OH)_3$ . . .	$35{\cdot}7$ „	2 „

Various attempts have been made to decide by experiment how far this conductivity is due to the sol, and how far to the "active" electrolyte. Malfitano[2] determined the electric conductivity of sols of ferric hydroxide from hydrolysed ferric chloride, and of arsenious sulphide, before and after filtration through a collodion membrane. As the latter retained the suspensoid, and allowed all (?) the rest to filter through, the conductivity of the filtrate should fall off, if it was due to the suspensoid, while, in the other event, it should remain unchanged by this process. No diminution of conductivity was observed in any instance, from which he concluded that the conductivity was due to the dissolved impurities. Applying the same method of collodion filtration, Duclaux[3] found the conductivity of a ferric hydroxide sol to be diminished by filtration, and regarded the difference as the conductivity of the suspensoid. It amounted to about 200×10^{-6} mho.

This method is open to the objection that the collodion filtration may change the concentration of the medium in addition to removing the disperse phase, and that the

[1] Billiter, *Sitzungsber. Kaiserl. Akad. Wiss. Wien.*, 1902, **111**, 1395; Bigelow and Gemberling, *J. Amer. Chem. Soc.*, 1907, **29**, 1576; Whitney and Blake, *ibid.*, 1904, **26**, 1339.

[2] *Compt. Rend.*, 1904, **139**, 1221.

[3] *Ibid.*, 1905, **140**, 1468.

small observed differences may as well be put down to this as to the removal of the disperse phase.

As electrolysis affords perhaps the most certain means of removing electrolysable impurities from a colloid, without any other appreciable alteration, the application of this method should solve the problem. By determining the electric conductivity of the original sol, and after subjection of the sol to successive electrolyses, Whitney and Blake[1] found that it diminished after each electrolysis, but did not finally approach zero. Instead, it converged to a definite value which they regarded as the true electric conductivity of the pure sol. The following values were obtained:

Gold sol.	$\kappa \times 10^6$.
After dialysis	13·2
„ 1 electrolysis . .	7·7
„ 2 „ . .	4·2
„ 3 „ . .	2·7
„ 4 „ . .	2·1
„ 5 „ . .	1·8
„ [6 „ . .	1·6]
„ [7 „ . .	1·4]
„ [8 „ . .	1·3]

The conductivity of the water was $1{\cdot}3 \times 10^{-6}$.

In the actual experiment, the sol was contained in a glass tube closed at both ends by gold-beater's skin. The lower end dipped into a glass dish; the electrodes were applied to the damp membranes, a wider glass tube being fixed by a rubber band to the upper end (Fig. 4, p. 77). The gold migrated to the anode (lower end) and was deposited on the membrane. On treatment with pure water, the gold again diffused into the liquid with regeneration of the sol. The conductivity of the water in the outer vessel rose considerably.

The above figures would seem to indicate that the

[1] *Loc. cit.*, p. 62.

pure sol would have the same electric conductivity as the water, since two or three further repetitions of the treatment should reduce the conductivity of the sol to that of the water. The figures in square brackets are values extrapolated from the curve plotted from the experimental values in the above table.

Kohlschutter's[1] silver sol (see Preparations, p. 187), had an initial conductivity of 129×10^{-6} mho. By purification with hydrogen gas in a platinum vessel the silver hydroxide present (no other electrolyte can be present) was reduced to silver, and the conductivity fell to *one-tenth* of its initial value, and then remained constant at about *three* times the specific conductivity of the water, viz. 7×10^{-6} mho. In a few instances it fell as low as 4 to 5×10^{-6}, and in some others could not be reduced below 10×10^{-6} mho.

In several silver sols prepared according to this method by the author, the conductivity fell as low as 7×10^{-6} in Jena glass flasks, without any treatment in platinum. The initial conductivity of the saturated silver hydroxide solution was about 38×10^{-6}.

Emulsoids. — The figure already given for ferric hydroxide sol may be taken as an indication that emulsoids have often a higher electric conductivity than suspensoids.

Although Pauli[2] found that albumin sol, carefully purified by dialysis, was practically a non-conductor, Whitney and Blake[3] obtained fairly high values for silicic acid sol, κ for a 1·47 per cent. sol being 100×10^{-6} mho, while a 0·2 per cent. gelatine sol gave $\kappa = 68 \times 10^{-6}$ mho. These are of the same order as

[1] *Zeitsch. Elektrochem.*, 1908, 14, 49.
[2] *Beitr. Chem. Phys. Path.*, 1906, 7, 531.
[3] *Amer Chem. Soc.*, 1904, 26, 1374.

the 200×10^{-6} mho. observed by Malfitano for ferric hydroxide sol.

It would appear from these results that there may be two classes of emulsoids, so far as electrical conductivity is concerned: some, comprising the electrically neutral sols, as albumin, have no electrical conductivity when they are pure, the variable value usually found being due to the impurities; while others, the electrically charged sols, possess a considerable conductivity. If the albumins are amphoteric substances, their vanishingly small electric conductivity is readily understood, for the conductivity of the simple amino-acids (*e.g.* glycocoll) is extraordinarily small in comparison with that of the parent acid.

From a theoretical point of view, a sol in which the disperse phase is electrically charged, whether positively or negatively, and the greater number of sols come into this category, must exhibit in some degree the phenomena of electric conductivity.

Electrical Migration

The migration of colloids in an electric field forms a special part of the general electrical phenomena, which occur at a boundary or interface between two phases, one of which at least is a liquid. Quite possibly the same phenomena occur at every interface, whether the phases are gas, liquid, or solid. The experimental difficulties are very great unless one phase is a liquid, and we shall only consider such cases.

At all such interfaces an electrical potential difference is established, of the nature of an electrical double layer. Consequently, displacement of one phase against the other takes place when the system is placed in an electric field. We have, therefore, two separate cases. In the one, the

solid is fixed, as in a capillary tube or a porous diaphragm, and all the displacement is thrown on the liquid, which is shown by a difference of level, or by a flow of liquid across the diaphragm. In the other, the solid is suspended in the liquid, and as no permanent difference of level can persist in the liquid, the solid moves through the liquid.

The terms "electroendosmosis" and "kataphoresis," frequently applied indiscriminately to both of these phenomena, may conveniently be employed to distinguish between them.

Electroendosmosis

Electroendosmosis, or the movement of a liquid across a diaphragm or through a capillary tube towards one of the electrodes when a current of electricity is passing, was noticed by Reuss[1] long ago, and has since been the object of many investigations, theoretical and practical. When a poor electrolyte is electrolysed with a porous cell, the difference of level on the two sides of the cell is very noticeable. Wiedemann[2] was led by this to inquire into the matter. He found that under comparable conditions the difference of level depended on the applied E.M.F. and also on the viscosity of the solution.

The latter fact suggested that the two electrically charged layers which suffer displacement are both liquid, the one adhering immovably to the solid, while the other moves with the rest of the liquid.

The experiment can also be so arranged that no difference of level is maintained, the liquid which is forced through the diaphragm being run off by a side tube. This

[1] For full historical references see Wiedemann, *Elektricität*, 1893, 1, p. 993.

[2] Wiedemann, *Pogg. Ann.*, 1852, [ii.] 87, 321.

is a convenient form of the experiment, the volume transferred in unit time being a convenient measure of the effect. The formulæ connecting the various factors concerned are given here (their deduction will be found at the end of the chapter). The equation for the *volume* of liquid transferred is

$$v = \frac{q\epsilon \mathrm{ED}}{4\pi\eta l}$$

in which q = area of diaphragm (or tube).
ϵ = potential difference of double layer.
E = E.M.F. at the electrodes.
D = dielectric constant of the liquid.
η = viscosity of the liquid.
l = distance between electrodes.

From it we see that the *volume* transferred is proportional to (1) the area of the diaphragm or the cross-section of the capillary, (2) the potential difference between the liquid and solid, (3) the fall of potential between the electrodes, and (4) the dielectric constant; it is inversely proportional to the viscosity of the liquid.

If, instead of allowing the liquid to escape, the *pressure* is allowed to rise, the equation is

$$\mathrm{P} = \frac{2\epsilon \mathrm{ED}}{\pi r^2}$$

The *height* to which the liquid will rise in tubes of the *same material*, is proportional to the applied E.M.F. and inversely proportional to the square of the radius of the tube.

Quincke[1] tested these results by measuring the difference of level on the two sides of a single glass capillary, when a known E.M.F. was applied. The equation shows

[1] *Pogg. Ann.*, 1861, [ii.] 113, 513; Tereschin, *Wied. Ann.*, 1887, [iii.] 32, 333.

that ϵ, the potential difference between glass and water, should be a constant. This is the case.

r (cm.).	E (volt).	h (cm.).	ϵ (volt).
0·0449	76	0·0125	0·054
„	152	0·0245	0·053
0·0188	154	0·0880	0·055

Other investigators have found ϵ to be constant, and of approximately the same value as Quincke obtained, *e.g.*—

r (cm.).	E (volt).	h (cm.).	ϵ (volt).
0·369	5,120	1·9	0·041
	7,220	3·1	0·048
	8,860	3·8	0·048
	10,200	4·3	0·046
	11,500	4·8	0·046

Since most substances become negatively charged in contact with water, the *water travels to the kathode.* This has been observed with capillary tubes of glass and shellac, and with diaphragms of porous earthenware, asbestos, carborundum, wool, cotton wool, arsenious sulphide, and many other substances. A small number have been found to be positively charged in water. They comprise basic oxides and hydroxides, *e.g.* aluminium oxide and cobalt oxide, etc.; and some salts, as anhydrous chromic chloride, barium carbonate, etc.

Effect of Acids and Alkalies.—The potential difference between the two phases may be changed by the addition of various substances to the water; and this change may be in either direction. The potential difference may increase or it may diminish, and in the latter case may be reversed in sign, passing through zero on the way. Perrin [1] has investigated this very fully, and some of his results are given below. The effect of acids and alkalies is very marked. The general effect is as follows.

[1] *J. chim. phys.*, 1904, **2**, 601.

Negative diaphragms become more negative in alkaline solutions; in acid solutions the diaphragm becomes less negative, and with increasing concentration of acid it becomes electrically neutral and finally is positive.

Positive diaphragms behave in the corresponding manner, *i.e.* they become less positive, and finally negative on the addition of alkalies, while they become more strongly positive in acid solutions.

In Perrin's experiments the variation or reversal of sign of the charge on the diaphragm was indicated by the volumes of liquid transported to the kathode or anode in unit time. The + or − indicates uniformly the sign of the charge on the solid (also migration of the liquid to the anode and kathode respectively).

Diaphragm.	Solution.	V (c.c./min.).
Carborundum	0·02 m. HCl	+ 10
	0·008	0
	0·002	−15
	water	−50
	0·0002 m. KOH	−60
	0·002	−105

Similar effects are observed with other diaphragms. It is worthy of note that the effect of acid and alkali is greatest at very small concentrations, rapidly falling off as the concentration increases, until practically a constant value is reached. The following figures for a naphthalene diaphragm show this very well.

Diaphragm.	Solution.	V (c.c./min.).
Naphthalene	0·02 m. HCl	+38
	0·01	+39
	0·001	+28
	0·0002	+ 3
	0·0002 m. KOH	−29
	0·001	−60
	0·02	−60

If the volumes are plotted (with due regard to sign) against the concentrations of acid and alkali ($H^{\cdot}$ and OH'), the two branches of the curve are symmetrical with respect to the point of electrical neutrality, which is very slightly displaced to the acid side, corresponding to the fact that the substances are negative in pure water.

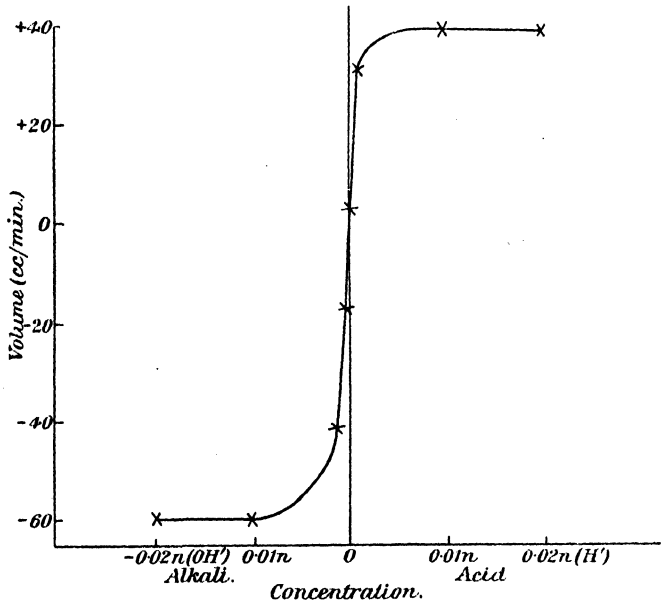


FIG. 3.

With positive diaphragms there would be a similar displacement to the alkali side.

Effect of Salts.—The influence of neutral salts has also been investigated by Perrin. For this purpose he used solutions which were already acid or alkaline owing to added acid or alkali. The effect of salts is very important in the case of kataphoresis, where, however, it is frequently complicated by other unavoidable effects, which mask or

even obliterate the primary effect. Some details will therefore be given in the corresponding case of electro-endosmosis.

NEGATIVE DIAPHRAGMS.

Carborundum in Alkali.

Salt.	V (c.c./min.).
0	−60
0·1 m. NaBr	−14
0·002 m. $Ba(NO_3)_2$	−26
0 0002 m. $La(NO_3)_3$	−18

Chromic Chloride in Alkali.

0	−76
0·001 m. $MgCl_2$	−10
0·001 m. $MgSO_4$	− 6

POSITIVE DIAPHRAGMS.

Chromic Chloride in Acid.

0	+90
0·1 m. KBr	+33
0·001 m. $MgSO_4$	+23
0·0005 m. $K_3Fe(CN)_6$	+ 3

The concentration effect is similar to that already noted with respect to acids and alkalies: very small concentrations have a very large effect, which is only slightly increased by subsequent increase of concentration This is shown below.

Carborundum in Alkali (negative).

Concentration of $La(NO_3)_3$ (mols. per litre).	V (c.c. per min.).
0	−60
0·00004	−58
0·0002	−18
0·001	− 1

Further addition of the salt must finally reduce the

electroendosmosis to zero, or reverse its direction. The latter actually occurs, just as addition of acid to a negative diaphragm, and of alkali to a positive one, reduces the potential difference to zero, and finally reverses the sign. The reversal is not so pronounced, and the reversed potential difference cannot be made so large as can be produced by acids and alkalies.

The Valency Rule.—The foregoing figures lead to a highly important generalisation regarding the influence of salts on the potential difference between the solid and the liquid. Considering the figures for the *negative diaphragm*, we find that the *valency of the kation* is the predominant factor. The concentration of the bivalent kation $Ba^{\cdot\cdot}$ which produces a given decrease in V, is very much less than that of the univalent kation $Na^{\cdot}$, and the concentration of the trivalent $La^{\cdot\cdot\cdot}$ is much less again. The figures for magnesium chloride and sulphate show that the valency of the anion does not matter, there being little difference between the univalent Cl' and the bivalent SO_4''.

With the *positive diaphragm*, on the other hand, the valency of the *anion* is the principal factor, the effect of the salt on the electrical charge of the diaphragm or on the volume of liquid increasing with increasing valency of the anion. This may be summarised as follows: the electric charge on the diaphragm is reduced by the ion of opposite sign; further, the magnitude of the effect increases with the valency of that ion, and is independent of the valency of the other ion.

This must be regarded as a broad generalisation, and it will subsequently be shown to hold in the case of kataphoresis, and also of the precipitation of suspensoids by electrolytes. It must be at once admitted that the matter is not so simple as this; ions of the same electric sign as the diaphragm do not have the same effect. There are

differences, again, between ions of the same valency, which cannot be explained by differences in ionisation. $H^{\cdot}$ and OH' in particular differ from other univalent ions. Instances of these will be found under kataphoresis, and more especially under precipitation of sols by electrolytes.

That the valency of the ion of opposite electric sign is the main factor in the alteration of potential on the diaphragm is plainly seen from the symmetrical nature of the figures obtained, when the results for + and − diaphragms are reduced to a common standard. This has been done by Freundlich,[1] who calculated the concentration of various salts which reduced V to one-half of the value when no salt was present.

Carborundum (negative).

Salt.	Concentration (millimols per litre).
$Na^{\cdot}Br$	50
$Ba^{\cdot\cdot}(NO_3)_2$	2
$La^{\cdot\cdot\cdot}(NO_3)_3$	0·1

Chromic Chloride (positive).

KBr'	60
$MgSO_4''$	1
$K_3Fe(CN)_6'''$	0·1

Other Liquids.—Quincke examined other liquids besides water; turpentine is negative to glass and carbon disulphide is positive to it. There was no migration of ether or petroleum. Methyl alcohol, ethyl alcohol and acetone all showed marked electroendosmosis. Perrin[2] extended the list very considerably. There was marked migration of methyl alcohol, ethyl alcohol, acetone, acetylacetone, and nitrobenzene; to a less degree of amyl alcohol and acetic acid; none of chloroform, ether, benzene, carbon disulphide, petroleum, and oil of turpentine.

[1] Freundlich, *Kapillarchemie*, p. 238.

[2] *J. chim. phys.*, 1904, **2**, 601.

The same general relations hold for these liquids as for water. The quantitative results[1] for methyl alcohol fully bear this out. Substances, such as chromic chloride, manganese dioxide, which are positive in water, are also positive in alcohol; the others are negative in alcohol, as in water. The addition of non-electrolytes does not affect the migration, but the addition of acids and alkalies has the same effect on positive and negative diaphragms, as in water. The valency rule applies equally in alcohol and in water.

Emulsoids.—Very little seems to be known regarding electroendosmosis of liquids in contact with emulsoid gels. Isolated observations have been made on the behaviour of semi-permeable membranes of aluminium hydroxide, ferric hydroxide and chromic hydroxide, all of which are probably emulsoid gels. Thus, in electrolysis through a film of aluminium hydroxide there was a very marked migration of liquid into the anode compartment[2]; the water was therefore negative, as was to be expected, since aluminium hydroxide is a positive sol, and wanders to the kathode. In a later research on the same subject, electroendosmosis took place across a diaphragm of filter paper soaked in gelatine; the direction was not recorded.

Kataphoresis

Suspensoids.—From the relation between electroendosmosis and kataphoresis, we should expect the general conclusions regarding the former, which have been discussed in the preceding section, to hold equally for kataphoresis. Except in so far as disturbing factors interfere with the observations, this is found to be true. Thus suspended particles of shellac, clay, cotton wool, starch,

[1] Baudouin, *Compt. Rend.*, 1904, **138**, 898.

[2] Taylor and Inglis, *Phil. Mag.*, 1903, [vi.] **5**, 301; Taylor and Millar, *Proc. Roy. Soc. Edin.*, 1906, **26**, 447.

sulphur, etc., in water migrate to the anode. Most suspensoid sols do the same, *e.g.* the metals, as gold, silver, platinum; the sulphides, as arsenious sulphide, zinc sulphide, etc.; while the hydroxides of the metals, as aluminium hydroxide and ferric hydroxide, and some other substances, migrate to the kathode. This is in agreement with the electroendosmosis results recorded in the previous section.

This migration of sols in an electric field was first observed by Linder and Picton [1] in arsenious sulphide sol, which migrated to the anode, and in ferric hydroxide sol, which migrated to the kathode. The behaviour of many sols has been investigated since. The following list, though in no way complete, may be useful:—

POSITIVE SOLS (to kathode).

Ferric hydroxide	Titanic acid
Aluminium „	Methyl violet
Chromic „	Methylene blue
Cadmium „	Magdala red
Zinc „	Some metals, Pb, Bi, Fe
Thorium „	(almost certainly hydr-
Zirconium „	oxide sols)
Cerium „	

NEGATIVE SOLS (to anode).

Metals, *e.g.* Au, Ag, Pt, Pd, Ir, Cd, etc. Most metallic compounds (except oxides, etc.), *e.g.* AgCl, AgI, As_2S_3, PbS, CdS, prussian blue, etc.

Sulphur, selenium, tellurium.

Silicic acid, stannic acid.

Vanadium pentoxide.

Molybdenum blue, tungsten blue, mastic, gamboge, fuchsin, eosin, indigo, aniline blue, methyl aniline green.

[1] *Chem. Soc. Journ.*, 1892, 61, 148.

The *velocity* of migration of particles suspended in a liquid, under a fall of potential, is given by the equation

$$u = \frac{\epsilon HD}{4\pi\eta}$$

where u = velocity, ϵ = the potential difference of the double layer, H = the fall of potential (volt/cm.), D = dielectric constant, and η = the viscosity of the liquid. The derivation of this formula is given at the end of the chapter. Inserting Quincke's value of ϵ for glass and water (0·05 V), and the values of the other symbols, Smoluchowski[1] calculated u for a fall of potential of 1 v/cm. to be 34×10^{-5} cm. per second.

$$u = \frac{0{\cdot}05 \times 1 \times 81}{300 \times 300 \times 4\pi \times 0{\cdot}0105} = 34 \times 10^{-5} \text{ cm./sec.}$$

The two factors 300 in the denominator are to convert ϵ and H into absolute units.

The velocity can be determined macroscopically, microscopically, or ultramicroscopically. In the first method, a vertical tube is filled with the sol (the ends may be closed with gold-beater's skin), and an electrode applied at each end. The direction of the current is such that the sol migrates to the under electrode, by which a sharp upper boundary is maintained. The distance travelled in a known time is read off on a scale (Fig. 4).

In the other methods,[2] the actual migration of a single particle is observed under the microscope, and the distance travelled by it in a known time is measured by means of a micrometer eyepiece. The ultramicroscope must be used if the particles are submicrons. Certain precautions

[1] *Bull. Acad. Scien. Cracow*, 1903, 182.

[2] Cotton and Mouton, *J. chim. phys.*, 1906, **4**, 363; Coward, *Trans. Faraday Soc.*, 1913, **9**, 142.

are necessary if correct results are to be obtained. The particles selected for observation must be near the middle of the liquid, for particles near the cell walls may even travel in the reverse direction. The reason is that electro-endosmosis occurs at the cell wall, and the liquid moving in the contrary direction to the sol (the cell wall, of glass or quartz, usually has the same sign as the sol) drags the particles along with it. Cotton and Mouton have described the diverse nature of the observations when the microscope is focussed on layers at different depths in the cell.

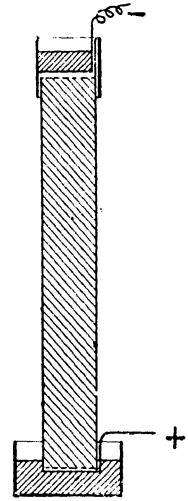


FIG. 4.

Then, the particles must be fairly equidistant from the electrodes, and the observations must be made immediately the current is applied. The disturbances due to neglect of these precautions are twofold. When charged particles reach an electrode of opposite charge, they usually give up their charges to the electrode, and remain precipitated in the vicinity of the electrode. They may, however, take up a charge of the same sign as the electrode, and then set off back to the other electrode. Reversal of the charge may occur in another way. As we have seen in electroendosmosis, very small changes in the concentration of electrolytes, and especially of $H^{\cdot}$ or OH', produce large changes in the charge on the solid, and may cause reversal. When a sol is submitted to prolonged kataphoresis, the traces of electrolytes accumulate at the electrodes, at the same time decreasing the $H^{\cdot}$ at the kathode, and increasing it at the anode. If, therefore, the original sol is neutral, the kathode liquid may become

alkaline, and the anode liquid will become acid, with corresponding changes in the charge on the particles.

This reversed migration, however caused, must obviously vitiate the results. Still another disturbing process may take place. The particles with reversed charge may come in contact with some of the original particles, and the two electrically neutralise each other, causing mutual precipitation. If the experiment is unduly prolonged this effect may cause serious error in the middle of the solution.

There is yet another disturbing factor, first indicated by Coward,[1] which must not be overlooked, viz. a charged particle may be attracted to an electrode of the same sign as the particle, if the potential difference between them is sufficiently great. For this reason, observations near the electrodes are always liable to error.

These sources of error apply also to the macroscopic methods, and their effects were noticed by Linder and Picton.

For demonstration purposes, the familiar apparatus of Nernst for demonstrating ionic migration may be used, a sharp boundary between the water and the coloured sol being obtained in the usual manner by loading the sol with a non-electrolyte (sugar or urea).

More convenient still is a small form of the Nernst apparatus, which can be mounted in the lantern and projected on the screen. The U tubes are of small thin-walled glass tubing. The filling tube has no tap, but is constricted to a very narrow opening just below its junction with the U tube. Instead of being placed centrally, it is better to bend it to one side, as shown in Fig. 5, but not in the same plane as the U tube. It is easier to work, and is out of the field of the lantern; the apparatus is clamped by this tube. By means of the

[1] *Loc. cit.*, p. 76.

rubber tube and small clip the sol can be introduced slowly and to the requisite amount. To use it, the side tube is quite filled with the loaded sol, and the clip is closed. The sol which has escaped into the U tube is washed out with water. Water is then placed in the U tube, and the electrodes (a flat helix of thin platinum wire) inserted. The apparatus is then mounted in the lantern. The clip is cautiously opened, and the sol flows equally into the two limbs with sharp interfaces. The clip is closed as soon as the electrodes are covered with water. The amounts of water and sol must be so adjusted that the interfaces are well below the electrodes. A suitable voltage is 110V or 220V.

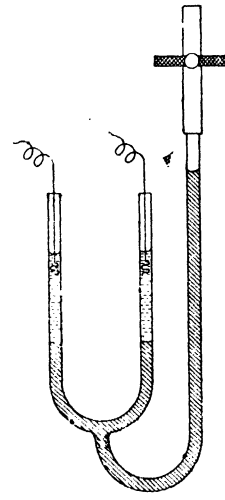


FIG. 5.

With this simple apparatus the direction of migration, the reversal of direction on reversal of the current, and the approximate velocity for a potential gradient of 1 volt/cm. can be easily obtained, as owing to the magnification, the migration is visible in a very little time. Some at least of the disturbances caused by prolongation of the experiment, such as the precipitation near the electrode, and the mutual precipitation by the particles of reversed charge, can also be observed.

Two such tubes may be shown on the screen at one time, and if a negative sol (gold or arsenious sulphide) is placed in one, and a positive sol (ferric hydroxide) in the other, the migration in opposite directions may be convincingly shown, as the electrode connexions can easily be shown on the screen at the same time.

Velocity of Migration.—The observed velocity is in good agreement with the value, 34×10^{-5} cm./sec., calculated from the formula, as the figures below show.[1]

Sol.	Size of particles.	u (cm./sec. per 1 v/cm.).	
As_2S_3 . . .	$50\mu\mu$	22×10^{-5}	(L. P.)
Quartz . . .	1μ	30	(W. B.)
Au	$< 100\mu\mu$	40	(W. B.)
„	„	21·6	(B.)
Pt	„	30	(W. B.)
„	„	20·3	(B.)
Ag	„	33	(C. M.)
„	„	23·6	(B.)
„ { 4 different preparations }	„	19·7	„
„	„	19·6	„
„	„	19·3	„
Fe	„	19	„
$Fe(OH)_3$ . .	„	30	(W. B.)

The agreement of these figures and the theoretical value shows that the potential difference between water and all these different substances is of the same order as that between glass and water. The values of ϵ calculated from the above values of u, vary from 0·028V. to 0·058V. The metals lead and bismuth give very low values of u and ϵ: they and iron are positive sols, like ferric hydroxide.

The velocity is practically independent of the size and form of the particles, as the formula requires.

Most remarkable of all is the fact that the average velocity is practically the same as the migration velocity of the average slow moving ions of electrolytes, $Na^{\cdot}$ being 45×10^{-5} cm./sec., and $Li^{\cdot} = 36 \times 10^{-5}$ cm./sec. for

[1] Linder and Picton, *Chem. Soc. Journ.*, 1897, **71**, 508; Whitney and Blake, *J. Amer. Chem. Soc.*, 1904, **26**, 1339; Burton, *Phil. Mag.*, 1904, [vi.] **11**, 425; Cotton and Mouton, *loc. cit.*, p. 76.

1 v/cm. fall of potential. The velocity of migration of suspensoids, whether microns or submicrons, and of ions is thus practically constant.

Effect of Electrolytes.—The presence of electrolytes, and especially of acids and alkalies ($H^{\cdot}$ and OH'), has such a marked effect on electroendosmosis that we naturally look for similar effects here. This expectation is justified in the few instances in which it is possible to test it. The difficulty is that another action of electrolytes comes in, which is wanting in electroendosmosis. Suspensoids are by no means so stable as a diaphragm-liquid system; they are very susceptible to electrolytes, undergoing a series of changes, which usually end in complete precipitation of the sol. As will be shown in the next chapter, these changes are almost certainly connected with the electrical changes, mainly the electrical neutralisation of the charged particles by the ions of the electrolyte, which we are led to infer from the behaviour of diaphragms, but which are difficult to verify by experiment.

Burton [1] investigated the influence of the trivalent kation, Al''', on negative gold sol and silver sol.

Silver Sol.

Concentration of $Al_2(SO_4)_3$ in millimols per litre.	u (cm./sec.) $\times 10^5$ at 18°.
0	− 22·4
0·0052	− 7·2
0·014	+ 5·9
0·0284	+ 13 8

Whitney and Blake had previously noticed that the addition of $H^{\cdot}$ (nitric acid) or of $Ag^{\cdot}$ (silver nitrate) to silver sol caused the particles to migrate to the kathode instead of to the anode.

[1] *Phil. Mag.*, 1905, [vi.] 12, 472.

The Electric Charge on a Particle.—An estimate of the charge on a single particle of gold sols and silver sols has been made by Burton, on the assumption that in the precipitation of these sols by aluminium salts, the amount of $Al^{'''}$ which just precipitates the gold or silver is such that the amount of positive electricity on it is equal to the amount of negative electricity on the particles precipitated.

The volume of a particle is 2×10^{-14} c.c., therefore 100 c.c. of a sol (with 6·5 mg. Ag) contains 3×10^{10} particles. This volume of sol required $3{\cdot}0 \times 10^{-5}$ and $2{\cdot}6 \times 10^{-5}$ $Al_2(SO_4)_3$ for precipitation, from which the charge on a particle is $2{\cdot}8 \times 10^{-2}$ electrostatic units, and the charge on 1 gm. equivalent of silver is 4 per cent. of the charge on $Ag^{'}$ (1 gm. equivalent of silver ion).

Other Liquids.—Quincke observed that most substances were positive in oil of turpentine, sulphur being the only exception. Lycopodium in ether migrates to the kathode; sulphur, vermilion, antimonious sulphide, to the anode. Billiter [1] found that alcohol reduced the migration in a platinum sol to zero, and then reversed the direction of migration.

To Burton [2] we again owe a series of quantitative experiments, which show the general relations quite plainly. The symbols in the table are the same as in the formula on p. 67.

[1] *Zeitsch. Elektrochem*, 1902, **8**, 638.
[2] *Phil. Mag.*, 1904, [vi.] **11**, 425.

Dispersion Medium.	Sol.	D.	η.	$u \times 10^5$.	ϵ (volts).
Methyl alcohol	Pb	33	0·00612	22	+ 0·046
	Bi			10·2	+ 0 021
Ethyl alcohol	Pb	25·8	0·0123	4·5	+ 0·024
	Sn			3·6	+ 0 019
	Zn			2·8	+ 0·015
Ethyl malonate	Pt	10·7	0·0223	2·3	— 0·054
	Ag			1·7	— 0·040
	Au			1·4	— 0·033

The value of u depends principally on the viscosity of the liquid; ϵ does not differ much from the values in water. The sols of the base metals in the alcohols are positive, as in water.

A broad generalisation regarding the sign of the charge on a solid in contact with a liquid, first put forward by Coehn,[1] may be stated: the substance with the greater dielectric constant is positive to the other substance. The D.C. of oil of turpentine is 2·23, that of glass is 4–7, according to its composition, and that of water is 81. In agreement with the rule, glass is positive in oil of turpentine, and negative in water. Water has a much higher dielectric constant than most other substances, and, as we have seen, most substances are negative in water.

Emulsoids.—When an emulsoid is placed in an electric field, migration is observed to take place as in suspensoids. But the disturbing factors are much more powerful than in the latter. The velocity is also much smaller, u for gelatine being $+ 25 \times 10^{-5}$, and for silicic acid $- 15 \times 10^{-5}$ cm./sec. It is partly due to this, that reversal at the electrodes, and mutual precipitation in the body of the liquid are more pronounced. Indeed, in a gelatine sol some of the particles were found to be travelling from each of the electrodes at the commencement of the experiment.

[1] *Wied. Ann.*, 1898, [iii.] **64**, 217.

This suggests that the charge on an emulsoid is largely an accidental matter, being determined by the medium in which it happens to be, and that its normal condition is electrical neutrality. Gelatine, if charged initially, is ready to lose its charge to the electrodes, or, if not, is ready to receive charges from the electrodes or from ions in the vicinity of the electrodes. Confirmation of this view is to be found in the observations on albumin. Coagulated egg-albumin does not migrate in either direction in neutral solutions, but migrates to the anode in alkaline solutions, and to the kathode in acid solutions.[1] We must conclude from this that albumin is electrically neutral in water and in neutral solutions, and that it becomes negative in alkalies (OH'), and positive in acids ($H^{\cdot}$).

Pauli's experiments[2] on a specially pure albumin sol still further confirm these conclusions. The albumin was dialysed until no more electrolyte diffused away. It was contained in three vessels connected together, the electrodes being in the two outer vessels. The concentration of the sol in the three vessels was determined by Kjeldahl's nitrogen method; the current was connected for periods up to twenty-four hours. There was no kataphoresis, from which we must conclude that the albumin is isoelectric with water. In solutions with an acid reaction ($H^{\cdot}$) the albumin migrated to the kathode, and was therefore positively charged; while in alkaline solutions (OH') it migrated to the anode, and was negatively charged. It remained unaffected by neutral salts.

It is quite open to explain this behaviour of albumin

[1] Perrin, *Compt. Rend.*, 1903, **136**, 1388; Hardy, *J. Physiol.*, 1904, **24**, 288.

[2] *Beitr. chem. Physiol. Path.*, 1906, **7**, 531.

by regarding it as an amphoteric substance, which as a base forms salts with acids, in which the albumin forms the kation, and as such migrates to the kathode, as all kations do. As an acid, it will form salts with bases, in which it functions as anion, and so travels to the anode. But when we recall Perrin's observations (p. 69) on the effect of H· and OH′ on electroendosmosis with diaphragms of such substances as carborundum and naphthalene, to neither of which can be ascribed acid or basic properties, or amphoteric electrolyte structure, we are forced to the opinion that the possible amphoteric character of albumin is not the essential factor in its kataphoretic behaviour. Rather, that pure albumin, perhaps like most pure emulsoids, is electrically neutral, and takes up + or — charges, especially in solutions containing H· or OH′ respectively. (See further, p. 90.)

Oil emulsions made by shaking two c.c. of petroleum (density 0·9) with 100 c.c. of water, or by boiling the oil and water together, or by dissolving the oil in alcohol, pouring the solution into water, and finally driving off the alcohol by boiling, were examined by Hatschek.[1] The dispersity was the same in all three cases, being 4×10^{-5} cm. The oil was negative to the water, and the velocity of kataphoresis was -43×10^{-5} cm./sec. per 1 v/cm.; from this the value of ϵ is 0·05V, and $e = 4{\cdot}4 \times 10^{-7}$ electrostatic units, values which are practically the same as for the negative metal sols.

Theoretical

In this section will be found first the deduction of the equations concerning electroendosmosis and kataphoresis already given in the two preceding sections; and following

[1] *Koll. Zeitsch.*, 1911, 9, 159; also Lewis, 1909, 4, 211.

it, a discussion of the various theories which have been suggested to account for the origin of the potential difference at the boundary between solid and liquid.

The Volume Equation.—In the steady state resulting when a constant E.M.F. is applied to electrodes in two vessels connected by a capillary tube, no increase of hydrostatic pressure occurring, the E.M.F. must be considered merely to overcome the initial resistance, and thus to impart the constant velocity. The force of friction is proportional to the viscosity, to the area of the moving surfaces, and to the velocity gradient. For the reason already given (p. 66) we may consider both the moving surfaces of the electrical double layer to be liquid, the liquid moving against a film of liquid, which firmly adheres to the solid. The viscosity is thus given by η, the viscosity of the liquid.

The mean velocity u is given by the length of the column of liquid which passes out of the tube in unit time, v being the volume of liquid; then

$$\pi r^2 u = v \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

in which r is the radius of the capillary.

The gradient of velocity $\frac{du}{d\rho}$ can be put $= \frac{u}{\delta}$ (ρ = the distance from the solid wall, and δ the distance of the moving side of the double layer from the wall), since δ is a small distance, and the liquid at δ moves with the velocity u, and the layer itself has zero velocity.

The frictional force for unit surface is thus:

$$\frac{\eta u}{\delta}, \quad \text{or, putting in } u = \frac{v}{\pi r^2}, \quad \frac{\eta v}{\pi r^2 \delta}$$

The electrical force acting on unit surface of the moving side of the electrical double layer is $e\mathrm{H}$, e being the charge

on this unit surface, and H the potential gradient produced by the external E.M.F.

These two forces balance in equilibrium, and we have

$$eH = \frac{\eta v}{\pi r^2 \delta} \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

The double layer may be regarded as a condenser of potential ϵ in a medium whose dielectric constant is D. Then

$$\epsilon = \frac{4\pi\delta e}{D}$$

this, with the preceding equation (2), gives

$$\frac{\epsilon DH}{4\pi\delta} = \frac{\eta v}{\pi r^2 \delta}$$

from which

$$v = \frac{r^2 \epsilon DH}{4\eta} \quad . \quad . \quad . \quad . \quad . \quad (3)$$

Substituting $\frac{E}{l}$ for H, E being the E.M.F. applied to the electrodes, and l their distance apart, and substituting q the cross-section of a diaphragm for πr^2 the cross-section of a single capillary tube, we finally have

$$v = \frac{q\epsilon ED}{4\pi\eta l} \quad . \quad . \quad . \quad . \quad . \quad (4)$$

in which form it is given on p. 67.

The Pressure Equation.—If the liquid is not allowed to escape at constant (zero) pressure, the hydrostatic pressure P produced by the migration of a volume v of liquid is given by Poiseuille's law:

$$v = \frac{\pi P r^4}{8\eta l}$$

The equilibrium pressure P is obtained by combining this with equation (3):

$$v = \frac{\pi P r^4}{2\eta l} = \frac{r^2 \epsilon E D}{4\eta l}$$

from which

$$P = \frac{2\epsilon E D}{\pi r^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

These are the two laws for electroendosmosis.

Velocity of Kataphoresis Equation.—The law for the kataphoresis of solid particles in a stationary liquid is readily deduced from the above relations.

Imagine the particle to be a small cylinder placed axially in the capillary tube, and to be stationary, while the liquid flows past the cylinder in the annular space between it and the tube. If the annular space be regarded as made up of a series of tubes, the velocity of the liquid is obtained by combining equations (1) and (3):

$$\pi r^2 u = v = \frac{r^2 \epsilon D H}{4\eta}$$

from which

$$u = \frac{\epsilon D H}{4\pi\eta} \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

If the cylinder be now regarded as moving and the liquid as stationary, the velocity must still be the same (equality of action and reaction).

Theories regarding the Electrical Properties

The formulæ which have just been deduced, have been shown in the preceding sections to be fully borne out by the experimental results. It is well, however, to state explicitly that they throw no light on the origin of the electrical phenomena described in those sections. The

development of the equations is based upon the assumption of "an electrical double layer," one layer of which can move, while the other remains stationary. The nature of the double layer, or how it comes into being, or is maintained, are quite immaterial.

These are, of course, questions of the greatest importance and interest. No final decisive answer can be given at the present time, but several very suggestive indications have been advanced, and are worthy of closer consideration.

On the well-established ground that the exceptions or irregularities most often afford the clue, we may first take the positive sols, those basic hydroxides of metals and basic dyes, which, unlike the great majority of hydrosols, migrate to the kathode. This peculiarity has been explained in various ways; *e.g.* being metallic hydroxides, they can form metallic (positive) ions, by electrolytic dissociation. This is true, but they must at the same time have produced an equivalent amount of OH' or of some other negative ion. Further, zinc sulphide (and most other metallic compounds) can also give rise to metallic ions (kations), but they, notwithstanding this, migrate to the anode.

Now if aluminium hydroxide, for instance, in pure water is positive, while the water is negative, it would appear that the hydroxide has in some way united with part of the $H^{\cdot}$ of the water, leaving the equivalent excess of OH' to produce the negative charge of the liquid phase. Pure water contains equivalent amounts of $H^{\cdot}$ and OH', though the actual concentrations are very small. From this we would infer that aluminium hydroxide dissolves, or adsorbs, or retains by permeation or diffusion, $H^{\cdot}$ more readily than OH'.

There is abundant experimental evidence to support this

view. The formation of a semipermeable membrane by reaction between aluminium salts and ammonia is evidence that aluminium hydroxide is impermeable by OH′, for otherwise, instead of a thin film, which does not increase in thickness, being formed, the reaction would continue until all the Al‴ or OH′ was used up. It has also been shown[1] that even a large E.M.F. fails to drive OH′ across such a film of aluminium hydroxide. We may thus take it as proved that aluminium hydroxide cannot dissolve OH′ to any extent, and that OH′ cannot diffuse into it. It has also been demonstrated that a film of aluminium hydroxide is permeable by H˙, both by simple diffusion and by the application of an E.M.F. It is immaterial whether this permeability is regarded as a solution effect or as a diffusion.

Thus, when aluminium hydroxide is suspended in even pure water, which contains equal concentrations of H˙ and OH′, the H˙ can dissolve in, or diffuse into it, while the equivalent of OH′ will be left behind, and will accumulate in the layer next the particles.

We will next consider the case of albumin, as the type of another set of exceptional substances. Highly purified albumin shows no kataphoresis in water or in neutral salt solutions; it therefore has no electric charge. From the present point of view, this indicates that albumin either cannot dissolve H˙ or OH′, or that both are equally soluble (or diffusible) in it. If the latter view is taken, the concentration of H˙ and OH′ in albumin will vary directly as their concentration in the liquid, *i.e.* in acids, which contain more H˙ and less OH′ than water, it will take up an excess of H˙, and will be positive. The positive charge will increase with increase in acidity of the liquid. In alkaline solutions there is more OH′ and less H˙ than in water; the albumin will become negative,

[1] Taylor and Inglis, *loc. cit.*, p. 74.

and the charge will increase as the alkalinity increases. In each case the effect of increasing acid or alkali will fall off, as a saturation limit may soon be reached.

Admittedly, these ideas cannot be carried much further, for practically nothing is known regarding solubility or diffusibility of ions in most substances. Nor does it follow because these "explanations" fit the facts, that they are correct. There may be many possible explanations, only one of which can be right. Indeed, the most probable of the suggestions is that one which substitutes *adsorption* for diffusion or solution: and this, partly because adsorption is a wider and more universal phenomenon than the others, and partly because it can be observed or assumed to occur in more instances than they.

The *adsorption theory* explains the predominant effect of $H^{\cdot}$ and OH' on the electric charge by stating that these ions are more readily adsorbed than other ions, and that, further, OH' is more readily adsorbed than $H^{\cdot}$; from which most sols are negative to water. It is not so clear why OH' is less readily adsorbed than $H^{\cdot}$ by those basic hydroxides which form positive sols, nor why albumin adsorbs both ions equally. Freundlich suggests that the basic substances produce OH' in the adherent layer, and that, owing to its greater diffusion velocity than the other ions present, it diffuses into the moving layer, imparting to it a negative charge, and leaving the particle positively charged; and similarly with the feebly acid substances and $H^{\cdot}$. The great influence of acid or alkaline reaction of the medium on the magnitude, and even on the sign of the charge on the sol, is readily seen from this point of view.

The fact that the effect of ions is relatively greatest at small concentrations is what would be expected from the relation between adsorption and concentration. It is

plain, too, that only adsorption of ions of opposite charge to that on the sol can reduce the charge on the sol, for the adsorption of the other ion would increase the charge. The valency rule also is capable of explanation from the same point of view (see p. 102).

In many instances electrolytic dissociation does not afford an explanation; *e.g.* drops of petroleum[1] in water are negatively charged, as also is aniline.[2] According to Perrin,[3] there is no electric charge at the interface of solids and liquids in non-ionising liquids, such as chloroform and ether. Again, transference of electrons at the interface may also occur.

CHAPTER IX

PRECIPITATION

ONE of the most striking features of certain of the sols prepared by Graham and other of the early investigators of colloids, and one which attracted their attention, is their extraordinary sensitiveness to chemical reagents. Aluminium hydroxide sol, for instance, prepared by Graham's method, gives a dense precipitate when one or two drops of dilute sulphuric acid are added to it; this precipitate is aluminium hydroxide. The sol is still more sensitive to neutral sulphates (*e.g.* sodium sulphate). Many other sols are equally sensitive.

In some cases this process can be reversed, and the

[1] Lewis, *Koll. Zeitsch.*, 1909, **4**, 211.
[2] Ellis, *Zeitsch. Physikal. Chem.*, 1912, **78**, 321.
[3] Perrin, *Jour. Chim. phys.*, 1904, **2**, 601; 1905, **3**, 50.

sol regenerated by merely washing away the reagent with pure water, but in others this cannot be done, there being apparently no direct method of regaining the sol. Between these extremes lie the majority of sols. In many cases the reversibility is a question of time; the precipitation is reversible at first, but, sooner or later, passes through stages of incomplete reversibility to complete irreversibility. The division of precipitations into reversible and irreversible depends on an arbitrary interval of time.

Instability, the tendency to undergo change either spontaneously or under the influence of very small amounts of reagents, appeared to be characteristic of colloids, though possessed by different colloids to very different extents. The metal sols, in whatever way prepared, are, as Faraday, Zsigmondy, and Bredig found, probably the most susceptible to changes, which seemed at first sight to be spontaneous, due to inherent instability, but which were later shown to be dependent on the method of preparation, and especially on the nature of other substances formed in the reaction simultaneously with the sol. On the other hand, many sols were extremely stable, and remained unchanged for years, although they were highly sensitive to small amounts of reagents.

This susceptibility to reagents is, as a rule, limited to electrolytes: salts, acids, and bases; indifferent substances, whether inorganic or organic, have usually no appreciable effect, until they are added in large quantity. Sols vary very much in their susceptibility to reagents; some are readily precipitated while others are not affected by some salts, and require large amounts of other salts to cause precipitation. They have accordingly been classed as hydrophobe and hydrophile sols, or more generally, as the distinction also applies to other dispersion media, lyophobe

and lyophile sols. Broadly, this division agrees with that into suspensoids and emulsoids. The propriety of the terms will be evident if the fundamental differences between suspensoids and emulsoids are recalled (p. 18). It is necessary also to bear in mind the present use of the term "*gel*" (Introduction, p. 5).

As the phenomena of precipitation are so varied, they will be dealt with in the following order:—

A. The action of electrolytes on suspensoids:
   (*a*) qualitative, (*b*) quantitative, (*c*) valency rule, (*d*) adsorption, (*e*) stabilising effect of ions.

B. The "complex" theory of colloids.

C. The action of reagents on emulsoids:
   (*a*) albumin, (*b*) gelatine, (*c*) silicic acid.

D. Protection of suspensoids by emulsoids.

E. Mutual precipitation of sols.

The Action of Electrolytes on Suspensoids

When successive small quantities of a salt are added to a sol, the sol becomes opalescent, and a flocculent precipitate finally appears, which settles out, and leaves the medium clear and free from the disperse phase. This behaviour, first observed by Selmi, and later by Graham, is well known to every student in the case of arsenious sulphide, which is obtained as a sol by interaction of arsenious acid and hydrogen sulphide solutions; no precipitate is obtained until acid or salts have been added. The changes are readily followed under the microscope; when opalescence commences, the particles, while visibly increasing in size by coalescence, are in rapid Brownian movement. As the size increases, the movement falls off, and when the particles settle out, they are no longer in motion.

The course of these changes can be followed more completely in the ultramicroscope. Commencing with an amicron sol, the first effect is the production of submicrons, seen as individual discs of light in active Brownian movement. On further addition of electrolyte, they decrease in number by uniting with each other to form microns. Along with this the Brownian movement becomes sluggish, and, as the micron stage passes into the macron stage, diminishes to complete cessation; sedimentation then occurs.

This cessation has been considered by some to be the cause of precipitation, the primary effect of the electrolyte being on the Brownian movement, slowing it down. It had, indeed, been observed that small concentrations of electrolytes actually do reduce it, and at last cause it to cease. Svedberg showed that the sequence is the reverse of that stated above, *i.e.* the electrolyte causes the particles to unite, and the Brownian movement becomes slower in consequence of the larger size. There was no change in the amplitude before and after the electrolyte was added, until the size began to increase. The following figures refer to a silver sol, to which increasing amounts of aluminium sulphate were added. It was possible to determine the amplitude before a sensible amount of precipitation had occurred. Even so great an amount of aluminium salt as to reverse the electric charge on the sol had no effect on the amplitude.

Kataphoretic velocity (cm./sec. × 10^5).	Amplitude in μ.	Kataphoretic velocity (cm /sec. × 10^5).	Amplitude in μ.
− 2·1	1·3	+ 0·43	1·2
− 2·6	1·3	+ 1·76	1·2

These figures make it quite clear that the alteration in the Brownian movement is due to antecedent changes in the sol.

The cause is rather to be sought in the electrical phenomena. Burton noticed in his experiments on the effect of Al''' on the kataphoresis of silver sols, that the latter appeared to be at *maximum instability* when the kataphoresis was reduced to zero, *i.e.* at the point of electric neutrality, the *isoelectric point.* Of the four silver sols in the table on p. 81, the pure sol was stable for indefinite periods, the two following ($u = -7{\cdot}2$ and $+5{\cdot}9 \times 10^{-5}$) precipitated in a few hours, and the last ($u = +13{\cdot}8 \times 10^{-5}$) was more stable, not being completely precipitated in four days. The effect of the electrolyte is first of all to diminish the potential difference between the disperse phase and the medium, and precipitation only occurs when the potential difference has been brought sufficiently near to zero; smaller amounts of electrolyte have practically no effect on the stability of the sol. Linder and Picton[1] added to a ferric hydroxide sol one-sixth of the amount of NaCl necessary for its complete precipitation; it remained clear even on boiling. As the sol could no longer be filtered unchanged through a porous plate, its dispersity must have decreased, although not so much as appreciably to diminish its stability.

The precipitation of sols by electrolytes has been recently worked out by Kruyt and Spek,[2] and, according to them, the processes concerned are as follows:—The particles unite after approaching on account of Brownian movement (probability of collision); the probability that collision leads to union depends on the electric charge on the particles, which, in turn, depends on the electrolyte added, corresponding to adsorption of the added ion. Decreased dispersity (by boiling, or change of initial concentration, as by dilution of a more concentrated sol)

[1] *Chem. Soc. Jour.*, 1905, **87**, 1992.
[2] *Koll. Zeitsch.*, 1919, **25**, 1.

causes an increase of precipitation value for $K^{\cdot}$ and $Ba^{\cdot\cdot}$, a decrease for $Al^{\cdot\cdot\cdot}$. With a lower total surface, a corresponding decrease of electrolyte is necessary for a given adsorbed amount; dilution or reduction of dispersity brings the particles further apart, so the probability of collision is less, and in equal conditions for precipitation a greater probability that collision leads to union, *i.e.* a less charge is required (lowering of critical potential). These opposing tendencies emerge to different extents for different ions.

We must conclude, then, that a definite concentration of electrolyte is necessary for precipitation, and that, since smaller concentrations may cause only partial precipitation or even none at all, it is not improbable that larger concentrations may also produce partial or no precipitation.

The Precipitation Concentration.—The existence of this limiting concentration was first demonstrated by Bodländer[1] in the case of kaolin suspensions. This is well shown by the following table:—

Acid concentration. $\frac{H_2SO_4}{2} \times 10^3$	Kaolin. g. per litre.	Acid concentration. $\frac{H_2SO_4}{2} \times 10^3$	Kaolin. g. per litre.
0·0	7·7	0·25	6·9
0·12	7·5	0·28	6·1
0·16	7·7	0·29	4·8
0·19	7·6		

The same holds for sols; below this limit of concentration there is no precipitation even after a long interval of time.[2] An arsenious sulphide sol contained 9·57 millimols per litre; in portions of this sol containing 1·219 and 2·438 millimols of potassium chloride per litre, the concentrations of arsenious sulphide at the end of 340 days were 9·60 and 9·45 millimols respectively. With

[1] *Gottinger Nachrichten*, 1893, 267.

[2] Freundlich, *Zeitsch. physikal. Chem.*, 1903, **44**, 141.

3·90 millimols of potassium chloride per litre, the sol was almost completely precipitated in this time.

It is a peculiar circumstance that the manner of adding the reagent has a marked effect on precipitation; when the reagent is added very slowly, or a little at a time, a much larger amount is necessary for complete precipitation. The sol appears to become "acclimatised." For instance, the amount of barium chloride necessary for complete precipitation of an arsenious sulphide sol in two hours was ascertained. When this amount was added in small quantities at a time, precipitation was far from complete in two hours, and a much larger amount was then necessary. The slower the reagent is added, the greater is this excess. This is a general occurrence.

If, as an experiment of Mines suggests,[1] the precipitant reverses the sign of part of the disperse phase, which then mutually precipitates the unchanged particles, *i.e.* if the action is due to irregular distribution of electric charges, it is evident that the effect produced by a given amount of electrolyte will depend on the rate at which it is added. For if it is slowly added, time is afforded for all the particles to be equally affected, and, therefore, there will be no precipitation.

The Valency Rule.—The most striking thing about the precipitation of sols by electrolytes is the enormous differences in the precipitation concentration of different salts. This is equally true of suspensions and of sols. The following figures, given by Bodländer,[2] illustrate this. The concentrations are not precipitation-concentrations, but are the concentrations which exactly doubled the rate of sedimentation in the pure suspension.

[1] *Koll. Chem. Beihefte*, 1912, **3**, 191.
[2] *Jahrb. Mineral.*, 1893, **2**, 147.

Electrolyte.	Kaolin Suspension. Mg. equivalents in 100 c.c. suspension.
HCl	0·0017
HNO_3	0·0016
$HCOO.CCl_3$	0·0016
H_2SO_4	0·0020
$H_2C_2O_4$	0·3700
H_3PO_4	0·0183
NaOH	1·186
$Ba(OH)_2$	0·3700
$NaNO_3$	0·0133
$CaCl_2$	0·0029
$MgCl_2$	0·0016

Similar results were obtained by both Hardy and Bechhold for mastic sols and a gold sol[1]:—

Electrolyte.	Mastic (Hardy). gm. equiv. per litre.	Gold sol (Hardy). gm. equiv. per litre.
HCl	0·004	0·008
HNO_3	0·004	0·008
H_2SO_4	0·004	0·008
$H_2C_2O_4$	0·009	—
NaCl	0·12	0·013
K_2SO_4	0 24	0·026
$BaCl_2$	0·022	0·004
$MgSO_4$	0 028	—
KOH	—	0·09

Mastic (Bechhold).

Electrolyte.	mg. equiv. per litre.	Electrolyte.	mg. equiv. per litre.
NaCl	1000	$BaCl_2$	50
$AgNO_3$	125	$CaCl_2$	50
HCl	10	$CdSO_4$	25
H_2SO_4	10	$Al_2(SO_4)_3$	0·5
$MgSO_4$	100	$Fe_2(SO_4)_3$	0·5
$ZnSO_4$	100	$Al(NO_3)_3$	0·6
		$FeCl_3$	0·9

[1] Hardy, *Zeitsch. physikal. Chem.*, 1900, **37**, 385; Bechhold, *Zeitsch. physikal. Chem.*, 1904, **48**, 385.

It is obvious from these results that these electrolytes fall naturally into three groups, the members of each group possessing the same precipitating power. As the same anions are to be found in all three groups, the enormous differences cannot be ascribed to them, but are either due to the unionised molecule or to the kations. The kations in each group are of the same valency; the univalent kations $H^{\cdot}$, $Na^{\cdot}$, $K^{\cdot}$, etc., in the first group, with the smallest precipitating power; followed by the bivalent kations $Ca^{\cdot\cdot}$, $Ba^{\cdot\cdot}$, $Mg^{\cdot\cdot}$, $Zn^{\cdot\cdot}$, etc., and by the third group, the trivalent kations $Al^{\cdot\cdot\cdot}$, $Fe^{\cdot\cdot\cdot}$, etc., with the greatest precipitating power.

All the sols in the above tables are negative; it is clear that the precipitation is mainly effected by the ion of opposite electric charge, and that the precipitation-concentration is a function of the valency of these ions.

If this conclusion is correct, the precipitation of positive sols should depend on the valency of the anion. Experiments made to test this have fully confirmed the valency rule. Hardy, who first established this rule, found the following figures:—

FERRIC HYDROXIDE SOL.

Electrolyte.	Concentration gm. equiv. per litre.	Electrolyte.	Concentration gm. equiv. per litre.
HCl	0·5	H_2SO_4	0·002
HNO_3	0·5	$H_2C_2O_4$	0·002
NaCl	0·5	K_2SO_4	0·0006
KOH	0·001	$MgSO_4$	0·0005
$BaCl_2$	0·001	H_3 citrate . . .	0·0007

Certain peculiarities in these results require explanation, but on the whole they confirm the valency rule, the three groups containing the univalent, bivalent, and trivalent anions respectively. A very extensive series of experiments by Freundlich[1] fully establishes the rule.

[1] *Loc. cit.*, p. 97.

FERRIC HYDROXIDE SOL (16 m.mols per litre).

Electrolyte.	Conc. mg. equiv. in 1 litre.	Electrolyte.	Conc. mg. equiv. in 1 litre.
NaCl	9·25	HCl	ca 400
KCl	9·03	$Ba(OH)_2$	0·42
$BaCl_2$	9·64	K_2SO_4	0·204
KNO_3	11·9	$MgSO_4$	0·217
KBr	12·5	$K_2Cr_2O_7$	0·194
$Ba(NO_3)_2$	14·0	H_2SO_4	ca 0·5
KI	16·2		

PLATINUM SOL (·7 m.atom per litre).

Electrolyte.	Conc. (m.mol per litre).	Electrolyte.	Conc. (m.mol per litre).
NaOH	130	$BaCl_2$	0·058
NaCl	2·5	$UO_2(NO_3)_2$	0·065
KCl	2·2	$Pb(NO_3)_2$	0·011
$AgNO_3$	0·22	$\frac{1}{2}Al_2(SO_4)_3$	0·013

ARSENIOUS SULPHIDE (7·54 m.mols per litre).

Electrolyte.	Conc.	Electrolyte.	Conc.
Univalent Kations—		Morphine chloride	0·425
$\frac{1}{3}K_3$ citrate	240	Crystal violet	0·165
$KC_2H_3O_2$	110	Neo fuchsin	0·114
$KClO_3$	86	*Bivalent Kations*—	
$\frac{1}{2}K_2SO_4$	65·5	$MgSO_4$	0·810
KCl	49·5	$MgCl_2$	0·717
KNO_3	50·0	$CaCl_2$	0·649
NaCl	51·0	$SrCl_2$	0·635
LiCl	58·5	$BaCl_2$	0·691
HCl	30·8	$Ba(NO_3)_2$	0·687
$\frac{1}{2}H_2SO_4$	30·1	$ZnCl_2$	0·685
		$UO_2(NO_3)_2$	0·642
Guanidine nitrate	16·4		
Strychnine „	8·0	Quinine sulphate	0·24
Aniline chloride	2·52	Benzidine nitrate	0·087
Toluidine sulphate	1·17	*Trivalent Kations*—	
p. chloraniline chloride	1·08	$AlCl_3$	0·093
		$Al(NO_3)_3$	0·095

Hardy's rule that the precipitating power of an electrolyte depends on the valency of the ion, whose electric charge is opposite to that on the sol, is thus fully established.

We thus have the same law applying to the amount and direction of electroendosmosis and kataphoresis on the one hand, and to precipitation on the other. It is then highly probable that the latter is a consequence of the reduction or elimination of the potential difference between the disperse phase and the medium. If the electric charge on the particles is due to the adsorption of kations or anions, according as the sol is + or —, it is easily seen that the neutralisation of this charge requires the adsorption of anions or kations. Further, the readily adsorbed $H^{\cdot}$ and OH', which we have seen to have so powerful an effect in electroendosmosis, should also have a greater precipitating power than other univalent ions. The data given above contain illustrations of such an effect. Not only so, but any ion which is readily adsorbed ought to have a lower precipitation-concentration than other ions of the same valency. Among such are the organic ions. We shall return to this later on.

Explanations of the Valency Rule.—Various explanations have been advanced. Qualitatively, there is little difficulty, if it is remembered that precipitation is a consequence of removing a definite electric charge from the disperse phase by means of ions of opposite charge. As the charges on uni-, bi-, and tri-valent ions are in the ratio 1 : 2 : 3, the equivalent amounts will be in the ratio 3 : 1·5 : 1.

The quantitative relation is not so easy. Whetham[1] applied the theory of probabilities, and reached the conclusion that the ratios of the molecular precipitation-

[1] *Phil. Mag.*, 1899, [v.] 48, 474.

concentrations of univalent, bivalent, and trivalent ions are

$$c_1 : c_2 : c_3 = k^3 : k^2 : k$$

k being a constant.

Freundlich assumes that neutral salts, whatever their valency, are equally adsorbed from equimolecular solutions, and that they follow the adsorption law. The charges on uni-, bi-, and tri-valent ions being in the ratio 1 : 2 : 3. the amounts to be adsorbed, in order to produce complete

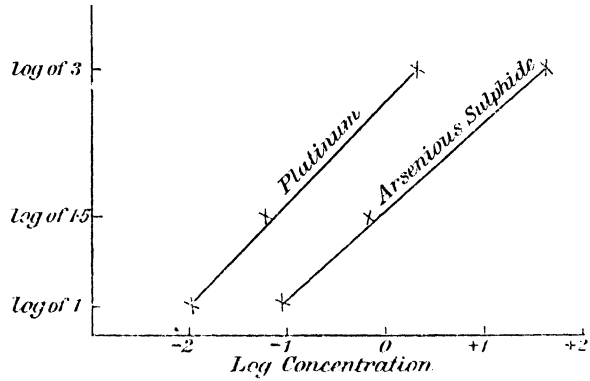


FIG. 6.

precipitation, will be in the ratio 3 : 1·5 : 1. The concentrations of solutions in which bivalent and trivalent ions will be adsorbed to these extents, compared with the necessary adsorption of univalent ions, can be read from the adsorption curve (p. 255). These should be approximately the precipitation-concentrations of the solutions. The simplest test of this is to plot the logarithms of the concentrations against the logarithms of 3, 1·5, and 1. The curve will be a straight line, if the adsorption law is followed. When this is done for the data for arsenious sulphide and platinum sols the curves are practically straight lines (Fig. 6).

Adsorption of the Precipitating Ion.—Perhaps the best confirmation of the above ideas as to the mechanism of precipitation is to be found in the fact, that when a sol is precipitated, the precipitate "carries down" with it part of the reagent, or rather, of the ion of opposite charge. This was first noticed by Linder and Picton [1] with arsenious sulphide sol and barium chloride. The supernatant liquid was found to be acid, and a corresponding quantity of barium was found in the precipitate. It was so firmly held by the precipitate that no amount of washing with water availed to remove it. It could be removed by washing it with a solution of some other salt, the kation of which took the place of the barium. These observations have been subsequently confirmed and extended.

According to the explanations of the preceding section, only the precipitating ions should be adsorbed, and in electrically equivalent amounts. The amounts of different ions adsorbed by a given amount of precipitate ought then to be chemically equivalent. This is the case.[2] Thus 100 c.c. of arsenious sulphide sol adsorbed the following weights of ions:—

Ion.	Weight adsorbed (gram), observed.	calculated.
Ba	0·0076	*0·0076*
Ca	0·0020	0·0022
Sr	0·0039	0·0049
K	0·0036	0·0043

The weights equivalent to 0·0076 g. Ba are given in the last column.

Freundlich [3] examined several organic ions, which also agreed with the rule. The number of milligram equivalents

[1] *Chem. Soc. Journ.*, 1895, **67**, 63.
[2] Whitney and Ober, *J. Amer. Chem. Soc.*, 1902, **23**, 842.
[3] *Koll. Zeitsch.*, 1907, **1**, 321.

of kations adsorbed by 100 millimols of arsenious sulphide is very nearly 2 (the number varies from 2·5 for Ca to 1·8 for aniline).

The impossibility of washing out the adsorbed ion with water, and the quantitative replacement of it by other ions, correspond closely with the behaviour of adsorbed substances in general. The positive sols afford further confirmation. Organic anions have an unusually low precipitation-concentration for ferric hydroxide sol, *e.g.*—

Sodium chloride	300
„ formate	56
„ acetate	30
„ benzoate	32
„ salicylate	20

Now organic acids are as a rule strongly adsorbed, and so the amount of anion necessary for electrical neutralisation and precipitation will be adsorbed from more dilute solutions.

The Stabilising Effect of Ions.—Attention has just been directed to the specially low precipitation-concentration of organic anions on a positive sol. A glance at the tables on p. 101 shows that these salts have an abnormally high precipitation-concentration for the negative sols. The same holds for OH', and the reverse for H'. Acids and bases occupy an exceptional position in all the tables, whether relating to + sols or — sols. Thus for ferric hydroxide the precipitation-concentrations are—

$BaCl_2$	9·64
HCl	400
$Ba(OH)_2$	0·42

The figure for barium chloride is about the same as that for any other chloride, except hydrochloric acid, and the figure for any univalent anion, except OH', is nearly the same as for Cl'.

It thus appears that $H^{\cdot}$ exerts an influence on a positive sol which is opposed to precipitation, while OH' has the opposite effect. The corresponding effect with negative sols will be that OH' hinders precipitation, while $H^{\cdot}$ favours it, and this is what actually happens. The precipitation-concentration of sodium chloride on a platinum sol was 2·5, of sodium hydroxide 130. The figures for a mastic sol were: sodium chloride = 0·12, and hydrochloric acid = 0·004. Bodländer's figures for kaolin are a good illustration, *e.g.*—

HNO_3	0·0016
$NaNO_3$	0·0133
$NaOH$	1·19
$CaCl_2$	0·003
$Ba(OH)_2$	0·37

In all these examples we see that $H^{\cdot}$ and OH' exercise opposing influences on both positive sols and negative sols, but that each of them has a similar effect on sols of the same sign as themselves, *i.e.* $H^{\cdot}$ stabilises positive sols, and OH' stabilises negative sols. This is what the facts of electroendosmosis, and the theories regarding the origin of the potential difference at the interface of liquid and solid, would lead us to expect. A positive diaphragm and a positive sol will have their positive charge increased by the presence in the liquid of a highly adsorbable kation, such as $H^{\cdot}$ and the organic kations; they will be more readily discharged by highly adsorbable anions, such as OH' and organic anions. The converse will hold for negative diaphragms and sols.

The precipitating effect of an electrolyte is due to a balance between two opposing influences: a suspending or stabilising effect due to the ion of the same sign as the sol, and a labilising or precipitating effect due to the ion

of opposite sign. The valency rule is approximately true because in the majority of cases, *i.e.* inorganic salts, the one force is much greater than the other. Still, even in the case of neutral salts the differences between univalent ions are far greater than the experimental error.

Many instances could be cited in illustration of this view, but two will suffice. Bredig discovered a method of preparing metallic sols by electrical dispersion of solid metals under water. These sols, which are negative, were not very stable, and Bredig recommends the addition of a trace of alkali to pure water, to increase the stability. In Kohlschütter's method of preparing silver sol (p. 187) there is always some unreduced silver hydroxide left. Most of this can be reduced by hydrogen gas in a platinum basin, but not quite all of it. The less hydroxide remains, the less stable is the sol. Unless very pure conductivity water is employed (electrolyte-free) the sols usually precipitate towards the end of the purification.

We must also revert to Burton's experiments on the kataphoresis of silver or gold sol, to which varying amounts of Al''' had been added (p. 81). The trivalent kation, which is so potent in discharging and precipitating the negative sols, reverses the direction of kataphoresis, and also increases the stability of the sol when added in larger quantity. In this connexion, his experiments with quadrivalent ions are interesting. He failed to obtain precipitation with stannic chloride or platinum chloride. There are two possible explanations for this failure. Probably in neither case does the solution contain a quadrivalent kation; stannic chloride is hydrolysed into stannic acid sol, which is emulsoid, and would "*protect*" the silver sol from precipitation by electrolytes (p. 130); if the platinum chloride was $PtCl_4$ (and not H_2PtCl_6), it was probably entirely converted into an oxy-acid (H_2PtOCl_4), in which

the kation is H· and the platinum is part of the anion. The other explanation is that, in accordance with the valency rule, the precipitation-concentration of a quadrivalent ion is exceedingly small, and a small excess over this amount would, as in the above case of Al‴, convert the silver sol into a stable positive sol.

The "Complex" Theory of Colloids

These relations between the stability of sols and the presence of ions or of electrolytes in the disperse phase have naturally led to the question whether a colloid is not essentially a complex made up of the two. Thus the above silver hydrosol will be either xAg, yAgOH, or more simply xAg.yOH′, and so for other sols. This idea is found quite early in the history of colloids. Graham observed that dialysis, however prolonged, did not remove all the chloride from his ferric hydroxide sol, the limit being 98·5 per cent. of ferric hydroxide to 1·5 per cent. of hydrochloric acid. The amount of chloride was later reduced to less than half this, 99·15 per cent. $Fe(OH)_3$ to 0·85 per cent. HCl, and recently again by Nicolardot[1] to 99·84 per cent. $Fe(OH)_3$ to 0·16 per cent. HCl.

The same thing occurs in many other instances, *e.g.* zirconium hydroxide sol,[2] prepared by hydrolysis of the chloride and dialysis, contained 0·0048 g. Cl′ to 0·667 g. ZrO_2. The sulphide sols prepared by Linder and Picton[3] were found by them to contain hydrogen sulphide, which could not be removed without precipitation of the sol. They determined both the metal and the sulphur; the excess of sulphur amounted to several per cent. They regarded the hydrogen sulphide as an essential constituent of the sols,

[1] *Recherches sur le sesquioxide de fer*, Thèse. Paris, 1905.
[2] Ruer, *Zeitsch. anorg. Chem.*, 1905, **43**, 232.
[3] *Chem. Soc. Journ.*, 1892, **61**, 114.

and assigned formulæ to them, *e.g.* $8As_2S_3$, H_2S; $22CuS$, H_2S; $12ZnS$, H_2S.

Wyrouboff[1] and pupils represented the various dialysed ferric hydroxide sols as chlorides of "condensed" ferric hydroxides, a reminiscence of Graham's "co" salts. This idea was further developed by Duclaux,[2] and extended to other groups of sols. In particular, copper ferrocyanide was shown to contain K', no matter what excess of $CuSO_4$ had been employed. The formula varied between $Cu_2Fe(CN)_6$, $\frac{1}{2}K_4Fe(CN)_6$ and $Cu_2Fe(CN)_6$, $\frac{1}{30}K_4Fe(CN)_6$. Similar results were found for cadmium sulphide from cadmium sulphate and hydrogen sulphide; the sol always contained all three substances, whether there was excess of either the one reagent or the other. The stability of the sol depends on the presence of these ions.

From this standpoint, precipitation by electrolytes becomes a chemical reaction, a double decomposition in fact, and the valency rule becomes obvious. The equivalence of the ions necessary for equal precipitation has already been dealt with, but Duclaux's figures for ferric hydroxide sol are so striking that they are given below.[2] The sol contained 0·0203 equivalents Fe, and 0·00166 equivalents Cl per litre. 10 c.c. of the sol ($= 16{\cdot}6 \times 10^{-6}$ equiv. Cl) required

17×10^{-6} equiv.	SO_4	19×10^{-6} equiv.	PO_4
16·5	$C_6H_5O_7$ (citrate)	16	OH
15·2	CrO_4	13	$Fe(CN)_6$
17	CO_3		

Similar figures were obtained for the negative copper ferrocyanide sol.

[1] *Bull. Soc. chim.*, 1899, **21**, 137.

[2] *Compt. Rend.*, 1904, **138**, 144, 809; 1905, **140**, 1468, 1544; 1906, **143**, 296, 344; *J. Chim. Phys.*, 1907, **5**, 29.

In the attempt to prepare pure silicic acid sol by Graham's method, Jordis[1] found that the more it was purified the more unstable it became, and formed the conclusion that sols are chemical compounds.

The amount of salt associated with the colloid varies with the concentration of the salt in the liquid,[2] which is contrary to chemical combination, but is in agreement with adsorption. Lottermoser[3] has shown that silver halide sols can be made from very dilute solutions of silver nitrate and KX. If silver salt is added to potassium iodide solution, a silver iodide sol is obtained, which is stable so long as there is an excess of potassium iodide; but so soon as $Ag^{\cdot}$ and I' are exactly equivalent, the sol is unstable and is precipitated. These sols are negative. Starting in the reverse order, the sol is stable so long as there is excess of silver nitrate, and is precipitated when there is none. These sols are positive.

We are thus led to conclude that the stability of sols is connected with the presence in the sol of small quantities of other substances, usually substances related to or derived from the colloid itself.

For one class of sols this seems improbable: the metal sols, especially the sols of noble metals, as gold and platinum, and most particularly when prepared by Bredig's method. The gold sols formed by reduction of auric chloride contain Cl', for after precipitation Cl' is formed in the liquid.[4] But in Bredig's and Svedberg's electrical dispersion methods (p. 217) the sols are formed at very high temperatures in the presence of air. It is by no means impossible for traces of oxides or hydroxides to be

[1] *Zeitsch. anorg. Chem.*, 1903, **35**, 16; *Zeitsch. Elektrochem.*, 1904, **10**, 509.

[2] Henri and Mayer, *Compt. Rend.*, 1904, **139**, 924.

[3] *J. pr. Chem.*, 1905, **72**, 39; 1906, **73**, 374.

[4] Steubing, *Ann. Physik.*, 1908, [iv.] **26**, 335.

formed under these conditions. The base metals when treated in this way give sols which, in appearance and general behaviour, are like hydroxide sols.[1] Even if air is excluded, the dispersion medium is undergoing chemical decomposition, owing to the high temperature, and so the possibility of the formation of compounds is increased. The instability of Kohlschütter's silver sol, when freed as far as possible from silver hydroxide, has already been referred to (p. 107).

The Action of Electrolytes on Emulsoids

The differences between suspensoids and emulsoids in their behaviour towards electrolytes are very marked, even more so than their electrical behaviour would lead us to anticipate. They are not merely differences between liquid and solid disperse phases, for ferric hydroxide sol, which is probably liquid, does not differ in this respect from other sols which are undoubtedly solid. As has been pointed out (p. 19), emulsoids are not only liquids, but partake more of the nature of solutions, part at least of the colloid probably being in solution. Whether this is the reason or not, the behaviour of emulsoids towards electrolytes is so diverse and so complex, that classification and comprehensive survey are (for the present) out of the question.

Although emulsoids generally are much less sensitive to electrolytes, the difference is mainly quantitative, for the dispersity of an oil emulsion is decreased by even small amounts of potassium chloride. The effect of multivalent ions is still more easily observed; and, as Mines[2] found, trivalent ions, *e.g.* $La^{\cdots}$, precipitate egg white at a concentration of 1·6 m. mol. per litre, although

[1] Burton, *Phil. Mag.*, 1906, [vi.] **11**, 425.
[2] *Koll. Chem. Beihefte*, 1912, **3**, 191.

univalent ions have no apparent effect. The corresponding concentration of $La^{\cdot\cdot\cdot}$ for the suspensoid arsenious sulphide is about 0·05 m.mol., or 0·09 m.mol. for $Al^{\cdot\cdot\cdot}$ (p. 101). If the Valency Rule is borne in mind, the relative insensibility to univalent ions is intelligible.

That there are other factors beside valency, is confirmed by another interesting observation of Mines. While suspensoids are affected equally by complex trivalent kations, as the cobaltammino, $Co(NH_3)_6^{\cdot\cdot\cdot}$, and simple ions as $Al^{\cdot\cdot\cdot}$ or $La^{\cdot\cdot\cdot}$, egg white is not precipitated by the former, even at 20 m mol. per litre. The chief differences between them are in mobility, and density of electric charge owing to the large surface, the ratio of the latter being estimated as 0·26 to 1·37.

All that can profitably be attempted is to present the more general features in a few of the most important and best-known cases. Even the classification of precipitation as reversible and irreversible is not justifiable, as reversibility is mainly a matter of time. It is rather unfortunate, too, that so much of the work has been done on the natural emulsoids, as white of egg, serum albumin, gelatine, frequently without any assurance as to the purity or even uniformity of the material. This circumstance makes the comparison of results a doubtful matter, and has surely retarded progress.

The oil emulsions of Hatschek (p. 85) are not particularly sensitive to electrolytes. Thus, the dispersity of a 1 in 5000 emulsion of light petroleum, whose dispersity is about 4×10^{-5} cm. was not changed by sodium chloride, but 155 m.mol of sodium sulphate per litre produced a clearing up. 19 m.mol of hydrochloric acid per litre had barely any effect on the sol, but a marked effect was produced at a concentration of 23 m.mol per litre. The particles became larger and the original reddish coloured

I. Albumin

The Action of Electrolytes on Albumin.—If we leave out of account acids and alkalies, salts may be grouped into three classes, according to their action on albumin sols. The first group produces precipitates, even when in small concentration; it comprises salts of the heavy metals. The other two groups only cause precipitation at really considerable concentrations; in the one group, the precipitation is reversible, while in the other it is not. The second group comprises the alkali salts: K, Na, NH_4, Li, and Mg; while the third group contains the alkaline earth salts. The difference is one of time, for in the former the precipitation becomes irreversible after a time, and in the latter it is reversible at first, but very rapidly ceases to be so.

Much of the work has been done on purified "natural" egg-white; egg-white is beaten up to a stiff froth, poured into a tall narrow cylinder, and the clear liquid which collects at the bottom is separated and diluted with water. This not only contains a mixture of albumins, but is not electrolyte-free; it is in fact alkaline. From the electrical differences between neutral and acid or alkaline albumin, it is not surprising that this preparation does not exhibit the same behaviour as pure albumin. It is necessary to bear in mind the possibility of these differences; only pure neutral albumin is suitable for experimental work. The three principal constituents of egg-white, egg-albumin, ovomucoid, and a globulin, differ widely in many respects, and yet are not very readily separated from each other. Pure crystallised albumin is prepared by Hofmeister's method, or by modifications of it. The properties of serum albumin, again, differ considerably from those of egg-albumin.

Reversible Precipitation, Salting Out.—When a saturated solution of ammonium sulphate is added, little by little, to albumin sol, no precipitate forms until an equal volume of the salt solution has been added, but precipitation is not complete until a further amount is added. To be more exact, precipitation commences when 10 c.c. of the mixture contain 6·2 c.c. of saturated ammonium sulphate solution, and is complete when 10 c.c. of the mixture contain 6·8 c.c. of the saturated solution. These limits are pretty close together, much more so than for many allied substances; the total amount required also differs from substance to substance. The figures for egg globulin are 2·9 and 4·6; this indicates a method of separation which is made use of.

If water is added, the precipitate dissolves, and will reappear on addition of sufficient ammonium sulphate solution. Hofmeister utilised this in the preparation of pure albumin.[1] The usual method is a modification which gives a larger yield, and is altogether more convenient. It is as follows: Mix equal volumes of egg-white and saturated solution of ammonium sulphate. Beat to a stiff froth, and let it stand overnight. Filter off the precipitate of globulin and mucoid, and add gradually to the clear filtrate, with gentle stirring, a 10 per cent. solution of acetic acid, until a slight permanent precipitate is formed. This mixture should be just acid to litmus. Then add 1 c.c. of the 10 per cent. acid for each 100 c.c.; a bulky precipitate is formed, which becomes crystalline in five hours. Allow to stand till next day, to obtain the full yield (60 g. per litre). To purify: filter, wash the precipitate three times with half-saturated ammonium

[1] Hofmeister, *Zeitsch. physiol. Chem.*, 1889, **14**, 163; 1891, **16**, 187. Hopkins, *J. Physiol.*, 1898, **23**, 130; 1900, **25**, 306. Schulz, *Zeitsch. physiol. Chem.*, 1899, **29**, 86.

sulphate solution containing 0·1 per cent. of acetic acid. Dissolve the crystals in the minimum of water, and add saturated solution of ammonium sulphate until a precipitate is formed; then add 2 c.c. more to each litre. The albumin recrystallises in 24 hours. Repeat this treatment as often as necessary. Schulz and Zsigmondy have shown that 3 to 6 recrystallisations are necessary to remove all the colloid impurities. Finally, the crystals are dissolved in pure water, and dialysed to remove the ammonium salts (p. 26).

This method has been given at length, because it may be of use, but mainly because it has been applied by von Weimarn, with suitable modification, to obtain in a crystalline state substances which are usually regarded as amorphous (p. 121).

This precipitation differs from that of suspensoids in the large precipitation-concentration, in reversibility, and also in the absence of a valency effect, either of kation or anion. The following figures[1] for purified native albumin show this.

Salt.	Concentration mols per litre.	Salt.	Concentration mols per litre.
Sodium citrate	0·56	Sulphate, Li	0·78
„ tartrate	0·78	K	0·79
„ sulphate	0·80	Na	0·80
„ acetate	1·69	NH_4	1·00
„ chloride	3·62	Mg	1·32
„ nitrate	5·42		
„ chlorate	5·52		

Sodium iodide and thiocyanate produce no precipitate.

Pauli[2] concludes from his extensive results that

[1] Hofmeister, *Arch. exper. path. pharm.*, 1888, **24**, 247.

[2] *Beitr. chem. physiol. path.*, 1903, **3**, 225.

kation and anion effects are independent, the former favouring precipitation, while the latter hinder it.

The order of anions arranged according to their precipitating power is thus—

citrate > tartrate > SO_4 > $C_2H_3O_2$ > Cl > NO_3 > ClO_3 > I > CNS

and of kations—

$$\text{Li} \quad \text{K} > \text{Na} > \text{NH}_4 > \text{Mg}$$

We shall come across this order of ions again. The order for salts of alkaline earths[1] is—

kations: Ba > Ca
anions: $C_2H_3O_2$ < Cl < NO_3 < Br < I < CNS

This is the reverse of the order of anions in the alkali salts. It is noteworthy that addition of barium chloride produces an acid reaction in a neutral albumin sol.

If an albumin, to which a trace of acid has been added, is used instead of neutral or natural albumin, the anion order is reversed; and if much acid is added, the precipitation is irreversible. With 0·03n HCl, the order is—

kations: Na > K > NH_4 > Mg
anions: SO_4 < NO_3 < Br < CNS

This difference of acid and alkaline albumin sols is undoubtedly connected with the change in sign of the electric charge on albumin in acid and alkaline liquids.

Irreversible Coagulation of Albumin.—The line of demarcation between reversible and irreversible coagulation is so indefinite that already some irreversible coagulations have been considered.

[1] Pauli, *Beitr. chem. physiol. path.*, 1904, **5**, 27; Posternak, *Ann. Institut Pasteur*, 1901, **15**, 85.

Coagulation by Heat.—When aqueous albumin sols are heated, coagulation takes place at some definite temperature, which is fairly constant for each kind of albumin. The nature of the change is unknown, but is apparently chemical, for natural albumins become more alkaline, and acid albumins become neutral or less acid. The two chief factors are the reaction of the sol, and the kind and amount of salt present.

Complete coagulation only occurs if the sol is faintly acid. If the sol is too acid, or is not acid at all, more or less albumin remains in the sol. Further, a dialysed salt-free egg albumin is not coagulated by heat. This was first noticed by Aronstein,[1] and has been frequently confirmed. It is, nevertheless, not quite accurate, for coagulation does occur, when the heating is continued for a sufficient time; it occurs at a constant temperature, too, which is close to the ordinary coagulation temperature. Serum albumin, if free from salts, is completely coagulated by heat; and the presence of traces of acid or alkali completely prevents coagulation.

The effect of salts on heat-coagulation has been closely studied by Pauli and others, both with natural albumin, and with pure dialysed albumin. The results with the former are very complicated, and will not be referred to. The following figures show the influence of salts; they were obtained with pure dialysed serum-albumin, the coagulation temperature of which was 60·3°. The table gives the coagulation temperatures of the albumin for the given concentrations of salts.

[1] *Pflüger's Archiv.*, 1874, **8**, 75.

COAGULATION TEMPERATURE.

Salt.	Equiv. concentration. 0·01	0·02	0·03	0·04	0·05
NaCl . . .	63·2°	65·7°	66·4°	67·2°	67·9°
Na_2SO_4 . .	66·7°	68·0°	68·5°	69·1°	69·7°
NaA . . .	66·9°	69·2°	70·6°	71·5°	72·1°
NaCNS . .	68·0°	69·7°	70·6°	71·6°	72·5°

These figures correspond to the adsorption curve (p. 255); in agreement with it, small concentrations produce relatively larger effects than do larger concentrations. In every case the coagulation temperature is raised; it slowly rises up to concentrations of 1–2n, in some cases to a constant value at 2–5n, *e.g.* alkali chlorides, bromides, nitrates. In another group (fluoride, sulphate, acetate, citrate) a maximum temperature is reached, after which it begins to fall, and may even be below that of the pure albumin. With iodide and thiocyanate the temperature rapidly rises after 1–2n, and at 2–3n no coagulation occurs even on boiling.

Here, again, we find the same lyotrope sequence of anions. There appears to be a connection between this effect of salts on heat coagulation, and the effect on viscosity (p. 23).

Acid and Alkaline Albumin.—As amphoteric substances, albumins unite with acids and bases, and become positive and negative sols. Consequently, they differ very much from neutral albumin; some of these differences have already been stated. One further instance will suffice. A trace of acid or of alkali completely prevents the heat-coagulation of serum-albumin, but the acid sol is completely coagulated by a trace of a salt, *e.g.* sodium chloride, and the alkaline sol is partially coagulated by salts, especially by traces of calcium.

Precipitation by Salts of Heavy Metals.—Here the effect

is wholly due to the kation, and precipitation takes place at very small concentrations. In all cases the precipitation is irreversible, except under certain special circumstances. The precipitate always contains the precipitating kation. Three types of reaction occur.

I. Silver salts precipitate at all concentrations from 0·1n, to 6n; the precipitate does not dissolve in excess of silver solution, but some remains in solution so long as excess of albumin is still present.

II. Copper salt solutions from 0·001n to 1n give a precipitate; above 1n no precipitate is formed. A secondary precipitate is formed with a 6n$Cu^{\cdot\cdot}$ solution.

III. Zinc salts from 0·001n to 0·5n give a precipitate; from 0·5n to 4n no precipitate; and beyond 4n a precipitate is formed.

This is for a 1 : 10 egg-albumin. If the sol contains more albumin, the region of non-precipitation is reduced. The behaviour of zinc sulphate is illustrated in Fig. 7.

In all these cases the precipitates contain metal as well as albumin, and have been regarded as chemical compounds. If so, their composition is remarkably variable, *e.g.* the copper albumin precipitates contain anything from 1·4 to 20 per cent. of CuO; the same applies to the others. A few examples are given, the figures give the percentage of metal in the egg-albumin metal precipitate.

(1) Ag 2·17, 3·3, 3·9, 4·3, 4·86, 6·26.
(2) Cu 0·7–2·2, 1·2, 1·2–1·35, 1·35–2·65, 2·24–2·65, 3·55, 3·95.
(3) Zn 0·9–3·7.

In conclusion, the precipitation of albumin by heavy metals bears a strong resemblance to the mutual precipitation of sols, and to the precipitating and stabilising action of multivalent ions (p. 139).

Coagulation by other means.—Many organic substances, *e.g.* alcohol, phenol, formaldehyde, tannin, coagulate albumin irreversibly. Alcohol does not coagulate pure salt-free albumin, but does so if a trace of salt is added. This follows the same regularities as heat-coagulation. Urea and many other indifferent organic substances hinder the coagulation by alcohol.

There are also many colouring matters, either basic or

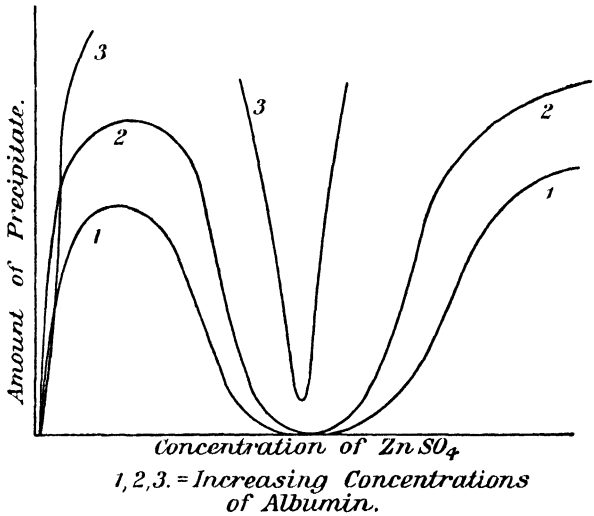


FIG. 7.

acid, which coagulate albumins. These reactions are of great importance in the staining of tissues; the mechanism is probably the precipitation of negative albumin sol by the positive sol (or by the kation) of the basic dyes, and conversely of the positive albumin sol by the negative sol (or by the anion) of the acid dyes (see below).

Albumins can be separated from the sol by mechanical

means:[1] shaking, bubbling air or a gas through it, etc. Ramsden also noticed that all albumins form in time a solid or a very viscous skin at a still surface. This is a general occurrence with substances which greatly lower the surface tension of the liquid, and so can pass into the surface layer (see Adsorption). This phenomenon is well shown by some dyes (fuchsin, methyl violet). A similar coagulation occurs at the interface between aqueous albumin and organic liquids insoluble in water (toluene, chloroform), especially when the interface is enlarged by shaking the liquids together. The action is the same as in air, accumulation of colloid in the surface layer until solidification occurs (p. 262). The skins are insoluble in water (the denaturising process appears to be spontaneous, and therefore irreversible).

II. Gelatine

While the main interest of the albumins centres in precipitation and coagulation, in gelatine and similar colloids, it is only of secondary interest, the chief problem being that of the reversible change—sol to gel, to which processes the terms solation and gelation are applied (see Introduction, p. 10). This process is entirely different from coagulation, as will appear immediately.

The properties of gelatine vary much with the presence of impurities. By adopting the principle of Hofmeister's original method of crystallising albumin, von Weimarn[2] has succeeded in crystallising gelatine and agar. A very dilute, quite clear gelatine solution in aqueous alcohol is maintained at 60°–70° in a desiccator. The water is slowly abstracted by, *e.g.*, dry potassium carbonate, which

[1] Ramsden, *Proc. Roy. Soc.*, 1903, **72**, 156; *Zeitsch. physikal. Chem.*, 1904, **47**, 336.

[2] *Grundzüge d. Dispersoid Chemie*, 1911, p. 106.

does not take up alcohol vapour. The solubility slowly decreases as the concentration of the alcohol increases. At last the gelatine commences to crystallise out. (See also p. 114.)

A further difficulty is that gelatine is not very stable, at least in presence of water, and especially if heated. This is shown by the change in viscosity which a gelatine sol undergoes when kept at constant temperature.[1]

Viscosity of 2 per cent. Gelatine at 100°.

Time (hours).	η
0	2·29
2	1·68
4	1·58
6	1·47
10	1·40
11	1·39

After 36 hours' heating, gelation no longer occurs (change to β gelatine). Ultramicroscopic investigations are in accord with this. A sol prepared at 60° contains submicrons, but after prolonged heating at 100°, only amicrons.

Gelatine is not amphoteric, like albumin, but is essentially acid;[2] notwithstanding this, it appears to be primarily a positive sol. It has also been shown[3] that gelatine undergoes a reversible transformation with temperature, as revealed by the muta-rotation of the solutions. The specific rotatory power of a sol is practically constant from 30° to 80°, but when the sol is cooled to 10°–15°, the lævo-rotation gradually increases to a constant value; the change being reversible if long heating to high temperatures is avoided (see p. 124).

Reversible Sol-Gel Transformation.—If a moderately

[1] Levitos, *Koll. Zeitsch.*, 1908, **2**, 240.
[2] Hofmeister, *Ber.*, 1878, **2**, 299.
[3] Trunkel, *Biochem. Zeitsch.*, 1910, **26**, 493.

strong sol of gelatine in water is made at high temperatures, on cooling it sets to a jelly, which is reconverted into the sol on warming. This change does not take place at a definite temperature (like a melting-point), for the process is a continuous one, as is shown by the cooling curve, or the temperature-viscosity curve. Fairly comparable results can be obtained by selecting some arbitrary standard of elasticity or of viscosity. Such a device was

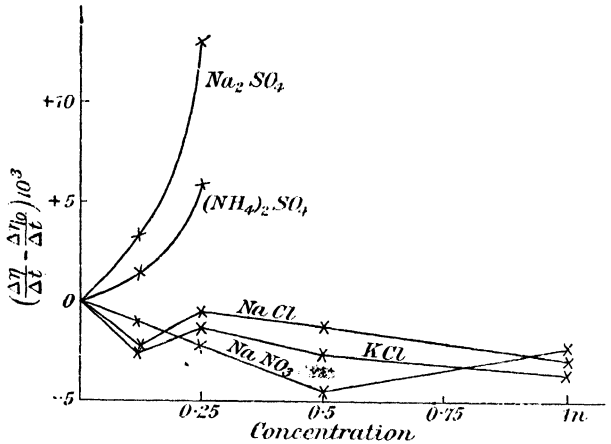


FIG. 8.

that adopted by Pauli,[1] who observed the temperature at which the thermometer was just held firmly by the gel; or by Levites,[2] who measured the times which elapsed before the viscosity became so great that the sol no longer ran out of the inverted vessel.

In the study of gelation, either the temperature or the time of gelation may be determined; the latter is preferable. Schröder[3] measured the power of setting by the

[1] *Arch. gesam. Physiol.*, 1898, **71**, 1.
[2] *J. Russ. Phys. Chem. Soc.*, 1902, **34**, 110.
[3] *Zeitsch. physikal. Chem.*, 1903, **45**, 75.

change in viscosity of the sol with time ($d\eta/dt$). Whatever method is adopted, it is essential that the previous treatment of the sol be uniform, as gelatine exhibits "hysteresis" in a marked degree, more especially after long heating. One cause of this is given above.

As just stated (p. 122) gelatine solutions exhibit muta-rotation, due to a reversible temperature transformation, and much of the uncertainty regarding the behaviour of gelatine is owing to neglect of this fact. In a recent investigation, the following important conclusions have been established.[1] There are two forms of gelatine—a sol form A, stable above 33°–35°, with $[a]_D^{35°} = -141°$; and a gel form B, stable below 15°, with $[a]_D^{15°} = -313°$; while between these temperatures there are equilibrium mixtures of A and B, the muta-rotation being due to the transformation. The increase in lævo-rotation, *i.e.* the change A → B, is closely parallel with the increase of viscosity. Above 35° gelation does not occur at any concentration; while the minimum concentration of gelatine in the form of B which will gelate at 0° is found to be 0·55 g. in 100 c.c. If the concentration is increased, there is a maximum temperature for each concentration, above and below which sol and gel respectively are stable for indefinite times; these are the true melting points, whereas the melting points of gels as usually determined are the temperatures at which the gels melt within an arbitrary interval of time, and are not the same as the setting temperatures, nor are they identical with the above maximum temperatures.

As the concentration increases, the maximum gelation temperature or melting point approaches 33°–35°, and above 35° no gel is formed at all. These conclusions are

[1] Smith, I. C. R., *Jour. Amer. Chem. Soc.*, 1919, **41**, 135.

in close agreement with the same author's experiments on precipitation of gelatine with alcohol, as also with the available data regarding the osmotic pressure and viscosity of gelatine. The time for half transformation is inversely proportional to the concentration, indicating that the reaction is of the second order, *i.e.* two molecules of A unite to form one molecule of B.

The temperature is also affected by salts and by organic substances. Some salts raise the gelation temperature, others lower it. The order is as follows:—

Raise . . $SO_4 > \overline{Ci} > \overline{T} > \overline{A}\ (H_2O)$
Lower . . $Cl < ClO_3 < NO_3 < Br < I$

The kation effect is very small, the order seems to be—

$$Na > K > NH_4 > Mg$$

Glucose and glycerol raise it, while alcohol and urea lower it. The same lyotrope order was found in Levites' investigation on the time of gelation, and by Schröder for the effect of salts on $d\eta/dt$ (Fig. 8). The effect of salts increases slowly at first with increasing concentration, and then more rapidly. The curves are somewhat irregular. Schröder found that if $\Delta\eta/\Delta t$ at 25° was $> 0{\cdot}0095$, the sol would form a gel within 24 hours, but if it was $< 0{\cdot}0075$, it would remain liquid ($\Delta\eta$ is the differences in viscosity at 25° at the times t_1 and t_2).

As the effect of salts on gelation is additive, many mixtures of salts will leave the gelation temperature unchanged.

Salting Out, and Precipitation of Gelatine by Salts.—This process is totally different from gelation. In the first place it is irreversible; further, it is produced by salts which favour gelation and by those which retard it. Organic substances influence gelation, but do not precipitate (certain exceptional substances, *e.g.* tannin excluded). It only

occurs at high concentrations of salts, in this respect resembling the salting out of albumins, *e.g.* precipitation is produced by 4nKCl (which lowers the gelation temperature about 13°), and also by 0·75nNa_2SO_4 (which raises the gelation temperature about 3°).

The order of anions, which alone have any considerable effect, is again lyotrope—

$$SO_4 > \text{Citrate} > \text{Tartrate} > \text{Acetate} > Cl$$

The action is not additive,[1] and the effect of mixtures is very complicated.

Effect of Electrolytes on the Osmotic Pressure.—Pure gelatine sols have a fairly high osmotic pressure (for 1·25 per cent. sol it is 6·2 mm. mercury), and this is not altered by non-electrolytes; but neutral salts lower it markedly.[2] The order is again lyotrope—

$$Cl(0{\cdot}44) > SO_4(0{\cdot}47) > NO_3(0{\cdot}47) > Br(0{\cdot}53) > I(0{\cdot}57) > CNS(0{\cdot}60)$$

The numbers are fractions of the osmotic pressure of the pure sol.

Both acids and alkalies greatly increase the osmotic pressure of gelatine, from 8 mm. to 39 mm. in 0·0024n HCl, and to 25 mm. in 0·0024n KOH.

Agar and other similar substances show the same characteristics as gelatine; in particular the effect of salts on gelation is very similar, the order being lyotrope.

In a series of researches Loeb and his co-workers have re-investigated the effect of electrolytes on certain properties of gelatine, as precipitation by alcohol, viscosity, osmotic pressure, gelation, and imbibition. According to

[1] Pauli, *Archiv. gesam. Physiol.*, 1898, **71**, 336.
[2] Lillie, *Amer. J. Physiol.*, 1907, **20**, 127.

their results,[1] the lyotrope effect is not observed in these properties, but as the conditions in their investigations were apparently quite different, it is not surprising if the conclusions are not the same.

III. Silicic Acid

This, the earliest artificial emulsoid, was discovered by Kühn[1] in 1853. Graham prepared it by dialysis, and noticed that its stability increased the longer it was dialysed. The pure sol is slightly acid (100 g. require 1·85 g. KOH for neutralisation), and is not so stable as a neutral sol, but its stability is increased by small quantities of hydrochloric acid. Kühn's sol and Graham's sol behaved quite differently to reagents; the former was irreversibly precipitated by sulphuric acid, or by freezing, the latter was not precipitated by acids or neutral salts, but by carbonates. These different results are characteristic of emulsoids.

Four main facts, however, stand out: the sol is unstable; gelation is irreversible; the stability is affected by acids and alkalies (as is also the sign of the charge on the colloid); the maximum of stability occurs at the isoelectric point, with a small $H^{\cdot}$ concentration.

Gelation is irreversible; all the investigations agree on this (except Kühn's method of preparation). The change takes place spontaneously, as the viscosity steadily increases with time until the gel is formed.[2] It is accelerated by rise of temperature, and by electrolytes. The temperature effect is not very large, *e.g.* boiling does not

[1] Loeb, *Jour. Biol. Chem.*, 1918, **33**, 531; **34**, 77, 395, 489; **35**, 497.
[2] *J. pr. Chem.*, 1853, [i.] **59**, 1.
[3] Garrett, *Dissertation*, Heidelberg, 1903, p. 51.

necessarily cause gelation. The effect of cooling is uncertain, some, as Kühn and Ljubawin,[1] state that complete gelation occurs on freezing the sol, while others, as Mylius and Groschuff,[2] did not find gelation to occur on cooling a sol to $-23°$.

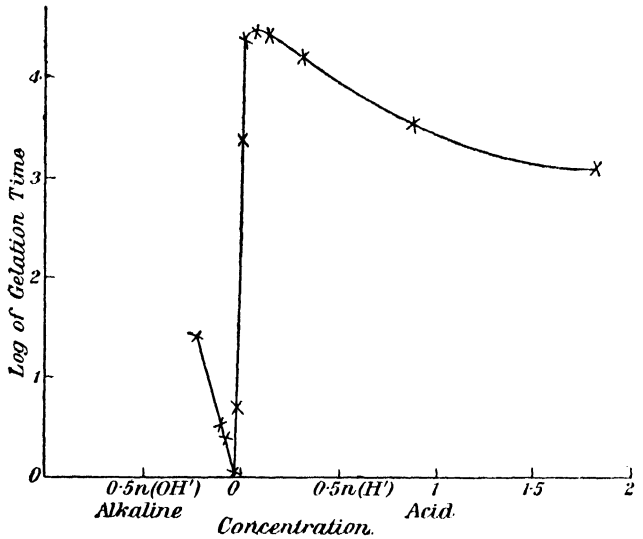


FIG. 9.

Effect of Electrolytes.—The action of acids and alkalies is the most important factor. Billiter[3] found kataphoresis to the anode in alkaline and feebly acid solutions; in these it is a negative sol, while at greater $H^{\cdot}$ concentrations it travels to the kathode, and is thus positive. The sol is therefore at its isoelectric point in feebly acid solution. Now Flemming,[4] who made a close study of the

[1] *J. Russ. Phys. Chem. Soc.*, 1889, **21**, 397.
[2] *Ber.*, 1906, **39**, 116.
[3] *Zeitsch. physikal. Chem.*, 1905, **51**, 150.
[4] *Ibid.*, 1902, **41**, 443.

effect of $H^{\cdot}$ and OH' on the rate of gelation, found the maximum velocity at small OH' concentration, and the minimum at small $H^{\cdot}$ concentration. With greater OH' concentration the velocity decreased, and it increased with greater $H^{\cdot}$ concentration (Fig. 9). We have thus a sol which, unlike the suspensoids, is most stable at its isoelectric point. In this respect it resembles egg-albumin.

According to Hardy's results,[1] the behaviour of silicic acid sols to neutral salts is very similar to that of negative suspensoids. This is probably true for alkaline sols, which are strongly negative. Thus, for instance, the pure sol (feebly negative) is not sensitive to kations, $K^{\cdot}$, $H^{\cdot}$, $NH_4^{\cdot}$, $Ba^{\cdot\cdot}$, etc., but becomes so on addition of ammonia, which increases the negative charge. It is then at once precipitated by barium chloride (this gel at once dissolves when excess of hydrochloric acid is added). Pappadà,[2] on the other hand, found that neutral salts only act at great concentrations, and accelerate gelation in accordance with the lyotrope series:

$$SO_4 > Cl > NO_3:$$
$$Cs > Rb > K > Na > Li$$

Stannic acid, titanic acid, tungstic acid, molybdic acid, and also starch sols are more or less like silicic acid sols in their general behaviour.

[1] *Zeitsch. physikal. Chem.*, 1900, **33**, 391.
[2] *Gazz. chim. ital.*, 1903, **33**, [ii.] 272; 1905, **35**, [i.] 73.

CHAPTER X

PROTECTION AND MUTUAL PRECIPITATION

Protection of Sols

Faraday, who prepared gold sols by reduction of auric chloride with phosphorus (p. 183), discovered that they were more stable when "jelly" (no doubt gelatine) was added to them.[1] The gold chloride was evaporated to dryness with the jelly; the resulting red-coloured jelly did not change colour with salt, as the "ruby fluids" did.

Purple of Cassius, too, which has long been known, is another example of increased stability of a colloid in the presence of another. Many other instances could be given in which use was made of this "protective" action, without any precise knowledge of its nature. The protection of less stable sols by organic sols (of suspensoids by emulsoids) was first definitely recognised by E. von Meyer and Lottermoser.[2] They observed that albumin prevented the precipitation of silver sol by salts. The latter subsequently reached the conclusion[3] that "on addition of very stable colloids, as albumin, gelatine, agar, or gum arabic, to a silver sol, no precipitation is caused by electrolytes until this stable colloid is gelatinised. The less stable silver sol is thus 'protected' against the electrolyte by the more stable colloid; it becomes more like the latter in its behaviour."

Zsigmondy then investigated the action quantitatively

[1] *Phil. Trans.*, 1857, 154. [2] *J. pr. Chem.*, 1897, [ii.] **56**, 241.
[3] *Anorg. Kolloide*, 1901, p. 50.

by means of his gold sol (p. 189), which is itself very stable, and is also very sensitive to salts. The degree of protection is expressed by the "gold number,"[1] which is the weight (in mg.) of colloid which just fails to prevent the change from red to violet in 10 c.c. of a gold sol (0·0053–0·0058 per cent.), when 1 c.c. of 10 per cent. solution of sodium chloride is added to it. The reciprocal of this number would be a more convenient expression of the protecting power. The following are taken from Zsigmondy's table:—

Colloid.	Gold number.
Gelatine	0·005–0·01
Isinglass	0·01–0·02
Casein (in NH_3)	0·01
Egg-albumin	0·15–0·25
Gum arabic	0·15–0·25; 0·5–4
Gum tragacanth	*ca.* 2
Dextrin	6–12; 10–20
Starch, wheat	*ca.* 4–6
,, potato	*ca.* 25
Sodium stearate	10 (at 60°); 0·01 (at 100°)
,, oleate	0·4–1
Stannic acid (old)	∞
Urea	∞
Cane sugar	∞

The gold number is a useful means of characterising substances, especially in cases which present difficulties to ordinary analytical methods. Thus 1 per cent. of gelatine will reduce the gold number of dextrin from 10 to less than 1. It has already proved useful in the fractionation of albumin.[2]

Preparation.	Gold number.
White of egg (fresh)	0·08
Albumin (Merck)	0·1–0·3
Globulin	0·02–0·05
Ovomucoid	0·04–0·08
Albumin (cryst.)	2–8
Alkali albumin	0·006–0·04

[1] *Zeitsch. anal. Chem.*, 1902, **40**, 697.

[2] Schulz and Zsigmondy, *Beitr. chem. physiol. path.*, 1902, **3**, 137.

If alkali is added to any of them, the differences disappear; all the alkali albumins have the same low gold number.

This protection is not confined to metal sols, nor is it exerted by organic colloids alone. The sulphide sols—arsenious sulphide, cadmium sulphide, etc.—are protected in the same manner,[1] though to different extents; further, the order of efficiency of the protecting colloid differs from sol to sol. Gold sol and silver sol have been prepared with silicic acid[2] as protective colloid, and zirconium hydroxide[3] sol exceeds even gelatine in its protection of gold sol. Another well-known example is that of ferric hydroxide sol; a basic ferric chloride solution when dialysed gives no visible precipitate with silver nitrate even when a considerable quantity of chloride is still present, as can easily be shown in other ways.

Paal's protalbic acid and lysalbic acid[4] (products of the action of alkali on albumin) are extremely active protectors. They have been used in the preparation of a large number of stable sols—comprising metals, metallic oxides and hydroxides, and salts—containing high percentages of colloid (see Preparations). These sols may be evaporated to dryness, and even after years will dissolve readily in water containing a little alkali.

We may thus say that a suspensoid sol, when mixed in suitable proportion with an emulsoid sol, loses most of its characteristic properties, and gains those of the protecting emulsoid. Bechhold[5] suggested that the protection is the result of adsorption. A thin layer of the emulsoid is adsorbed at the interface, and thus confers its stability on the adsorbing particle. Thus only substances which are readily adsorbed (*i.e.* which lower the surface tension of

[1] Müller and Artmann, *Österr. chem. Zeit.*, 1904, **7**, 149. Küspert, *Ber.*, 1902, **35**, 2815, 4066. [2] Biltz, *ibid.*, 4431. [4] *Ibid.*, 2195. [5] Bechhold, *Zeitsch. physikal. Chem.*, 1904, **48**, 385.

the dispersion medium) can act in this way. The objection that the amount of the very active colloids is too small to cover the particles is only an apparent one, for the concentration of most of the sols protected is very small; *e.g.* in the Zsigmondy test, the amount of gold is 0·5 mg. and of gelatine required for protection is 0·005–0·01 mg. The difference is still less if account is taken of the difference in density of gold and gelatine. According to Zsigmondy the coating of gelatine is invisible in the ultramicroscope, and there is no apparent diminution of the Brownian movement.

If the action is due to adsorption of the protecting colloid, it is clear why their protective power is not parallel with their stability, for adsorption, and possibly other factors too, will come into play.

The protection is not merely against electrolytes, for the stability of the mixture is practically the same as that of the protector, *e.g.* as regards solation and gelation; heat; evaporation; imbibition; solation by digestion with water, acid, alkali, etc.; ultrafiltration. Gold hydrosols protected by an emulsoid are as insensitive to complex trivalent ions as the emulsoid itself (see p. 112).

The relative amounts of the two colloids are of the utmost importance, for precipitation takes place with smaller amounts of the protective colloid[1] (see p. 137). Owing to the small concentration of metal sols it is not easy to get this effect with them, and so the protection is very marked. The addition of gelatine to hydrosols of gold, mastic, or oil, to a concentration of 1 in 100,000,000 increases the precipitating effect of hydrochloric acid. In these cases the sign of the charge on the sol remains unchanged, but when enough gelatine is added to protect the sol, the negative sols become positive on addition

[1] Friedemann, *Archiv. Hygiene*, 1906, **15**, 376.

of the acid.[1] It may be added that the reverse of protection has been effected.[2] By adding excess of a mastic sol to an albumin sol, the albumin could be readily precipitated by means of electrolytes, etc. (See also next section.)

Mutual Precipitation of Sols

When Lottermoser mixed various sols with a view to obtaining mixed gels by precipitation of the mixture with salts, some of the sols precipitated each other without the addition of any salt. On making a table of these incompatible sols, he was surprised to find that the classification was the same as he had already obtained from their electrical migration.[3] In other words, a positive sol will precipitate a negative sol, while sols of the same electric sign will not do so. The precipitate contains both colloids, but, owing to experimental difficulties, he was unable to determine their amounts. Very little ferric hydroxide sol sufficed to precipitate a large amount of silicic acid sol; with 20 c.c. of the latter (0·144 g. SiO_2) and 10 c.c. of the former sol (0·040 g. Fe_2O_3), the liquid above the precipitate was still brown. The experimental difficulties are three in number: difficulty of filtration without adsorption (or precipitation), spontaneous precipitation of the excess of colloid in the sol, and slowness of the reaction. Occasionally spontaneous solation occurred.

The mutual precipitation of certain dyes had previously been noticed by Linder and Picton;[4] they also knew that these dyes were colloids of opposite electric charge.

Suspensoids.—A quantitative method was devised by

[1] Walpole, *Jour. Physiol.*, 1913, **47**, 14; *Biochem. Jour.*, 1914, **8**, 170.
[2] Michaelis and Rona, *Biochem. Zeitsch.*, 1906, **2**, 219.
[3] *Anorg. Kolloide*, 1901, p. 77.
[4] *Chem. Soc. Journ.*, 1897, **71**, 568.

Biltz; it is a synthetic method,[1] whereas Lottermoser's unsuccessful ones were analytical. Varying known amounts of the one sol are added to a constant amount of the other, and the result noted. Very small amounts cause no visible change, more causes partial precipitation, larger amounts cause complete precipitation, while still larger amounts give less precipitate, and at last no precipitation occurs. The region of complete precipitation is fairly narrow, while, with large excess of either sol, no precipitation occurs at all. The following shows this.

10 c.c. gold sol (= 1·4 mg.) + 5 c.c. thorium hydroxide sol of variable concentration.

mg. ThO_2.	Appearance. Immediate.	30 minutes later.
0·5	no precipitate	slight opalescence
1·0	trace of precipitate	trace of precipitate
2·0	slow precipitation	slow precipitation
2·5	rapid complete precipitation	complete „
3·0	slow „ „	„ „
4·0	trace of precipitation	„ „
5·0	no „	no change

The optimum amounts of various positive sols for gold sol differ considerably, as also does the optimum amount of a positive sol for various negative sols, but the order is always the same, *e.g.* :

Negative sol.	Optimum of positive sol (in mg.).					
	Fe_2O_3.	ThO_2.	CeO_2.	ZrO_2.	Cr_2O_3.	Al_2O_3.
Au 1·4 mg. .	3	2·5	4	1·6	0·3	0·1–0·2
As_2S_3 24 „ .	13	6	4	2·0	0·5	2·0
Sb_2S_3 28 „ .	32	20	11	6·5	3·0	2·0

[1] *Ber.*, 1904, **37**, 1095.

There is obviously an amount of one sol which is equivalent to a given amount of the other; it is not, however, a chemical equivalence, nor is the precipitate, which must contain the two colloids in practically constant proportions, to be regarded as a chemical compound, in spite of its constant composition. The equivalence is electrical; as Billiter first suggested,[1] the maximum precipitation occurs when the positive charge on the one sol exactly equals (and neutralises) the negative charge of the other. This is in agreement with what we learnt regarding the precipitation of suspensoids by electrolytes, and the maximum of instability at the isoelectric point (p. 96). The optimum precipitation may not correspond exactly to electrical equivalence, for obviously the number of particles required and their size (*i.e.* the electric charge and the dispersity) as well as the relative concentrations of the two sols, must affect the precipitation, as also does the rate at which they are mixed (p. 98). In accordance with this, the composition of the precipitate is not quite constant. It always contains both, but so does the remaining sol, unless complete precipitation has occurred, *i.e.* the precipitate on either side of the optimum does not contain the whole of the component which is in defect. This distinguishes it from ordinary chemical reactions.

In fact, if the positive and negative sols are standardised by means of barium chloride (the change of titre on precipitation, p. 104), complete precipitation is found to occur when the volumes are inversely proportional to the titre, which is directly proportional to the electric charge.

Henri[2] had already tried the effect of two sols of the same electric sign upon each other. As would be anticipated from the protection effect, they not only did not

[1] *Sitzungsber. Kaiserl. Akad. Wiss. Wien.*, 1904, 113, 1159.
[2] *Compt. rend. Biol.*, 1904, 55, 1666.

precipitate each other, but the mixed sol acquired the stability of the more stable component.

On either side of the optimum mixture, the sol is negative or positive, according as one or other component is in excess, although the sol still contains both; and this holds whether partial precipitation has taken place or not. The following observations of Billiter[1] illustrate this.

$Fe(OH)_3$ sol + As_2S_3 sol.

10 c.c. of the mixture contain		Observation.	
Fe_2O_3(mg.).	As_2S_3(mg.).	Optical.	Kataphoresis.
0·61	20·3	opalescence	to anode
6·08	16·6	immediate precipitation	„
9·12	14·5	complete „	none
15·2	10·4	immediate „	to kathode
24·3	4·14	slight opalescence	„
27·4	2·07	no change	„

The curve Fig. 10 is of the same form as that for the action of zinc sulphate on albumin (p. 120).

Emulsoids.—So far we have considered mainly the action of suspensoids on suspensoids. When we come to emulsoids, their behaviour, as might be anticipated from their electrical properties and behaviour on precipitation, is not so simple. The mutual precipitation of positive and negative gelatine (and other similar emulsoids) during kataphoresis has been referred to already (p. 83). Albumin (electrically neutral) is precipitated by basic emulsoids, as histone, and basic dyes, because in them the albumin becomes negative, while they are positive sols. Similarly, it is precipitated by acid emulsoids, as silicic acid sol, and acid dyes, in which it becomes positive, while the acids are negative.

[1] *Zeitsch. physikal. Chem.*, 1905, 51, 142.

Similar reactions occur with tannin and gallic acid,[1] which precipitate both albumin and gelatine.

Suspensoids and Emulsoids.—The action of emulsoids on suspensoids has been described in the previous section. As there stated, the protection stage is preceded by precipitation, when the emulsoid is added slowly, or in small amount. The reason is now evident. It is also clear that there may be a balance between the precipitation and protection effects. Here, possibly, the acid nature of gelatine and its protective power together more than balance the precipitation effect. On addition of

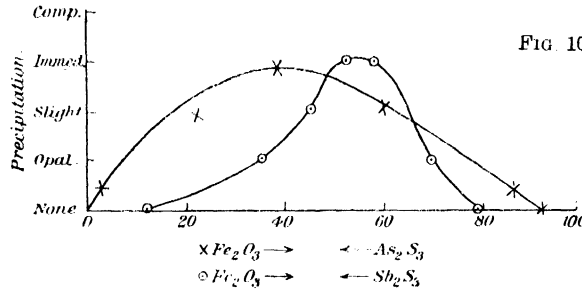


FIG. 10.

ammonia to the gelatine, which makes it more negative, the ferric hydroxide sol is precipitated; if instead, the ammonia is added to the mixture of sols, no precipitation occurs, but the mixed sol migrates to the anode.[2]

Similar anomalies have been observed with albumin,[3] which is precipitated by both positive and negative sols.

The essential feature, then, of the action of a positive sol on a negative sol, is that excess of either sol protects, while precipitation only occurs in a middle zone, which is usually narrow (Fig. 10).

[1] Dreaper and Wilson, *J. Soc. Chem. Ind.*, 1906, **25**, 515.
[2] *Sitzungsber. Kaiserl. Akad. Wiss. Wien.*, 1904, **113**, 1159.
[3] Friedemann, *Zeitsch. physikal. Chem.*, 1905, **51**, 146.

Action of Multivalent Ions on Sols.—This takes us back to the remarkable phenomenon observed by Burton in the action of $Al^{\cdots}$ on gold sol and silver sol (p. 107). A very small concentration of $Al^{\cdots}$ does not precipitate the sol, at slightly larger concentrations precipitation is complete, while with excess of $Al^{\cdots}$ no precipitation occurs. The original sols are negative; they pass through the isoelectric point, and then become positive. This is very similar to the protection of sols, which can also precipitate each other. In each case, there is a middle zone of precipitation, and on either side of it stable sols, but of opposite electric charge. Other multivalent kations behave like $Al^{\cdots}$. Now these salts are hydrolysed, and thus contain positive hydroxide sols. Their action on negative sols may therefore be due to protection at the two extremes, with mutual precipitation at intermediate concentrations. As Burton showed, the greater the excess, the greater the (reversed) charge and the stability. A new effect, however, must now come in: the precipitating effect of the anion on the now positive sol. The second region of non-precipitation is accordingly followed by a second zone of precipitation, which is finally complete. The whole series of changes on successively increasing the hydrolysed salt is: (1) first zone of non-precipitation; (2) first zone of precipitation; (3) second zone of non-precipitation (4) second zone of precipitation (Fig. 11).

The following illustrate this[1]:—

Mastic sol + $Al_2(SO_4)_3$

$\frac{Al_2(SO_4)_3}{2}$ (millimols in 1 litre).	Precipitation.
0·008–0·033	none
0·083	slight
0·167	complete
0·33–0·83	none
1·67–33·3	complete

[1] Friedemann and Neisser, *Münch. medizin. Wochenschrift*, No. 1

The accompanying change in kataphoresis is shown below[1]—

Platinum sol (Bredig) + $FeCl_3$

$FeCl_3$ (millimols in 1 litre).	Precipitation.	Kataphoresis.
0·021–0·056	none	to anode
0·083–0·222	complete	none
0·333–6·67	none	to kathode
16·3–666·7	complete	none

Fig. 11 illustrates this behaviour.

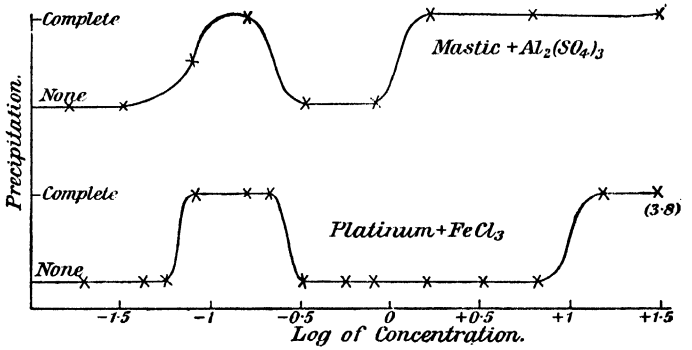


FIG. 11.

A very complete example of these "irregular" series is given by Kruyt and Spek,[2] for a ferric hydroxide sol and sodium hydroxide or phosphate. The sol was dialysed for $3\frac{1}{2}$ days, and contained 0·33 per cent. Fe_2O_3 and 0·028 per cent. Cl_2; 50 c.c. sol + 150 c.c. water.

$Fe(OH)_3$ sol + NaOH.

NaOH (m.mol. in 1 litre).	Precipitation.	NaOH (m.mol. in 1 litre).	Precipitation.
1·27, 1·40	incomplete	5·59	none
1·55, 1·75	immediate complete	8·36	,,
2·00, 2·16	complete	13·9	opalescence
2·33, 2·80	,,	20·9, 23·2	incomplete: yellow colour of liquid gradually diminishes
3·10	almost complete	24·6, 26·1	
3·99	opalescence	27·9	
		30·3, 32·4	complete

[1] Buxton and Teague, *Zeitsch. physikal. Chem.*, 1907, **57**, 76.
[2] *Koll. Zeitsch.*, 1919, **25**, 1.

That the second precipitation zone is due to the action of the anion of the salt on the reversed sol is borne out by the above tables. In each case, the first precipitation zone begins at 0·083 m.mol Al''' and Fe''', and ends at 0·333 m.mol; in the former the second precipitation zone commences at 1·67 m.mol Al''', while in the latter it is ten times as great, 16·3 m.mol Fe'''. In the former the anion is SO_4'', and in the latter Cl'; the difference is in agreement with the valency rule.

This phenomenon is easily seen in the case of dyes, for they comprise all three cases: (*a*) true solutions, as eosin and methylene blue, which act on sols in the same manner as other electrolytes; (*b*) most dyes exert protection, *i.e.* there is a precipitation zone, with a non-precipitation zone on each side of it. Frequently the middle zone is very sharply defined and within very narrow limits; (*c*) Nile blue and mastic sol behave in a similar manner to aluminium salts and mastic.

As we have seen, the behaviour of albumin with zinc salts and salts of heavy metals is very similar, the curves being of the same kind (*cf.* Figs. 7 and 11).

It has been suggested that salts of multivalent ions possess greater precipitating power because of the hydrolysis, *i.e.* that the precipitation is really produced by the hydroxide sol, and not by the ion, but this is not the case. The charge on a sol is very much less than on an equivalent amount of the corresponding ion (p. 82), and a correspondingly larger amount of the former will be required. Biltz showed that 24 mg. of arsenious sulphide required 2 mg. Al_2O_3 as hydroxide sol for precipitation, while, as Al''', 0·13 mg. Al_2O_3 were sufficient. Even complete hydrolysis, which is far from being the case, could not give the required amount of sol. It is not probable that the increased positive charge on the

sol will be increased to a sufficient extent by the presence of $H^{\cdot}$, to make up for such large differences in amount.

Proof that the relative amounts of positive and negative sols for optimum precipitation vary with the dispersity is afforded by the recent experiments of Galecki and Kastorskij.[1] The ferric hydroxide sol contained amicrons only, and was opalescent, its concentration was 10·28 mg. in 1 c.c. and its kataphoresis velocity was $+ 35{\cdot}7 \times 10^{-5}$ (cm. sec. volt cm.). Of the two gold sols, the one, Au_f, prepared by reduction with formaldehyde, contained submicrons; its concentration was 0·07 mg. in 1 c.c. and its velocity was $- 39{\cdot}3 \times 10^{-5}$. The other, Au_p, prepared by reduction with phosphorus, was of the same concentration, and had almost the same velocity ($- 36{\cdot}2 \times 10^{-5}$), but contained amicrons only.

On the average 1 mg. Au_f = 4·98 mg. Fe_2O_3
and 1 mg. Au_p = 18·4 mg. Fe_2O_3

When the amount of gold sol added was insufficient to cause any precipitation, the Au_f sols contained amicrons only, while Au_p at first cleared up the opalescence of the ferric hydroxide, but submicrons appeared later. The following figures require no further explanation.

Fe_2O_3. (in mg.)	Au.	Velocity (cm. sec. volt cm.). Au_f.	Au_p.
0	0·7	— 39·3	— 36·2
Optimum for precipitation (as above).			
61·68	0·28	+ 30·1	+ 22·77
92·52	0 07	+ 33·4	+ 26 20
102·8	0·0	+ 35·7	+ 35·7

[1] *Koll. Zeitsch.*, 1913, **13**, 143.

CHAPTER XI

THE PROPERTIES OF GELS

GELS are usually obtained when emulsoid sols are cooled or evaporated down; when suspensoids are treated similarly, the disperse phase is usually obtained as a loose powder. The former contain both disperse phase and dispersion medium, and form two fairly distinct types: the gels which retain their elasticity and coherence on drying, and those which lose their elasticity and become powdery on drying. The sol-gel reversible transformation has already been dealt with (p. 122) and will not be again referred to; there still remain the two important subjects of imbibition and hydration and dehydration of gels, and the structure of gels, including the relation between amorphous and crystalline solids. But before these are discussed, it may be useful to present a summary of the general properties of gels.

As emulsoids are generally recognised to be two-phase liquid systems, it seems reasonable to conclude that gels are also two-phase liquid systems with extremely great viscosity, since there is no apparent decrease in the number of phases on cooling or evaporating down emulsoid sols. As the viscosity of emulsoids indicates, there is in emulsoids a gradual and continuous transition from sol to gel (p 123). This conclusion was reached empirically by Bütschli (1892 onwards) as a result of microscopic observations on the structure of gels of starch, gum, gelatine, and

other substances. Many of the characteristic properties of gels are connected with this two-phase structure.

Density.—There is always contraction when a dry gelatinous colloid and water unite to form a gel; but the gel considered alone undergoes considerable expansion when it takes up water.

This initial contraction on imbibition has long been known, and was accurately determined by Lüdeking[1] in the case of gelatine. The density of the sample of gelatine he used was 1·412, and the density calculated from the density of gels of 14 per cent. and 35 per cent. gelatine was 1·9. The actual figures are—

Concentration g. in 100 g. of gel.	*d.* observed.	*d.* calculated.
13·6	1·069	1·041
32·0	1·135	1·103
58·5	1·242	1·206

This behaviour of gels is in agreement with that of emulsoid sols (p. 21), and is further evidence of the similarity of their nature.

Thermal Expansion.—The thermal expansion of gels is practically the same as that of the water or other liquid which makes up the greater part of the gel.

A gelatine gel becomes warmer when it is stretched, and cooler when it is compressed; this is also the case with rubber.

Compressibility.—The compressibility of gelatine gel is much higher than that of solids,[2] $\beta = 10 \times 10^{-6}$, instead of about 1×10^{-6} in the case of solids. The compressibility rises as the temperature is raised, and when the gel becomes sol, $\beta = 48 \times 10^{-6}$, which is the value for water.

It is not improbable that the high value of β for the

[1] *Wied. Ann.*, 1888, [iii.] **35**, 552.

[2] Barus, *J. Amer. Chem. Soc.*, 1898, **6**, 285.

gel is due to the phenomenon being the sum of two effects, the compressibility of the dilute liquid phase which forms the larger part of the gel, and the elasticity of the more concentrated liquid phase which forms the containing walls of the gel.

Elasticity and Viscosity.—The modulus of elasticity of a cylinder of gel is given by

$$E_d = \frac{Pl}{\pi r^2 \Delta l}$$

P = weight attached to the cylinder to cause extension.
Δl = the increase in the length l.
r = radius of the cylinder.

This is the modulus of elasticity for extension, the modulus for shearing strain is

$$E_s = \frac{E_d}{2(1+\mu)}$$

μ being the ratio of the relative contraction of the diameter to the relative change in length. The value of μ for gelatine is 0·5, hence there is no actual change in volume when a gelatine gel suffers extension, even when the extension is great.

The value of E_d in gelatine gels increases as C^2, the square of the concentration of gelatine. The relaxation time increases much with increase of concentration, being 10 minutes for a 10 per cent. gel, and 40 minutes for a 20 per cent. gel.

Since $E_s \times$ relaxation time = viscosity, the viscosity of gels must show enormous increases with increase of concentration.

The addition of other substances to the gel affects the elasticity just as it affects gelation (p. 125). Sulphate and polyhydroxyl organic compounds, as sugar, glycerol, act

in the one direction (increase of E), while chloride and nitrate have the opposite effect. This is as might be expected: the substances which increase the elasticity of the gel favour gelation, the others favour solation.

The viscosity must also be affected by the addition of substances to a gel, as they affect both the modulus of elasticity and the relaxation time.

Optical Properties.—Double Refraction on Mechanical Deformation.—This is another property which gels have in common with emulsoid sols, and as it was not referred to in describing sols, some detail may be given here. It is well known that glass becomes doubly refracting when subjected to strain, such as unequal pressure. As glass is a super-cooled, highly viscous liquid, it occurred to Clerk Maxwell [1] that other highly viscous liquids, which yet have the ordinary properties of liquids, ought to show the same effect. The apparatus consists essentially of a massive cylinder rotating coaxially inside a larger hollow cylinder, which is stationary. The liquid is placed in the annular space and is thus subjected to the mechanical deformation. Polarised light is sent through the liquid and the emergent light is analysed by a suitable eyepiece.

No double refraction was observed with cane sugar solution or glycerol, but it was produced in even very dilute sols of gum, gelatine, collodion, etc. The effect therefore cannot be due to ordinary viscosity, as the glycerol and the sugar had much greater viscosities than the sols. It most probably arises from the peculiarity of emulsoids and gels in being two-phase liquids, the interface between the phases of which is possessed of elastic properties, to which also the peculiarities of the viscosity of emulsoids is also almost certainly due.

The double refraction, $D = n - n_0$, is the difference

[1] Maxwell, *Proc. Roy. Soc. Edin.*, 1856. See also Kundt, *Wied. Ann.*, 1881, [iii.] 13, 110.

of the refractive indices of the extraordinary ray and the ordinary ray, and is given by

$$D = \frac{\lambda\Delta}{a}$$

where λ is the wave-length of the monochromatic light employed,
Δ the difference of phase, and
a the thickness of the plate or layer of gel.

D is proportional to $\Delta l/l$, the relative lengthening, and this ratio may be taken as a measure of the effect. It is approximately proportional to the concentration of the gel, and salts have the same effect on it as on the modulus of elasticity, *i.e.* chloride and nitrate diminish it, sulphate has practically no effect.[1]

Gelatine is optically active; chloride and nitrate diminish the rotation, while sulphate does not alter it.

Diffusion in Gels.—The early observations on the diffusion of solutions in gels have already been referred to at some length (p. 24). It may be recalled that Graham concluded that the rates of diffusion of salts in gelatine gels were the same as in pure water, but that his results did not really bear him out in this, the differences he found being greater than his experimental error. Others, too, arrived at the same conclusion for salts in other gels, *e.g.* in silicic acid and agar. It was demonstrated later that the differences are not large so long as the gel is dilute, but become much greater in concentrated gels.[2]

Substances which influence the sol-gel transformation and the elasticity of the gel, also affect the permeability of the gel by other substances. Alcohol and glycerol

[1] Lieck, *Ann. Physik.*, 1904, [iv.] **14**, 139.
[2] Bechhold and Ziegler, *Zeitsch. physikal. Chem.*, 1906, **56**, 105.

reduce the diffusion in gelatine or agar, while urea, chloride, and iodide increase it.

Liesegang's Rings.—This complicated phenomenon has given rise to much discussion. A glass plate is coated with gelatine sol containing ammonium bichromate; when the gelatine is set and partly dry, a drop of silver nitrate solution is placed in the middle of the plate, and the plate kept in a horizontal position in a moist atmosphere, to prevent evaporation. The silver nitrate diffuses out from the drop, and silver chromate is deposited in concentric rings at ever increasing distances from each other.

Ostwald[1] explained their formation as an effect of supersaturation: a certain excess of $Ag^{\cdot}$ is required to produce the supersaturation in the metastable region, which will necessitate the formation of nuclei of the precipitate. When this has happened, the whole of the excess of silver chromate will separate out, and so the adjoining region becomes poorer in chromate ion and the silver ion has further to go before the next crystallisation can take place. There are other factors, however, some of which have been indicated by Liesegang, and by Bechhold.[2]

In the first place, there is the protective action of emulsoids on the precipitation of suspensoids, and this is exceptionally strong in the case of gelatine (p. 131). It is thus probable that silver chromate will remain as a suspensoid sol long after the metastable concentration (if it exists at all) has been passed.

Ostwald's explanation does not explain why the centre of the plate, where the drop of silver nitrate is put on, always remains clear, the first deposit being a ring near

[1] *Lehrbuch*, 2, II. p. 778.

[2] *Zeitsch. physikal. Chem.*, 1907, **59**, 444; 1905, **52**, 185.

the margin of the drop; for it cannot be owing to want of $Ag^{\cdot}$. Nor does the protective action of the gelatine afford an explanation, unless the question of time is introduced. The clear centre may, however, be a result of the protecting action of an excess of either ion in the precipitation of sols of insoluble silver salts, *e.g.* in the titration of silver by chloride or of chloride by silver, the silver chloride remains as sol so long as there is excess of the ion to be precipitated, and it is precipitated only when there is no excess of either ion (p. 110). It may well be, then, that the very reverse of Ostwald's explanation takes place, and that precipitation only occurs when the amounts of silver ion and chromate ion are equivalent.

There is still another effect which may exert a powerful influence, viz. the permeability, not merely of the gelatine, but of the ring of precipitated silver chromate by salts. This itself is a subject of great complexity, and the few generalisations which have been made out will be discussed below. Only it may be said here that a gel consisting of a semi-permeable precipitation film is, as a rule, impermeable by the ions which make up the film, otherwise a thin continuous film would not be produced by the reaction. Accordingly, if the silver chromate is first of all precipitated as a gel or a two-phase liquid, it will certainly not be without effect on the diffusion of silver ion from the centre to the region beyond the ring last deposited. It may even cause decomposition of the silver nitrate, the silver ion being retained while the nitrate passes through, thus clearing out the chromate and causing silver ion to diffuse further before the next ring can be formed. It might be inferred from the above, that no silver ion could get past the first ring; but this is not the case, for the precipitated silver chromate gel will, sooner or later (and probably assisted by the excess of silver ion),

break down, either by crystallisation or other diminution in dispersity, and will thus lose its impermeability.

This does not exhaust all the possibilities, but enough has been said to show that the phenomenon is by no means a simple one, and that a full and satisfactory explanation is not yet possible.

Precipitation Films.—The properties of precipitation membranes, which came into prominence during the development of the osmotic pressure theory of solution, have been the subject of many investigations, without any finality having been reached. The structure of the membrane must be an important factor in the behaviour of any particular film, and this must depend to a large extent on the conditions under which it is precipitated, and these again must largely affect the stability of the form in which the precipitate first separates out. As a rule these membranes are unstable, and liable to change, to deteriorate in impermeability, under influences which are mainly unknown; hence it is not surprising that the results of investigations on them are frequently not in close agreement.

The state in which a precipitation film first separates from solution, and its subsequent changes, are indicated by von Weimarn's Theory (p. 178). The more insoluble the substance, the easier it is to obtain it in the form of a cellular jelly, which will under suitable conditions form a coherent semi-permeable membrane. The more dilute the reagents, the more likely is the precipitate to separate out in a crystalline form, or, if it is very insoluble, as an incoherent powder or open network.

The permeability will vary with the structure of the film, and as this is often much altered by the action of salts (ions), the film may change very rapidly when salts are present, although it had previously remained unchanged

for long periods. These changes may be either reversible or irreversible; if the former, it may be very difficult to detect the change. The permeability of a film by substances may be connected with the molar weight of the diffusing substance, or with the influence of the substance on the nature of the membrane, increasing or decreasing its elasticity, which, as we have just seen, affects the diffusion of substances in gels. There is also the possibility of irreversible coagulations or other changes brought about by the action of ions on the colloid films, which may act in the direction either of diminishing or increasing the permeability, and may even produce the one effect at low concentrations, and the reverse at higher concentrations.

Notwithstanding this, a few general conclusions have been arrived at concerning such semi-permeable membranes. No one now maintains that the permeability is connected with the size of the pores in the film, *i.e.* that the films function as molecular or ionic "sieves." It is much more likely that the principal factor is the lyotrope character of the particular solute. Thus acids and alkalies, chlorides, bromides, iodides, nitrates, and chlorates are more or less able to pass through most precipitation films; sulphates, phosphates, carbonates, salts of organic acids, salts of bivalent kations as Ca, Mg, Zn, etc., and salts of heavy metals are less so, and often cannot do so at all, while polyhydroxy organic compounds also come into the same class.

This grouping seems to point to lyotrope influences, especially the classification of the organic substances, though the effect of salts might also point to a valency influence, as in the precipitation of sols (p. 98).

Adsorption must likewise play a part in the phenomena, and along with it the mutual precipitation of positive

and negative sols. The nature of the semi-permeable membrane may be temporarily or permanently changed in consequence of either adsorption or of the precipitation of other substances on the membrane.

Hydration and Dehydration of Gels

Non-Elastic Gels

The question of the composition and chemical nature of the hydrates of metallic oxides, such as ferric oxide, manganese dioxide, and stannic oxide, has always been a difficult one, and there is little doubt that many such "compounds" still find a place in the dictionaries, in spite of the evidence of their indefinite nature. For instance, J. M. van Bemmelen,[1] to whom is due a great part of our knowledge of this subject, showed as long ago as 1878 that the amount of "hydrate water" of ferric oxide was variable, an accidental amount, and that the substance continuously lost water in dry air, and gained it in moist air, the amount depending, among other things, on the temperature and the moisture. The following figures show this:—

Mols of Water to 1 of Oxide.

State of gel.	*t.*	SiO_2.	SnO_2.	Al_2O_3.	Fe_2O_3.
Just dry	15°	4·4	3·0	5–6	> 6
In air	15°	1·5	2·6	4·4	5–4
In dry air	15°	0·5	1·0	2·6	1·6
In air	100°	0·2	1–0·6	2·3	1·2–1

The vapour pressure curves show decisively that the solid is not a definite hydrate, a chemical individual, for according to the phase rule a hydrate, which, on giving up some of its water as vapour, is in contact with a lower

[1] *Ber.*, 1878, **11**, 2232; 1880, **13**, 1466.

hydrate, or the anhydrous compound, forms a univariant system (two components, three phases), the vapour pressure of which is constant at constant temperature. As this is not the case, there can be only two phases, the gas phase and one solid phase, in which the vapour pressure varies with the temperature and the concentration in the phase, just as in the case of an unsaturated solution.

The water in the solid phase (from the phase rule point of view, it is immaterial whether the phase be regarded as solid or liquid) is therefore not in the form of a chemical compound, but is adsorbed or dissolved. Real compounds are formed under certain conditions, *e.g.* BeO,H_2O, and $Al_2O_3,3H_2O$, which separate out in a crystalline state with a definite composition, and behave as true compounds.

Hydration and Dehydration of Silicic Acid Gel.—The system SiO_2,H_2O has been systematically investigated by van Bemmelen,[1] who determined the isothermal at 15°. The gels were obtained by the action of dilute hydrochloric acid on sodium silicate, a little ammonia being added; the gels were then well washed. Gels of various concentrations were obtained by varying the concentration of the sodium silicate. The results were the same, whether the gel was in powder, in grains or in clumps. The gels were placed in desiccators containing sulphuric acid of thirty-six different concentrations (from $H_2SO_4,0{\cdot}25H_2O$ down to $H_2SO_4,90H_2O$).

The amount of water was ascertained by weighing at stated intervals of time. The results are given in Fig. 12 for a gel which originally contained $100H_2O$ to $1SiO_2$. The temperature was 15°.

The *dehydration* follows the curve AOO_1O_0, which is made up of two similar curved portions, separated by an intermediate linear portion. From A to O the loss of

[1] *Zeitsch. anorg. Chem.*, 1896, **13**, 233.

water is a continuous process, but is in no sense an equilibrium, for though at any point the system can take up water, it does not follow the curve, but strikes out towards the saturation pressure (indicated on the diagram) which it reaches in a very little time. This latter process is more nearly reversible, as subsequent dehydration follows a slightly divergent curve to reach the curve AO near the point at which it left it.

At O the middle portion of the curve, OO_1, is reached; it is approximately a horizontal straight line, indicating that large quantities of water can be removed without making much difference in the vapour pressure. This part

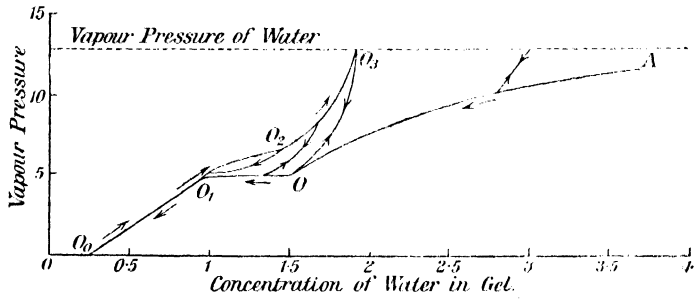


FIG. 12.

of the curve corresponds to a curious change in the appearance of the gel, which up to this point had been clear and transparent. At O it becomes opalescent, commencing in the interior and gradually spreading through the mass, until it is yellow by transmitted light and bluish by reflected light. These colours suggest the appearance of a new highly disperse heterogeneity, and this proves to be the case. The opalescence is caused by bubbles of air or of water vapour appearing where there had previously been liquid water. A similar appearance has been observed with many other gels and transparent substances with

very fine porosity, as meerschaum. As dehydration proceeds the gel becomes white as porcelain, and then opaque. At O_1 the reverse series of changes commences, the gel becoming white, then opalescent, and finally clear as glass.

Between O and O_1 the reaction is irreversible; at any point the gel can take up water, but it does so, as before, by a short cut to saturation. As before, this hydration is approximately reversible, the system returning to a point on OO_1.

From O_1 the curve O_1O_0 is a continuation of AO, but differs from it in the reaction being reversible, both hydration and dehydration being represented by the same curve.

Hydration of the Dry Gel.—The gel dried over concentrated sulphuric acid still has about $0{\cdot}2H_2O$ to SiO_2. Starting at O_0 the hydration follows the dehydration curve as far as O_1 from which point it lies above O_1O; this portion O_1O_2 is not a straight line, like O_1O, but is much flatter than the rest of the hydration curve. The process is not reversible along O_1O_2, the dehydration follows the paths shown on the diagram. The characteristic opalescence and opacity also make their appearance in this region, but not to so marked an extent as on dehydration.

From O_2, which is about $0{\cdot}2H_2O$ above O, and the vapour pressure 2–3 mm. higher, the third portion of the curve O_2O_3 begins; the curve ends in O_3 at the vapour pressure of water. Dehydration from O_3 does not exactly follow the hydration curve, but comes down to O if the gel is far past O_2. If it is near O_2 it comes down to an intermediate point on OO_1. All these are indicated on the diagram by the direction arrows.

Silicic acid gels are unstable systems of the general formula SiO_2,nH_2O, the value of n depending on the physical conditions and also on the previous history of

the system. The latter, known as hysteresis, is of great importance, not only in this particular property of gels, but in many of the properties of colloids generally. The hydration and dehydration of other non-elastic gels, as ferric hydroxide, stannic acid, etc., show the same characteristics as silicic acid gel, although there are many individual differences in each case.

Alcogels.—Gelatine with alcohol or benzene as dispersion medium forms series of gels which have been examined by Bachmann.[1] Alcogels and benzogels of gelatine show—apart from certain special features which arise from the mechanical properties of their structure—a marked similarity in the course and hysteresis-cycle of their vapour pressure isotherms with those of silicic acid hydrogel, and others. The common cause is the similarity of the processes involved—the reduction of vapour pressure of the imbibed liquid owing to the action of capillarity in an amicroscopic hollow-spaced system. The same cycle of events must always occur with a liquid and a porous substance with capillary spaces and walls of adequate resistance, provided no secondary changes, such as chemical reactions, occur. By applying the theory of capillarity, it is possible to estimate approximately the size of the spaces; they are 30–100 times smaller than Bütschli's network, *i.e.* 2–30 $\mu\mu$ in diameter.

Elastic Gels

The differences in the hydration phenomena of elastic gels, of which gelatine or agar may be taken as the type, and the non-elastic gels are sufficiently great to warrant their separation, although they have much in common, and the groups merge into each other. Perhaps the most outstanding differences are the absence in the elastic gels

[1] *Koll. Zeitsch.*, 1918, **23**, 85.

of the middle portion of the dehydration curve (OO_1, Fig. 12), and the fact that an elastic gel which has taken up all the water it can from water vapour, can still take up large amounts of liquid water, much more indeed than it has already taken up from the vapour.

As with non-elastic gels, there is no evidence of chemical combination, no fixed ratio of solid to water which is reproduced under varying external conditions. The amount of water imbibed depends on many conditions: the temperature, whether the water is liquid or vapour, the presence of other substances in the water, and the previous history or treatment of the gel.

The process of imbibition is accompanied by contraction, if the total volume of the gel and water is considered, but in many cases the solid experiences a large expansion, and can then give rise to large pressures. This and the other phenomena of imbibition are clearly very important from the biological side, as many of the tissues of plants and animals possess the power in a marked degree. Other elastic gels are starch, agar, proteins, gelatine. One difficulty of investigation is that the substances examined are not pure, many of them are mixtures, and most of them are easily decomposed; in addition to which equilibrium is often very slowly reached.

Hofmeister considered imbibition to be made up of three distinct processes: capillary, endosmotic, and molecular imbibition. The last, which is of the nature of adsorption in its not being chemical combination, is what is now ordinarily meant by imbibition. He arrived at the following generalisations. The quantity of liquid which can be taken up reaches a maximum, which depends on the gel, on the liquid, on the temperature, and on the viscosity of the liquid. There is always contraction, and always evolution of heat; from which, according to le

Chatelier's theorem, heat will hinder or diminish imbibition, while cold and pressure will favour it.

Weight and Volume Change.—A plate of dry gelatine weighing 0·904 g.[1] was placed in an atmosphere saturated with water at ordinary temperature. The gain in weight in eight days was 0·37 g. and no further gain took place in twenty days. When the plate was immersed in water at ordinary temperature, it took up 5·6 g. of water in one hour, and still more on prolonged soaking. The one maximum is about 50 per cent. of the dry weight, the other is 1000 per cent. This extra water is easily given up to dry air, or even in moist air. The greater part of it is so loosely held that the gel has the same vapour pressure as water, and under constant conditions loses water at the same rate as a similar surface of water; only a small residue is more firmly held, which cannot be removed at all at 15°, but is slowly given up at 95°.

The greatest changes in volume occur with the first additions of water, hence really dry materials must be employed. Assuming that all the contraction is of the water, Rodewald[2] found the following for starch dried over sulphuric acid :—

g. water to 100 g. starch.	Vol. in cc. of 1 g. water.	g. water to 100 g. starch.	Vol. in cc. of 1 g. water.
1·17	0·33	9·20	0·29
2·69	0·29	13·4	0·49
5·02	0·31	14·95	0·55
7·40	0·36	19·24	0·49

The volume change is easily demonstrated, if a 50 c c. flask with long narrow neck is filled loosely with shreds of gelatine, water added up to a mark on the neck, and the stopper inserted. The level of the water falls as imbibition proceeds. The temperature must be kept constant, as heat is evolved during the reaction.

[1] Schroeder, *Zeitsch. physikal. Chem.*, 1903, **45**, 109.
[2] *Zeitsch. physikal. Chem.*, 1897, **21**, 193.

If gelatine is hardened by alum or alcohol or formaldehyde, it largely loses its power of imbibition, becoming more like the non-elastic gels. Imbibition also depends on the liquid, *e.g.* alcohol is not imbibed by gelatine. There is no imbibition by starch in petroleum, or by albumin in alcohol, benzene, ether, or turpentine. This alone is sufficient to mark off imbibition from adsorption, for there would be some adsorption with these liquids, although probably not so large as with water. There must be some connexion between imbibition and the solubility of the liquid in the gel, as the liquid must pass through the walls of the gel to dilute the liquid in the interior.

Further examples of imbibition are rubber in ether, chloroform, or other organic liquids, and pyroxylin (collodion) in ether or alcohol. The same behaviour is observed here as with gelatine and water. To make a gelatine sol from dry gelatine and water, it is much quicker to soak the gelatine in cold water, and to apply heat only when imbibition is fairly complete; hot water and dry gelatine form a sol very slowly. Similarly with collodion (see p. 27): it is soaked in either alcohol or ether, and after imbibition has taken place, the other liquid is added, when solation is rapid.

The Pressure of Imbibition.—As the total volume change is a contraction, the pressure due to the expansion of the gel by water is not observed at all unless the gel is separated from the water by a semi-permeable membrane. If gelatine is packed in a porous earthenware cylinder, connected with a manometer, and placed in water, the pressure bursts the cylinder.[1]

Reinke determined the pressures by means of the oedometer. Circular discs of dry seaweed (*Laminaria*)

[1] Schroeder, *loc. cit.*

were placed in the bottom of a steel cylinder, the piston of which was pierced by a number of very fine channels, which allowed free passage of water to or from the seaweed (the latter really provided the semi-permeable membrane, the steel piston only acting as a strong support, as when pressure was applied to the piston, the holes would be closed by the outer membrane of the seaweed). Weights were placed on the top of the piston, and the height to which the piston was raised was measured. As the discs increased only in thickness and not in area, the height gives the volume and hence the amount of water which has been taken up. Ten layers of Laminaria, 0·1 mm. in thickness, and 50 sq. mm. area, gave the following pressures :—

P (atmospheres).	h (mm.).	W (per cent. H_2O in vol. per cent. of air-dry substance).
1	3·3	330
3·2	2·05	205
7·2	0·97	97
21	0·35	35
41	0·16	16

These pressures are equilibrium pressures, for similar values were obtained for the pressures at which water was just pressed out from seaweed containing varying amounts of water. The pressures required to remove water when the amount present is very small, become enormous. A rough idea of the pressure of imbibition is got from the contraction of starch and water (p. 155). The product of the internal pressure P, and the compressibility β, is approximately constant: $P\beta = c = 0{\cdot}572$. ($P_0 = 1{\cdot}1 \times 10^4$, $\beta_0 = 5{\cdot}2 \times 10^{-5}$.) As the 9·8 g. of water contract to 3·01 c.c., the average pressure producing this contraction is

$$\log \frac{9{\cdot}8}{3{\cdot}01} = 0{\cdot}572 \log \frac{P_1}{1{\cdot}1 \times 10^4}$$

which gives $P_1 = 8{\cdot}6 \times 10^4$. From this value we get an approximate heat of imbibition of $1{\cdot}2 \times 10^4$ cal., which gives 120 cal. per g. of starch, the experimental value being only 30 cal. Similar forces come into play when elastic gels are dried in other ways: *e.g.* glass plates coated with gelatine and then dried often become double-refracting, owing to the strain, and if the glass is thin it may become very curved. Similarly, if an elastic gel in a glass or porcelain dish is dried up in a desiccator over sulphuric acid or in very dry air, it not infrequently happens that the surface of the basin is torn away with the gel as it contracts.

Heat of Imbibition.—When a gel takes up water heat is given out, as the following figures show :—

	cal. per g. gel.
Gelatine	5·7
Starch	6·6
Gum arabic	9·0
„ tragacanth	10·3

Now the solation of a gel absorbs heat, as heat is evolved when emulsoids are coagulated; hence it is difficult to arrive at correct values of the heat of imbibition. Experiments on starch with known amounts of water show that the greatest amount of heat is evolved for small amounts of water, as is only to be expected, since only a small fraction of the water is difficult to remove, and requires a high temperature to do it (p. 158).

The value for gelatine is for air-dried sheet, which contains about 15 per cent. of water. A re-determination by Bradford with sheet dried at 110° for 24 hours gave a mean value of 33 cal. per g. corrected for the solation of part of the gelatine, the value of which is $-3{\cdot}7$ cal. per g. solated. This agrees with the value of 30 cal. per g.

which Rodewald obtained for starch dried over sulphuric acid.[1]

Velocity of Imbibition.—Reinke used the oedometer, by means of which he measured the pressure of imbibition, to determine the velocity of the process. Since the discs of seaweed do not change in area, only in thickness, it is easy to find the velocity by determining the change of h with the time, the pressure on the piston being constant and the amount of gel being known.

If w_t is the amount of water taken up in the time t, and w_∞ the maximum amount which can be taken up under the conditions, we have—

$$\frac{dw}{dt} = k(w_\infty - w_t)$$

or

$$k = \frac{1}{t} log \frac{w_\infty}{w_\infty - w_t}$$

The table contains the results of such an experiment.

t (min.)	w.	k.	t (min.)	w.	k.
1	40	0·108	16	306	0·095
4	121	0·092	20	345	0·106
8	201	0·090	24	372	0·121
12	258	0·090	∞	392	—

Hofmeister[2] determined the velocity of imbibition of water by thin plates of agar and gelatine (0·5 mm. in thickness) by weighing the plates at stated intervals of time. As the weighing took some time, the times are not very exact. The same formula holds for his results, *e.g.*

[1] Wiedemann and Lüdeking, *Ann. Phys. Chem.*, 1885, **25**, 147; 1888, **35**, 552; Bradford, *Biochem. Jour*, 1918, **12**, 351; Rodewald, *loc. cit.*, p. 158.

[2] *Arch. exp. Physiol. Path.*, 1890, **27**, 395.

GELATINE PLATE.

t (min.).	w (g.).	k.	t (min.).	w (g.).	k.
5	3·08	0·090	20	4·58	0·064
10	3·88	0·084	25	4·67	0·075
15	4·26	0·084	∞	4·96	

Imbibition in Solutions.—Hofmeister[1] extended his investigations on imbibition to salts in water, in order to find the distribution of the solute between the gel and the solution. He found, however, that both the velocity of imbibition and its amount varied considerably with the nature of the solute. He used thicker plates of gel, so that maximum values were not obtained. The plates were soaked in solutions of salts and of indifferent substances, the concentrations varied from 0·5 m to 4 m. Remarkable differences were observed, the imbibition in some solutions being as much as five times as great as in other solutions of equivalent concentration.

Arranged in order of increasing effectiveness in promoting imbibition, the series is—

sodium—sulphate, tartrate, citrate, acetate; alcohol, glucose, cane sugar;
(water);
chlorides—potassium, sodium, ammonium; sodium—chlorate, nitrate, bromide;

to which might be added iodide and thiocyanate, both coming after sodium bromide.

The substances before water hinder imbibition, less water being taken up in the same time, and also less water taken up in the maximum, while the salts after water favour imbibition. The order is again the lyotrope series which we have come across so often. As already seen, the modulus of elasticity is affected by salts in the

[1] *Arch. exp. Physiol. Path.*, 1891, **28**, 210, 238.

lyotrope order; this is the same series in the reverse order. As was to be expected, a substance which renders a gel more easily deformed (reduction of E) will favour imbibition. There is a still closer connexion between the effect of salts on gelation and imbibition, so that the curves representing the effect of any salt on these processes are practically reciprocal, *i.e.* what favours gelation hinders imbibition, and conversely.

The effect of salts on imbibition by gelatine has been the subject of much research and criticism. The existence of a maximum of imbibed water is called in question, as is also the lyotrope influence in imbibition, as well as in other properties of gelatine (p. 125). It has been found by Shreve[1] that though the Hofmeister series holds when gelatine is made up with water, and placed in solutions of *m* ammonium chloride, *m* sodium chloride, *m* sodium bromide, (*water*), 2 *m* and *m* ethyl alcohol, 2 *m* and *m* sodium citrate, 2 *m* and *m* sodium tartrate, *m* and 0·5 *m* sodium sulphate, yet when dry gelatine is made up with these solutions, or when a 28 per cent. gel is allowed to absorb 0·2–0·3 of its volume of these solutions at 10°–35°, the *rate* of imbibition is increased.

She also found that between 10° and 35°, heat favours imbibition, although the reaction is exothermic, but that Le Chatelier's law does not apply, since the equilibrium is apparent only. Further research is necessary in these directions, but it seems unlikely that imbibition does not approach a definite maximum, in solutions at least, unless some other phenomenon, as solation, intervenes.

When a gel undergoes imbibition in a solution, it takes up both solute and solvent, but in different amounts which depend to different extents on the concentration of the solution. The water taken up increases with the con-

[1] *Science*, N.S. 43, No. 1239; *Jour. Franklin Inst.*, 1919, p. 319.

centration of the solution to a maximum (at about 14 per cent. solution of NaCl), and then decreases slowly as the concentration increases. The amount of salt taken up increases with the concentration, and always approximately proportionally to the concentration.

In the presence of salt (NaCl), the amount of water imbibed exceeds that taken up in pure water, the increase being from 0·2 to 18 per cent. Not only is the amount larger, but the velocity is also increased. In a 5 per cent. solution of NaCl, the total amount was greater, and the rate much greater.

The action of acids and bases on the imbibition by gelatine is similar to the action of salts. At small concentrations (0·005–0·01m), imbibition is less than in pure water, reaches a minimum and increases to a maximum at 0·025m, both the rate and the amount being greater; the latter is 3–4 times as great as in water.

The Structure of Gels

As emulsoid sols are two-phase liquids, and as gels are obtained from them by cooling or by evaporation, the conclusion is natural that gels possess the same structure, *i.e.* the two liquids persist from the sol stage. The structure then is cellular, the walls being a highly viscous solution enclosing a more dilute solution.

This is confirmed by observations in many directions, at least so far as the cell walls are concerned. Van Bemmelen and Bütschli, in particular, have examined the micro-structure of a series of precipitates and gels. These structures are more or less after the honeycomb pattern, and are recognisable in plant and animal cells and tissues, and also in albumin or gelatine acted on by heat, tannin, alcohol, chromic acid, etc. Albumin structures are open network, with a mesh of 0·5–1·5 μ;

gelatine gels over 7 per cent. form closed nets, and open network below 7 per cent.[1]

Pauli and others have expressed doubt as to this structure, maintaining that it is not pre-existent in the sol or gel, but is a secondary structure of the altered gel.[2] According to von Weimarn, these structures are secondary, the honeycomb appearance being probably an optical effect due to overlapping of grains, "exhibiting various structures—network, honeycomb, rayed, dendritic—under the microscope, unless the preparation consists of a single layer of detached grains. *All these structures are of secondary formation, the only original structure of these precipitates is the fine-grained crystalline structure.*"

Hatschek [3] has shown, from the stress-elongation curve, that the two-liquid phase hypothesis is not valid. He also investigated the shape of gas bubbles generated in gels, and found that the bubbles are at right angles to pressure, and parallel to tension applied to the gel; the simplest structure conforming to the conditions is that of piled shot, which agrees with the globulitic structure observed by Bachmann [4] in the ultra-microscope. Zsigmondy and Bachmann,[5] in examining the gelation of soaps with the ultra-microscope, also observed the formation of aggregates with crystalline properties.

Finally, Bradford,[6] in a series of researches, has applied von Weimarn's theory to the gelation of emulsoids with conspicuous success, showing that the process is

[1] Bemmelen, *Ber.*, **1878, 11**, 2232; 1880, **13**, 1466.

[2] Pauli, *Der Kolloidale Zustand*, 1902.

[3] Hatschek, *Koll. Zeitsch*, 1912, **11**, 158; 1914, **15**, 226; *Trans. Farad. Soc.*, 1917, **12**, 17.

[4] Bachmann, *Zeitsch. anorg. Chem.*, 1911, **73**, 150.

[5] Bachmann and Zsigmondy, *Koll. Zeitsch.*, 1912, 11, 145.

[6] Bradford, *Science Prog.*, 1916, **10**, 369; 1917, **12**. 63. *Biochem. J.*, 1916, **10**, 169; 1917, **11**, 14; 1918, **12**, 351; **1920**, **14**, 91.

one of crystallisation. The small diffusion constant of the emulsoid retards the crystallisation of the sol, so allowing the accumulation of a large excess concentration, which, along with the large value of K in von Weimarn's formula, causes gelation on cooling. The small crystallisation velocity, which also is due to small diffusion constant, is responsible for the permanency of the gel and the hysteresis of the sol, since it prevents subsequent development of larger crystals in the former, and retards changes in the aggregation of the latter. A gel thus comprises two phases: an ultra-microscopic solid phase, bathed in a liquid dispersion medium, from which it has crystallised, and which it retains partly by molecular and partly by capillary forces. The ultimate solid particles of gels are probably spherites, this being in agreement with their ultra-microscopic appearance, and also with the possibility that gelatine can be obtained in this form.

It is curious to note this return to the earliest theories of gels, put forward by Frankenheim in 1835,[1] and von Nägeli in 1858.[2]

[1] Frankenheim, *Die Lehre v. d. Kohäsion*, 1835.
[2] Nägeli, *Pflanzenphysiolog. Untersuchungen*, 1858.

PART II

METHODS OF PREPARATION

CHAPTER XII

INTRODUCTION

THE preparation of a sol, a disperse system the dispersity of which lies between certain limits, must obviously follow one of two lines: either the dispersity is increased, or it is diminished. In the former case, we start with the (massive) solid, in the latter, with the substance in the form of molecules or ions in solution or vapour. If the process of solution of a crystalline solid in a liquid is regarded as a continuous change, the dispersity of the solute continuously increasing, and the crystallisation of a solid from solution regarded as the reverse process, it is evident that every system during the processes of solution and crystallisation passes through the degree of dispersity corresponding to the sol stage.

There are then two main groups into which the methods of preparation fall,

I. Crystallisation Methods, and

II. Solution Methods.

All the known methods come under these two heads. The electrical dispersion method of Bredig, and the later modifications of it, may appear to be possible exceptions,

but are almost certainly to be regarded as crystallisation methods. It is, however, convenient to treat them as a separate group.

Svedberg[1] has prepared hydrosols of mercury by various methods, and has ascertained the range of size of the particles in each, with a view to ascertaining the mechanism of electrical synthesis of colloids. The methods were:

(1) shaking mercury with water or aqueous solutions, thin lamellæ of mercury being disrupted.

(2) Super-heated mercury vapour passed into water.

(3, *a*) Direct current arc.

(3, *b*) Alternating current arc.

The order is as follows:—

(3, *b*) 23 per cent. $< 105\ \mu\mu$; 6 per cent. $> 1500\ \mu\mu$. maximum: *very acute*, 100 $\mu\mu$.

(2) 5 per cent. $< 85\ \mu\mu$; 3 per cent. $> 2500\ \mu\mu$. maximum: good, 100 $\mu\mu$.

(3, *a*) (At 9° C.) 3 per cent. $< 110\ \mu\mu$; very few $> 2000\ \mu\mu$. maximum: very good, 135 pp.
(At 50° C.) 0·6 per cent. $< 110\ \mu\mu$.
maximum: poor, 170 $\mu\mu$.

(1) 4·7 per cent. $< 120\ \mu\mu$; 1 per cent. $> 2500\ \mu\mu$. maximum: poor, 120 $\mu\mu$.

He concludes, therefore, that solation by electric arc

[1] *Koll. Zeitsch.*, 1919, **24**, 1. Van Marum in Ostwald's *Geschichte d. Elektrochemie.* Faraday, *Phil. Trans.*, 1857, p. 18, **147**, 152. Threlfell, *Phil. Mag.*, 1894, [5], **38**, 450. Ehrenhaft, *Wien. Ber.*, 1910, **119**, (II*a*), 830.

is due to the formation of vapour, with subsequent condensation.

The classification is due to von Weimarn, and is similar to that adopted by Svedberg, who classifies the methods as Condensation Methods, and Dispersion Methods. In the former the disperse phase is produced by "condensation" from ions in solution, and the latter includes all those methods which start from a solid phase of low dispersity. It therefore takes in the electrical dispersion methods. In spite of a formal similarity, there is a considerable difference between the two classifications; the latter is somewhat arbitrary, especially as regards dispersion methods, some of which, as Svedberg states, are more probably condensation methods. von Weimarn, on the contrary, bases his classification on the continuity between coarse heterogeneity and the apparent homogeneity of solutions, so that every crystallisation begins with the formation of a highly disperse system, a sol, and in every process of solution the solid phase, just before complete solution, forms a highly disperse system, a sol. Thus, to prepare a sol it is merely necessary to arrest the process of crystallisation or of solution at the appropriate stage.

Simple as this may appear, in practice it is not always easy to effect, and the art of preparing sols consists in so arranging the conditions that—

(1) The disperse system is obtained in a fairly stable condition, and

(2) Its concentration is not too small.

As a brief historical sketch will amply show, the early preparations were mainly a matter of chance; some one accidentally discovered the conditions under which a particular sol was obtained in a stable form. As these

were multiplied, certain general conditions were, of course, recognised, more especially after the general properties of sols had become better known. It thus became possible to classify methods, and to apply known methods which were likely to be successful in any given case.

It was not, however, until von Weimarn elaborated his theory regarding the processes of crystallisation and solution that systematic treatment became possible. As his theory has had highly important results, and has already led to the preparation of a very large number of sols, and is capable of almost indefinite application, it will be briefly described.

von Weimarn's Theory.—Two stages in the separation of a crystal solid from a solution must be taken into consideration. The one is the "initial condensation" of the solid from the solution, which must take place in the form of a highly disperse phase, the size being approximately that of the molecules or ions of the substance in solution. These "amicron" particles increase in size by two distinct processes: aggregation crystallisation, and ordinary recrystallisation. In the former, when two particles come near enough to each other, they become similarly oriented, and unite to form a larger particle. In the latter, each crystal grows at the expense of the substance in the surrounding solution. The concentration and the stability of the disperse system depend on these two factors: the initial velocity of the condensation, and the velocity of the growth of the crystals. Doubtless other factors are also concerned, which have been as yet unconsidered, and, in consequence of their omission, the results are not quantitatively exact.

For crystallisation to take place at all, there must be an excess of solute present, above that necessary for saturation under the conditions of experiment. If Q is

the total amount of solute in unit volume of the solvent, and L is the solubility of the solute in the solvent, Q — L, the number of mols which must finally appear as a solid of constant solubility L, may be regarded as the "condensation pressure," or the pressure under which the molecules begin to condense to crystals. Against this pressure we have the resistance of the system to condensation, which is not the same for different solids or solvents. With a given condensation pressure, the "condensation resistance" will vary with the solubility of the disperse phase, *i.e.* with the molecular cohesion of the dissolved molecules to those of the dispersion medium.

Since, at the outset, the disperse phase is practically of the same dimensions as the molecular complexes of the solution (it is invisible or barely visible in the best ultramicroscope), the initial reaction may be treated as homogeneous, and the velocity of initial condensation

$$W = k\frac{\text{condensation pressure}}{\text{condensation resistance}} = k\frac{Q - L}{L} = k\frac{P}{L} = kU$$

in which k is a constant, Q and L, as above, the amount of solute in unit volume of the solution, and the solubility of the disperse phase in the dispersion medium. $P = Q - L$ is the actual excess of mols of solute in unit volume, and $U = \frac{P}{L}$ is the specific supersaturation at the initial condensation.

The second factor, the velocity of the growth of the particles of the disperse phase, is expressed by the Noyes-Nernst formula—

$$V = \frac{D}{\delta} S(c - l)$$

in which D is the diffusion coefficient;

δ the thickness of the adhering layer (of uniform concentration, equal to the length of the diffusion path);

S the surface of the disperse phase;

c the concentration of the solution;

l the solubility of the disperse phase of given dispersity;

$c - l$ the absolute supersaturation.

For the crystallisation of a pure liquid the corresponding equations are—

$$W = k\frac{T - T_1}{R} = kU$$

where $T - T_1$ = the absolute over-cooling;

R = the latent heat of crystallisation;

U = the specific over-cooling.

And

$$V = \frac{H}{\delta} S(t - T_1)$$

where H = the coefficient of thermal conductivity;

t = the melting-point for given dispersity;

and the other symbols have the same significance as above.

Let us first consider the velocity of condensation. In the first place, the factor of primary importance is not P, the absolute excess of solute, but $\frac{P}{L}$, the specific excess. An example will make this clear. With a given value of P (say, a few grams per 100 c.c.), a very soluble substance, as, *e.g.*, sodium chloride, will deposit nothing at first, and finally a few crystals will be formed. With the same value of P, an almost insoluble substance, as silver chloride, will give an immediate curdy precipitate. Owing to the large value of L in the former case, the

velocity of condensation is much smaller than in the latter case.

The value of P, nevertheless, is not without influence. The results are very different, according as a given value of U is given by a large P or by a small L. In the one case, a large amount of disperse phase must be produced, in the other very little; if U is large, the former will give a concentrated gelatinous precipitate (a gel), the latter a large number of highly disperse particles (a sol). Thus, by suitable alteration of P or L or of both, we can secure the initial separation of the disperse phase in any desired form.

The duration of the disperse phase in this form is governed by the second formula, which expresses the rate of growth of the disperse phase under the conditions prevailing. The smaller the absolute supersaturation $(c - l)$ is, the smaller is V and the greater the stability of the disperse phase. The same result is attained by decreasing D, the rate of diffusion; this occurs if the solution is very concentrated, in which case the disperse phase is also very concentrated, and further increases the stability.

The conditions for obtaining a stable highly disperse phase are, therefore, small value of P and a corresponding small value of L, in order that U may be sufficiently large to give a large number of points of crystallisation. Suitable values of P may be obtained by any of the usual means, as, *e.g.* (*a*) rapidly cooling a concentrated solution to a sufficient extent; (*b*) adding a solution of the substance to a liquid in which the solvent is completely soluble, but in which the solute is practically insoluble; (*c*) production of the disperse phase by a chemical reaction between substances which are sufficiently soluble to give the desired value of P.

A series of illustrative examples may now be given.

(1) Sodium chloride is so soluble in water (L large) that, even if it were possible to obtain a sufficiently large value of P, the suspensoid stage would be of short duration, owing to the rapid growth of the crystals in the concentrated solution.

(2) But if sodium chloride is produced by the interaction of sodium ethylate or sodium thiocyanate and hydrochloric acid in, say, a mixture of ether and amyl alcohol, in which sodium chloride is practically insoluble, a curdy or gelatinous precipitate, similar to silver chloride, is formed.

(3) If the concentrations in the above reaction are so chosen that P is not too large, a stable suspensoid sol of sodium chloride will be formed.

(4) If an aqueous solution of silver nitrate, saturated at 20°, is cooled in liquid air, a clear glass is obtained, which contains the silver nitrate in the form of a highly disperse phase along with ice. This system is stable at low temperature in spite of the large value of P, because diffusion is reduced to zero.

A fuller examination of the case of barium sulphate will be found of interest. The solubility of barium sulphate at 18° is 0·00024 g. in 100 c.c.; this is not very insoluble, compared with, *e.g.* aluminium hydroxide or even silver iodide. It is so large that with solutions of barium nitrate or chloride (the ordinary reagents) and the ordinary laboratory solutions of sulphates, the values of P obtainable are not large enough to give large values of U; and for the same reason the subsequent growth of the crystals is rapid. Under ordinary conditions of precipitation, therefore, barium sulphate is obtained as a more or less immediate, crystalline precipitate, which, of course, is exactly what is wanted for analytical purposes.

By making use of more soluble salts, as, *e.g.* barium thiocyanate ($Ba(CNS)_2,3H_2O$), and manganous sulphate ($MnSO_4,4H_2O$), it is possible to obtain barium sulphate in any form, from a clear gelatinous mass to a clear solution. The equivalent solutions are mixed in equal volumes; correspondingly large volumes of the very dilute solutions must be used, otherwise there will not be a visible quantity of barium sulphate to separate out. Strictly, the product of the volume and the concentration should be a constant.

The following table, given by von Weimarn, indicates the nature of the precipitate:—

Equivalent concentration of the reagents (n).	P excess of $BaSO_4$ (g. in 100 c.c.).	$U = \frac{P}{L}$ ($L = 0{\cdot}0002$ g. in 100 c.c.)	Nature of the precipitate.
0·00005 to 0·00014	0	0	No precipitate in a year—micro-crystals to be expected in a few years (macro-crystals from large amounts of solution).
0·00014 to 0·0017	0·0006 to 0·0096	3 to 48	Slow precipitation at U = 8. Suspensoid stage at U = 25 (momentary). Complete separation in months to hours.
0·0017 to 0·75	0·0096 to 4·38	48 to 21,900	Precipitation in a few seconds at U = 48. Beyond this, instantaneous precipitation. Crystal skeletons and needles. At U = 21,900 crystals are barely recognisable.
0·75 to 3	4·38 to 17·51	21,900 to 87,500	Immediate formation of "amorphous" precipitates.
3 to 7	17·51 to 40·9	87,500 to 204,500	Cellular clear jelly.

It is clear from this that to get a suspensoid of barium sulphate, it is necessary to diminish L, since to increase P leads, as was to be anticipated, to the formation of a (concentrated) gel. This can be done by the addition of

alcohol to the water. The suspensoid stage appears to be most stable at about U = 8. Retaining this value, and reducing L to one-tenth of its value in water by means of alcohol, we must also reduce Q to one-tenth ; the velocity of growth will also be reduced to the same extent. The excess of barium sulphate in 100 c.c. is reduced to 0·00018 g. and the stability of the disperse phase is greatly increased. For the sol to be stable, the solubility of the disperse phase must not exceed 0·0001 g. in 100 c.c. of the dispersion medium.

The differences in the nature of the precipitate, according as the appropriate value of U is attained by change in P or in L, are further illustrated by a comparison of the barium sulphate gel obtained by the above method with 7 n. solutions in water (P large, L unchanged) with the gel obtained by Kato's method (p. 206), in which solutions of sulphuric acid and of barium acetate in a mixture of alcohol and water (P smaller, L reduced) also produce a gelatinous precipitate of barium sulphate. The two precipitates are very similar in appearance, but their behaviour on dilution with water is strikingly different. The former gives at once a dense white crystalline precipitate, while the latter forms a clear sol, or is at least converted into an opalescent bluish sol, which is very stable. On the addition of an acid, as hydrochloric acid, a white precipitate is at once produced, owing to the increased solubility of the barium sulphate in the acid liquid, and the consequent rapid growth of the particles.

One further instance may be given which shows clearly how the necessary conditions for a sol or a gel may be calculated. The solubility of aluminium hydroxide is so small that it is impossible to determine it. We may assume it to be 10 times less soluble than silver

iodide, say, 10^{-8} g. in 100 c.c., which is 20,000 times less than that of barium sulphate. With the latter gels are obtained at P = 17·5; a similar precipitate of aluminium hydroxide will be obtained at $P = \frac{17{\cdot}5}{20000} = 0{\cdot}0009$. This is confirmed by experiment. At a concentration of 0·0005 g. $Al(OH)_3$ in 100 c.c. the precipitate is highly disperse, above 0·01 g. it is a gel. When, as here, the amount which separates out is so minute, there is not enough to form a skin on the drops, and a network or a fine-grained gel or gelatinous precipitate is obtained. The third stage of the table is not attainable at ordinary temperatures, as the concentrations are too small; but at the boiling-point a microcrystalline precipitate is formed at P = 0·0005 g. Ammonia increases the solubility to such an extent that large microcrystals are readily obtained.

Summarising, we have—

1. Substances which are very soluble. The suspensoid stage is only reached at large values of U, and the result is a concentrated suspensoid sol, a gel. If U is small the suspensoid stage is not recognisable.

2. Substances of small but measurable solubility (about 10^{-4} g. in 100 c.c.). The suspensoid state is reached at both large and small values of U: the former gives a gel as in 1, the latter a suspensoid sol of small concentration.

3. Substances which are practically insoluble. At small values of U, the suspensoid stage is not recognisable; with large U dilute sols are obtained. A gel is obtained only at extremely large values of U.

4. However small the solubility, the precipitate is obtained as crystals with small values of U, if the volume and interval of time are sufficiently large.

5. Every highly disperse system obtained by the crystallisation method strives to diminish its dispersity,

because the smallest particles are more soluble than the larger.

A brief discussion of von Weimarn's theory of the solution method will be found on p. 210.

The crystallisation methods may be classified as follows, and will be described in this order :—

1. Cooling a solution or liquid.
2. Replacing one liquid by another.
3. Reduction methods—
   - (*a*) By hydrogen, carbon monoxide, acetylene, hydrazine, etc.
   - (*b*) By phosphorus.
   - (*c*) By organic substances, with or without protection.
   - (*d*) By metals, or kations.
   - (*e*) By kathode reduction.
4. Oxidation—
   Sulphur from hydrogen sulphide and air or sulphur dioxide.
5. Hydrolysis—
   - (*a*) Of metallic salts.
   - (*b*) Of other compounds, *e.g.* silicon sulphide, ferric ethylate, etc.
6. Precipitation methods—
   - (*a*) No electrolyte produced.
   - (*b*) Electrolytes produced, with or without protection.

CHAPTER XIII

CRYSTALLISATION METHODS

I. Cooling Solution

A FEW c.c. of a 0·02 per cent. solution of *sulphur* (or *phosphorus*) in alcohol is cooled in liquid air; a clear glass is obtained, which is a highly disperse solid sol. This is evident when the tube is allowed to warm up to room temperature. The liquid becomes opalescent blue, changing to white as the temperature rises. This is succeeded by a blue opalescence, and the sol gradually passes into a solution.

An *ice* sol can be prepared in a similar manner. When a very dilute solution of water in ether, chloroform, or xylene (or other liquid of low melting-point) is rapidly cooled in liquid air or in a mixture of alcohol and solid carbon dioxide, the water crystallises out as highly disperse ice, and a liquid sol is obtained.

This method can be extended indefinitely to either low or ordinary temperatures, and to gases, liquids, or solids.

II. Replacement of Solvent

In this method the solvent is replaced by a liquid in which the solute is insoluble, and thus appears as a disperse phase. The preparation of a mastic sol or a gamboge sol is the classical example of this process.

Gum mastic is insoluble in water, but is readily soluble in alcohol or ether. When a dilute alcoholic solution is added gradually to a quantity of water, with constant stirring, the gum is suddenly precipitated in a

highly disperse condition, and, owing to its insolubility, the dispersity does not appreciably diminish. Here we have a small value of P, while L is very small, and U is large, which fulfil the necessary conditions. If the mastic solution is concentrated, or if a large quantity of it is added to the water, a gel is obtained which is also fairly stable. The method is obviously capable of almost indefinite extension. A few instances will suffice.

(1) *Sulphur* (*Selenium*, *Phosphorus*)

The solubility of sulphur in alcohol is 0·05 g. in 100 g. at 18°, and 0·4 g. at 78°; of phosphorus in alcohol, 0·3 g. at 18°, and 0·4 g. at 78°. Both are practically insoluble in water. Crystallised selenium is insoluble in alcohol, but dissolves in carbon disulphide, its solubility being 0·02 g. in 100 g. at 46°.

To prepare sulphur or phosphorus sols, 5–25 c.c. of cold saturated solution are slowly added to 1000 c.c. of cold water, with vigorous stirring. The sols are colourless, with a bluish opalescence, and are stable for days or weeks.

For the selenium sol, 5–25 c.c. of a hot saturated solution are similarly added to 1000 c.c. of cold ether (water cannot be used, as carbon disulphide also is insoluble in it). It is of a beautiful rose colour with a metallic sheen, and is as stable as the others.

(2) *Silver Iodide*

Complex salts or double salts, one of whose components is an insoluble salt, and which are decomposed by water into their components, may yield sols. Thus, if silver iodide is dissolved in potassium iodide, and the solution poured into a large volume of water, a silver iodide sol is obtained. Its stability is increased by the potassium iodide, which at very small concentrations diminishes the solubility of silver iodide.

(3) *Gelatine* (or *Agar*)

If a very dilute solution of gelatine or agar in boiling water is poured into a large volume of boiling alcohol, extremely stable suspensoid sols are obtained.

III. Reduction Methods

Historical Sketch.—The potable gold of the alchemists was probably a gold sol, since it was a solution of gold salts in ethereal oils; these slowly reduce gold chloride with production of gold sols. The production of a red gold solution by the action of a tin solution on gold chloride was described in a text-book so long ago as 1749. In 1794 was published an elaborate research on the colours produced on silk dipped in solutions of gold salts, and subsequently treated with hydrogen or phosphorus in ether. Red and purple shades were obtained.

Out of many early references, mention may be made of reductions with hydrogen and phosphine (1811); of the action of egg-white and of isinglass, which gave reddish-purple sols; and of starch, which gave blue sols. We have here very early (1821) the action of "protective" colloids in conferring stability. Gold chloride was also reduced by hydrogen and hydrogen sulphide, by gallic acid, and by oxalic acid, etc. (1822). Finally, Berzelius, in his *Lehrbuch* (1844), gave many recipes for the preparation of gold sols of different colours.

Curiously enough, in spite of this wealth of recorded observations on gold sols, they were discovered anew by Faraday[1] in 1856, who obtained them by reduction with phosphorus in ether, and were rediscovered once again by Zsigmondy[2] in 1898. The latter also rediscovered Faraday's work, while both apparently knew nothing of all the early work. All the earliest work seems to have been confined to gold, no doubt partly because of its

[1] *Phil. Trans.*, 1857, 145. [2] *Annalen*, 1898, 301, 29.

alchemistic importance, partly because of its ready reduction. Wöhler[1] reduced dry silver mellitate or citrate by means of hydrogen gas at 100° ; a brown mass was obtained, which dissolved in water with a yellow-brown colour (1839). Carey Lea's[2] reduction of silver solutions with strong solutions of ferrous citrate gives gels containing also ferric ion (which probably acts as a "protector"), from which the sol is obtained by washing out the citrate. From the precipitating effect of citrate, the sol would appear to be positive, *i.e.* the negative silver sol + excess of $Fe^{\cdots}$ (see p. 139). Carey Lea regarded the gels as "allotropic" forms of silver.

The modern history of reduction methods begins with Zsigmondy's rediscovery of gold sols by the reduction of a faintly alkaline solution of auric chloride with formaldehyde. He sought out the conditions for obtaining, as often as required and with small risk of failure, a uniform highly disperse gold sol, which was at once stable and sensitive to reagents. Further, his method could be applied with but slight modification to other noble metals. This was done by Lottermoser[3] (1901), who prepared platinum, palladium, rhodium, and iridium sols by this method. By taking advantage of the supersaturation, Zsigmondy[4] has devised a method by which a gold sol may be prepared of any desired uniform dispersity. A small amount of a highly disperse sol is prepared by reduction with phosphorus; a little of this is added to induce reduction in a mixture of gold salt, carbonate, and formalin; and finally a little of the latter is added in the

[1] *Pogg. Ann.*, 1839, [ii.] **36**, 629.

[2] *Amer. J. Science*, 1889, [iii.] **37**, 476; **38**, 47.

[3] *Ueber anorg. Koll.*, 1901.

[4] *Nachr. K. G. d. Wiss. Göttingen*, 1916, p. 177; ref. *Koll. Zeitsch.*, 1919, **24**, 75.

same manner to the required amount of gold solution. A highly disperse, very stable sol is thus obtained.

According to von Weimarn's theory, the preparation of stable highly disperse sols of metals by reduction of their ions in solution should be an easy matter, for the metals are insoluble in the dispersion medium; thus it is easy to have a large value of U with very small P, and vanishingly small L, and practically no D. Hence there will be a very large number of points of condensation, and no subsequent growth in the solution, for all the ion will have been changed into metal, which is insoluble.

This is the actual experience, but there is a difficulty of a different origin. The highly disperse sols are precipitated by traces of electrolytes, and these may be produced by the reduction or be present as impurities in the water. On this account many inorganic reducers are inadmissible, especially acids and salts, as their ions are usually powerful precipitants. If they are used, protective colloids must also be present. When stannous ion is used as the reducer, stannic acid is formed along with the metal sol, and so stable sols are obtained. Examples of this are the purple of Cassius, the alchemical preparations of gold, and Lottermoser's preparation of mercury, by means of stannous chloride. Pure suspensoid sols are usually not stable unless very dilute, so that if concentrated sols are wanted, as they may be for medical or technical purposes, recourse must be had to the stabilising action of protective colloids.

Paal[1] has elaborated a method which makes use of two degradation products of egg-albumin, which he names protalbic acid and lysalbic acid. Their sodium salts are obtained by the action of sodium hydroxide on albumin;

[1] *Ber.*, 1902, **35**, 2206.

they exert a powerful protection, and at the same time are strong reducers. They may be used alone, or in conjunction with other reducers, as hydrazine, sodium amalgam, etc. Others, too, have employed protective colloids for the same purpose. These sols are not so useful for many scientific purposes, as their properties differ so much from those of the pure sols, but they are extraordinarily stable, and may be dried up to hard, metallic-looking grains, which after years will completely solate when placed in water. It is very doubtful whether their physiological activity is at all comparable to that of the unprotected sols.

Kathode reduction may give rise to sol formation. Billiter[1] obtained a yellow-brown mercury sol at the kathode when a 0·004 n. solution of mercurous nitrate was electrolysed. He employed a U tube with side tubes, the bend being plugged with glass wool. On prolonged electrolysis at 220 volts and 0·2–0·3 ampere, the solution was converted into a turbid gray liquid.

The purity of the water is an important factor in the production of stable sols. Bourdillon's method of distillation[2] is simple and most effective. Using this water ($\kappa = 0{\cdot}3$ to 1×10^{-6} mho), the author has obtained brilliant stable sols of gold, silver, ferric hydroxide and arsenious sulphide. Naturally it must also be used for the dialysis.

It is quite impossible to deal exhaustively with all the reducers which have been employed successfully. Full details are to be found in Svedberg's invaluable book.[3]

Among the reducers which have been found effective are the following:—

[1] *Ber.*, 1902, **35**, 1929.
[2] *Chem. Soc. Journ.*, 1913, **103**, 791.
[3] *Methoden z. Darstellung Kolloider Lösungen*, 1909.

Reducer.	Sol.	Author.
H_2	Ag	Kohlschütter [1]
CO	Au, Pd	Donau [2]
	Ag	Kohlschütter [1]
SO_2 }	Ag	v. d. Pfordten [3]
H_3PO_3 }	Se	Schulze [4]
	Te	Gutbier [5]
P	Au	Faraday [6]
		Zsigmondy [7]
Terpenes, alcohols	Au	Vanino [8]
Acetylene	Au	Blake [9]
Formaldehyde	Au	Zsigmondy [7]
	Pt, Pd, Rh, Ir	Lottermoser [10]
,, + silicic acid	Au, Ag	Küspert [11]
Acrolein	Au, Pt, Pd, Os, Ru	Castoro [12]
Carbohydrates	Au	Vanino [13]
N_2H_4	{ Ag, Au, Pt, Pd. Ir, Se, Te }	Gutbier [14]
NH_2OH	Au, Te	,,
$C_6H_5N_2H_3$	Au, Te	,,

With Protective Sols.

Protalbates and lysalbates + N_2H_4	Ag_2O (to 80%)	Paal [15]
	Ag (93%)	,,
	Au (93%)	,,
	Pt (78%)	,,
Protalbate + H_2 or N_2H_4	Pd (76%)	,,
Lysalbate + NaHg	Ir (40%)	,, [15]
,, + N_2H_4	Cu (red and blue)	,,
	Cu (brown and blue)	,,
	Se	,,
Polyphenols	Au, Pt, Ag, Hg	Henrich [17]
Phenol acids	Au, Ag, Pt	Garbowski [18]
$Fe^{\cdot\cdot}$ (citrate)	Ag	Carey Lea [19]
$Sn^{\cdot\cdot}$	Hg, Bi, Cu	Lottermoser [10]

[1] *Zeitsch. Elektrochem.*, 1908, **14**, 49.
[2] *Monatsh.*, 1905, **26**, 525; 1906, **27**, 71. [3] *Ber.*, 1885, **18**, 1407.
[4] *J. pr. Chem.*, 1885, [ii.] **32**, 390.
[5] *Zeitsch. anorg. Chem.*, 1902, **32**, 51, 91, 105. [6] *Loc. cit.*, p. 179.
[7] *Loc. cit.*, p. 179; also *Zeitsch. anal. Chem.*, 1901, **40**, 697.
[8] *Ber.*, 1906, **39**, 1696; 1905, **38**, 463.
[9] *Amer. J. Science*, 1903, [iv.] **16**, 381. [10] *Loc. cit.*, p. 179.
[11] *Ber.*, 1902, **35**, 2815, 4066. [12] *Zeitsch. anorg. Chem.*, 1904, **41**, 126.
[13] *Koll. Zeitsch.*, 1907, **2**, 51.
[14] *Zeitsch. anorg. Chem.*, 1905, **45**, 77; 1902, **31**, 448; *J. pr. Chem.*, 1905, [ii.] **71**, 358, 452; *Zeitsch. anorg. Chem.*, 1902, **32**, 51, 91, 106, 347; 1904, **39**, 112. [15] *Ber.*, 1902, **35**, 2206, 2224, 2236; 1904, **37**, 124.
[16] *Ber.*, 1906, **39**, 1545, 1550; 1905, **38**, 534, 526.
[17] *Ber.*, 1903, **36**, 609, 1215. [18] *Ibid.*, p. 1215. [19] *Loc. cit.*, p. 179.

A detailed account of the following methods is given as being the most generally useful and illustrative:—

1. Kohlschütter . silver sol with hydrogen.
2. Donau . . . gold sol with carbon monoxide.
3. Zsigmondy . . „ „ formalin.
   „ „ phosphorus.
4. Castoro . . . platinum sol with acrolein.
5. Gutbier . . . red and blue gold sols with hydrazine.

(1) Silver Sol by reduction with Hydrogen (Kohlschütter)

The method consists in the reduction of silver oxide or hydroxide in presence of water by means of hydrogen gas. As the two products are silver and water, the method is one which yields an electrolyte-free sol—

$$2AgOH + H_2 = 2Ag + 2H_2O$$

Hydrogen gas is bubbled through a hot (50°–60°) saturated solution of silver oxide, contained in a round-bottomed flask, which is preferably of Jena glass. Solid silver oxide is present to keep up the concentration. In 8–10 hours about 0·5–1 litre of intensely coloured sol is obtained. Reduction is too slow below 50°, while above 60° the sols are very unstable. Analysis showed the presence of some unchanged silver oxide.

As the action appeared to take place mainly at the interface between the liquid and the vessel, Kohlschütter tried the effect of various surfaces. In a platinum vessel a crystalline deposit was obtained in place of the sol. This suggested a means of purification, as follows.

About 80 c.c. of the sol is placed in a blackened platinum basin, and protected from air by a bell-jar. Pure hydrogen is passed through the liquid by means of a tube with a platinum tip. In 12 hours the residual silver

oxide was reduced, the silver being deposited as bright crystals which firmly adhered to the basin. During this treatment the electric conductivity fell to $7\text{–}8 \times 10^{-6}$ mho, a tenth of its former value. The specific conductivity of the water was about 2×10^{-6} mho.

(For other interesting details of this work, see p. 107.)

This preparation can be made as a lecture experiment, if a saturated solution of silver oxide is substituted for the suspension. About 150–200 c.c. of filtered solution are heated to 60° in a Jena flask fitted with Jena glass tubes, and a brisk current of pure hydrogen passed through it. In 20–50 minutes a perfectly clear, intense yellow sol is obtained, which presents a most brilliant appearance in the ultramicroscope. It contains about 0·03 g. Ag in 1000 c.c.

(2) Gold Sol by reduction with Carbon Monoxide (Donau)

Pure gold, precipitated by oxalic acid, is dissolved in aqua-regia, evaporated on a water-bath, and dissolved in pure water to form a 0·002–0·05 per cent. solution. If ordinary distilled water is used, a protective colloid must be added. The carbonic oxide, prepared from oxalic acid and sulphuric acid, may be used along with the carbon dioxide, or freed from it; the mixed gas gives a better colour. The gas is stored in a gasometer, and, after bubbling through water, is passed into the gold solution by means of a capillary tube. The solution may be cold or warm; in a few minutes a red colour is noticeable. The reduction is complete and the end of it is ascertained by the electric conductivity. Large quantities can be made at a time, if the gas is led in slowly. A litre of 0·002 per cent. sol may be had in about 2 hours. The sol is of a clear red colour, and is very stable. The carbon

dioxide can be removed by boiling, and the hydrochloric acid by dialysis.

A very stable **palladium** sol is obtained by treating a palladous chloride solution (0·0005–0·05 per cent.) in the same manner. The reaction is quicker, and is complete. Most of the acid can be removed by dialysis.

Kohlschütter made a **silver** sol by reduction of silver oxide solution with carbon monoxide. It was not very stable.

(3) Gold Sol by reduction with Formaldehyde (Zsigmondy)

The following are Zsigmondy's later directions, and by adhering to them it is easy to prepare a pure red gold sol.

About 120 c.c. of pure water are put into a Jena glass beaker of 300–500 c.c. capacity, and raised to boiling point. During the warming 2·5 c.c. of the gold chloride solution (6 g. of crystallised $HAuCl_4,3H_2O$ in a litre), and 3–3·5 c.c. of pure potassium carbonate solution (0·18 n.) are added. As soon as it boils, 3–5 c.c. of formaldehyde solution (0·3 c.c. of commercial formalin in 100 c.c. of water) are added moderately quickly, a little at a time, with constant vigorous stirring (a soft glass rod must not be used; a Jena glass tube closed at the ends will do). The reaction commences in a few seconds, or, at longest, a minute; the liquid turns a pale red, rapidly changing to an intense bright red, which undergoes no further change. The sol may be purified by dialysis.

It appears to be impossible to prepare more than 120–150 c.c. at a single operation, with larger quantities the colour is not so good or clear. If a large quantity is required, the individual samples are collected and submitted to purification together.

(4) Gold Sol by reduction with Phosphorus (Zsigmondy)

Faraday's gold sols, prepared by adding a solution of phosphorus in ether to aqueous solution of gold chloride, varied very much in colour and stability. Zsigmondy, by combining it with his formaldehyde method, has devised a method which gives, without difficulty, gold sols of the highest dispersity.

The directions and quantities are the same as in the formaldehyde method (see above), except that the solution is not boiled, as reduction takes place at the ordinary temperature, and that a few drops of a solution of white phosphorus in ether are added instead of the formalin. The action is slow, the liquid turning first pale yellow-brown, then gradually a pure red, which is perfectly clear, without a trace of opalescence by either transmitted or reflected light.

The Tyndall effect is scarcely observed in it. The size of the particles is about 1·2–1·5 $\mu\mu$, and is exceedingly uniform. In the ultramicroscope a few isolated gilded dust particles are observed, and beyond that, only a feeble cone of light which gradually fades away on dilution. The sol is very sensitive to electrolytes.

(5) Platinum Sol by reduction with Acrolein (Castoro)

About 500 c.c. of a solution of H_2PtCl_6 (1 g. in a litre) are made slightly alkaline with a few drops of potassium carbonate solution, and raised to boiling point. The flame is removed, and 2–4 c.c. of acrolein solution (Kahlbaum's 33 per cent. solution) are added. The yellow colour disappears in a few seconds, and is succeeded by a brown colour, which finally becomes black. It is filtered, diluted with its own volume of water and dialysed. The sol is quite clear in thin layers, and is very stable.

For dilute sols it is better to make 50–60 c.c. of the platinum solution up to 200 c.c. with pure water, and to proceed as above, using correspondingly less acrolein.

Gold, palladium, osmium, and **ruthenium** sols may also be prepared by this method.

(6) Blue Gold Sol by reduction with Hydrazine (Gutbier's Methods)

In these hydrazine, phenylhydrazine, and hydroxylamine are employed as reducers.

1 g. gold chloride is dissolved in 1000 c.c. of pure water, and exactly neutralised with very dilute sodium carbonate. A solution of hydrazine hydrate (1 c.c. of Kahlbaum's commercial 50 per cent. solution to 2000 c.c. of water) is added drop by drop. The reaction begins at once with production of a deep blue sol. In all a few c.c. of the hydrazine solution are required for complete reduction.

The sol is deep blue by both transmitted and reflected light, is clear, and very stable. If too much reducer is added, the sol is not clear and soon settles out. A peculiarity of the phenylhydrazine reduction of gold is that stable sols of different colours can be obtained by simply adjusting the amount of reducer. The following is a striking experiment:—

Dilute 5 c.c. of gold solution (0·1 per cent.) with 300 c.c. of water in a large beaker, and run in from a burette 0·2 to 0·5 c.c. of a freshly prepared solution of phenylhydrazine hydrochloride (0·4 per cent.). On stirring the liquid becomes deep red. Now add more reducer, drop by drop, when the colour changes to violet; after addition of 5 c.c. the colour is violet-blue, a further quantity changes the colour to blue, and finally to deep blue when 12 c.c. have been added.

Silver, platinum, palladium, iridium, tellurium, and

selenium sols, with gum arabic as protective colloid, have been made by this method.

The colour of the gold sols produced by reduction with hydrazine hydrate depends on the reaction of the solution. If the solution is faintly acid the sol is bright blue, if it is almost neutral the sol is violet or purple, while a brilliant red sol is obtained if the reaction is alkaline (author's unpublished results). Thus—

100 c.c. water,
1 c.c. gold solution (1%),
1–1·5 cc. potassium carbonate solution (0·18 n.),
1–2 c.c. hydrazine hydrate (1 c.c. of 50% solution to 2000 c.c. of water),

give a bright blue sol. If 2 c.c. of potassium carbonate are used the sol is violet, and with 2·5 c.c. of potassium carbonate and 3 c.c. of hydrazine hydrate solution the colour is a brilliant clear scarlet. All three sols are very stable, and are easily reproduced.

Paal's Method. Protalbic Acid and Lysalbic Acid as Protective Colloids

This method is important because of the highly concentrated sols which can be prepared by it (for "Protection," see p. 128). There are two ways in which these substances have been employed; in the earlier method they were used both as reducers and protectives, while in the later they are simply protectives, other powerful reducers, such as hydrazine, sodium amalgam, etc., being used to effect the reduction. The latter method is the more useful. Two examples will suffice.

Silver Oxide Sol and Silver Sol.—1 part of sodium protalbate is dissolved in 15 parts of water, and some sodium hydroxide is added. Silver nitrate is then added until a

precipitate forms, which is dissolved by more sodium hydroxide. Silver nitrate and sodium hydroxide are added alternately until the desired concentration is reached (up to 3·2 parts of $AgNO_3$, or 2 parts Ag). If a silver oxide sol is wanted, this solution is dialysed. For silver sol the undialysed silver hydroxide sol is heated on the water-bath until reduction is complete; this is known by the absence of any reaction with one drop of hydrazine solution. The sol is then dialysed and evaporated in a flat basin on the water-bath. It consists of shining grains with a beautiful blue-green metallic sheen, and is completely soluble in water, even after two years if a drop of sodium hydroxide solution is added.

Gold, platinum, and other metal sols are obtained in a similar manner, with the aid of hydrazine as reducer.

Selenium.—3 g. of sodium protalbate are dissolved in 45 c.c. of water, and 1·63 g. of SeO_2 (=1 g. Se) dissolved in water is added, along with sodium hydroxide in sufficient quantity to redissolve any precipitated protalbic acid. 2 g. of commercial hydrazine hydrate solution are added, and the liquid then rendered just acid in reaction by means of dilute hydrochloric acid. The liquid froths up and becomes blood-red in colour. Alcohol is added to diminish the frothing. The reduction is aided by gentle heat, which causes red flocks of colloid selenium and free protalbic acid to settle out. These are dissolved by addition of sodium hydroxide, and the solution is then dialysed. The sol is quite clear and of the colour of arterial blood. It can be evaporated on the water-bath and dried in a vacuum over sulphuric acid. It is a dark red, shining, and enamel-like substance, and is completely soluble in water.

It contains 33 per cent. of Se, and 5 per cent. of Na. The solubility in water is retained for several years.

Mercury (Lottermoser).

A very dilute solution of mercurous nitrate is poured into a dilute solution of stannous nitrate. An excess of stannous salt is necessary, and neither solution should contain more free acid than will just prevent the separation of basic salts. The liquid becomes deep brown in colour. The mercury sol is precipitated by a strong solution of ammonium citrate as a fine black precipitate, and the liquid carefully neutralised with ammonia. The liquid is syphoned off, the rest being sucked out by means of a porous earthenware filter. The precipitate is dried in a vacuum over sulphuric acid. It has a silvery lustre and forms in water a deep brown sol.

This preparation owes its stability, no doubt, to the protection exerted by the emulsoid stannic acid, which is produced at the same time by the hydrolysis of the stannic nitrate. This accounts for the salting out and the subsequent regeneration of the sol.

Bismuth and **copper** sols have also been prepared by modifications of this method.

IV. Oxidation Methods

The oxidation of hydrogen sulphide to water and sulphur seems to be the only instance of this method. When a solution of hydrogen sulphide is exposed to air, a bluish opalescent sol is first noticed, which subsequently turns yellowish-white and deposits sulphur. Or a solution of hydrogen sulphide is acted on by a solution of sulphur dioxide, when a series of complicated reactions occurs, one product of which is sulphur gel and sol (Wackenroder's solution, 1846).[1] Wackenroder prepared it by passing hydrogen sulphide into a saturated solution of sulphur dioxide at room temperature; he observed that

[1] *Annalen*, 1846, 60, 189.

the opaque yellowish-white liquid is very stable, and is apparently homogeneous, as it can be filtered unchanged.

Selmi and Sobrero (1850)[1] passed sulphur dioxide and hydrogen sulphide simultaneously into a flask full of water. The yellow precipitate of sulphur dissolved in water and was reprecipitated by salts. If sodium salts were used, the precipitate redissolved in water, but not if potassium salts had been used. In the latter case the precipitate is elastic and remains so for months. The precipitate contains potassium sulphate which cannot be washed out. The acid liquid contains sulphur sol, which is precipitated by potassium or sodium salts. They considered it to be an emulsion (like soap, starch, prussian blue, in Selmi's previous researches).

Debus[2] fully investigated Wackenroder's solution and gave details of the preparation.

Recently Raffo[3] prepared sulphur sol from sodium thiosulphate and sulphuric acid as follows: 50 g. of pure $Na_2S_2O_3,5H_2O$ are dissolved in 30 c.c. of water, and added, drop by drop, with constant stirring to 70 g. of sulphuric acid (of density 1·84) contained in a 300 c.c. cylinder, which stands in cold water. Hydrogen sulphide is first formed, then sulphur dioxide, followed by a whitish precipitate, changing to lemon yellow. When the action is over, 30 c.c. of water are added and the whole shaken up and heated to 80° for 10 minutes. The sulphur dioxide is expelled, and the thick turbid mass clears up to a sulphur yellow liquid, which is filtered through glass wool, kept cold for 12 hours, is reheated and then refiltered. This treatment is repeated until all the insoluble sulphur is removed. At this stage the sulphur is a yellow mass which dissolves on warming to a perfectly clear yellow

[1] *Ann. Chim. Phys.*, 1850, [iii.] **28**, 210.
[2] *Chem. Soc. Journ.*, 1888, **53**, 278. [3] *Koll. Zeitsch.*, 1908, **2**, 358.

sol. It is allowed to settle out, centrifuged, washed with cold water, centrifuged again, dissolved in water, precipitated by sodium carbonate, centrifuged, and so is obtained as a sediment of almost pure soluble sulphur, which solates in distilled water. One such sol contained 4·6 per cent. of S and 1·5 per cent. of Na_2SO_4.

Its stability is not very great, and is diminished if the sodium sulphate is dialysed away. With sodium salts a gel is precipitated, which solates in pure water, or on heating to 80°. With potassium salts the gelation is irreversible. A sol which had been neutralised by sodium carbonate remained clear when kept in a stoppered vessel.

V. Hydrolysis Methods

The hydrolysis of salts is really a special case of double decomposition, in which water is one of the reagents; this is clearly seen if the reaction takes place in non-aqueous solution. Theoretically, all salts undergo hydrolysis, but not to a recognisable extent unless the acid or the base, or both, of the salt is a weak electrolyte.

The equations

$$Fe'''Cl_3' + 3H'OH' \rightleftharpoons 3H'Cl' + Fe(OH)_3$$

and

$$Na'CN' + H'OH' \rightleftharpoons Na'OH' + HCN$$

illustrate the reaction. In the latter instance the acid is very weak, but is soluble. In the former the base is probably very weak, but is certainly very insoluble, and thus the equilibrium point is very far on the right side.

Hydrolysis is, as indicated in the above equations, reversible, and increases with the dilution, and also with rise of temperature. When, as in the first reaction, one product is an insoluble substance, we have the necessary conditions for obtaining a stable sol. Even in cases

where the hydrolysis is slight, a sol may be obtained by dialysis, if the salt is not nearly so diffusible as the acid, which is usually the case. Or the acid may be volatile, in which case hydrolysis can be completed by boiling off the acid. The salts which have been most frequently utilised for preparations are those of organic acids (acetate chiefly, because acetic acid is both volatile and a weak acid), and nitrates and chlorides, owing to their solubility and the ready diffusibility of the acids. Another factor of importance is the precipitating effect of anions on positive sols, which all the hydroxide sols formed by hydrolysis of these salts are. Sulphates are more readily hydrolysed than chlorides or nitrates, but ferric sulphate cannot be used to prepare a ferric hydroxide sol, owing to the precipitating effect of the bivalent anion SO_4'' on the positive sol, and this in spite of the stabilising effect of the $H^{\cdot}$; in consequence a precipitate of so-called basic ferric salt is produced instead of a sol.

The earliest preparation of a sol by hydrolysis was the hydrolysis of silicon sulphide, which was discovered by Berzelius (1833).[1] Crum[2] then prepared an aluminium hydroxide sol from aluminium acetate by boiling off the acetic acid. He failed to get ferric hydroxide sol in the same way, but this was done by Pean de St. Gilles a year later.[3] Then followed the dialysis researches of Graham, but these processes are really solution processes, as he digested the solution with precipitated hydroxide before dialysis.

The hydrolysis of ferric chloride was fully investigated by Debray,[4] and more especially by Krecke.[5] The latter found that with solutions containing over 4 per cent. of

[1] *Lehrbuch*, 3 Edition, II., 122. [2] *Annalen*, 1853, **89**, 156.
[3] *Compt. rend.*, 1855, **40**, 568. [4] *Compt. rend.*, 1869, **68**, 913.
[5] *J. pr. Chem.*, 1871, [ii.] **3**, 286.

ferric chloride the hydrolysis is reversed on cooling, while below 1 per cent. it is quite irreversible. The temperature at which hydrolysis is complete also depends on the concentration, thus:

Concentration. g. $FeCl_3$ in 100 g. of solution.	Temperature.
32	130°
8	110°
4	100°
1	83°
0·25	64°
0·06	36°

Most of the free acid can be removed by dialysis. Goodwin[1] showed by measurement of the electric conductivity that the hydrolysis of ferric chloride is a time reaction. The same holds for zirconium chloride, and for aluminium acetate.

As usual, a few typical preparations will be given.

(1) Hydrolysis of Acetates

Aluminium Hydroxide Sol[2]

A solution of aluminium acetate (containing not more than 0·5 per cent. of $Al(OH)_3$) is heated to 100° in a closed vessel for 10 days. The liquid is diluted in a wide flat basin, and is kept boiling vigorously until all the acetic acid is driven off, water being constantly added to replace that boiled off. If the depth of the liquid does not exceed 5 mm., 1 to 2 hours' boiling will be sufficient.

The final concentration should be about 1 part of $Al(OH)_3$ in 1000 parts of water. The sol is transparent, tasteless, and neutral.

[1] *Zeitsch. physikal. Chem.*, 1896, **21**, 1.
[2] Crum, *Annalen*, 1853, **89**, 156.

(2) Hydrolysis of Nitrates

(*a*) *Zirconium Hydroxide Sol*[1]

30 g. of zirconium nitrate are dissolved in 500 c.c. of water, and evaporated to dryness on a water-bath. The residue is dissolved in 500 c.c. of water and again taken to dryness; this treatment is repeated several times. The final product is a clear gum, which swells up in water, and forms a very viscous sol. On dilution an opalescent sol is obtained.

(*b*) *Ferric Hydroxide Sol*[2]

A solution of iron in nitric acid is freed as far as possible from acid. It is then dialysed in a parchment-paper tube, the external water being changed three times a day. The dialysis is continued until nitric acid can no longer be detected in the exterior water. This takes about four to six days. The sol is clear brown, with a slight opalescence by reflected light.

Sols of the following metallic hydroxides have also been prepared by this method: chromium, aluminium, tin, bismuth, cerium, thorium, zirconium. In every case the sol contained traces of nitrate.

(3) Hydrolysis of Chlorides

Ferric Hydroxide Sol[3]

A few c.c. of a 32 per cent. solution of ferric chloride are added slowly to 1000 c.c. of boiling water. The liquid becomes dark red-brown, and remains so on cooling; it

[1] Müller, *Zeitsch. anorg. Chem.*, 1907, **52**, 316.
[2] Biltz, *Ber.*, 1902, **35**, 4431.
[3] Krecke, *J. pr. Chem.*, 1871, [ii.] **3**, 286.

contains ferric hydroxide sol and hydrochloric acid. It will serve many purposes without purification. Practically all the acid can be removed by dialysis.

(4) Hydrolysis of Silicon Sulphide[1]

Berzelius, and later Frémy, obtained silicic acid sol by the action of water on silicon sulphide. Hydrogen sulphide is evolved and β silicic acid remains in solution. It is very stable (it is an electrolyte-free preparation, as the gas escapes), but becomes gelatinous if it is concentrated or boiled, or if alkaline salts are added.

(5) Hydrolysis of Organic Compounds

(*a*) *Ferric Hydroxide Sol from Ferric Ethylate*[2]

Anhydrous ferric chloride is dissolved in absolute alcohol, and treated with sodium ethylate. Sodium chloride is precipitated, the ferric ethylate remaining in solution. This is poured into a large quantity of water, when a clear brown sol is obtained.

(*b*) *Silicic Acid Sol from Methyl Silicate*[2]

A solution of 8 g. of methyl silicate in 200 c.c. of water is boiled under a reflux condenser. The methyl alcohol is then removed by boiling off one-fourth of the liquid. A 2·25 per cent. sol is obtained, which, as the method indicates, is very stable against heating.

[1] Berzelius, *Lehrbuch III.* Auf. 2, 1832, 122; Frémy, *Ann. Chim. Phys.*, 1853, [iii.] **38**, 312.

[2] Grimaux, *Compt. rend.*, 1884, **98**, 105, 1434.

VI. Other Crystallisation Methods

This section contains all the crystallisation methods which are not reductions or hydrolyses. As already suggested, there is no scientific importance in this sub-grouping.

These methods are mainly double decompositions, one product of which is insoluble. They are thus typical cases of von Weimarn's theory, and special attention is again directed to it, and to the examples already described in detail, which properly come into this section (p. 175). The stability of the sol depends to a great extent on the nature of the other product. If it is an electrolyte, the sol may soon be precipitated by it, unless the solutions are very dilute; or it may not be obtained at all unless a protective colloid is present. We have thus three classes:

(*a*) The other product of the reaction is a non-electrolyte.

(*b*) The other product is an electrolyte, and the concentrations must be very small.

(*c*) A protective colloid is added to increase the stability of the sol.

Historical Sketch.—In the third edition of his *Lehrbuch* (1833) Berzelius described the preparation of soluble arsenious sulphide from arsenious oxide and hydrogen sulphide, and its precipitation by hydrochloric acid. He also states that osmium sulphide is obtained as a brown solution by the action of hydrogen sulphide on osmic acid, and that it, too, is precipitated by acids.

Then Graham (1867) in his classical experiments prepared many sols by the action of acids or alkalies on soluble salts, as *e.g.* hydrochloric acid on silicate, stannate, molybdate, or potassium hydroxide on stannic chloride; also by double decomposition of salts in dilute solution

and subsequent dialysis to remove the electrolyte product, *e.g.* copper ferrocyanide, prussian blue.

Schulze (1882) returned to the action of hydrogen sulphide on oxides of arsenic and antimony. In the latter case no sulphide sol was formed, and he investigated the action of hydrogen sulphide on tartar emetic; other salts are produced in the reaction, and the concentration is an important factor. No sol is obtained if the tartar emetic solution is more than 1·6 per cent., and partial precipitation occurs between 1·25 and 0·5 per cent.

Winssinger (1888) prepared many sulphide sols by the action of hydrogen sulphide gas on very dilute solutions of salts, *e.g.* of platinum, palladium, gold, silver, thallium, lead, bismuth, iron, nickel, cobalt; other sulphides, *e.g.* of tungsten and molybdenum, by dissolving the sulphide in ammonium sulphide and reprecipitation with acetic acid. The salts were removed by dialysis. Zinc sulphide sol was prepared by passing hydrogen sulphide into a suspension of zinc hydroxide. It is doubtful if this last method is not a solution method; it may at least become one if excess of hydrogen sulphide is passed in. Linder and Picton (1892) substituted hydrogen sulphide solution for the gas, at the same time keeping up the concentration by passing in more gas. They employed hydroxides in suspension, and also salts.

Lottermoser, acting on mercuric cyanide and copper glycine with hydrogen sulphide, obtained stable sols of mercuric sulphide and copper sulphide, the other products being hydrocyanic acid and glycine (amino-acetic acid), both non-electrolytes. He also prepared organosols from the same substances by substituting organic liquids for water as solvent.

He also discovered later that, at sufficiently low concentrations, silver nitrate gives sols with many salts which

form insoluble silver salts, provided that one or other of the reagents is present in slight excess (see p. 110). In this way he prepared many silver sols, *e.g.* AgCl, AgBr, AgI, AgCN, AgCNS, AgOH, Ag_2CO_3, Ag_2CrO_4, Ag_2S, etc. Solution processes may also play a part in some at least of these preparations.

Many sols prepared by double decompositions are not very stable, and none are so except at great dilution. If more concentrated sols are required, an emulsoid must be added to confer stability. For instance, Paal's protalbic acid and lysalbic acid methods are equally effective for other insoluble metallic compounds. By the action of the appropriate sodium salt on silver protalbate or lysalbate, Paal prepared sols of AgOH, Ag_2CO_3, Ag_3PO_4, Ag_2S, AgCl, AgBr, AgI; he also prepared Hg_2O sol by the same method. Other emulsoids may be used; HgCl, HgBr, HgI, Ag_2CrO_4 sols have been made with albumin as protector; with the aid of gelatine Lobry de Bruyn (1898) obtained sols of AgCl, AgBr, AgI, Ag_2CrO_4, sulphides and hydroxides of many heavy metals, lead iodide, prussian blue, copper ferrocyanide, manganese dioxide, etc. According to him concentrated sugar solution also protects.

In some instances, a protective colloid may be produced by the reaction. Michael observed that the reaction between chloracetic ester and sodiomalonic ester (and other similar compounds) in benzene solution gave clear solutions of a pale yellow colour, with a faint opalescence, and concluded that an addition compound had been formed, as no sodium chloride separated out as usual. Paal (1906) showed it to be a sol of sodium chloride, which is precipitated as a gel by ligroin; this gel is re-solated in benzene. An organic bye-product is supposed to act as protector; sols of sodium bromide and iodide have been

obtained by similar reactions in anhydrous benzene or ether. The presence of a protective colloid does not seem necessary for the stability of sodium chloride sol in organic liquids, such as benzene, in which it is practically insoluble (see p. 174).

As before, a few typical or important preparations are given in detail.

A. Electrolyte-free Sols

I. *Arsenious Sulphide Sol*[1]

Pure arsenious acid is dissolved in water, which is kept boiling; in this way a strong solution is obtained. This solution is allowed to flow into a saturated solution of hydrogen sulphide, through which a current of the gas is continuously passing. The uncombined hydrogen sulphide is removed by a current of hydrogen (Linder and Picton).

Schulze obtained very concentrated sols by adding arsenious oxide to the sol, after the saturated solutions had been treated with hydrogen sulphide, then adding more H_2S. After several repetitions the sol contained 37 per cent. of arsenious sulphide.

II. *Zinc Sulphide Sol*[2]

A current of hydrogen sulphide is passed into water containing in suspension pure zinc hydroxide, which has been precipitated by ammonia and washed with cold water by decantation. The sol is very slightly opalescent. Copper sulphide sol is prepared in a similar way.

[1] Linder and Picton, *Chem. Soc. Journ.*, 1892, **61**, 137; Schulze, *J. pr. Chem.*, 1882, [ii.] **25**, 431.

[2] Winssinger, *Bull. Soc. Chim.*, 1888, [ii.] **49**, 452.

III. *Mercuric Sulphide Sol*[1]

Hydrogen sulphide is passed into a cold saturated solution of mercuric cyanide (12 g. in 100 c.c.). The hydrocyanic acid cannot be completely removed by a current of hydrogen sulphide or carbon dioxide, and the sol becomes unstable if it is dialysed. The best way is to distil off the hydrocyanic acid under reduced pressure in an atmosphere of hydrogen sulphide. The sol is deep brown in colour.

Copper glycine treated in a similar manner gives copper sulphide sol.

Organosols are obtained by using ether or benzene as solvents instead of water.

B. Sols containing Electrolytes

I. *Silicic Acid Sol*[2]

A solution of sodium silicate (112 g.) is poured into an excess of dilute hydrochloric acid (67·2 g. HCl), the total amount of water being 1000 c.c. The sodium chloride and the excess of acid are dialysed away; the dialysis is complete in four days (no precipitate with silver nitrate). The sol contained 60·5 g. of silicic acid, 6·7 g. had escaped during dialysis, and the concentration was 4–9 per cent. of silicic acid.

II. *Antimonious Sulphide Sol*[3]

4·3 g. antimonious oxide and 13 g. of tartaric acid are made up to 1000 c.c. of solution; this will give a 0·5 per cent. sol. The solution is saturated with hydrogen

[1] Lottermoser, *J. pr. Chem.*, 1907, [ii.] **75**, 293.
[2] Graham, *Phil. Trans.*, 1861, **151**, 183.
[3] Schulze, *J. pr. Chem.*, 1883, [ii.] **27**, 320.

sulphide gas. The sol is deep red, and may be purified by dialysis.

III. *Metallic Sulphide Sols*[1]

For sols of *platinum sulphide* or *gold sulphide*, the solution of the corresponding chloride is made as neutral as possible, and hydrogen sulphide is passed in. In spite of the hydrochloric acid, the dark brown sols are fairly stable, remaining unchanged for many weeks. A gold sol contained 0·55 g. Au_2S_2 in a litre.

A *silver sulphide* sol from silver nitrate contained 0·6 g. Ag_2S in a litre; a slightly more dilute sol remained unchanged for over two months. Dialysis increases the stability.

IV. *Barium Sulphate in Aqueous Alcohol*[2]

A 1 m. sulphuric acid solution is diluted with 2 volumes of alcohol, and there is added an equivalent amount of a 1 m. barium acetate solution, which has been diluted with 6 volumes of alcohol. A transparent gel of barium sulphate, which forms a clear sol with a large quantity of water, is obtained. If the gel is dried below 40° C. it will still solate in water.

C. A Protective Colloid is present

I. *Gelatine (or Sugar)*[3]

A 10 per cent. solution of gelatine, purified from electrolytes, is mixed with an equal volume of the solutions (0·1–0·05 n.), which by their interaction will produce an insoluble compound.

[1] Winssinger, *l.c.*, p. 200.

[2] Kato, *Mem. Coll. Sci. Eng. Kyōtō*, 1909, **2**, 187. [*Chem. Soc. Journ.*, 1910, A. ii., 850.]

[3] Lobry de Bruyn, *Rec. trav. chim.*, 1900, **19**, 236; *Ber.*, 1902, **35**, 3079.

II. *Sulphide Sols* with *Casein* or *Gum Arabic*[1]

If hydrogen sulphide gas is passed through a solution of silver salt or cadmium salt, to which gum arabic or casein have been added, stable sols of the sulphides are obtained.

III. *Paal's Protalbic Acid and Lysalbic Acid Methods*[2]

(*a*) For silver hydroxide sols, see p. 192.

(*b*) Hydroxides of Bi, Co, Ni, Fe, Mn; Ag_2CO_3, Ag_2S, AgCl, etc., may all be prepared by the action of the appropriate sodium salt on the corresponding metallic salt of protalbic acid or lysalbic acid.

IV. *Sodium Chloride Sol in Benzene*

5 g. of malonic ester and 0·7 g. of sodium are added to 30 c.c. of anhydrous benzene, cooled, and 4 g. of chloracetic ester added; and heat is applied till all has dissolved. The orange coloured opalescent liquid is cooled and the gel is precipitated by adding 5–6 volumes of petroleum ether. It solates completely in benzene, but is insoluble if dried in a vacuum.

The dried substance contained 58 per cent. of NaCl, and 26 per cent. of Na. There is thus excess of sodium, and a large amount of (adsorbed) organic substance.

[1] Müller, *Oesterr. Chem. Zeit.*, 1904, **7**, 149.

[2] *Ber.*, 1906, **39**, 1436, 2859, 2863; *ibid.*, 1908, **41**, 51, **58**.

CHAPTER XIV

SOLUTION METHODS

THE process generally known as "peptisation" (Graham) is a typical example of the solution method. As the term gelation has been used to express the transformation of sol into gel, solation might appropriately be applied to the reverse process.

Lottermoser,[1] starting from his observations on the formation of suspensoid silver compounds, in which he found that excess of one or other ion was necessary for the production of the sol (p. 110), considers that a peptiser (or sol-former) must contain one, or, in some cases, either of the ions of the disperse phase. Thus, silver chloride, as a fine precipitate, forms a sol on digestion with a solution containing either $Ag^{\cdot}$ or Cl'. When aluminium hydroxide is peptised with aluminium chloride solution, it is because of the Al''', or with sodium hydroxide because of the OH'. Müller[2] showed that ferric chloride, thorium nitrate, chromium nitrate peptise aluminium hydroxide as well as hydrochloric acid does.

Equal quantities of aluminium hydroxide (= 1·224 g. of Al_2O_3) in 250 c.c. of water required for complete peptisation—

[1] *Zeitsch. physikal. Chem.*, 1908, **62**, 359; *Koll. Zeitsch.*, 1908, **3**, 31.

[2] *Koll. Zeitsch.*, 1907, **2**, supplement 6-8; *Zeitsch. anorg. Chem.*, 1908, **57**, 311.

20 c.c. of 0·05 n. HCl.

1 c.c. of $FeCl_3$ solution (containing 3 per cent. of Fe_2O_3).

4·5 c.c. of $Cr(NO_3)_3$ solution (containing 1·45 per cent. of Cr_2O_3).

10 c.c. of $Th(NO_3)_4$ solution (containing 2·55 per cent. of ThO_2).

Calculating back to $(H^{\cdot})Cl'$ or $(H^{\cdot})NO_3'$, the amounts required for peptisation were—

Hydrochloric acid . . .	0·001 HCl
Ferric chloride	0·0012 HCl
Chromic nitrate	0·0026 HNO_3
Thorium nitrate	0·0038 HNO_3

while the amount of aluminium hydroxide peptised requires 0·036 HCl or HNO_3 to form normal salt.

These results are not necessarily at variance with Lottermoser's theory, for it is quite probable that the first action between ferric chloride and aluminium hydroxide is the formation of some ferric hydroxide and aluminium chloride. Or ferric chloride, like all the above salts, is hydrolysed into basic hydroxide and free acid, which is thus in a position to act on the aluminium hydroxide with production of Al'''. It is rather curious that hydrochloric acid and ferric chloride are apparently equally effective in peptising aluminium hydroxide.

The amount of peptiser required is not proportional to the amount of the precipitate, but depends largely on the previous treatment of the precipitate.

Some metallic hydroxides are peptised by alkalies; thus Hantzsch [1] showed that zinc hydroxide and beryllium hydroxide form sols when treated with alkalies, and do not dissolve in them. Many metallic sulphide precipitates are peptised by treatment with hydrogen sulphide.

[1] *Zeitsch. anorg. Chem.*, 1902, **30**, 289.

In all these instances, as von Weimarn indicates, we have, as peptiser, substances which are capable of forming soluble compounds with the substance which is peptised; *e.g.* with aluminium hydroxide we have aluminium chloride and the aluminates; with silicic acid, we have silicates formed with alkalies, and with acids, a soluble complex of unknown composition. In the silver salts, soluble complex salts are formed with both silver nitrate and the soluble halides.

The solution theory of Noyes and Nernst must therefore apply to this process, as it does to the crystallisation process. The formula is—

$$V = \frac{D}{\delta} S(L - c)$$

in which L is the solubility, c the concentration of the solution at any given time, and the other symbols have the same significance as on p. 168. [It is the same equation, except that L and c are reversed, in order to apply it to the process of solution (increase of c), instead of to crystallisation (decrease of c)]. If V is large, the sol stage will soon be passed; V will be small only when D or $(L - c)$ is small. Substances of high molar weight diffuse slowly, and their sol stage is of long duration, as, *e.g.* gelatine. Even if $(L - c)$ is small, the sol stage will not be stable, unless D is also small, since the larger particles will grow rapidly at the expense of the smaller ones.

The Noyes-Nernst formula, however, only applies when the processes are reversible, and when diffusion is slow in comparison with the other processes. If then the solid undergoes a slow change before passing into solution, or if the actual process of solution is much slower than the rate of diffusion, the sol stage may be comparatively stable. Peptisers, as we have seen, are substances which

can, if in sufficient concentration (or if sufficient time is allowed), dissolve the solid, which is insoluble in the dispersion medium. This being so, the velocity of solution can be slowed down to any desired extent by simply reducing the concentration of the peptiser. When the sol stage is reached, the peptiser may be removed, wholly or in part, by dialysis.

The method is a very general one. As already explained, the crystallisation method indicates how a substance may be obtained as a highly disperse precipitate (gel). By means of a suitable peptiser and dispersion medium, this can be converted into a sol. For instance, barium sulphate and carbonate and other insoluble salts of the alkaline earths can be peptised by the corresponding acid (which forms soluble acid salts) in a mixture of alcohol and water, in which the disperse phase is sufficiently insoluble to prevent subsequent decrease in dispersity by recrystallisation. Many other examples of a similar kind will be found below.

There is another method of preparation which is difficult to place. As the dispersity certainly increases, it has this much in common with the solution process. Svedberg classes it along with peptisation as mechanical-chemical dispersion under the heading "washing-out" method. Many reactions give rise to an insoluble substance which is not obtained as a sol, except with very dilute solutions, because it is precipitated by the other product, which is an electrolyte (see previous section). In some of these instances the insoluble precipitate is converted into a sol when the excess of this electrolyte is removed by washing or dialysis. The phenomenon of a precipitate coming through the filter on thorough washing is well known.

There are many other reactions also in which a

substance is produced in a highly disperse state, and only requires the removal of electrolytes to pass into the sol. Davy,[1] *e.g.*, reduced boron oxide with potassium, and found that the boron washed through the filter before the potassium hydroxide was completely removed. The same happens with silicon and zirconium (Berzelius). The latter also prepared sols of silicic acid and molybdic acid. The silicic acid gel produced by the action of water on silicon fluoride passes into a sol on washing with water. Molybdenum tetrachloride is precipitated by ammonia as a gelatinous precipitate, for it is insoluble in salt solutions; when these are washed out, a clear reddish-yellow sol is obtained.

The dispersity of the precipitate is of great importance in solution methods. Kühn[2] noticed that silicic acid gel formed a sol only if it was dilute and had not lost much water. The same difference has been noted between a gel of freshly precipitated antimonic oxide ($Sb_2O_5,6H_2O$), and one which has been air dried.

Berzelius[3] also described the solation of sulphides by washing sulphide precipitates with water. Many other instances could be given, one will suffice. Platinum black, prepared by means of formic acid, often forms a stable sol when thoroughly washed.

Berzelius seems to have been the first to observe the solation of a gel in the case of silicic acid. Finely divided silicic acid dissolves in potassium carbonate solution, forming β silicic acid, which dissolves in water. The potassium carbonate is not decomposed, for no carbon dioxide is given off; and when it is neutralised with acid, the silicic acid does not separate out, proving it to be

[1] *Schweigg. J.*, 1811, **2**, 48.
[2] *J. pr. Chem.*, 1853, [i.] **59**, 1.
[3] *Pogg. Ann.*, 1824, [ii.] **2**, 139.

dissolved by the water and not by the alkali. The solation of stannic acid, titanic acid, and prussian blue were all known to Berzelius.

Then come Graham's important researches[1] on peptisation (1861, 1864). He prepared aluminium hydroxide, ferric hydroxide, and chromic hydroxide sols by digestion with the chlorides, titanic acid by means of hydrochloric acid, ferrocyanides of iron and copper by means of oxalic acid or oxalates. The sols were purified by dialysis.

Reference has already been made to A. Müller's researches, as also to the peptisation of sulphides by hydrogen sulphide, which was first observed by Spring.[2] Kužel has recently (1907) described an important method of peptisation. The substance, usually a metal, as *e.g.* chromium, platinum, is very finely powdered by mechanical means, and treated with moderately hot dilute solutions of different etching reagents. Usually an acid reagent is followed by an alkaline one. A detailed example is given below. von Weimarn's method for insoluble salts of alkaline earths has already been given (p. 175). A similar method of Neuberg will be found below.

I. Boron (silicon, zirconium)[3]

An oxide of the element is reduced by potassium at red heat. The fused mass is treated with water, and the precipitate washed with pure water until the filtrate begins to run through coloured. Subsequent washing gives the sol.

II. Ferric Hydroxide Sol[1]

A solution of ferric chloride is saturated with freshly

[1] *Phil. Trans.*, 1861, **151**, 183.
[2] *Ber.*, 1883, **16**, 1142.
[3] Davy, *l.c.*, p. 208.

precipitated ferric hydroxide, or ammonium carbonate is added to it so long as the precipitate redissolves. The red solution is dialysed; after 19 days there were 30·3 equivalents of Fe to 1 of HCl.

III. Aluminium Hydroxide[1]

50 c.c. of a solution of aluminium chloride (= 2·45 per cent. of Al_2O_3) are diluted with water and precipitated by ammonia, as in gravimetric analysis. The precipitate is well washed with hot water, and is then transferred to a flask containing 250 c.c. of water. 0·05 n. HCl is added from a burette, the solution being heated to boiling. After each addition water is added to replace that boiled off. The opalescent liquid can be filtered unchanged.

IV. Cadmium Sulphide[2]

An ammonia solution of cadmium sulphate is completely precipitated with hydrogen sulphide. The precipitate is thoroughly washed by decantation with water, suspended in pure water and a current of hydrogen sulphide passed in. The precipitate becomes milky and finally disappears. The sol is then boiled until no more hydrogen sulphide is driven off.

V. Tungsten[3]

10 kg. of tungsten, mechanically powdered as fine as possible, are heated for at least 5 hours, better for 24–48 hours, on a water-bath with 75 kg. of 15 per cent. hydrochloric acid, with vigorous stirring and frequent renewal of the acid. The acid is run off, and the metal washed by decantation with distilled water until a sol begins to form.

[1] Müller, *l.c.*, p. 204.
[2] Spring, *Bull. Acad. Roy. Belg.*, 1887, [iii.] **14**, 312.
[3] Kužel, *D. R. P.*, 186980, 1907.

It is then treated for 5–24 hours with 75 kg. of 1 per cent. potassium cyanide solution. After being washed with water it is again heated for 24 hours with 75 kg. of 1 per cent. ferrous sulphate. After complete removal of the iron by washing with water, the metal is again heated with an alkaline liquid, *e.g.* a 2 per cent. solution of methylamine, or a 0·5 per cent. solution of sodium hydroxide in alcohol. After two or three repetitions of this treatment with acid followed by alkali the tungsten forms a perfect sol with water.

By this method sols of chromium, manganese, molybdenum, uranium, tungsten, vanadium, tantalum, titanium boron, silicon, thorium, zirconium, platinum, and other metals can be obtained. Suitable reagents for the method are—*acid:* organic acids, phenols, salts with acid reaction, as ammonium chloride, aluminium chloride; *alkaline:* caustic alkalies, alkaline carbonates, potassium cyanide, ammonia, organic bases as pyridine, methylamine. Other liquids may be used instead of water, as methyl alcohol, ethyl alcohol, glycerol.

VI. Barium Carbonate in Methyl Alcohol[1]

Carbon dioxide passed into a solution of barium oxide in methyl alcohol gives a thick gel of barium carbonate. If more gas is passed in, the gel dissolves, forming an opalescent liquid. On evaporation in a vacuum it leaves a clear gel, which re-solates on addition of methyl alcohol.

Unclassified Methods

I. *Conversion of one Sol into Another*

One example has already been given in Paal's preparation of silver sol from silver hydroxide sol (p. 193).

[1] Neuberg, *Koll. Zeitsch.*, 1908, **2**, 321, 354.

Schneider[1] acted on stannic acid sol with hydrogen sulphide, and so obtained the sulphide sol. Meyer and Lottermoser[2] converted silver sol into silver halide sols by means of free halogens, or of salts which readily give up halogen. Lottermoser also obtained cupric oxide sol from copper sol by oxidation in air. As already stated, the sols of base metals (as prepared by the electrical dispersion methods) are really oxide or hydroxide sols.

II. *Sols formed by the solution of Alloys*

(1) Some alloys give rise to a highly disperse sol, when one constituent is insoluble in an acid and the others are soluble in it. Schneider[1] made a gold-tin-silver alloy, and treated it with nitric acid. A black powder was left which was well washed with water. This residue gave a beautiful ruby sol with ammonia. On dialysis, purple of Cassius sol was obtained.

In this case the stannic acid protects the highly disperse gold; perhaps the alloy is to be regarded as a highly disperse gel (cp. pp. 175 and 180).

(2) Wedekind[3] reduced zirconium oxide with magnesium. A part of the black reduction product begins to go through the filter when treated with moderately strong hydrochloric acid and washed with water. The sol is deep blue and opalescent.

[1] *Zeitsch. anorg. Chem.*, 1894, **5**, 80.
[2] *J. pr. Chem.*, 1897, [ii.] **56**, 247; *ibid.*, 1898, [ii.] **57**, 513.
[3] *Zeitsch. Elektrochem.*, 1903, **9**, 630.

CHAPTER XV

ELECTRICAL DISPERSION METHODS

THERE are two distinct methods of electrical dispersion, kathode dispersion and dispersion in an electric arc between two metallic conductors in the dispersion medium. The latter, which is by far the more important, was discovered by Bredig so late as 1898. The former goes back to the times of Ritter and Davy.

A tellurium kathode in water with a platinum anode sends out a cloud of brown powder. Using a high potential, Davy obtained a purple-red liquid which spread through the water. This has been fully investigated by E. Müller.[1] He found that a rod of pure tellurium as kathode, 5 cm. distant from a platinum anode in pure water, gives at 200 volts brown clouds, which form a brown sol. Selenium and sulphur sols were obtained by partially covering a platinum kathode with fused selenium or sulphur. The sol is formed at the junction of the platinum and the other element. High voltages are not necessary; sols are formed at even 4 volts.

Bredig,[2] who was engaged in an investigation of the decomposition of organic substances by the electric arc, tried the effect of passing an arc between metal wires under water. Dark-coloured liquids resulted; gold wires gave red or violet liquids, which were very similar to Zsigmondy's gold sols. Some metals, *e.g.* mercury and

[1] *Zeitsch. Elektrochem.*, 1905, **11**, 521, 931.

[2] *Ibid.*, 1908, **4**, 51; *Anorg. Fermente*, Leipzig, 1901.

tin, gave suspensions of low dispersity; platinum, palladium, iridium, silver, and cadmium gave metal sols; thallium gave a hydroxide sol. Later, it was found that many metals give rise to hydroxide sols only, as zinc, iron, aluminium. Metals with high solution pressures (> hydrogen) are not likely to yield metal sols in water. When Bredig substituted organic liquids as the dispersion medium, another difficulty was encountered, the decomposition of the liquid with production of carbon, of which the sol contained a large amount, *e.g.* 75 per cent. of the solid in a platinum sol was carbon. Burton dispersed several metals (copper, lead, bismuth, tin, iron, zinc) in methyl and ethyl alcohol, and platinum, silver, gold in ethyl malonate, but all these sols were very impure.

These difficulties were satisfactorily overcome by Svedberg.[1] In the first place, in applying Bredig's method to the preparation of organosols, he found that increasing the active surface of the metal was favourable to sol formation. Insertion of a condenser in parallel with the electrodes was a still further improvement. These methods worked with the kathodically softer metals, silver, gold, copper, lead, tin, but failed with the "hard" metals, *e.g.* aluminium. Very positive metals, as calcium, caused greater decomposition than negative metals; the catalyser metals, cobalt, nickel, platinum, also gave rise to strong decomposition, while bismuth and tin had the least effect in this direction.

Svedberg gives a list of 28 metal sols in isobutyl alcohol, with their colour and relative stability. The sols are mostly dark coloured, perhaps because of the

[1] *Ber.*, 1905, **38**, 3616; *ibid.*, 1906, **39**, 1705; *Koll. Zeitsch.*, 1907, **1**, 229, 257; *ibid.*, 1908, **2**, xxix–xliv; *Methoden zur Herstellung Kolloider Lösungen*, Dresden, 1909.

0·2—2 per cent. of carbon which they contain. A few examples may be given.

Metal.	Colour. Transmitted.	Reflected.	Stability.
Ag . . .	green brown	black	24 hours
Al . . .	brown black	black	∞
Au . . .	dark violet	black	28 hours
Cd . . .	brown	grey black	∞
Cr . . .	brown black	black	1–2 weeks
Cu . . .	grey black	blue black	20 hours
Pt . . .	brown black	black	∞
Zn . . .	brown red	grey black	∞
C . . .	yellow brown	grey brown	∞
P . . .	colourless	flesh	—
Se . . .	vermilion	pale red	1–2 days
Si . . .	brown yellow	dark grey	∞
Te . . .	brown	black	a few hours

Svedberg then used oscillatory discharges instead of a direct current arc, and with care was able to prepare pure metal sols in water and other liquids. By means of it, organosols of the alkali and alkaline earth metals have been obtained. The best conditions for sol formation are—

Capacity	as large as possible
Self-induction . .	as small „
Ohm's resistance .	„ „
Length of spark .	„ „

Related metals are dispersed to a similar extent; ease of dispersion in any series increases with the atomic weight. The order is—

Cu, Ag, Au; Mg, Zn, Cd;
Al, Th; Ni, Pt.

As already mentioned, the amount of decomposition of the dispersion medium depends on the nature of the metal.

The following figures for alcohol sols indicate the superiority of Svedberg's method.

Comparison of Alcohol Sols prepared by Bredig's Method (Degen), and by Svedberg.

Metal.	Percentage of Carbon. Degen.	Svedberg.
Bi	—	0·25
Cd	15	0·33
Mg	62	1·4
Pt	73	1·2
Al	—	1·6

1. Gold Sol and Silver Sol by Bredig's Method

An ammeter (*A*), a rheostat (*R*), which will afford 4–12 amperes with the voltage (220 V.) and two electrodes

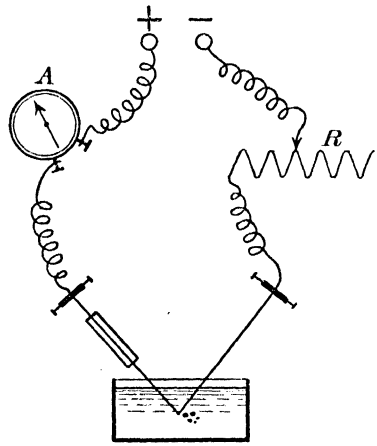


Fig. 13.

of pure gold wire, 1 mm. in thickness, and 6–8 cm. in length, are connected in series with the lighting circuit. The gold wires are pushed through narrow glass tubes for convenience in handling. The resistance is adjusted until

8–10 amperes pass with a 1 mm. arc between the wires under water. The wires are momentarily touched and drawn apart.

A better sol is obtained if a 0·001 n. solution of sodium hydroxide is used instead of pure water, but in either case salts should not be present. So long as the arc passes, purple red clouds are sent out from the wire; if the arc is extinguished, the wires are short-circuited again. The metal comes from the kathode alone; the anode usually gains slightly in weight.

In this manner Bredig prepared sols of gold, silver, platinum, iridium. Silver sol is the easiest to prepare:—

"Wires of 1 mm. diameter easily disperse in pure water, without addition of alkali, with a current of 4–8 amp. The dark sol is sometimes red-brown to deep olive-green in colour; the dilute sol is yellow. They are very stable."

Cadmium sol could only be prepared with pure water and in an oxygen-free atmosphere.

2. Billiter's Modification of Bredig's Method[1]

A thin layer of the metal is electrolytically deposited on another metal, *e.g.* lead, copper, nickel, zinc, on iron; iron on zinc; mercury on zinc or iron; or aluminium foil is wrapped round zinc or iron wire. These are used as kathodes in Bredig's process, the anode is iron or aluminium wire.

All the sols thus obtained are brown in colour; most of them are oxides or hydroxides.

3. Svedberg's First Method

Small pieces of thin metal foil are suspended in the dispersion medium in a cylindrical vessel. The electrodes

[1] *Ber.*, 1902, **35**, 1929.

are wires of "hard" metal, *e.g.* iron or aluminium, and are connected with the 220 volt circuit. The foil is kept in rapid movement, and sparks readily pass from one piece to another. The current is read off on an ammeter, 20–50 milliamperes being sufficient.

If a condenser of 0·32 microfarad capacity is joined in parallel with the electrodes, the dispersion is quieter and there is also less decomposition of the liquid.

By this method sols of gold, silver, copper, lead, tin can conveniently be obtained in water or organic liquids, as alcohol, acetone, ether, chloroform.

4. Svedberg's Second Method

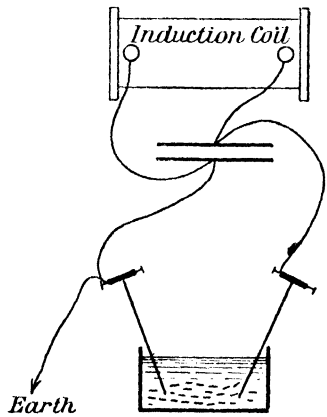


FIG. 14.

The secondary terminals of a large induction coil (12-15 cm. spark) are connected with the electrodes, and in parallel with a glass condenser of 225 sq. cm. surface. The electrodes dip into the liquid contained in a basin, at the bottom of which is placed the metal in the form of grains or small pieces (Fig. 14); the electrodes need not be

of the same metal. Dispersion takes place rapidly and quietly, and many sols can be prepared in this manner. The contents of the basin may be kept in gentle motion by means of one electrode.

5. Sodium Sol in Ether

The apparatus consists of a small flask with a long neck, and a hard glass tube which just fits into the neck. A rubber tube slipped over the junction makes it gas-tight. The lower end of the tube is closed up except for one or two minute holes, which afford communication between the tube and the flask. Platinum wires are stretched on the inside of the tube from bottom to top, where they are fused in. Dry ether and small pieces of sodium, the latter to a depth of 0·5–2 cm., are placed in the flask. The top of the tube is connected with a supply of pure dry hydrogen, which is passed through the apparatus for 1–5 hours, after which the ether is sucked by means of a pump into the tube, and the current turned on.

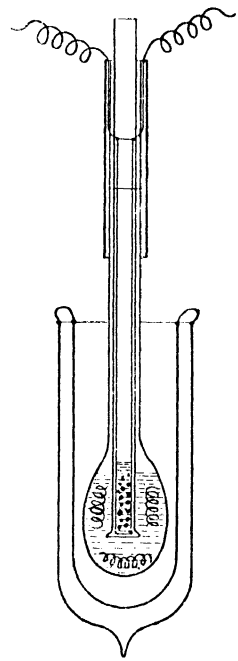


Fig. 15.

For other metals, as potassium, rubidium, cæsium, a low temperature is necessary. The flask is placed in a mixture of solid carbon dioxide and acetone, or, better, of liquid air and alcohol, in a Dewar vessel. The ether must be very pure and dry.

Other liquids may be used, *e.g.* pentane, methane, chloroform. Isobutyl alcohol is the most generally useful alcohol, as lower ones may give alcoholates, and higher ones are decomposed.

6. Electrical Dispersion of Non-metals (Svedberg)

Any solid element or compound which has a moderate electric conductivity can be dispersed by this method, *e.g.* carbon, silicon, selenium, tellurium; and minerals, as magnetite, copper sulphide.

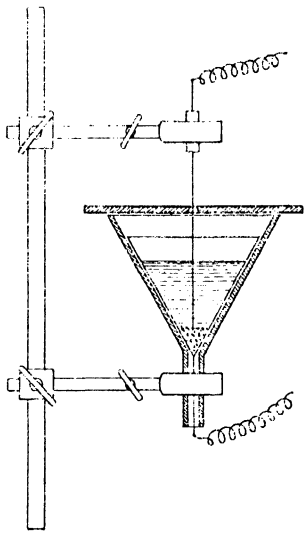


FIG. 16.

The following is a convenient form of apparatus for poor conductors: a glass funnel with a ground edge is fitted with a conical vessel of aluminium, in which is placed the powder and the liquid. The funnel is covered with a perforated glass plate, through which an aluminium wire is led. The glass funnel acts as a convenient insulator; the conical vessel and the wire are connected with the induction coil, and the wire may also be earthed. The powder is dispersed as sparks pass between the electrodes.

Sols of sulphur, phosphorus, mercuric oxide, copper oxide, and prussian blue in isobutyl alcohol were prepared with this apparatus. The sols are very dilute, but can be concentrated by evaporation.

PART III

ADSORPTION

CHAPTER XVI

SURFACE PHENOMENA

SOME justification may seem necessary for the departure, in this section, from the principle adopted in the rest of the book, in which the phenomena are described first, and then the various theories and explanations which are deemed of sufficient importance are discussed. Here what is to some extent the reverse procedure has been preferred, for the reason that it seemed of the utmost importance to have a guide through the mass of facts and observations, and because there is, in this case, one central idea round which these ascertained facts can be ranged, and which therefore effects the necessary simplification.

This essential fact is that there is always a difference in concentration at the boundary between two heterogeneous phases, whether the phases be gas, liquid or solid. This "surface concentration" is the principal factor in adsorption, from which all the generalisations may be deduced; the deviations from these laws are due to secondary disturbing factors, which vary from case to case; or, in certain instances, the phenomena are not really adsorptions, but bear a more or less close general resemblance to them.

This being the position, we will in the first place ascertain the facts regarding surface concentrations, and to do this, we must take into consideration surface energy and surface tension. From them we will deduce the empirical generalisations regarding adsorption, and finally, will consider the other phenomena which are liable to be classed as adsorptions.

Surface Energy and Surface Tension.—The surface of a liquid, *i.e.* the interface between it and the gas phase, whether its own vapour or any other gas, is the seat of a form of energy, the surface energy. This energy may be regarded as characteristic of the liquid state, just as volume energy is of the gas state. Its two factors are surface tension and the area of the surface, the former being the "intensity" factor, and the latter the "capacity" factor; the corresponding factors of volume energy are pressure and volume. Surface energy is therefore the product of the area and the tension—

$$\text{surface energy} = \text{surface} \times \text{surface tension}.$$

It may be well to note here that, contrary to the case of gases, where the energy decreases as the volume increases, the surface energy of a liquid increases with increase of surface, and that, therefore, the surface of a liquid tends to diminish spontaneously, while to extend the surface energy must be supplied to the liquid. This, as we shall see later, is of fundamental importance in the consideration of surface concentration and adsorption.

Owing to the small numerical value of the intensity factor, surface energy forms an insignificant fraction of the total energy of a liquid, unless the development of the surface is extraordinarily great.

Specific Surface.—The relation of the surface of a system to its volume can be conveniently expressed by the specific

surface, a conception introduced by Wo. Ostwald. It is obvious that the actual surfaces of equal volumes of a substance may vary enormously, from the minimum surface of a single sphere to indefinitely high values in the case of thin sheets, rods or very small particles, whether drops or powder.

The specific surface is the surface divided by the volume. For a cube with length of side l, the surface is $6l^2$, and the volume is l^3, and the specific surface is $6/l$, from which it follows that a 6 cm. cube has unit specific surface.

Surface energy is negligibly small, unless the specific surface is at least 10,000.

Surface Tension of Pure Liquids.—For a detailed account of surface tension and the methods of measurement, the larger textbooks of Physics or of Physical Chemistry should be consulted. All that can be done here is to present those aspects which are of immediate importance from our present point of view. The methods of measurement fall into two classes, the static and the dynamic methods. The former include the rise in a capillary tube, the weight of the hanging drop, the adhesion of a disc to the surface, and direct measurement of the curvature of the surface. The latter include the oscillating jet, the oscillating drop, and the capillary waves methods. As a rule all the methods give concordant values in the case of pure liquids, but not in the case of solutions, for which the static methods do not agree with the dynamic methods, although each class gives practically concordant results.

The numerical values of the surface tension of liquids are usually small; for water, which has a greater surface tension than most liquids, it is 77 ergs at 0° C.; *i.e.* 77 ergs are necessary for the production of 1 sq. cm. of water surface.

Below are given the surface tensions of a few typical liquids.

Surface Tension.

I.—Liquids at 20° C.

Water	73·0	Formic acid	37·1
Methyl alcohol	23·0	Acetic „	23·5
Ethyl „	22·0	Propionic „	26·2
Propyl „	28·6	n-Butyric „	26·3
Isobutyl „	22·5	Aniline	43·8
Isoamyl „	23·5	Pyridine	38·0
Ether	16·5	Nitrobenzene	41·8
Acetone	23·0	Benzene	28·8
		Toluene	28·2

II.—Metals.

Mercury	15° C.	436	Cadmium	365° C.	810
Sodium	90°	520	Iron	1200°	1000
Tin	277°	610			

III.—Fused Salts.

KI	700° C.	86	KNO_3	338° C.	110
KCl	790°	100	$NaNO_3$	339°	106

IV.—Liquefied Gases.

H_2	−252° C.	2	Cl_2	−72° C.	33·6
N_2	−196°	8	CO	−190°	11
O_2	−183°	13	CO_2	+15·2°	2

The Temperature Coffiecient.—The variation of surface tension with the temperature is given by the formula—

$$\sigma_1 = \sigma_0(1 - at)$$

from which there must be a temperature at which $\sigma = 0$. This is most probably the critical point (Frankenheim), at which the difference between liquid and gas disappears. As a matter of fact, the critical temperature can be

calculated fairly well by determining the surface tension at two temperatures, and extrapolating to $\sigma = 0$.

It also follows that liquids which are near their critical points, *e.g.* condensed gases, will have small surface tensions, while liquids far removed from their critical points, as molten metals and fused salts, will have large surface tensions. The value of a also depends to some extent upon the value of σ; for ordinary liquids $a = 0\,003$, while it is much larger for substances with small σ, as gases, for which $a = 0{\cdot}015$, and much smaller for those with large σ, as metals, for which $a = 0\,0003$.

The Molar Surface Energy.—Reference may be made to this in passing, as it is of interest and importance. The molar surface energy is a colligative property of liquids, and is as general as the gas constant R is for gases.

The molar surface energy is the product of the molar surface and the surface tension. If V is the molar volume the molar surface is proportional to $V^{\frac{2}{3}}$, since the volume of a sphere is as the cube of the radius, while its surface is as the square; the molar surface energy is thus $V^{\frac{2}{3}}\sigma$, omitting the numerical factor $\sqrt[3]{36\pi}$.

Eötvös and Ramsay and Shields found that it decreases proportionately with rise of temperature, becoming zero at the critical temperature (see above), and that the temperature coefficient is the same for all liquids. If then w_t is the molar surface energy at the temperature t, and w_0 that at 0°, we have—

$$w_t = w_0 - Bt$$

where B is a constant independent of the nature of the liquid. This equation becomes identical in form with the gas equation if the temperature is counted from the critical temperature as zero, at which $\sigma = 0$.

Expressing these temperatures by D, and the molar surface by ω, the equation becomes—

$$\sigma\omega = BD$$

analogous to $pv = RT$

The value of B is 2·12 in absolute units. By means of it we can determine the molar weights of liquids, and if they are associated liquids, the deviation in their value of B affords a measure of the degree of association.

Thickness of the Surface Layer.—The thickness of the surface layer can easily be deduced from the fundamental consideration of Stefan, that to bring a liquid particle into the surface requires half the work necessary for its transformation into vapour. From this the total amount of energy which can be imparted to a liquid in the form of surface energy is $\frac{1}{2}W$ (W being the heat of vaporisation), while the surface tension gives the energy required to form unit surface.

In the case of water $\frac{1}{2}W = 2{\cdot}5 \times 10^{10}$ erg for 1 g., and $\sigma = 77$ erg, from which 1 g. of water can cover 16×10^7 sq. cm., and the thickness of the layer is $0{\cdot}6 \times 10^{-8}$ cm.

This also is the limit at which the properties of the substance perceptibly differ from those of the substance in bulk. This will become more apparent if we consider the variation of vapour pressure of a liquid with the curvature of the surface.

Vapour Pressure of Curved Surfaces.—Since the effect of surface tension is to reduce the surface to a minimum, and since the surface of two drops of a liquid is greater than that of the united drop, while the volume and mass remain the same, the tendency is for a system consisting of an assemblage of drops to unite into a single drop. This may be effected either by coalescence of the drops by

actual contact, or by the transference of vapour from the smaller to the larger drops.

The simplest method of getting at the difference of vapour pressure between a curved surface and a plane surface of a liquid is as follows:—

A capillary tube is placed in the liquid, which is contained in a vessel so large that the surface in it is plane. The height to which the liquid will rise is

$$h = \frac{2\sigma}{rd}$$

σ being the surface tension, r the radius of the tube, and d the density of the liquid. The vapour pressure at the curved surface in the tube is equal to the vapour pressure at the plane surface, less the hydrostatic pressure of a column of the vapour, whose height is h. This pressure is equal to hD, if D is the absolute density of the vapour. Thus

$$dp = p - p_1 = h\mathrm{D} = \frac{2\sigma}{rd}\mathrm{D}$$

The meniscus of the liquid is concave, and dp is negative, *i.e.* the vapour pressure at a concave surface is less than that at a plane surface. Conversely it is greater to the same extent at a convex surface. Thus the smaller the drop the greater its vapour pressure; consequently small drops will distil isothermally over to the larger ones.

The actual differences are very small, *e.g.* the vapour pressure of a drop of 0·001 mm. radius is about 1 per cent. greater than that of the plane surface.

The Pressure in the Surface Layer—The surface layer is under a greater pressure than the bulk of the liquid, owing to the contractile force of the surface tension. It can be calculated in the following manner:—

A quantity of the liquid under the pressure p is connected with a spherical drop of the same liquid by means of a capillary tube. In equilibrium the pressure p, which tends to increase the size of the drop, is counterbalanced by the surface tension which diminishes the surface, and consequently the size of the drop, *i.e.* for a small change in radius of the drop dr, the work done by the pressure pdv is equal to σdw, the opposing work done by the surface tension, v being the volume of the drop, and w its surface. We thus have

$$\sigma dw - pdv = 0$$

since increase of volume and increase of surface denote loss and gain of energy respectively. For the change in radius dr, the increase in volume dv is $4\pi r^2 . dr$, and the increase of surface dw is $8\pi r . dr$. Thus

$$\sigma . 8\pi r . dr = p . 4\pi r^2 . dr$$

whence

$$p = \frac{2\sigma}{r}$$

In the case of water, with $\sigma = 77$ erg, $p = 154/r$. Since atmospheric pressure is about 10^6 units, a drop of water whose surface pressure is 1 atmosphere will have a radius of $1{\cdot}5 \times 10^{-4}$ cm. or a diameter of 0·003 mm. or 3μ. This must be reflected in the other properties, *e.g.* the density. The compressibility of water is 0·00005 for 1 atmosphere, hence the density of the above drop will be 0·00005 times greater than that of water in bulk. The other properties are changed to a proportionate extent.

Surface Concentration.—From these and other considerations, for instance, of the "internal pressure" of liquids which is produced by the great difference in the molecular forces on the two sides of the interface, and

which attains enormous magnitudes, it has been concluded that the surface layer is a layer of great compression, a conclusion which has many important corollaries. One illustration must suffice.

If the surface is a layer under great pressure, the concentration in the surface of a solution must be different from that in the bulk of the liquid, or briefly the "volume concentration." For just as unequal temperatures in a dilute solution cause an unequal distribution of the solute, a fact experimentally demonstrated by Soret, and later theoretically deduced by van't Hoff, who found Soret's results to be in agreement with the gas law as applied to solutions, so from the same law unequal pressures at constant temperature must also produce an unequal distribution. Only here, owing to the peculiarities of hydrostatic pressure, it is not so easy to perform the corresponding experiment. The subject will be referred to later (p. 254), where the converse view is adopted, that the experimentally proved differences between surface concentration and volume concentration in solutions are taken as proof of the existence of a layer of compression in the surface.

It is plain that in a pure liquid too, the surface concentration will be greater, if the surface layer is under great pressure.

The Surface Tension of Solutions.—There are thus important differences between the surface tension of pure liquids and of solutions, which until recently had not received the attention they merit, although they were clearly indicated in the conclusions reached by Willard Gibbs.

As we have already seen, every free liquid surface tends to diminish its energy. In the case of a pure liquid this can take place in only one way, viz. by the diminution of the surface (the capacity factor), since the

intensity factor, the surface tension, is a constant. But in a solution, it may be effected in this manner, or by decrease in the intensity factor, the surface tension. And this in general can always occur, for increase in concentration of the one component will produce an increase of surface tension, and of the other component a decrease. A solution can therefore always decrease its surface tension, and its surface energy, by the appropriate change in concentration of the surface layer. In other words, a solution can diminish its surface energy, with a fixed area of surface, by an excess of that component which reduces the surface tension entering the surface layer.

Thus the composition of the surface layer of a solution is different from that of the rest of the solution, the "molar fraction" of that component which lowers the surface tension being increased. It is desirable, for the sake of clearness, to adhere to the use of the term "molar fraction" in expressing the composition of a solution, thus avoiding the arbitrary and unjustifiable distinction between the components, which the terms "solvent" and "solute" imply. If a solution contains 100 mols of solvent and solute together, of which a mols are solute, the molar fractions of solute and solvent are a and $100 - a$ respectively.

It is clear from the above that the surface may contain either an excess or defect of solute. There is an important difference between the two cases; the former, surface excess, may be very large even in dilute solution, but surface defect is necessarily small.

Static and Dynamic Surface Tensions.—This surface concentration manifests itself in many ways, one of the most important of which is that since time is required for the necessary readjustment of concentrations when a fresh surface is produced, or an existing one extended, the

surface tension of solutions is not constant, but varies with the time which has elapsed since the surface was produced. In consequence of this, the various methods of measuring surface tension usually give different results according as they depend on dynamic or static methods (p. 227). In the former fresh surfaces are always being formed, while in the latter the surface is an old one. The dynamic surface tension is nearer that of the solvent, while the static surface tension is usually smaller, since a solution usually has a smaller surface tension than the solvent. The values of the former will not as a rule be the real dynamic surface tension, but will lie somewhere between it and the static surface tension.

The latter presents no special difficulty, except in certain cases, where the difference in concentration is accompanied or followed by slow chemical changes, as with the soaps, where the surface tension may continue to change for hours or days.

The following figures illustrate the differences between the dynamic and static surface tensions of some solutions.

	σ (Dynamic).	σ (Static).
Water	75	75
Sodium oleate	26	79
Heptylic acid	54	68

The static values were obtained by the capillary tube method, and the dynamic values by the oscillating jet method.

Sodium Sulphate in Water.

Static (capillary tube). $t = 10°$.		Dynamic (capillary waves). $t = 15°$.	
%	σ	%	σ
0	74·0	0	73·3
4·01	74·8	5	72·8
5·07	75·1	10	73·4
6·53	75·6	15	72·6

CHAPTER XVII

SURFACE CONCENTRATION

The Surface Concentration Formula.—The equation connecting the surface concentration and the surface tension of the solution was first developed by Willard Gibbs (1876–78),[1] later by J. J. Thomson (1888),[2] and in the form given here by Milner (1907).[3]

Consider a solution, the surface and volume of which are capable of independent reversible alteration, the latter by means of a semi-permeable membrane, which separates it from water. If s is the surface, v the volume, σ the surface tension, and p the osmotic pressure, the work done on the system by increasing s by ds at constant v is σds, and that done by increasing v by dv at constant s is $-pdv$. Since the final result is independent of the order in which these reversible changes are performed

$$\sigma ds - \left(p + \frac{dp}{ds}ds\right)dv = -pdv + \left(\sigma + \frac{d\sigma}{dv}dv\right)ds$$

from which

$$\frac{d\sigma}{dv} = -\frac{dp}{ds}$$

i.e. the surface tension will vary with the volume (and therefore with the concentration) only when the osmotic pressure depends on the surface.

[1] *Trans. Connecticut Academy*, vol. III., 439.
[2] *Applications of Dynamics to Physics and Chemistry*, p. 190.
[3] *Phil. Mag.*, 1907, [vi.] **13**, 96.

The surface excess u is derived as follows: u is the number of mols in each sq. cm. of surface withdrawn from the volume, and ineffective on the osmotic pressure. If N is the number of mols in the original solution, the volume concentration, on which alone σ and p depend, is—

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

Changing to c as the variable we have—

$$\frac{d\sigma}{dv} = \frac{d\sigma}{dc}\frac{dc}{dv} = -\frac{c}{v}\frac{d\sigma}{dc}$$

and

$$\frac{dp}{ds} = \frac{dp}{dc}\frac{dc}{ds} = -\frac{u}{v}\frac{dp}{dc}$$

from which

$$\frac{d\sigma}{dc} = -\frac{u}{c}\frac{dp}{dc}$$

If the gas law holds, $\frac{dp}{dc} = RT$; or if not, $\frac{dp}{dc} = iRT$, whence

$$\frac{d\sigma}{dc} = -iRT\frac{u}{c}$$

or

$$u = -\frac{c}{iRT}\frac{d\sigma}{dc}$$

The relation between concentration and surface tension is perhaps more easily derived in the following manner.[1]

The surface w of the solution contains 1 mol of the solute in virtue of surface concentration, and σ is the surface tension. A very small quantity of solute enters the surface from the solution and diminishes σ by $d\sigma$; the corresponding energy is $wd\sigma$. Now this energy must exactly balance the energy required for the separation of the same quantity of solute from the solution, *i.e.* to

[1] Ostwald, *Outlines of General Chemistry*, 3rd English Edition, 1912, p. 499.

overcome the osmotic pressure due to this quantity of solute in the solution. If v is the volume which contains unit weight, and dp is the difference between the osmotic pressures of the solution before and after its removal, the energy is vdp. We thus have—

$$wd\sigma + vdp = 0$$

If the gas law is assumed to apply to these solutions, $v = RT/p$, hence

$$wd\sigma = -\frac{RT}{p}dp$$

or

$$\frac{d\sigma}{dp} = -\frac{RT}{wp}$$

and since p is directly proportional to the concentration, the formula gives the desired relation between σ and c—

$$\frac{d\sigma}{dc} = -\frac{RT}{cw}$$

As w is the surface which contains 1 mol excess of solute, u the excess of solute in unit surface is $1/w$, which gives finally—

$$u = -\frac{c}{RT}\frac{d\sigma}{dc}$$

It should be noted that the surface tension concerned here is the equilibrium, *i.e.* the static, surface tension.

This equation shows that if σ increases with increase of concentration, u is negative, *i.e.* the molar fraction of the solute in the surface diminishes, while if σ diminishes with increase of concentration, u is positive, and the molar fraction of solute in the surface increases. The same conclusion has already been reached qualitatively (p. 234).

Verification of the formula presents serious difficulties,

and so far only qualitative agreement has been attained, *i.e.* the molar fraction changes in the direction indicated by the equation.

The experimental demonstration of the equation, which was first derived by W. Gibbs in 1876–78, was long in being realised. In 1896 the author, working in Ostwald's laboratory, observed that the electric conductivity of a dilute aqueous solution of sodium oleate changed when the solution was stirred up with the electrodes, so as to produce foam on the surface, and gradually returned to its initial value as the bubbles slowly collapsed. This could be repeated as often as desired. Attempts to separate the foam on a large scale, in order to prove the difference by analytical methods, were unsuccessful. Zawidski [1] (1900) effected the analytical proof in the case of salts and acetic acid by the simple expedient of adding saponin, and analysing the foam carried over by bubbles of air. The differences in concentration were considerable. Miss Benson [2] (1903), working with aqueous amyl alcohol, which, like soap solutions, does not require extraneous substances to produce foam, found the surface concentration to be 0·0394 n., the original concentration being 0·0375 n.

Milner's [3] results are as follows:—

Sodium Chloride.—The increase in σ is 1·72 dynes per sq. cm. for increase in c of 1 mol per litre, $i = 1{\cdot}74$, $R = 8{\cdot}32 \times 10^7$ erg per degree, $T = 290$, whence

$$u = -4{\cdot}09 \times 10^{-11} \text{ mol per sq. cm., or}$$

0·024 mg. per square metre.

Acetic Acid.– $i = 1{\cdot}08$, and $u = +3{\cdot}3 \times 10^{-10}$ mols per sq. cm., or

0·20 mg. per square metre.

[1] *Zeitsch. physikal. Chem.*, 1900, 35, 77.

[2] *Amer. J. Phys. Chem.*, 1903, 7, 532. [3] *Loc cit.*, p. 236.

Sodium Oleate.—No finite value for $\frac{d\sigma}{dc}$ could be obtained, as the following figures show:—

Concentration.	Relative surface tension.	Concentration.	Relative surface tension.
0·02	2·330	0·00225	2·305
0·066	2·300	0·00206	2·240
0·0082	2·275	water	6·15

u was estimated by determining the decrease in electric conductivity produced by bubbling air through the solution and removing the foam. This estimate came to about $1{\cdot}2 \times 10^{-10}$ mol per sq. cm., or

0·4 mg. per square metre.

Milner observed that the static and dynamic surface tensions of the soap solution were very different.

In spite of this want of quantitative agreement, the generalisation is one of extreme importance in its bearing upon adsorption, which is primarily and in the main a matter of surface extension, and therefore of surface concentration. Before passing on to adsorption it is accordingly necessary to inquire into the surface tension of solutions, with especial reference to the variation of surface tension with concentration.

Surface Tension of Solutions; the σ, c curve.—Reference to the table of surface tensions on p. 228 will show that, of ordinary liquids, water has the largest surface tension, and clearly only a solvent with a comparatively large value of σ can show much variation of σ, at least in the direction of diminution. And so it is that, apart from other properties of water as a solvent (unless, indeed, these are connected in some way with the large value of σ), water differs markedly from many other solvents in that

very large decreases of surface tension do occur, and that most aqueous solutions have a smaller surface tension than water. All the possible varieties of curve between two components with different surface tensions are known, but for the present, at least, these variations of type are of no particular moment.

Gibbs pointed out that a small quantity of solute may cause a large decrease of surface tension, but cannot increase it to any great extent (see p. 245). Accordingly, the majority of σ, c curves lie below the straight line joining the values of σ of the two components; further, they either pass through a minimum or exhibit a tendency to a minimum. Naturally there are instances where the σ, c curve is the connecting straight line, but this only occurs when the two substances are chemically similar and when their surface tensions are not far apart.

Surface Tension of Solutions.—The surface tension of aqueous solutions of salts, and especially of inorganic salts, is greater than that of water, and increases linearly with the concentration. This is in accordance with the general rule, for the surface tension of salts is undoubtedly greater than that of water. Solutions of hydrogen chloride and hydrogen bromide, which as pure liquefied gases have smaller values of σ, have slightly smaller surface tensions than water.

Surface Tension of Electrolytes in Water.

$t = 18°$; $c = 1{\cdot}5$ mol per litre; $\sigma_{H_2O} = 75{\cdot}3$.

HNO_3	74·2	KNO_3	76·9
HCl	74·9	KCl	77·6
H_2SO_4	76·0	K_2CO_3	79·9
NaOH	78·3	$NaNO_3$	77·2
KOH	78·0	NaCl	77·8
NH_3	72·2	NH_4NO_3	77·0

The following figures show the types of variation of surface tension with concentration:—

Conc.	Cane Sugar (19°).	HCl (20°).	NaOH (20°).	$NaNO_3$ (15°).
0	78	73·0	72·8	73·5
5	63	72·5	74·6	75·0
10	57	72·3	77·3	
15		72·0	80·8	
20		71·4	85·8	77·6
25	51	70 7	90·6	
30	59			
35			99·7	80·8

The σ, c curves are straight lines, being exactly expressed by—

$$\sigma_{\text{solution}} = \sigma_{\text{water}} (1 + kc)$$

Similar behaviour is shown by all kinds of solutes in solvents which have a much smaller surface tension than the solute, *e.g.* camphor and benzoic acid in ether or acetone give curves which increase linearly with concentration in precisely the same manner as salts and water. Salts in alcohol also follow the same law.

There are many substances which exert a very slight effect on the surface tension of water in either direction, such are salts of fatty acids, of hydroxy acids, and of amines; polyhydroxy compounds generally also belong to this group.

The active substances, which, as stated above, are only active when the solvent has a large surface tension, are the fatty acids, alcohols, amines, esters, and many other organic compounds. In all these cases the surface tension falls very rapidly with very small concentrations of solute, while comparatively large amounts of water are required to increase the surface tension of the other substance. This is in accord with the views already set forth

regarding the change in molar fraction and change in σ. This is shown in the tables below and in Figs. 17 and 18.

Acetic Acid in Water.

$t = 20°$

Concentration (%).	σ
0	75·1
10·6	57·4
20·3	49·6
43·9	37·1
50·2	37·0
67·8	33·6
78·0	30·3
87·6	28·8
97·5	26·4
99·7	24·3

Ethyl Alcohol in Water.

$t = 15°$.

Concentration (%).	σ
0	72·2
10	51·2
20	40·6
30	34·7
40	31·2
50	29·1
60	27·7
70	26·6
80	25·4
90	22·1
100	22·5

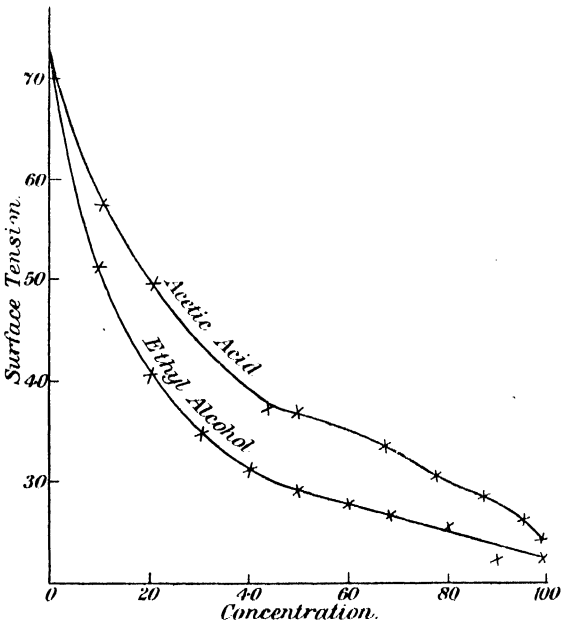


FIG. 17.

v (litres per mol).	Isobutyl alcohol.	Butyric acid.	Propylamine.
1	26·99	33·07	46·30
2	36·01	40·82	52 6
4	44·92	48·87	59·1
8	53·81	56·1	63·6
16	60·03	62·7	67 9
32	65·76	67·1	69·8
64	68·7	69·9	
128		71·3	

α (water =) 72 ·95.

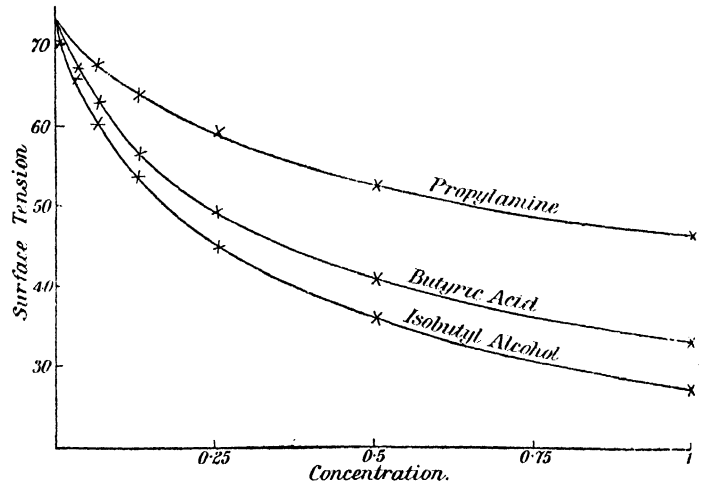


FIG. 18.

Extreme examples of the diminution of surface tension of water are given by soap and nonylic acid; the surface tension of 0·002 n. sodium oleate is 28·5, and of a 0·0008 n. nonylic acid 40.

The effect of mixtures of two substances on the surface tension of a solvent appears to be additive, both in the case of salts and of fatty acids.

Dynamic Surface Tension of Salt Solutions.—In view of the above σ, c tables, the dynamic surface tension of salt solutions presents an interesting problem. As stated above (p. 234) the surface tension of a fresh surface usually differs from that of an old surface, in which equilibrium has had time to become established. Quincke noticed that in salt solutions σ changed with time, the differences being fairly large, but these may have been due to traces of grease. Others have observed changes which they attributed to increase in molar fraction of the water, but in one case the change is in the wrong direction, and in the other the results show very considerable fluctuations. It is not surprising that Milner found very great differences in the surface tensions of fresh and old surfaces in the case of sodium oleate (p. 240).

Magnitude of Surface Excess and Defect.—A small quantity of solute may cause a large diminution of surface tension, but not a large increase. If the surface tension of a dilute solution is greater than that of water, and increases with concentration, the molar fraction of the solute in the surface layer must diminish. Clearly the limit is reached when the surface is pure water, *i.e.* when the molar fraction of the solute is zero. In the opposite case, the molar fraction of the solute must increase, and in the limit the whole of the solute will be present in the surface, and may, as shown above, produce extremely large diminutions of the surface tension.

The problem may be discussed from a different point of view. To remove solute from the volume of the liquid the osmotic pressure must be overcome, and the corresponding amount of energy must be supplied. If the surface tension (the surface remaining constant) is reduced by increase of concentration, the addition of this amount of solute will set free a corresponding amount of surface

energy, which is thus available for the osmotic work. But if the surface tension is increased with increase of concentration, the addition will increase the surface energy in the surface (for constant surface), and both operations can continue only if energy is supplied from without. In the former case, one process requires energy and the other liberates it, while in the latter both processes require energy.

CHAPTER XVIII

ADSORPTION

ADSORPTION, in its most general sense, implies the unequal distribution of a substance at the boundary between two heterogeneous phases. At the interface of a solid and a gas or vapour, it is usually called gas adsorption, as the difference in distribution of the solid phase is negligibly small, or, in any case, eludes observation. There is probably uneven distribution on both sides of the interface between liquid and gas phases. The surface concentrations dealt with in detail in the previous chapter are instances of this. Finally, we have the case of the boundary between solid and liquid phases, and especially of solutions, which comprises the cases most usually referred to as adsorptions.

Here, too, the inequality of concentration is on the liquid side of the interface, although the substance adsorbed has frequently been regarded as bound to the solid. This is because the surface layer in which this concentration difference exists is a very thin layer, and is the layer which wets the solid, and remains wetting it when the rest of the liquid is poured away.

From the facts given in the previous chapter, it is plain that, since the surface concentration differs from the volume concentration, any considerable extension of surface in a fixed volume of solution, such as occurs when

a quantity of solution is shaken up with a very fine insoluble powder, must produce a very considerable change in the volume concentration. And further, if this surface extension is the main factor in adsorption, the main features of adsorption should be capable of prediction from the known facts of surface concentration. This is what we propose to show in the present section.

The General Phenomena of Adsorption.—(1) The surface excess in a solution is usually positive (p. 241); such solutions will give rise to positive adsorption, *i.e.* when they are shaken up with a fine insoluble powder, the volume concentration will diminish. This is what is observed. It was a long time before negative adsorption was observed at all, while positive adsorptions have been known for a very long time.

(2) Further, surface excess may be large even in dilute solutions, while surface defect is necessarily small. This also is what is found in adsorption generally. Positive adsorption may be very large, almost all the solute may be removed, especially from dilute solution, by shaking it up with the adsorbent. Negative adsorption is usually so slight that it is difficult to determine it with accuracy.

It should be borne in mind that the simplest way of expressing surface concentrations is in terms of the molar fraction, *i.e.* the molar fraction of the component which lowers the surface tension increases in the surface, and adsorption follows the same rule. Negative adsorption of solute is thus really positive adsorption of solvent. This is of real importance, for serious errors have arisen from overlooking the fact that the adsorbent may adsorb either or both of the components.

(3) The adsorption should be proportional to the actual extension of surface; if an adsorbent is of approximately uniform size, the same weight of adsorbent will

effect the same amount of adsorption. That is, the adsorption for any substance is a function of its specific surface. The kind of uniformity attained by sieving is not sufficient, for all efficient adsorbents possess in addition an enormous surface, due to porosity.

(4) It follows from this, too, that adsorption is an equilibrium, *i.e.* that if a given volume of solution of known concentration is shaken up with a given weight of a certain adsorbent until equilibrium is attained, and the solution is then diluted by addition of a known volume of solvent, the amount adsorbed is also reduced, until it is the same as would have been adsorbed directly from a solution of the same concentration by the same weight of adsorbent. This has been fully established by Ostwald, Schmidt, and by Freundlich; *e.g.* 1 g. of charcoal shaken up with 100 c.c. of a 0·0688 m. solution of acetic acid for 20 hours gave a final volume concentration of 0·06078 m., while 1 g. shaken up for the same time with 50 c.c. of a 0·1376 m. acetic acid, to which 50 c.c. of water were then added, and shaken up again for 3 hours, gave a final concentration of 0·06064 m.

(5) The specific surface of an adsorbent is not known, and as pointed out above, cannot be estimated from the average size of the particles. It is clear, however, that the same extension of surface ought to produce the same amount of adsorption in any given solution, independent of the nature of the adsorbent, but not independent of the nature of the solution. The amounts adsorbed by equal weights of two different adsorbents (or two different samples of the same substance), from equal volumes of the same solution, will thus be in the ratio of their specific surfaces. The method may be looked upon as one for fixing the relative specific surfaces of solids.

This deduction is fully borne out by the experimental

data. It is a well-established empirical rule that the order of efficiency of adsorbents is comparatively independent of the nature of the adsorbed substance and of the solvent, and is not obviously related to the chemical nature of the adsorbent.

The adsorption equation is—

$$\frac{x}{m} = ac^{\frac{1}{n}}$$

x is the weight of substance adsorbed by m the weight of adsorbent.

c is the volume concentration after adsorption is complete.

a and $\frac{1}{n}$ are constants.

The ratio of the values of a for two adsorbents and different solutions ought, according to the above, to be a constant. This is the case, *e.g.*—

	Crystal violet.	Patent blue.	New fuchsin.
$\frac{a \text{ charcoal}}{a \text{ wool}}$	8·2	9·9	
$\frac{a \text{ charcoal}}{a \text{ silk}}$	21·1	26·9	23·2
$\frac{a \text{ charcoal}}{a \text{ cotton}}$	156	155	

Further confirmation is afforded by Walker and Appleyard's results for the adsorption of picric acid from water and alcohol solutions by charcoal and silk.

	0·01 n. picric acid in Water.	Alcohol.
$\frac{\frac{x}{m} \text{ charcoal}}{\frac{x}{m} \text{ silk}}$	7·3	5·2

(6) The adsorption should depend largely on the solvent: the smaller the σ of the solvent, the smaller the decrease of σ in the solution. Adsorption must therefore be stronger in aqueous solutions than in alcohol. Thus we have the following empirical rules, all of which are simple deductions from the theory.

(*a*) A solvent in which other solutes are strongly adsorbed, is itself feebly adsorbed when dissolved in other solvents: its σ is large and so it gives rise to small positive or negative adsorption in solutions of liquids with smaller σ (p. 242).

(*b*) Substances which are strongly adsorbed from solutions are themselves solvents in which adsorption is feeble. This and the preceding rule are contained in the statement that the molar fraction of that component which lowers the surface tension of the solution is increased in the surface layer, whether that component be present as solvent or solute (p. 234).

(*c*) Inorganic salts, acids and bases, polyhydroxy organic compounds, etc., are feebly adsorbed from water; the adsorption is usually positive, but may be negative.

(*d*) Most organic substances, organic acids and bases, especially aromatic compounds, dyes, etc., are adsorbed either moderately strongly, or to a very marked degree.

(*e*) Adsorption from solutions in alcohol or other organic solvents is usually small. The amounts adsorbed, x/m, from solutions of picric acid in water, alcohol and benzene were—

	x/m	
Water	1·31	millimol
Alcohol	0·77	„
Benzene	0·49	„

(*f*) A substance adsorbed from a solution is very difficult to remove from the adsorbent by washing with

the solvent. But it can be readily extracted with a solvent of smaller surface tension. For instance, the platinum black on electrodes of conductivity vessels strongly adsorbs picric acid (and also other acids) from dilute aqueous solution, and it is practically impossible to remove it completely by even prolonged soaking in water. If the electrodes are placed in alcohol, the liquid soon becomes bright yellow from the presence of picric acid.

This behaviour is frequently made use of in technical chemistry. Many organic bases (alkaloids) are strongly adsorbed from aqueous solution by animal charcoal, and can be recovered from it by extraction with alcohol or other organic liquid, whose σ is sufficiently small.

The Adsorption Isothermal.—It might seem to be the simplest method of approaching adsorption to consider it as a special case of the general Partition law or Distribution law of Nernst, of which Henry's law of the solubility of gases is also a special, though simple, case.

The Distribution law as frequently formulated is

$$\frac{c_1}{c_2} = k$$

which expresses that if a substance is shaken up with two immiscible liquids in each of which it is soluble, the ratio of its concentrations in the two layers is a constant, independent alike of the total amount of solute and of the relative quantities of the two liquids. In this form the equilibrium only holds for substances whose molar weight is the same in the two liquids. If it is associated in the one and not in the other, or if it is associated in both but to different degrees, the formula becomes

$$\frac{c_1}{c_2^n} = k$$

where n is the association factor, and is obviously a simple integer. The two following tables illustrate the two equations.

Succinic Acid in Ether and Water.

c_1	c_2	c_1/c_2
0·024	0·0046	5·2
0·070	0·013	5·2
0·121	0·022	5·4

Benzoic Acid in Water and Benzene.

(c = g. in 10 c.c.)

c_1	c_2	c_1/c_2	$c_1/\sqrt{c_2}$
0·0150	0·242	0·062	0·0305
0·0195	0·412	0·048	0·0304
0·0289	0·970	0·030	0·0293

The adsorption equation is of the same form as this

$$\frac{c_1}{c_2^{\,n}} = k, \quad \text{or} \quad \frac{x}{m} = ac^{\frac{1}{n}}$$

but differs from it in the values of n. Here it may vary within fairly wide limits, but is always greater than 1, $1/n$ being between 0·1 and 0·5. The adsorption of arsenious acid by freshly precipitated ferric hydroxide is expressed by the equation [1]

$$\frac{y}{x^{\frac{1}{2}}} = 0{\cdot}631$$

y and x being respectively the amounts of acid adsorbed and remaining in the solution—

y	x (obs.).	x (calc.).
0·251	0·010	0·010
0·415	0·107	0·123
0·549	0·495	0·498
0·615	0·952	0·881
0·712	1·898	1·826
0·824	3·875	3·740

[1] Biltz, *Ber.*, 1904, **37**, 3138.

To explain this as a case of partition of solute, would imply that the arsenious acid in ferric hydroxide gel has one-fifth the molar weight it has in water. But it is normal in the latter, and there is no chemical justification for supposing it to be dissociated in such a manner.

The following may be taken as typical examples of adsorption from solution.

(a) *Acetic Acid in Water by Charcoal at* 25° C.

Concentration.	$\frac{x}{m}$
0·018	0·467
0·031	0·624
0·0616	0·801
0·126	1·11
0 268	1·55
0·471	2·04
0·882	2·48
2·79	3·76

(b) *Benzoic Acid in Benzene by Charcoal at* 25° C

Concentration.	$\frac{x}{m}$
0·0062	0·437
0·025	0·78
0·053	1·04
0·118	1·44

The corresponding curves are given in Fig. 19. As already explained (p. 103), the best test of the validity of the adsorption law is to plot the logs of the concentrations against the logs of x/m; if the law holds, these curves are straight lines. The lower part of Fig. 19 shows that this is the case in both the above examples. Similar curves for the adsorptions of carbon dioxide by charcoal are given in Fig. 20.

Lagergren's Theory of Adsorption.—Starting from the idea of the surface layer being a layer of compression,

Lagergren applied the le Chatelier theorem to adsorption, and deduced that the surface concentration would be greater

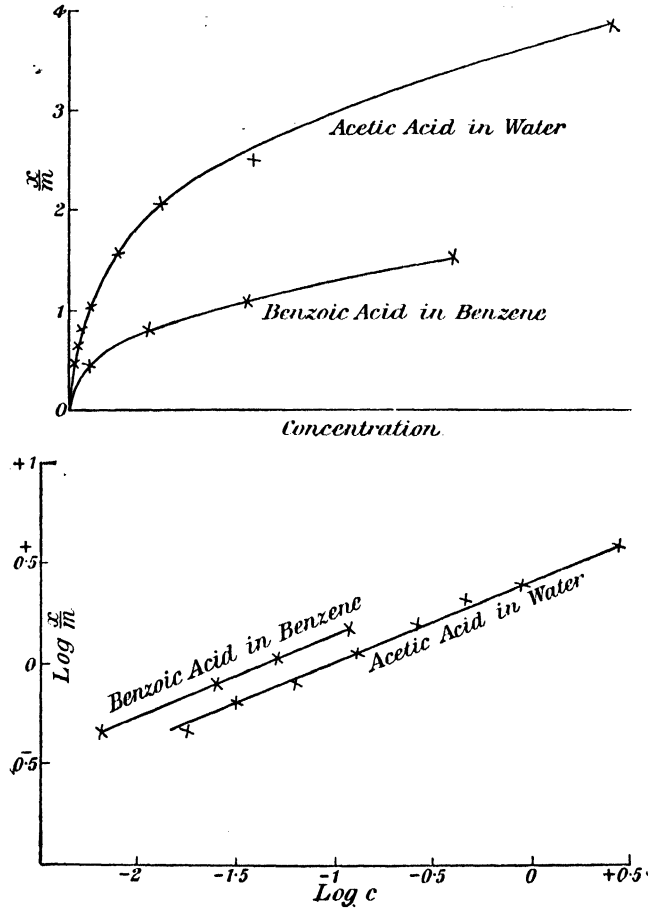


FIG. 19.

ADSORPTION BY CHARCOAL FROM SOLUTIONS.

or less than the volume concentration according as the change in concentration of the solution is accompanied

by increase or decrease of density, which would give rise to positive and negative adsorption respectively.

Now this is a perfectly correct deduction, although it was adversely criticised by Ostwald on the ground that the theorem did not apply to a dilute solution, but only to the solubility, *i.e.* to the equilibrium between the saturated solution and the solid phase. But just as a uniform dilute solution which is unequally heated becomes unequally distributed until the osmotic pressure of the more dilute part, at the higher temperature, is the same as the osmotic pressure of the more concentrated part at the lower temperature, so, too, with unequal pressure at constant temperature. Solute or solvent will enter the layer under pressure according as the one or the other causes an increase in density (p. 232).

Lagergren had previously measured the adsorption of salt solutions by various adsorbents, and had found that some of them were negatively adsorbed, sodium chloride being one of those which are so. The total effect is very slight, but there is no doubt that it exists. But sodium chloride does not appear to be a substance which according to the theory ought to be negatively adsorbed, though both ammonium chloride and bromide ought to be negatively adsorbed, and were found to be so.

There can be no doubt, however, as to the relation between the compression and uneven distribution, so that, since the latter has been experimentally demonstrated beyond question, it may be concluded that the surface layer is in a state of compression, as Lagergren had assumed on other grounds.

Pseudo-adsorption Phenomena.—It cannot be over-emphasised that true adsorption is an equilibrium, which can be approached from either side, and is therefore reversible. There are many phenomena which are

superficially similar to adsorption, but which are really very different in character, and ought not to be classed along with adsorption. They are not equilibria, and are irreversible. Some of them may be adsorptions at the beginning, but secondary changes, which are not reversible, supervene.

To take an extreme case first, by way of illustration: charcoal, as is well known, adsorbs many substances from aqueous solution, and among them many metallic salts. Some salts of heavy metals are so completely removed from solution by it that not a trace of the metal can be detected in the liquid, which becomes strongly acid; but what has been taken out by the charcoal cannot be removed from it by washing with water. Clearly, the salt has been decomposed, the metallic ion has actually been deposited as metal (or in some cases hydroxide, owing to interaction with water) on the charcoal. The first action may be adsorption, especially as salts of heavy metals are powerful precipitants of sols, and are thus probably strongly adsorbable, but the final state cannot be put down to adsorption.

The formation of metal from metal ion need not even be ascribed to chemical action, whether of the charcoal or of the adsorbed gases, for charcoal, which is highly porous, is negatively charged in contact with water, while the water is positively electrified. At each capillary tube (pore), therefore, the water in the tube will be positive, and the charcoal at the entrance to the tube will be negatively electrified. A metal ion, $M^{\cdot}$, which tries to diffuse into the tube may have its electric charge neutralised by the negative charge on the charcoal, and be deposited there as metal. This is, at least, the only probable explanation of the deposition of metal from solutions in very fine cracks in glass apparatus, where chemical action seems quite out of the question.

A similar explanation holds in many of the phenomena commonly classed as adsorptions. Thus a positive sol, dyestuff, or other substance, will be easily precipitated in the pores of wet filter paper; for the paper will be negative, and the water positive, and the positive sol will be precipitated as electrically neutral particles, and will be held there so firmly that it cannot be washed out by water. A great many of the separations of dyes by the capillary action of filter paper (Goppelsröder and others) depend on this same fact. A positive dye will be precipitated on the paper, while a negative one will not, and can therefore diffuse or spread out over the paper.

It seems not unlikely that some of the exceptionally powerful adsorption effects of gels which are acids or bases, are to be put down to the same cause. The basic gels are positively charged, and will cause precipitation on their surface of negative sols, while acids are negatively charged. Adsorption is frequently very strong with these adsorbents, and it is well known that with them, the adsorption of salts is usually accompanied by decomposition, one ion being held, while the other remains in solution; usually water enters into the reaction. For example, silicic acid sol shaken up with potassium carbonate adsorbs alkali, and an equivalent quantity of potassium hydrogen carbonate remains in solution. Similarly, manganese peroxide decomposes potassium sulphate, adsorbing $K^{\cdot}$, and leaving free sulphuric acid.

Adsorption of Gases

Concentration differences at the interface are not confined to solids and liquids, but occur also at all other interfaces. The surface tension of mercury varies with the gas in contact with it, *e.g.*—

Gas.	t	σ (dynamic).
Vacuum	15°	436
Hydrogen	21°	470
Oxygen	25°	478
Nitrogen	16°	489
Carbon dioxide . . .	19°	480
Air (dry)	17°	476
„ (moist)	17°	481

With a solid and a gas there is no such perceptible difference in the solid, but there is in the concentration of the gas.

The same equation applies here as in liquids—

$$\frac{x}{m} = \alpha p^{\frac{1}{n}}$$

only p, the pressure, takes the place of c, the concentration. The value of $\frac{1}{n}$ for any temperature is practically independent of the nature of the gas and of the adsorbent; thus α becomes a characteristic of the gas. It runs roughly parallel with the compressibility or the ease of condensation of the gas. The properties of the gas seem to have much more influence on the amount of adsorption than the nature of the adsorbent. The order of different adsorbents is generally the same, whatever the gas may be, the agreement being more or less quantitative.

The adsorption of mixtures shows that one gas can turn out another, a further proof that adsorptions are equilibria. A quantity of charcoal adsorbed 284 c.c. of carbon dioxide and 24 c.c. of hydrogen from a mixture of carbon dioxide and hydrogen. The same quantity of charcoal was first saturated with hydrogen, and was then placed in a mixture of hydrogen and carbon dioxide, when it finally contained 268 c.c. of carbon dioxide, and 27 c.c. of hydrogen.

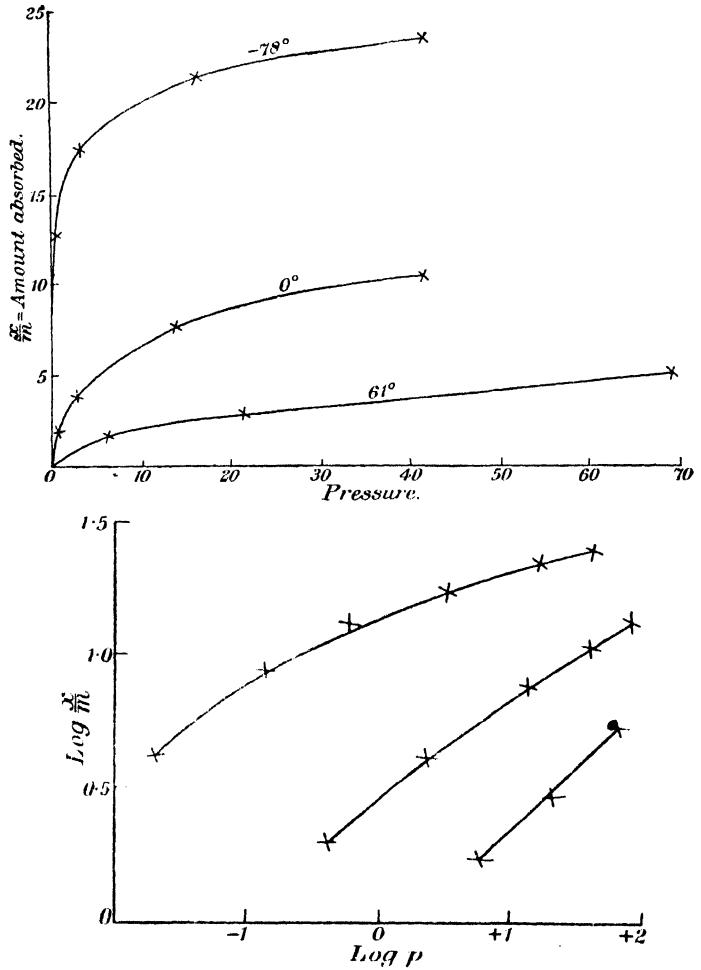


FIG. 20.

ADSORPTION OF CARBON DIOXIDE BY CHARCOAL.

Oxygen is more strongly adsorbed than nitrogen. Accordingly there is a greater concentration of oxygen on a surface than in air. This is probably the explanation

of the increased oxidation so frequent at surfaces. Dewar[1] found the air adsorbed by charcoal at —190° to contain over 50 per cent. of oxygen.

Temperature and Adsorption.—The adsorption isothermal applies at all temperatures down to —78° in the case of charcoal and carbon dioxide, as was shown by Travers[2] (Fig. 20). The quantity adsorbed decreases as the temperature rises; a also changes, but the change in $1/n$ has the greater effect—

t	a	$\frac{1}{n}$
—78	14·29	0·133
0	2·96	0·333
35	1·236	0·461
61	0·721	0·479
100	0·324	0·518

As the adsorption decreases with rise of temperature, heat must be evolved during adsorption. This is in agreement with the results of Dewar's observations; the heats evolved when 1 c.c. of charcoal adsorbed all it could were—

	v (0° and 760 mm.) per c.c. of charcoal. 0°	−185°	Cal. per c.c. of charcoal.
Hydrogen . .	4 c.c.	135 c.c.	9·3
Helium . .	2	15	2·0
Nitrogen . .	15	155	25·5
Oxygen . .	18	230	34·0

The velocity of adsorption is extremely rapid, over 90 per cent. of the total adsorption taking place in a few seconds. With charcoal and carbon dioxide at —78°, the manometer is steady in a few minutes (Travers). In some cases slow chemical actions occur, when the pressure

[1] *Proc. Roy. Soc.*, 1904, **74**, 126.
[2] *Ibid.*, 1906, **78**, A. 9.

may continue changing for months, as with oxygen and charcoal (oxidation). Carbon dioxide appears to act slowly on glass, causing a similar slow change.

Dewar's[1] application of adsorption to produce high vacua depends on the facts that adsorption is much greater at low pressures than at high, and that it also increases at low temperatures. If, then, a quantity of gas at small pressure is exposed to charcoal at very low temperatures practically the whole of the gas will be adsorbed.

Adsorption at Liquid Interfaces.—The methods of determining the surface tension applicable to the surface between two liquids are the oscillating jet, surface waves, curvature of surface, size of large flat drops, capillary rise, adhesion discs, weight of drop, and pressure of drop. As is to be expected, there are frequently large differences between the dynamic and static surface tensions. The changes in surface tension produced by different liquids are often very considerable.

Surface Tension at Liquid Interfaces.

	t.	Method.	σ (static).
Mercury-water	20°	flat drop	370
-benzene	20°	pressure of drop	342
Water-paraffin oil	16°	weight of drop	48
-benzene	20°	,, ,,	32·6
-ether	20°	,, ,,	9·7
-isobutyl alcohol	18°	,, ,,	1·76
Methyl alcohol-carbon disulphide	18°	,, ,,	0·82

It is plain that the mutual solubility of the liquids has a marked influence here, as might be predicted, for when two liquids become completely miscible at the critical solution point, the interface and therefore the surface tension disappear. The values are also influenced

[1] *Loc. cit.*, p. 261.

to a marked extent by the addition of acids and alkalies, and still more by substances like soap.

Lewis[1] investigated the adsorption of sodium glycocholate and methyl orange in water-paraffin oil, having shown that these substances greatly lower the surface tension, *e.g.*—

Sodium Glycocholate in Water-petroleum.

Concentration.	σ.	Concentration.	σ.
0	33·6	0·00357	22·0
0·0000357	32·2	0·00643	16·8
0·000357	28·1	0·0118	12·6

There was a decrease in volume concentration, *i.e.* a surface excess of solute, which is in accord with theory, but no quantitative agreement was found, as direct determination gave $u = 4{\cdot}7 \times 10^{-6}$ g., while the calculated value is $u = 5{\cdot}5 \times 10^{-8}$ g., and similar discrepancies were shown by methyl orange.

The Distribution of a Sol between Two Liquids.—A knowledge of what takes place when a sol is shaken up with a liquid which is not miscible with the dispersion medium, is obviously of great importance in many directions; to mention one only, the connexion between adsorption and dyeing. It was certainly not justifiable to treat the removal of the disperse phase from a sol by contact with a solid surface as an adsorption, comparable with the removal of solute from a solution at such a surface. The distribution of a disperse phase, whether suspensoid or emulsoid, between two dispersion media may be regarded as an extension of adsorption. The question has recently been attacked by Reinders,[2] who

[1] *Phil. Mag.*, 1908 [vi.], **15**, 506.

[2] *Koll. Zeitsch.*, 1913, **13**, 235; see also Hofmann, *Zeitsch. physikal. Chem.*, 1913, **83**, 384.

was probably led to it by his investigations into the nature of dyeing (p. 285).

The possibilities depend upon whether the disperse phase is liquid or solid. If the former, it may leave the original dispersion medium without entering the other liquid, forming a separate layer between the other two. This will happen if the surface tension at one interface is greater than the sum of the other two. But if no one of the surface tensions at the interface between the pairs of liquids is greater than the sum of the other two, the three liquids will meet at a common angle. But if one phase is solid, it cannot spread out as an intercepting layer, and will collect at the liquid interface as solid particles.

Considerations of the kind employed to solve the problem of liquids wetting solids in contact with air,[1] lead to the following conclusions. If a sol (disperse phase 3 in liquid 1) is shaken up with an immiscible liquid 2, one of three equilibria will be established :—

(*a*) If $\sigma_{2,3}$ is $> \sigma_{1,2} + \sigma_{1,3}$, the sol will remain unchanged.

(*b*) If $\sigma_{1,3}$ is $> \sigma_{1,2} + \sigma_{2,3}$, the second liquid will completely remove the disperse phase from the original sol.[2]

(*c*) If $\sigma_{1,2} > \sigma_{2,3} + \sigma_{1,3}$, or if no one σ is greater than the other two together, the disperse phase will collect at the interface between the two liquids.

These conclusions have been verified by Reinders, both in the case of suspensions and of sols. With the latter

[1] *Cp.* Freundlich, *Kapillarchemie*, 1909, p. 137.

[2] This case corresponds to the "wetting" of a solid by a liquid. If

$$\sigma_{s,g} > \sigma_{l,g} + \sigma_{s,l}$$

the liquid will spread over the surface of the solid until there is no direct contact between the solid and the gas. The interface between solid and gas will disappear in favour of the solid-liquid interface and the liquid-gas interface, since the free energy of the former is greater than the sum of the other two.

any of the three can happen, provided the dispersity is low, but if the dispersity is high, a sol may exhibit anomalies, one part behaving in one way, and the rest in one of the others. In addition, emulsoid sols may form a separate layer between the others. A few illustrations will suffice.

In *gold* hydrosols isobutyl alcohol produced no effect until the separate layer was formed, when the gold separated out at the interface in a thin layer. The colour by transmitted light was violet-blue to blue-green, and by reflected light a brilliant gold. The layer creeps up between the alcohol and the glass, causing the alcohol to appear coloured, although it is not so. Amyl alcohol, benzene, benzine, ether, carbon disulphide, and carbon tetrachloride behave similarly.

A *gold* sol in amyl alcohol (produced by reduction of auric chloride in amyl alcohol with phosphorus), which was yellow-brown in colour and very stable, was shaken up with water. No gold entered the water layer, but violet-red gold separated out at the interface and on the glass. Ether sols were prepared in the same manner, but were not stable; when shaken up with water, all the gold left the ether, forming a yellow-red sol in the water, and a slight brown precipitate at the interface. A freshly prepared hydrosol (from gold chloride and phosphorus in ether) which was brown-red in colour, was quite indifferent to ether, no separation occurring at the interface.

The effect of gum arabic as a "protecting" colloid was as follows:—

Gold sol + gum arabic.

2nd liquid.	No gum.	0·001 per cent.	0·005 per cent.
isobutyl alcohol	blue at interface.	blue at interface, slow, some red sol in the water.	blue at interface, very slow, most of the gold red in the water.
ether	blue at interface.	red, all in the water.	red, all in the water.

As was to be expected, the protection of the gum arabic, which is hydrophile, hinders the transference of the disperse phase (hydrophobe) into the alcohol or ether in which the gum is itself lyophobe.

Of other sols which were examined, *ferric hydroxide* hydrosol was unaffected by any of the other liquids, and *arsenious sulphide* hydrosol was completely separated out at the interface with isobutyl alcohol and amyl alcohol, and was not changed by the others.

Frequently part of an apparently uniform sol would remain in one liquid (usually the original dispersion medium) while the rest was precipitated at the interface. The separation of the disperse phase at the interface appears to be an exceedingly common occurrence, and forms a good criterion for sols; for example, alkali blue, the blue acid of congo red, the acid of erythrosin, all go to the interface when the hydrosols are shaken up with carbon tetrachloride.

Analogous phenomena must often occur at interfaces between solids and liquids, *e.g.* gold sol when shaken up with charcoal, barium sulphate, aluminium hydroxide, fibres, and particularly colloid dyes on fibres. They commonly pass under the name of adsorptions, but a more suitable name would be adhesions. As with increasing dispersity there is a continuous change from sols to solutions, there is no abrupt division between adhesions and adsorptions.

PART IV

APPLICATIONS OF COLLOID CHEMISTRY

CHAPTER XIX

SEMI-COLLOIDS

THERE is an extensive series of substances which are intermediate in properties between emulsoid sols and solutions (the emulsides and solutides of von Weimarn's nomenclature). In accordance with this position, their character is indefinite, as they exhibit some of the properties of each, and so far as is known, there is no clue as to which class they belong in respect of any given property. Naturally, the first idea is to look for some connexion between the molar weight of the substance and its general behaviour, but this at once fails, for substances of practically the same molar weight, and not widely different composition, are frequently to be found in different classes, as a glance at the table on p. 274 will show.

Among the important classes of substances which come into this category are some of the highest importance in technical science, as casein, the soaps, dyes and colouring matters, tannins, degradation products of albumin, etc.

While albumin is a genuine emulsoid, the products of the action of alkalies (NaOH) on it, Paal's protalbic acid

and lysalbic acid (p. 132) are semi-colloids, *e.g.* the latter, which is soluble, diffuses in water and through parchment paper; the molar weight, deduced from the freezing point, is 700–800. But the solutions are opalescent, and syrupy when concentrated. Further, they are strongly "protective," as their use in Paal's method of preparation testifies. Peptones, on the other hand, do not "protect," but diffuse slowly; their molar weight, determined by the freezing point method, is about 500–1000. They are usually regarded as amphoteric electrolytes.[1]

The electrical behaviour of semi-colloids is of considerable interest, for many of them are fairly good electrolytes, even when osmotically they are remarkably inert; this aspect of the question has been but little studied.

Owing to the individual peculiarities of the semi-colloids, it is impracticable to give a systematic account of them. A brief description of some technically important ones is all that is attempted.

Casein.—Casein is insoluble in water, but is essentially acid, as is shown by the reddening produced by pressing moist casein on to blue litmus paper. It dissolves in alkaline solutions, which might be attributed to solation by peptisation; it appears, however, to combine with a definite amount of alkali irrespective of the concentration (1 g. casein requires 0·88 millimol of NaOH). The resulting solution is opalescent, which is usually put down to hydrolysis, casein being reformed. The addition of acids to the alkaline solution produces turbidity, casein being precipitated, while excess of alkali removes the opalescence.

From the electric conductivity, *i.e.* by the application of Ostwald's rule for determining the basicity of an acid from the variation of the equivalent conductivity (μ)

[1] Neumann, *Zeitsch. physiol. Chem.*, 1905, **45**, **216**.

of the sodium salt with the dilution (v), Sackur concludes that casein is a tetrabasic acid, which, together with the above equivalence with sodium hydroxide, gives a molar weight of about 5000.[1] It does not diffuse through parchment paper, though a substance with this molar weight should diffuse to a measurable extent (p. 36), and should also exert a considerable osmotic pressure.

Soaps.—The soaps constitute a highly complicated chapter in chemistry. From the present point of view, their interest centres in the fact that they are representative of a class of substances which

(1) Are themselves probably non-colloid, but may undergo changes in certain liquids, giving rise to colloids, and hence have been termed colloidogens;

(2) Exhibit very different behaviour at low and high concentrations;

(3) Are known as electrolyte colloids, for the reason that, while the aqueous solutions are good electrolytes, their osmotic properties (boiling point, vapour pressure, etc.) are so far abnormal that not only do they not indicate the ionisation, which the electric conductivity leads us to expect, but they differ so slightly from those of the pure liquid, that the idea of solution is precluded. In other words, while the solutions are fair electrolytes, their boiling point and vapour pressure are approximately the same as for water.

Thus, Krafft[2] found no elevation of boiling point for concentrated solutions of soaps, while there were slight rises for dilute solutions. Smits[3] obtained similar results for sodium palmitate at concentrations from 0·3 to 0·6

[1] *Zeitsch. physikal. Chem.*, 1902, **41**, 672; *Beitr. chem. Physiol. Path.*, 1903, **3**, 193.

[2] *Ber.*, 1894, **27**, 1747; 1895, **28**, 2566; 1896, **29**, 1328; 1899, **32**, 1584.

[3] *Zeitsch. physikal. Chem.*, 1903, **45**, 608.

mols per litre. For higher concentrations he used a tensimeter owing to the experimental difficulties of the boiling point method. There was no diminution of vapour pressure in a 28 per cent. (1 mol per litre) solution, and only 1·3 mm. diminution in a 14 per cent. solution.

For the osmotic pressure of soap solutions, see p. 318.

Concentrated solutions are clear when hot, and gels are formed on cooling. Dilute solutions are frequently opalescent, and the opalescence is increased by heat. All the solutions have electric conductivity; the soap is therefore ionised or hydrolysed, or probably both. Hydrolysis is proved by the extraction of fatty acid from the solution by shaking up with toluene; the hydrolysis is not into acid and base, but into acid salt and base, and occurs even when excess of base is added. In absolute alcohol the soaps give normal molar weights by the boiling point method.

A comparative study of the sodium salts of the fatty acids shows that the soap character begins with the C_{12} acid. Oleic acid is more soluble than the saturated acids, and its salts are less hydrolysed.

MacBain and Taylor[1] were unable to get any satisfactory determinations of the boiling point (which the author can corroborate from personal experiences), so they studied the electric conductivity at 90° of solutions of sodium palmitate, using silver vessels, as others were attacked chemically by the soaps at this high temperature. They appear to have obtained the same value for the conductivity, whether the solution was made up from solid soap and water, or from acid and sodium hydroxide. This is a very important observation, for it indicates that a true, *i.e.* a reversible, equilibrium is established between

[1] *Zeitsch. physikal. Chem.*, 1911, 76, 179.

electrolytes in solution and colloids in the sol condition. There is a maximum conductivity (89·47) at 0·5 m., and a minimum (82·37) between 0·2 m. and 0·1 m.

Addition of sodium hydroxide to the solutions produces a precipitate, which is a mixture of sodium palmitate and an acid salt, $NaHP\bar{a}_2$, in spite of the alkaline reaction of the liquid. Whether this precipitation is the precipitation of a sol, a salting out, or a gelation, is not very clear. The precipitation of the acid salt by alkali from alkaline solution seems to be similar to the gelation of silicic acid by small quantities of alkali (p. 129). As the reaction takes place with solutions up to 56 per cent. (2 m.), it is plain that the hydrolysis of sodium palmitate is—

$$2NaP\bar{a} + HOH \rightleftharpoons NaOH + NaHP\bar{a}_2$$

and not

$$NaP\bar{a} + HOH \rightleftharpoons NaOH + HP\bar{a}$$

The nature of "*salting out*" of soaps by adding a mixture of sodium chloride, carbonate and hydroxide, seems to be as uncertain as the above action of sodium hydroxide. It has been variously described as salting out proper, analogous to the action of ammonium sulphate on albumin, or of many salts on organic substances not necessarily colloid; as a precipitation of a sol by electrolytes; and as a "common ion effect," *i.e.* the precipitation of a sparingly soluble salt by adding a large amount of a soluble salt with a common ion (*e.g.* the decrease in solubility of silver acetate on adding sodium acetate or silver nitrate to the solution).

Dried soap swells in water, becoming a gel[1]; this process is accelerated by alkali, and this fact is made use of by the manufacturer. The cuttings of soap to be remade up are treated with dilute alkali instead of with water.

[1] Goldschmidt, *Koll. Zeitsch.*, 1908, **2**, 103, 227.

The surface tension of soap solutions is dealt with on p. 240. As the solutions are so complex, it is not surprising that the surface tensions are not well-defined. While sodium oleate lowers the surface tension of water to a great extent, sodium palmitate, according to Bottazzi,[1] does not lower it at all, and the addition of a little sodium hydroxide produces no change. He concludes that the lowering of the surface tension is due to the undissociated sodium oleate, while the hydrolytic products are much less active, or are quite inactive.

Among semi-colloids other than those mentioned above are substances used in dyeing and tanning. Owing to their importance they will form the subject of separate chapters.

Indicators.

Wo. Ostwald[2] has suggested a colloid theory of indicators. Congo rubin turns blue with acids, its range being similar to congo red. In water it forms a highly disperse system, which is between typical colloids and molecular dispersoids, *i.e.* the velocity of dialysis, diffusion, and ultrafiltration lies between them, but is greater than congo red. It is also, like congo red, electro-negative. It is changed to blue by acids, but also by neutral salts, alkaline salts like sodium carbonate, and even by alkalies like barium hydroxide. In these cases the colour change is followed by precipitation of the dye. Non-electrolytes are inactive. The valency law is followed, *e.g.*

$\frac{1}{2}$ Na_2SO_4	:	$MgSO_4$	:	$\frac{2}{3}$ $Al_2(SO_4)_3$
1	:	39·4	:	1530
1	:	39·4	:	1552

The change can be prevented by addition of "protective" colloids, and they have similar values in this case, as hold for gold sols.

[1] *Atti. R. accad. Lincei*, 1912, 365 (abstract in *Koll. Zeitsch.*, 1913, 12, 205).

[2] *Koll. Zeitsch.*, 1919, 24, 67.

CHAPTER XX

DYEING

THE question whether dyeing is a chemical or a physical process is one which has agitated scientists and practical men alike as long as there has been a science of chemistry, and the main effect of the advent of colloid chemistry has been to render the question still more complicated by providing yet another set of explanations to those already existing, without increasing materially the prospect of a final answer. Still, it affords several points of attack, and there is little doubt that many of the phenomena of colloids must be concerned in some of the processes of the dyer's art. The fibres cotton, silk, wool, are more or less comparable with gels, both in structure and general properties; they exhibit the phenomena of imbibition and dehydration, and possess great development of surface. Many dyes are true colloids or semi-colloids in water, and of the others, many greatly lower the surface tension of water, and are thus readily adsorbed from water, as also are the other two classes of colloids and semi-colloids.

Notwithstanding this, it is vain at the present moment to expect that colloid chemistry can provide a single or simple explanation of dyeing, or an answer to the question whether dyeing is a chemical or a physical process. The reason of this is to be found in the question. As Ostwald well expresses it, "We are not justified in speaking of 'a theory of dyeing,' as if any single theory can be applied to all the processes of dyeing. Dyeing is not a scientific, but a technical notion, which denotes uniform results

without regard to the means employed. Science is bound to take into consideration the means, and, if they are found to be different, it must put forward correspondingly different theories of the dyeing processes which depend on them."[1]

The original rival explanations were physical action, with solid solution as a later extension, and chemical reaction between the fibre and the dye. To these are now added colloid reactions and adsorption at interfaces, the latter naturally taking first place, though the mutual precipitation of colloids of opposite electric charges, and the various types of pseudo-adsorption (p. 256) must also be important factors, especially though not exclusively when mordants are used. But before entering on this, the main subject of interest, it is desirable to outline briefly the colloid properties of dyes.

The Colloid Nature of Dyes.—As stated in the previous chapter, many dyes form semi-colloids in water, others are undoubtedly colloids, *i.e.* form emulsoid or suspensoid sols with water as dispersion medium, while others again form true solutions. The following table shows to which group a number of important dyes belong.

Colloid.	Semi-colloid.	Crystalloid.
Alkali blue	Capri blue	Alizarin red
Aniline blue (soluble)	Fuchsin	Auramine
Azoblue	Methyl violet	Bismarck brown
Benzazurin	Neutral red	Chrysoidin
Benzopurpurin	Nile blue	Eosin
Carmine		Fluorescein
Congo red		Magdala red
,, fast blue		Methylene blue
,, brown		Patent blue
Diamine green		Picric acid
,, blue		Pyronine
Induline (soluble)		Rhodamine
Naphthol yellow		Safranine
Night blue		Thionine
Violet black		

[1] *Outlines of General Chemistry*, 3rd English Edition, 1912, p. 495.

The colloids show distinct microns and submicrons in the ultramicroscope, and otherwise behave as typical sols; usually the emulsoid or hydrophile character predominates, but in some (*e.g.* congo red), the dye is precipitated by small amounts of salts, and, as they are mostly negative sols, the precipitating power of the salt depends on the valency of the kation (p. 98). As a rule the sol is electropositive or electronegative according as the colouring substance forms the kation or anion of the dye.

According to Keller,[1] methylene blue in water migrates feebly to the anode with a voltage of 60–70 V., although it is a basic dye; in alkaline solutions it migrates to the anode, while in acids it travels to the kathode. Acid fuchsin in water goes to both anode and kathode.

The semi-colloids exhibit the irregularities associated with the class to which they belong (see Chap. XIX.); their molar weight in water is 2–3 times the normal, while, like the soaps, the molar weights in alcohol are normal.[2] The aqueous solutions are good electrolytes, and submicrons are visible in the ultramicroscope. Michaelis[3] observed that the addition of salts to sols of semi-colloids, and even to solutions of the soluble dyes, produces submicrons, *i.e.* they shift the dye from one class to the next. Thus a dilute fuchsin contained no submicrons, but when sodium chloride was added to the hot solution and the solution rapidly cooled, many submicrons were visible. This change no doubt plays an important

[1] *Koll. Zeitsch.*, 1919, **25**, 60.

[2] Krafft, *Ber.*, 1899, **32**, 1610.

[3] *Virch. Arch. Anat. Physiol.*, 1905, **179**, 195.

part in the effect of neutral salts on the taking up of dyes by fibres from the dye-bath; neutral salts, as is well known, increase in some cases to a remarkable extent the amount of dye taken up by the fibre, and colloid dyes are among the most readily taken up dyes. The chemical theory has failed to supply any plausible explanation of this action.

A similar transference from one class to the next more colloid class can also take place in other ways. The dye salt may form true solutions, but give rise, by hydrolysis or other reaction, to colloid base or acid (or it may be to colloid ion) in a manner analogous to the action of water on soaps (p. 269), or by the production of insoluble salts, *e.g.* of fatty acids, in the form of sols.

Precipitation of Dyes by other Colloids.—The mutual precipitation of colloids is strikingly exemplified in the case of dyes.[1] Among dyes are to be found all types of colloids—suspensoids and emulsoids, semi-colloids and colloidogens—and salts which form true solutions. Of the three types of action (p. 137) (1) simple precipitation, and (2) precipitation with protection and consequent non-precipitation when excess of either sol is present, are well known; the third type with two zones of precipitation and two of non-precipitation does not appear to have been observed.

(1) Eosin (anion) and methylene blue (kation), being electrolytes and non-colloid, precipitate suspensoids sols—eosin, the positive sols such as aluminium hydroxide and ferric hydroxide, methylene blue, the negative sols such as platinum and mastic—so soon as the critical concentration has been reached.

A similar action occurs with emulsoids under the conditions which convert them into positive or negative

[1] Buxton and Teague, *Zeitsch. physikal. Chem.*, 1907, 60, 469.

colloids, the negative emulsoids are precipitated by basic dyes, the positive by acid dyes. Methylene blue precipitates sols of hæmoglobin, serum albumin (native and heated), congo red, etc., at high, but not at low concentrations.

(2) The colloidogen, semi-colloid and colloid dyes with suspensoids and emulsoids, such as gelatine, tannin, albumin, etc., are examples of the second type: a zone of precipitation with a zone of non-precipitation on each side of it.

The possibility of titrating one dye with another, as night blue with eosin, or with other colloids, as night blue with tannin, depends on this reaction, the precipitation zone being very sharply defined, and the ratio of the two substances remaining the same when the absolute concentration is changed. The ratio corresponds in the former case to the chemical equivalents, but that there is not true salt formation is indicated by the fact that the ratio varies with the rate at which the precipitant is added.

Solid Skins on Solutions of Dyes.—Solutions of many dyes, *e.g.* fuchsin, form a skin on the surface, when they are kept for some length of time. The nature of this skin is not always known, but is due to increase of surface concentration. These substances lower the surface tension of water to a very considerable extent, and so, even in dilute solutions, the concentration of the surface layer may be extremely high; and as they are mainly emulsoid or hydrophile colloids, they form gels or even solid skins on the surface.

They may also be formed at the interface of two immiscible liquids in which the colloid is insoluble. Ramsden,[1] who has investigated this phenomenon, especially in the

[1] *Zeitsch. physikal. Chem.*, 1904, 47, 336.

case of albumins, has applied it to the separation of colloids from liquids by simply shaking up with air or a suitable liquid (toluene or chloroform in the case of albumins). The method applies to albumins, soaps, and saponins, as well as to dyes.

This concentration of the colloid in the surface or interface is certainly followed in many instances by irreversible changes, *e.g.* albumin and dyes become insoluble, in whole or in part, or become incapable of solation, etc.

Two classes of substances which are nearly related remain to be discussed; they are lakes and mordants. We will take the latter first.

Mordants.—As a broad generalisation mordants may be said to be "colloidogenic" substances, *i.e.* they are themselves truly soluble, but by various changes give rise to colloids, either sols, or more usually gels. These gels produced on or in the fibre of the fabric to be dyed then react with the colouring matter of the dye-bath, whether by chemical action, by adsorption, by solid solution, or, as is extremely likely in some cases, by mutual precipitation of colloids of opposite electric charge, is immaterial at present. By this means dyes which are not fast when used alone are more firmly fixed. The mere mention of the substances chiefly used as mordants is sufficient evidence of their colloid character: aluminium salts, chromic salts, ferric salts, stannic chloride, tannin, etc.

Let us take *aluminium mordanting*, for instance. A solution of aluminium acetate is partly hydrolysed in solution into aluminium hydroxide sol and acetic acid. This, when brought into contact with, say, cotton, will probably deposit some aluminium hydroxide on the surface of the fibre, for the sol is positive and cotton in contact with water is negative; we should thus expect precipita-

tion of the sol on the cotton. But whether this takes place or not, some aluminium acetate will soak into the fibre, and will there hydrolyse, depositing aluminium hydroxide gel in the fibre, the acetic acid escaping either by diffusion or by evaporation, if the fabric is steamed or dried. If the former action, mutual precipitation of the aluminium hydroxide on the surface, takes place, the formation of the gel in the fibre could take place as follows. The aluminium acetate which has soaked into the fibre before the precipitate has been deposited on its surface, cannot diffuse out again, for the film is impermeable by Al''', but acetic acid can easily dialyse out, leaving an aluminium hydroxide gel impregnating the fibre. Thus the mordant would be both embedded in the fibre, and also to some extent deposited on its surface.

The fact that the basic sulphates are good mordants while the basic chlorides are not so, is probably connected with the precipitating effect of the bivalent anion, SO_4'', on the positive aluminium hydroxide sol in the former, while in the latter the stabilising effect of the hydrogen ion H', or of the Al''' on it prevents its precipitation by the univalent anion Cl' (pp. 139, 196). In the case of the basic acetate, which also is a good mordant, the salt is more fully hydrolysed than the chloride or sulphate, and the acetic acid is so weak that it can have only a feeble stabilising effect on the aluminium hydroxide sol.

The use of *bichromate* as a mordant appears to depend ultimately on the precipitation of chromic hydroxide gel on or in the fibre. The bichromate is decomposed in dilute solution into chromate and chromic acid ; the latter is adsorbed by the fibre and is probably partially reduced by the material of the fibre, but the reduction is completed *e.g.* by sulphurous acid. Chromic chloride and chromic fluoride are also used as mordants for wool.

Stannic chloride by similar reactions can deposit stannic acid gel in the fibre, for in water it is practically completely hydrolysed into hydrochloric acid and stannic acid sol.

Tannin as a mordant deserves separate mention. It is an emulsoid sol in water, and is readily adsorbed. Its adsorption is increased when free acid is added to the solution, but this soon reaches a maximum, and further addition of acid reduces the amount adsorbed, as the following figures show :—

Adsorption of Tannin by Cotton.

	Amount adsorbed.
Tannin + no acid	30 per cent.
+ 1 g. acetic acid per litre	35 „ „
+ 2 „ „ „	40 „ „
+ 5 „ „ „	50 „ „
+ 10 „ „ „	33 „ „
+ 20 „ „ „	31 „ „

Lakes.—Tannin forms lakes with basic dyes; these may be salts, but are more likely formed by the mutual precipitation of the negative tannin and the positive (basic) dye. According to Witt[1] there is no definite molecular ratio between the dye and the tannin. The ratio will obviously depend on the electric charge on the particular gel and sol, and will in any case not necessarily approximate to molecular ratios (p. 136). That this is the nature of the reaction is supported by the fact that the tannin lakes are soluble in excess of tannin, for a sol which precipitates when the appropriate amount is added protects the other sol if added in excess (p. 135).

The lakes proper are formed from alizarin (a weak dibasic acid, dihydroxy anthraquinone, $C_{14}H_8O_4$) and

[1] *Chem. Zeit.*, 1885, 12.

metallic oxides, of which aluminium hydroxide is the type. The presence of an oxide of a bivalent metal, *e.g.* CaO, is also necessary for a proper colour and fast dyeing. The chief lake is Turkey red on cotton, which contains aluminium, and calcium, and also a fatty acid. A pure aluminium mordant on wool also requires an oxide of the MO type to give the colour; here magnesium oxide is found to be the best.

Pure aluminium ricinoleate powder, if heated with water and alizarin, begins to attract the colouring matter at 40° C., at which it melts, and the bright red colour is gradually developed.

The formation of lakes with dyes and aluminium hydroxide may be compared with the action of the latter on red gold sols, which gives bright red precipitates.

The Theories of Dyeing

The essential fact on which the chemical theory of dyeing is based is that there is a decomposition of the dye salt, especially in the case of basic dyes, the coloured kation being fixed on the fibre, while the anion remains in the bath. This is represented as a chemical reaction[1] between the dye and the fibre, which is stated to be an amphoteric electrolyte, and so functions as an acid to basic dyes, and a base to acid dyes, an insoluble product being deposited on or in the fibre. The following objections appear to be fatal to this theory.

(1) The dye is not insoluble, for it can in many cases be readily removed by treatment with water or other

[1] Knecht, *Ber.*, 1889, **21**, 1556, 2804; **22**, 1120. Suida, *Sitzungsber. kaiserl. Akad. Wiss. Wien.*, 1904, **113**, 724; *Zeitsch. Angew. Chem.*, 1909, 2131.

liquid, and there is, in fact, reversible equilibrium between the dye on the fibre and in the bath.

(2) That the same decomposition occurs with other substrates in which chemical action (amphoteric or otherwise) must be considered improbable. Such are pure cellulose, charcoal, glass, asbestos, and other silicates.[1]

(3) According to Losev it is doubtful if a similar decomposition of acid dyes takes place, and it certainly does not occur with the substantive dyes, so that in these cases the chemical reaction is quite lacking.

As the facts relating to the first of these objections are of fundamental importance, they may be stated at once. In an investigation on the behaviour of picric acid to various adsorbents, Walker and Appleyard[2] found that the amount of dye taken up from the bath varied continuously with the concentration of the bath, relatively larger amounts being taken from weak baths than from strong ones. The formula expressing the relation was found to be—

$$\frac{c_{\text{silk}}}{c_{\text{water}}^{2\cdot7}} = k$$

This is the well-known adsorption formula. If the dyed silk was treated with water, the action was reversed, and the same end result was obtained whether the dye was on the silk or in the solution. Further, less picric acid was taken up by silk from alcohol solutions, and none at all from benzene solutions.

From these results, it would appear that the action of picric acid on silk is purely an adsorption effect, the amount adsorbed depending not only on the nature of the substance adsorbed, but also on that of the solvent.

[1] Georgievics, *Färberzeit.*, 1894–5, **19**, 9, 129, 188, 286. Freundlich and Losev, *Zeitsch. physikal. Chem.*, 1907, **59**, 284.

[2] *Chem. Soc. Journ.*, 1896, **69**, 1334.

Adsorption generally is greater from liquids whose surface tension is large (as water) than from those with small surface tensions (as alcohol and benzene), the decisive factor being the effect of the particular solute on the surface tension of the liquid (p. 242).

It is very difficult to reconcile some of the well-known facts of dyeing with the chemical theory, *e.g.* the effect of adding neutral salts to the bath (p. 275), but above all the increased dyeing produced by adding bases to basic dyes, and acids to acid dyes. The stronger the acid and the greater its concentration, the greater is the dyeing action.

Adsorption of Dyes.—In the chapter devoted to adsorption (p. 247) will be found several references to dyes, which show that the *initial* stage at least of the reaction between dye and fibre may be regarded as an adsorption. One only will be repeated here. The ratio of the amounts of two adsorbed substances is practically independent of the nature of the adsorbent (p. 250), and this applies equally to fibres (wool, cotton, silk) as to the substances usually employed as adsorbents (charcoal, aluminium oxide, silica, etc.).

Again, as pointed out above, there is apparently equilibrium between fibre and solution, just as there is with the other adsorbents. Lastly, the connexion between the concentration of the dye-bath and the amount taken up is expressed by the adsorption formula, the numerical values of the index being similar to those of other adsorptions. This, the result of the work of Walker and Appleyard, already referred to, of Schmidt,[1] and especially of Freundlich and Losev,[2] is the main objection to the theory of solid solution, first suggested by Witt.[3]

[1] *Zeitsch. physikal. Chem.*, 1894, 15, 56.
[2] Freundlich and Losev, *loc. cit.*, p. 282.
[3] *Färberzeit.*, 1890-1, 15, 1.

The Solid Solution Theory.—According to this view, the dye is distributed between the two immiscible solvents —the liquid and the fibre—being in the ordinary solution state in the one, and as a solid solution in the other. Many arguments have been adduced in favour of this theory, but the above objection led to the general abandonment of this theory in favour of the adsorption theory, although many of the properties of dyed fibres were not in agreement with what was to be expected, if the process of dyeing was purely an adsorption. In particular, the microscopic appearance on the whole gave the impression of solution throughout the fibre, and not of a surface adsorption. For example, starch grains are uniformly coloured,[1] and microscopic sections across dyed fibres have revealed in some cases the existence of irregular deposits on the external surface of the fibre, or mainly in the outer layers, but in many others the dye was uniformly distributed through the fibre.[2] The former structure occurs with the insoluble dyes as Turkey red (see Mordants, p. 278), and with inorganic pigments; the latter occurred especially in direct dyeing on wool and silk with basic dyes. It also occurs with cotton and mercerised cotton with substantive dyes, and with basic dyes if the cotton is previously mordanted with tannin.

As in many other cases there is evidence that adsorption, which is a rapid process, is followed by slow changes, such as diffusion into the interior of the adsorbent. Examples of this are found in hydrogen and platinum or palladium, acids in various adsorbents both fibres and inorganic substances,[3] iodine and hydrogen in

[1] Fischer, *Zeitsch. physikal. Chem.*, 1908, **63**, 480.

[2] Suida, *loc. cit.*, p. 281.

[3] Georgievics, *Koll. Zeitsch.*, 1912, **10**, 31; *Zeitsch. physikal. Chem.*, 1914, **87**, 669.

charcoal,[1] though in the case of iodine and charcoal later research has failed to find any evidence of solid solution, the equilibrium being rapidly attained in benzene; in carbon disulphide it was very slow, owing to decomposition of the carbon disulphide with liberation of sulphur which combined with the iodine.[2] On the whole, then, it is not improbable that in dyeing, too, adsorption is followed by similar processes.

According to Reinders[3] pure adsorption only occurs with those dyes which form sols, and in the fibre are also colloid (gels ?), among which he classes precipitation of gold sol or arsenious sulphide sol on charcoal or barium sulphate, or of charcoal suspension on paper, and also the dyeing of wool and cotton with true colloid dye sols, such as the blue acid of congo red. These dyeings are not fast, and the dye can be removed by washing.[4]

Reinders and Lely have recently shown that the fact that the distribution of dye between fibre and bath follows the adsorption law instead of the distribution law (Henry's law) cannot be accepted as a criterion in this question, for the distribution of dyes between two immiscible liquids frequently follows the same adsorption law. They investigated the distribution of a number of dyes between water and isobutyl alcohol, both with and without the addition of acid (HCl), and alkali (KOH); the dyes were—

Basic dyes: methylene blue, fuchsin, crystal violet, new fuchsin.

Acid dyes: crystal ponceau, patent blue, erythrosin A, roccellin, quinoline yellow, alkali blue.

Substantive dye: congo red.

[1] Davis, *Chem. Soc. Journ.*, 1907, **91**, 1666. MacBain, *Zeitsch. physikal. Chem.*, 1909, **68**, 471.

[2] Dora Walter, *Koll. Zeitsch.*, 1914, **14**, 242.

[3] *Koll. Zeitsch.*, 1913, **13**, 96.

[4] Pelet Jolivet, *Die Theorie des Färbeprozessen*, Dresden, 1910, p. 142.

They found (1) that the distribution of the dyes between water and isobutyl alcohol is expressed by the adsorption formula—

$$\frac{c_{\text{alcohol}}}{c_{\text{water}}^{\frac{1}{n}}} = k$$

in which $\frac{1}{n}$ is less than 1. The value of $\frac{1}{n}$ varies from 0·3 for erythrosin A to 1 for alkali blue and crystal ponceau. In most cases it is not constant, but rises with increased concentration.

(2) The addition of potassium hydroxide to the basic dyes, and of hydrochloric acid to the acid dyes increase the concentration of dye in the alcohol layer, just as they increase the amount of dye taken up by fibres.

(3) Wool and silk which are dyed with basic dyes are readily decolorised by the alcohol (compare the non-dyeing of silk by picric acid in benzene, p. 282).

(4) A colourless solution of rosaniline in water dyes wool and silk a deep red, *i.e.* the colour of the salts; the same thing happens when the solution is shaken up with isobutyl alcohol or amyl alcohol. In this case salt formation is excluded. It is probable that there are two modifications of the base, colourless and red, the former more soluble in water, the latter more soluble in alcohols (and in fibres), and so taken up from the aqueous layer.[1]

Reinders explains the small value of $1/n$ as partly due to the differences in molar weight of the dyes in the two

[1] A similar thing occurs with picric acid, which is readily adsorbed from the yellow aqueous solution by, *e.g.*, platinum black on platinised electrodes, and is not extracted from them by washing with water. It is extracted by alcohol and benzene, but in the form of a colourless solution, which resulted in the extraction being overlooked, until it was noticed that the addition of water to the alcohol produced an intense yellow colour. (Private communication from Professor Sir J. Walker.)

layers, for as already stated their molar weights in alcohol are usually normal, while in water they are 2–3 or more times the normal, as the following figures show [1] :—

Dye.	Molar weight.		
	In water.	In alcohol.	Theoretical.
Fuchsin	520–620	320–340	337
Methyl violet . . .	800–870	400–420	408
Benzopurpurin . .	3000	—	724
Diamine blue . .	3400	—	999

The change in molar weight with concentration may be the cause of the change in the value of $\frac{1}{n}$ with concentration.

Or the explanation may be that the dyes are both hydrolysed and ionised in water, and not in the alcohol; the ions would not be extracted from the water layer by the alcohol, and thus the distribution would vary with the concentration of the ions; similarly, the distribution of the hydrolytic products between the two solvents would depend on their solubility in each, and, naturally, to a different extent from that of the undissociated dye. That this must have some effect on the distribution is borne out by the effect of acid on acid dyes, and of bases on basic dyes, the results of which are as would be expected from the above considerations. The addition of acid to basic dyes, or of base to acid dyes, often causes an increase in the concentration of the dye in the alcohol layer. This may be referred to the decreased hydrolysis, and consequent increase in concentration of the undissociated dye salt in the water layer, which, of course, means an increase in the alcohol layer also. The effect is not so great as in the

[1] Krafft, *Ber.*, 1899, **32**, 1608.

other case, where acid is added to acid dye and base to basic dye, and the changes in colour point to other effects. The following figures illustrate the effect of acid and alkali on methylene blue :—

	HCl.						KOH.			
Equivalents to 1 of methylene blue	Large excess	8	4	2	1	0	0·8	2·6	6·2	10
$\frac{\text{Calcohol}}{\text{Cwater}}$ . . .	1·08	0·86	0·50	0·41	0·41	0·41	0·41	0·57	1·25	3·33

Finally, the adsorbability of the three dyes, crystal violet, new fuchsin, and patent blue, follows the above order, independently of the nature of the adsorbent, whether it is charcoal, silk, wool, cotton, or cellulose (p. 250), and the same order is retained in their distribution between water and isobutyl alcohol.

We are thus forced to conclude that the invalidity of the simple distribution law and the validity of the adsorption formula cannot be considered a decisive objection to the solid solution theory in favour of the adsorption theory. On the other hand, the adsorption theory affords a reasonable explanation of the striking differences in the adsorption of dyes in water and in other liquids such as alcohol and benzene. It seems probable that the initial stage in most instances is an adsorption pure and simple, but that, if the dyeing is to be fast, it is succeeded by other stages which may in some cases be chemical changes and physical in others, resulting in a decrease in solubility of the dye in the original solvent.

CHAPTER XXI

TANNING, THE SOIL, AND PURIFICATION OF SEWAGE

TANNING

AFTER so lengthy a discussion of the main processes of dyeing, which, however, makes no claim to be exhaustive or complete, it is unnecessary to devote much space to tanning, since to a great extent the main problem is the same, viz. how far the actions of the chemicals on the skin are to be regarded as chemical reactions, adsorptions, or mutual precipitations of colloids.

The colloid nature of the substances concerned in tanning is even more pronounced than in the case of dyeing. The skin contains albumin- and gelatine-like substances in the form of gels, which swell in water, this being influenced to a marked degree by acids, alkalies, and salts. The tanning materials are mainly colloids, and hydrophile rather than hydrophobe. Tannin, *e.g.*, forms undoubtedly an emulsoid sol in water, for it is opalescent, does not dialyse, and does not lower the freezing point of water. It is interesting to note that Paterno,[1] who first discovered this, also stated that its molar weight in acetic acid was normal. He has quite recently, however, found this to be erroneous.[2] the lowering of the freezing point being due to impurities and moisture in the tannin; it is as much a colloid in acetic acid as in water. One result of

[1] *Zeitsch. physikal. Chem.*, 1889, **4**, 457.

[2] Paterno and Salimei, *Koll. Zeitsch.*, 1913, **13**, 81.

its colloid nature is that a larger amount of tannin is extracted from tanning material by distilled water than by ordinary water, the presence of small quantities of salts preventing solation, bivalent ions ($Ca^{\cdot\cdot}$ or CO_3'') being more powerful than univalent ions.

In the treatment preliminary to tanning proper, the swelling during the treatment with lime, and the persistence with which the last traces of lime are retained, necessitating extraction with acid, are both instances of colloid reactions.

Proctor and Wilson[1] consider that acids act on gelatine with formation of ionised salts, the anions of which, owing to diffusion into the mass of gelatine, exert an outward pressure, hence an increase of volume or swelling. This is applied by Proctor and Burton to the processes of pickling, lime extraction, and mordanting. According to Proctor's colloid-chemical theory, a compound of skin and tanning material is formed because of the presence of an electrical potential, *i.e.* a membrane potential. Electrical neutralisation takes place with mutual precipitation of oppositely charged colloids—hide and tanning agent.

According to Möller,[2] true solutions cannot tan, only peptised sols. Tannin is the peptiser in plant materials, the peptised substances being ellagic acid, katechin and its polymers. Tanning consists in the separation of the peptiser from the peptised substance. Tannin possesses a great solubility for skin substance, diffuses into the skin, and forms with it a solid solution, while the peptised substance attaches itself to the surface of the fibres of

[1] *Jour. Amer. Leather Chem. Assoc.*, 1916, 261; also Proctor and Burton, *Jour. Soc. Chem. Ind.*, 1916. Proctor and Wilson, *Chem. Soc. Jour.*, 1916, **109**, 1327.

[2] *Collegium*, 1916, p. 549. *Koll. Zeitsch.*, 1919, **24**, 32.

skin. This is only possible because of the peptised condition of the tanning solutions. The peptiser acts on the surface of the particles of the peptised substance, to form a soluble complex compound, which coats the particles and so prevents reunion.

The process of "**pickling**" has been very fully studied by Proctor;[1] it consists in treating the skin before tanning with very dilute sulphuric acid, during which a large amount of water is imbibed, the fibres swelling to a considerable extent. The skins are then placed in a strong solution of salt, when dehydration takes place, the skin becoming leather-like in texture. This action of neutral salts only takes place after acid imbibition. Proctor made out the general relations in the simpler case of the imbibition of water by gelatine under the influence of acids and salts.

A gelatine which took up about eight times its weight of water, took up about fifty times its weight of water in very dilute hydrochloric acid; very weak acids scarcely altered the amount imbibed. Salts in neutral solution increased imbibition, but in acid solution they dehydrated the gelatine; the process of dehydration was very susceptible to traces of acid. This is another general characteristic of colloids; such processes as gelation and solation, imbibition and dehydration of gels are generally greatly influenced by very small quantities of acids and alkalies (p. 165). The action of the acid on the gelatine, according to Proctor, is to form a salt-like substance.

In tanning proper, adsorption and mutual precipitation of sols in the liquid by the gels in the skin are undoubtedly the primary processes in the case of tannin and the vegetable extracts. The nature of the leather depends on the state of the skin (due to differences in the preliminary

[1] *Koll. Chem. Beihefte*, 1911, 2, 243-284.

treatment) and the materials in the tanning liquor; in the latter the colloids which are most readily adsorbed are deposited in great concentration on the surface, leaving the interior unaffected, while those which are less adsorbable and more diffusible have time to penetrate into the skin. As a general rule what is aimed at is a gradual tanning. This is attained in several ways, by appropriate selection of less adsorbable reagents at the commencement of the tanning, followed by more adsorbable ones. The same is effected by systematic exhaustion of the liquor; fresh extract is used with skins which are almost completely tanned, thus removing the most adsorbable substances and depositing them on the surface, while the fresh skins are treated with the almost spent liquor, which naturally contains only the least adsorbable substances. The adsorption is greatly influenced by the nature of the previous swelling of the skin; if acid has been used, adsorption is much quicker and much greater than after alkaline treatment.

In **mineral tanning**, in which chromium, aluminium, and iron alone are concerned, there is probably precipitation of a hydroxide sol contained in the basic salts employed by the colloids in the skin, although there is also the possibility of diffusion of salt into the skin, followed by decompositions similar to those occurring in mordanting which result in the deposition of metallic hydroxide gel in the fibres. In the two-bath process of chrome tanning, as in bichromate mordanting (p. 279), chromic hydroxide is produced in the fibre by the reduction of chromic acid by reducing agents, and if thiosulphate and acid are used as the reducing agent, sulphur sol is also formed (soluble hydrophile colloids from the skin or the chromic hydroxide "protecting" it), and some of it is also adsorbed.

Secondary Changes.—Whatever the initial process, there are, in the case of both vegetable and mineral tanning, secondary changes, which are slow and irreversible. At first a considerable amount of tannin, or of chromium, aluminium, or iron, can be extracted with water, and the skin has not fully acquired the properties of leather. As the latter increase, the amount of tanning agent extracted by water decreases. In tanning with fats, as with tannin, there is the possibility of oxidation, and in the former case it has been suggested that the oxidation products are the actual tanning agents. Other actions supposed to take place are dehydration and polymerisation, it being further suggested that these actions are catalytically accelerated by the fibre. There is apparently little direct evidence bearing on these suggestions.

Iron tanning is not so satisfactory as aluminium, and still less so than chromium. According to Stiasny, ferric salts are too fully hydrolysed, and therefore too indiffusible, and too quickly precipitated, while the inferiority of aluminium is due to its salts not being hydrolysed enough. If hydrophile colloids, such as soap, blood, albumin, gelatine, are added (as "protectors"), iron tanning is improved. It is quite possible, too, that the iron catalytically oxidises the fibre, and so causes brittleness. The superiority of chromium may be connected with the presence in chromic salts of complex ions, no similar substances being known in the case of ferric and aluminium solutions.

Just as Proctor[1] was enabled to throw light on the action of acids and salts in "pickling," by a study of the behaviour of gelatine (p. 291), so Abegg and Schroeder obtained valuable information from an investigation of the action of tanning agents on gelatine.

The melting point of the gelatine was 36°. Formalin

[1] *Koll. Zeitsch.*, 1907, 2, 85.

acted slowly, raising the melting point; the maximum attained was 48°. The time necessary for this to be reached was inversely proportional to the concentration of the formalin. Alum and chrome alum do not harden the gelatine as formalin does, and the melting point is lowered, by 10 per cent. alum to 34°, and by 10 per cent. chrome alum to 32°; the action is very rapid (a few minutes), and previous treatment of the gelatine with sodium carbonate was of no effect. Iron alum, with or without sodium carbonate, caused the gelatine to become hard and brittle; the melting point was 40°–38° in very dilute solution.

Bichromate followed by sodium thiosulphate, picric acid, and tannin were tried, but the melting point remained unchanged.

The lowering of the melting point by the alums is due to the action of salts on the melting point of gelatine (p. 125); this effect is superposed on the tanning effect.

Washing out the tanned gelatine produced a curious effect—the melting point of the mineral-tanned gelatine rose well above the original melting point after brief extraction with water and fell on prolonged washing to the original melting point. The following figures are of interest:—

Gelatine (m.p. 36°).

Tanning agent.	Melting point. At once.	30 min. washing.	Long washing.
10% Cr. alum .	32°	37°	36°
„ Al alum .	34°	42°	36°
„ Fe alum .	48°	45°	41°
Tannin . . .	34°	—	—
Formalin . . .	—	48° (48 hrs.)	46° (55 hrs.)

The Soil

The application of colloid chemistry to the study of soils has been attended with marked success. The colloid nature of one of the chief constituents of soil, humus, has long been known, and to its colloid properties its importance is mainly due. There are also other colloids present in soil, the chief being

(*a*) Humus, and decayed organisms.

(*b*) Ferric hydroxide and aluminium hydroxide, etc.

(*c*) Amorphous silicates, resulting from the weathering of crystalline silicates.

(*d*) Bacteria.

Humus is, perhaps, the most important of all; it is emulsoid in character, resembling albumin in many respects—in salting out, imbibition with water, adsorption of salts, migration to the anode; it acts as a substrate for bacteria, and as a "protective" colloid for suspensoid colloids in the soil. The question whether it is an acid or not seems at last to be definitely settled. It has frequently been held that its neutralisation with bases was simply the formation of adsorption compounds, but recent work leaves little room for doubt. The solution has a greater electric conductivity than oleic acid solution; it is said to invert cane sugar, and to react with iron, hydrogen being liberated. Oden prepared humus acid suspension, and a colloid-free ammonium humate, and concludes that alkali first peptises humus, and subsequently acts upon it chemically, for alkali humate is certainly not a colloid, since no particles are visible in the ultramicroscope; further, salts do not cause precipitation, the solution diffuses, and there is no change in concentration when it is shaken up with charcoal or barium sulphate. The gelation of humus sols gives rise

to membranes which make the soil impervious to air and water.

As a negative colloid humus is precipitated by kations and in accordance with the valency rule more readily by $Ca^{\cdots}$ and $Fe^{\cdots}$ or $Al^{\cdots}$. They alter the permeability, the amount of water taken up by imbibition, and also the way the soil "works." The adsorption of potassium is probably also affected.

The adsorption of dyes by humus is made use of in soil analysis, *e.g.* methyl violet serves to distinguish colloids from finely-divided crystalloids; colloid aluminium silicates and aluminium hydroxide can be distinguished from amorphous silica (silicic acid) by means of alizarin, and the two former from each other by naphthol yellow + acetic acid, which colours the aluminium hydroxide alone. All these reactions depend on the attraction of colloids for basic or acid dyes according to the sign of the electric charge on the colloid. As Rohland has shown, colloid clays adsorb prussian blue, organic dyes, colouring matters from fæces and urine, and also albumins, oils, soaps, etc., from drainage waters.

A knowledge of the amount of clay in a soil is thus an important matter. Plasticity tests afford only a rough guide to the amount, and better results are obtained by ascertaining the hygroscopicity, *i.e.* the adsorption of water vapour by the surface. It is, however, difficult to apply, as the extent of surface changes on drying, and humus imbibition also vitiates the results. The adsorption of malachite green by the clay affords a good and reliable estimate of the amount of clay.

The adsorption of salts, of calcium and potassium in particular, by soil is highly important; potassium is strongly adsorbed by clays, phosphate by calcium carbonate (no doubt some chemical action in this case), also precipitated

calcium phosphate precipitates ferric oxide and aluminium oxide. The adsorption of potassium is a very rapid process, as pure adsorptions usually are, while the adsorption of phosphate is much slower, as is to be expected, since, as stated above, the adsorption of phosphates may be partly a chemical action. Another important action of fertilisers is the solation of silicic acid gel (probably also of other colloid gels), usually stated as dissolving silicic acid; the sol rises by capillary action to the surface, and is there again gelated, and encrusts the surface.

The weathering of rocks gives rise to colloids, mainly in the form of gels. The precipitated colloids produced during weathering are not chemical compounds of alumina with silica, *i.e.* amorphous aluminium silicates, but are mixtures of the single gels, produced by the mutual precipitation of positive and negative sols.

Purification of Sewage and Water

The oxidisable impurities in sewage are colloids in the form of sols. This was first suggested by Biltz and Kröhnke,[1] who proved it to be the case by dialysis, and by the migration of the substances to the anode when subjected to a fall of potential. They are thus negative colloids, and are precipitated by positive sols, such as ferric hydroxide sol and aluminium hydroxide sol. They are also rapidly precipitated by ferric salts and aluminium salts; and this not because of the hydrolysis of these salts into the above positive sols, but because of the powerful precipitating effect of trivalent kations, as $Fe^{\cdots}$, $Al^{\cdots}$, etc., on negative sols (p. 141). Biltz applied the adsorption formula, but without much success.

The methods of chemical purification of waste water

[1] *Ber.*, 1904, **37**, 1745.

in chemical manufactures are usually based on the above reaction. For example, aluminium hydroxide is used as a clearing agent in the waste waters in starch factories. According to Rohland (p. 296), some kinds of native plastic clay can be used instead of artificial colloid aluminium hydroxide in these purification processes.

The purification of water for town supplies by filtration through beds of sand, charcoal, etc., affords examples of adsorption from solutions at the enormous surface of the filter. The addition of alum to water before mechanical filtration has several effects. In the first place, the acid solution will affect the electric charge on the colloids in the water, especially the emulsoid colloids, and so will increase their precipitation by salts. Then, as mentioned above, aluminium ion has a very powerful precipitating action on negative sols, and if positive sols are present the bivalent sulphate ion will also rapidly precipitate them.

Some of the impurities which may occur in water are very strongly adsorbed. For instance, lead may be dissolved from the lead pipes, and find its way into the water supply. It is completely taken out by a single filtration through a layer of closely-packed cotton wool (a single filter paper will not do it). This is extremely convenient for analysis, as the lead is easily removed from the cotton wool by means of acid. The lead is apparently present as a sol of lead carbonate or hydroxide.

Rohland states that the yellow colouring matter from the sulphite cellulose process is not adsorbed readily, as it is not a colloid. It must be turned into a colloid by oxidation in air and addition of potassium ferrocyanide before it can be removed by adsorbents.

CHAPTER XXII

APPLICATIONS OF COLLOID CHEMISTRY TO BIOLOGY

The Equilibrium between Blood and Oxygen.—The question of the solubility of gases, especially the important gases oxygen and carbon dioxide, in blood has long engaged the attention of scientists. The variation in the amount taken up with the external pressure does not follow Henry's law (that the solubility of a gas in a liquid varies directly as the pressure), very large amounts being taken up at low pressures in comparison with those at high pressures. The amount taken up at any pressure is enormously greater than that dissolved by water under the same conditions,[1] as the following figures show: at a pressure of 150 mm. 100 c.c. of water take up 0·7 c.c. of oxygen, while 100 c.c. of dog's blood take up 24 c.c.; as the centrifuged plasma takes up only 0·65 c.c., the corpuscles are responsible for the difference, and not the salts or other substances in the blood.

Since Liebig's time, the accepted explanation of this deviation from Henry's law has been that it is due to the formation of a chemical compound of hæmoglobin and oxygen. There are several difficulties in accepting this explanation. Not only does the composition of this compound vary with the pressure, but also with other

[1] Bohr, *Nagel's Handbuch d. Physiol.*, 1905, I., 1, p. 54; Loewy, *Physikal. Chem. u. Medizin*, 1907, I., p. 231; also Philip, *Physical Chemistry: Its bearing on Biology and Medicine*, 1913, p. 26.

varying conditions of preparation; further the maximum amount that can be taken up is by no means constant. Thus the maximum amount of oxygen that can be taken up should bear some constant relation to the amount of iron (representing hæmoglobin), but 1 g. of Fe corresponds to—

328–468 c.c. in dog's blood.
301–450 „ „ ox „
280–401 „ „ pig's „
379–426 „ „ horse's „

Again, in any given case, the maximum saturation is not reached even at a pressure of 10 atmospheres[1]:—

p cm. Hg.	c.c.	p atmospheres.	c.c.
17	7·3	1	20·0
25	10·1	2	20·9
34	10·8	3	21·6
44·5	15·6	5	22·7
56	16·9	7	23·1
		10	23·4

The first of these difficulties was apparently solved by Donders, on the basis of chemical dissociation, analogous to the dissociation of calcium carbonate. But to "explain" all these phenomena, it was necessary to assume more than one kind of hæmoglobin, and several dissociation products of hæmoglobin, one containing iron (hæmochromogen), another one iron-free. The former again dissociates into a part containing oxygen, and another which is oxygen-free.

As Wolfgang Ostwald[2] pointed out, all the available data for the amounts both of oxygen and of carbon dioxide

[1] Bert, *La pression barométrique, etc.*, Paris, 1878, p. 643.
[2] *Koll. Zeitsch.*, 1907, **2**, 264, 294.

in blood are expressed by the adsorption formula, and give typical adsorption curves; the following example will suffice[1]:—

p mm. Hg.	x in per cent. of total saturation.	x calculated.
2	32·5	26·1
16	52·0	52·9
25	63·5	61·5
45	74·0	75·1
63	83·0	84·2
82	93·5	92·1

The figures in the last column are calculated from the adsorption formula—

$$\frac{x}{m} = k\ c^{\frac{1}{n}}$$

with $k = 20{\cdot}6$ and $\frac{1}{n} = 0{\cdot}34$. The curve in Fig. 21, represents p and x in columns 1 and 2.

There can be little doubt that the gases are adsorbed by the blood, probably at the surface of the disperse phase.

The effect of artificial colloids on the solubility of gases has been the subject of investigation by Geffcken.[2] With ferric hydroxide sol there was no difference between the solubility of oxygen in water and in the sol, while nitrous oxide was less soluble in the sol. And more recently, Findlay[3] and co-workers have carefully investigated the problem, using carbon dioxide and nitrous

[1] Loewy, *Engelmann's Arch. Physiol.*, 1904, 231.

[2] *Zeitsch. physikal. Chem.*, 1904, 49.

[3] *Chem. Soc. Journ.*, 1910, **97**, 536; 1912, **101**, 1459; 1913, **103**, 436; 1914, **105**, 291.

oxide, and a large variety of colloid sols, as starch, egg albumin, gelatin, dextrin, ferric hydroxide, silicic acid, and suspensions of silica and charcoal, at pressures from 250 mm. to 1000 mm. of mercury. At low pressures the solubility of the gas may be greater or less than in water, but diminishes with rise of pressure, falling to a constant minimum or passing through a minimum and rising slightly after it. As there is no effect at all comparable

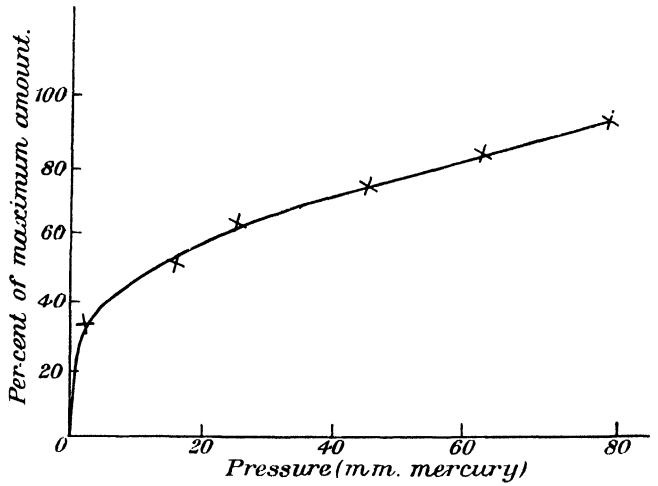


FIG. 21.

with the case of oxygen in blood, it is evident that some other factor must be operative in the latter case, and this may be chemical in its nature.

Enzymes and Inorganic Ferments.—The organic ferments which have been isolated are amorphous, albumin-like substances; it is usually impossible to remove them from organic tissues with which they are associated. During reaction they must be either in the form of gel on the surface of the tissue, or in the form of a sol (probably

emulsoid or hydrophile). In either case the reaction is obviously heterogeneous, and adsorption, surface concentration, and diffusion must therefore take an important part in the changes. If the chemical change is a rapid one, the Nernst-Brunner principle must also apply, and if the enzyme is a sol, Brownian movement will come into play, as will also changes in the specific surface under the influence of reagents, especially of acids, alkalies and salts.

When Bredig discovered his method of preparing sols of pure platinum and other metals, whose action as catalysts in the massive state was known, he was naturally led to examine their catalytic properties in comparison with the same metals in the solid state on the one hand, and with the organic catalysts, the enzymes, on the other. The results obtained by Bredig and his pupils are embodied in his interesting book, *Anorganische Fermente* (Leipzig, 1901).

Qualitatively the metal sols were found to catalyse the same reactions as platinum black, *e.g.* the union of hydrogen and oxygen, the oxidation of hydriodic acid by atmospheric oxygen, and the decomposition of hydrogen peroxide, which is also catalytically decomposed by many organic ferments. The activity of the sols is enormous; thus 1 c.c. of a platinum sol, containing from 0·0001 mg. to 0·000003 mg. of metal, showed marked catalytic properties. Sols of other substances which act upon hydrogen peroxide were much less active than this, the concentrations corresponding to the above being—

Pt . . .	20 million litres	for	1 g. atom
MnO_2 . .	10	„	„
Co_2O_3 . .	2	„	„
CuO . .	1	„	„
PbO_2 . .	0·1	„	„

These concentrations are comparable with those at which the activity of ferments, etc., is perceptible.

Quantitatively there is a close resemblance between decompositions by metal sols and by enzymes. The decomposition of hydrogen peroxide into water and oxygen is a very convenient reaction to study; it is a reaction of the first order if platinum black is used, and remains so whether the solution is acid, alkaline, or neutral. Here the chemical reaction is extremely rapid, and the velocity actually measured is the diffusion of the hydrogen peroxide across the adherent layer, the temperature coefficient being correspondingly small.

The reaction with platinum sol in neutral solution is not strictly one of the first order, although it is approximately so, for if the sol is a very active one, the velocity increases as the amount of hydrogen peroxide falls off. This is not due to the formation of a compound of platinum and oxygen, since the rise is repeated, even if the platinum has been previously treated with the peroxide. In acid solution the reaction is also of the first order.

There is a difference in this connexion between the enzymes and the metal sols. O'Sullivan and Tompson,[1] and Tamman[2] have shown that the inversion of sugar by enzymes approximates to the logarithmic law (reaction of the first order), but is not in exact accordance with it, because of changes in the condition and activity of the ferment, which are functions of time, and in some instances of the amount of substance catalysed.

In *alkaline* solution very peculiar results were obtained. The activity is very much increased, so that the sol must be 3–30 times more dilute than in water, a suitable concentration being 1 g. atom in 300,000 litres. Dilute

[1] *Chem. Soc. Journ.*, 1890, **57**, 926.
[2] *Zeitsch. physikal. Chem.*, 1889, **3**, 35; 1895, **18**, 436.

alkali therefore increases the velocity, which increases at first with the concentration of sodium hydroxide to a maximum, and then diminishes, finally becoming less than in neutral solution, *e.g.*—

$0{\cdot}05\ H_2O_2 + 0{\cdot}000003$ Pt

Concentration of NaOH	0	$\frac{1}{512}$	$\frac{1}{256}$	$\frac{1}{128}$	$\frac{1}{64}$	$\frac{1}{32}$
Time (min.) for 50% decomposition	255	34	28	24	25	22
Concentration of NaOH	$\frac{1}{16}$	$\frac{1}{8}$	$\frac{1}{4}$	$\frac{1}{2}$	1 normal	
Time (min.) for 50% decomposition	34	34	70	162	520.	

Fig. 22A is the corresponding curve.

Thus in normal sodium hydroxide the velocity is reduced to half the velocity in neutral solution. This is very similar to the effect of alkali on the decomposition of hydrogen peroxide by emulsin. Jacobson[1] had found that the enzymes of malt and of pancreas, and emulsin decomposed hydrogen peroxide much more rapidly in weak alkaline solutions, *e.g.*—

Emulsin + H_2O_2

Concentration of KOH	0	$\frac{1}{130}$	$\frac{1}{70}$	$\frac{1}{40}$	$\frac{1}{30}$	$\frac{1}{25}$ normal
Time (min.) for 170 c.c. O_2	30	3	6	15	20	> 30

The curve (Fig. 22B) is very similar to that for platinum.

The order of reaction cannot be determined, for in very dilute alkali solutions the velocity is independent of the concentration of the peroxide; at greater concentrations the order of reaction comes out between 0–1. The cause

[1] *Zeitsch. physiol. Chem.*, 1892, 16, 340.

of this may be the stabilising effect of hydroxyl ion on negative sols (p. 105), changing sub-microns to amicrons, and causing an increase in the specific surface and Brownian movement. A similar explanation may also hold for the analogous case of enzymes. Confirmation of this view may be found in the observation that ferric hydroxide sol, which has marked catalytic powers, is quite inactive in alkaline solution, according to Bredig's observations. It is a positive sol, and the effect of hydroxyl ion upon it

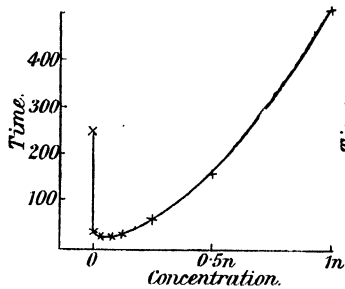


FIG. 22A.

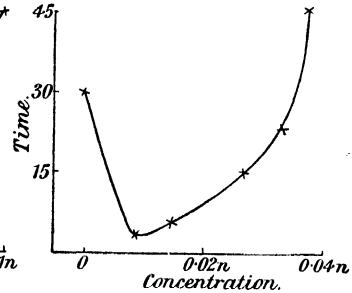


FIG. 22B.

should be the direct opposite of the effect on negative sols.

If the concentration of the platinum sol is diminished in the ratio 2 : 1, the velocity constant k decreases in the ratio 3 : 1, *e.g.*—

Pt concentration.	k.
$28{\cdot}16 \times 10^{-6}$	0·115
21·12 „	0·072
14·08 „	0·040
10·56 „	0·024
5·28 „	0·0084
2·64 „	0·0027

Finally, there is a striking parallelism between the "poisoning" action of various substances on platinum sol

and on enzymes. Substances such as hydrogen sulphide, mercuric chloride, hydroxylamine, hydrocyanic acid, etc., even at very small concentrations, reduce or entirely stop the catalysis: *e.g.*—

$$0{\cdot}06\ H_2O_2 + 0{\cdot}00001\ Pt$$

Concentration HCN (mol. per litre)	0·0	0·00000005	0·0000001	0·0000002
Time in minutes for 50% decomposition	7·5	15·4	22·0	40·9

i.e. 0·0014 mg. of hydrocyanic acid in 1 litre reduces the velocity to half. Jacobson finds the same for the catalysis of hydrogen peroxide by emulsin and by pancreatic ferment, and Kobert found a similar sensitiveness of the catalysis of hydrogen peroxide by blood (hæmase) to hydrocyanic acid (0·002 mg.). It is interesting to note that the order in which the reagents are mixed makes a great difference to the result; the poisoning of the catalyser, whether platinum or enzyme, is always more severe when the hydrocyanic acid is added to it before the hydrogen peroxide. Both the platinum and the enzymes "recover" their activity after a time. As Freundlich points out, the variation of the "poisoning effect" with the concentration of the poison is in accordance with the adsorption formula, though it is, of course, not suggested that the mere adsorption of the substance on the surface slows down or prevents the action (by offering a resistance to diffusion).

Agglutination.—An enormous amount of work has been done during the recent development of colloid chemistry towards the elucidation of some of the perplexing and complicated reactions of biology in accordance with the newly acquired ideas, and in no direction have more strenuous efforts been made than in the case of toxins and antitoxins, and the other reactions of a similar nature.

So extensive is the subject that entire books have been devoted to it; obviously, then, nothing can be done here beyond indicating how far the outstanding features of these reactions are colloid in nature, whether adsorptions or mutual precipitations of sols and gels.

A word of warning may not be out of place here, although it may be equally necessary in other subjects. There is an undeniable tendency not only to apply a new idea or theory in many new directions in a loose and vague manner, but also to regard such applications as "explanations." Mass-action, osmotic pressure, ionisation, hydrolysis, amphoteric electrolytes, and now colloids, adsorption, and surface tension, have been successively thus employed, and often in cases of so complex a nature that it was *a priori* highly improbable that any one explanation could take in all the relations concerned. Particularly is it necessary to remember this in dealing with adsorption. The adsorption formula is merely an empirical expression, which more or less closely fits a large number of facts, which are by no means necessarily the same in nature, and to show that a particular phenomenon can be expressed by the adsorption formula certainly does not explain the phenomenon.

What are commonly known as emulsions of bacteria are really suspensions, varying in dispersity according to the kind of bacteria, and are precipitated by quite definite amounts of electrolytes, as are suspensions generally. They are, as a matter of fact, not very sensitive, as they are not precipitated by kations of the alkalies or of light metals, but are precipitated by acids (hydrion), by kations of heavy metals, and by aluminium and ferric ion (see table, p. 310). They thus stand between suspensoid and emulsoid sols, and on this account have been represented as suspensoids, protected by an emulsoid

sol. This is supported by the fact that bacteria sols are not "protected" to any considerable extent by emulsoids, such as gelatine or dextrin, which are usually so powerful in this respect.

When the immune serum is added to the bacteria sol, the latter becomes much more sensitive to electrolytes. Indeed, no clumping of the bacteria or sedimentation occurs on the addition of the immune serum, unless salts are present; hence, if the sol and the serum have been dialysed, there is no precipitation. It would thus appear that the agglutinin in the immune serum destroyed the "protecting" part of the bacteria sol, which thus became a suspensoid sol.

The method of working is as follows. The bacteria sol (typhus, cholera, etc.) is treated with formalin, which kills the bacteria, the sol is repeatedly centrifuged, changing the water, or it is dialysed. The sol is opalescent, and remains without sedimentation for a long time. To obtain the agglutinin-bacteria, the serum of animals, which have been injected with the same bacteria as the sol, is added to a culture of the bacteria, and the resulting agglutinin-bacteria sol is treated in the same manner as the bacteria sol.

The agglutinin-bacteria sol is not precipitated by hydroxyl ion, but is readily precipitated by acids and salts of heavy metals. The valency rule applies, the precipitating power increasing with the valency of the kation. There is an "optimum" of precipitation at one definite ratio of bacteria sol to agglutinin, and no precipitation occurs if there is a large excess of either. This is analogous to the mutual precipitation of positive and negative sols (p. 134). The following table illustrates the differences between bacteria sol (typhus) and the corresponding agglutinin-bacteria in their precipitation by

electrolytes. For comparison, the corresponding figures[1] for a mastic sol are added :—

Electrolyte.	Concentration (m.mol. per litre) for precipitation in 24 hours. Bacteria.	Agglutinin-bacteria.	Mastic.
$NaCl$ . . .	∞	25	1000
$NaNO_3$ . . .	—	25	—
$\frac{Na_2SO_4}{2}$ . . .	—	55	—
KOH . . .	∞	∞	
HCl	1	0·5	10
$\frac{H_2SO_4}{2}$ . . .	1	0·25	10
$H.C_2H_3O_2$ . .	1	1	—
$AgNO_3$ . . .	25	1	125
$MgSO_4$ . . .	∞	1·3	50
$CaCl_2$ . . .	∞	2·3	25
$BaCl_2$ . . .	∞	2·5	—
$CdSO_4$ . . .	5	0·5	12
$Ni(NO_3)_2$ . .		1·3	—
$HgCl_2$ . . .	1·3	0·25	—
$\frac{Al_2(SO_4)_3}{2}$ . .	0·08	0·08	0·15
$\frac{Fe_2(SO_4)_3}{2}$ . .	0·2	0·04	0·15

The change from emulsoid to suspensoid is also shown by the precipitation of agglutinin-bacteria by dyes. Similar changes occur when egg-albumin is coagulated by heat. The mutual precipitation with its zone bounded on both sides by zones of non-precipitation is accompanied by the analogous behaviour towards multivalent ions, *e.g.* Al''' and Fe''' (p. 139), and also towards acids (H'); the latter of which, however, has not been observed with

[1] Bechhold, *Zeitsch. physikal. Chem.*, 1904, **48**, 385.

inorganic sols. Its occurrence in this instance is probably connected with the anomalous position of an albumin-like substance with suspensoid properties, the albumin character rendering the sol very susceptible to hydrion ($H^{\cdot}$) as emulsoid sols of albumin are known to be.

Henri[1] pointed out an important difference between the mutual precipitation of sols and agglutination in that the former only occurs between sols of opposite electric charge, while the latter occurs with both. For instance, red blood corpuscles, which are negative, can be precipitated by both positive and negative sols. He assumes that the corpuscles are surrounded by a pellicle which can fix salts (by adsorption ?), especially magnesium sulphate and calcium sulphate. These salts act upon any precipitable sol, producing a coagulum round the corpuscle; they can be removed by diffusion into an isotonic sugar solution, after which the blood corpuscles are much less susceptible to precipitation by sols. Similarly by soaking them in solutions of salts, especially of chlorides and sulphates, they become more readily precipitated by sols, and especially by ferric hydroxide sol.

The nature of the combination between the bacteria and the agglutinin is a problem of much the same kind as that of the combination of fibres and dyes. From the constancy of the ratio of the two which is necessary for optimum precipitation, it was at first concluded that the combination was chemical in nature. But this alone is of no value as a criterion, since, to mention only one instance, the mutual precipitation of positive and negative sols also fulfils this condition, even in cases where chemical reaction in the ordinary sense cannot possibly be supposed to take place. Biltz[2] then suggested that they were

[1] *Compt. rend.*, 1904, **138**, 1461.

[2] *Zeitsch. physikal. Chem.*, 1904, **48**, 615.

adsorption compounds formed from a highly disperse emulsion and a sol. He showed further that the distribution of agglutinin between the bacteria and the immune serum followed the adsorption law, as the following figures show:—

Typhus Bacillus and Agglutinin.

Agglutinin in solution.	Agglutinin in agglutinin-bacilli.	
	Observed.	Calculated.
20	180	170
60	340	360
500	1500	1520
3500	6500	5960
9000	11000	11400

The figures in column 3 are calculated from the adsorption formula

$$\frac{x}{m} = ac^{\frac{1}{n}}$$

in which the constant $a = 21{\cdot}9$, and $\frac{1}{n} = 0{\cdot}637$.

The action between bacteria and agglutinin can thus undoubtedly be expressed as an adsorption. But there are difficulties in the way of accepting this as a final explanation, for a most important feature of the whole reaction is the fact that sols of any one kind of bacteria are affected only by the agglutinin produced in serum by the injection into the animal of the same kind of bacteria, and by no other. Gelatine, however, acts as a specific agglutinin to both typhus and cholera bacilli. This, while confirming the colloid nature of the reaction, is difficult to work out on the line of chemical combination, although, as Proctor found in investigating the action of acids and salts

[1] Biltz, *Med. naturverein. Archiv.*, 1907, **1**, 363, calculated from Elsenberg and Volk, *Zeitsch. Hygiene*, 1902, **40**, 155.

on gelatine, gelatine forms a chemical compound of a salt-like nature with acids (p. 291). This specific character of the reaction is generally considered to be strongly in favour of a chemical reaction between the two, a point of view advocated throughout by Arrhenius in his book on *Immunochemie*. If the combination is chemical in nature, it must be of a peculiar and restricted kind. The probability of deciding the problem in the meantime seems to be somewhat remote.

Toxins and Antitoxins.—The nature of the reaction between a toxin and its antitoxin has, like the similar reaction of agglutination, attracted much attention in recent years, and the position concerning it is very similar to that in the case of agglutination.

The substances concerned in the toxin-antitoxin reaction are undoubtedly colloid in nature more so on the whole than in the agglutination reaction, some of them, indeed, being so far removed from the dispersity associated with emulsions that they diffuse fairly rapidly. The diffusion coefficients of some toxins and antitoxins in gelatine have been determined by Arrhenius.[1]

Diphtheria toxin . .	$D = 0{\cdot}016 \times 10^{-5} \frac{cm^2}{sec.}$.
„ antitoxin .	0·0017 „
Tetanus lysin . . .	0·043 „
„ antilysin . .	0·0024 „

The substances are thus colloids, and the antitoxins apparently more so than the corresponding toxins. No conclusions regarding molar weight by the application of Thovert's relation (p. 35) are permissible, as the diffusions were carried out in gelatine and not in water.

The first striking similarity between the colloid

[1] *Immunochemie*, p. 17.

reactions and the toxin-antitoxin reaction is what is known in the latter as the Danysz effect. When a diphtheria toxin is treated with its antitoxin, the reduction in toxicity depends on the manner in which it is added, *i.e.* an amount of antitoxin which is exactly sufficient to neutralise a given amount of toxin when added all at once, is not nearly sufficient to neutralise the same amount of toxin when added little by little, with moderate intervals between each addition. And the longer the intervals, the greater is the insufficiency. This is a well-known characteristic of colloid reactions, *e.g.*, in the precipitation of suspensoid sols by electrolytes,[1] and in the salting out of emulsoids, as albumin.[2] If the salt is added all at once, more albumin is precipitated than if it is added gradually; when 5 c.c. of a saturated solution of ammonium sulphate were added at one operation to 5 c.c. of a white of egg sol, the filtrate contained 0·17 g. of albumin; when the addition was spread over twenty-four hours the filtrate contained 0·214 g., and over forty-eight hours it contained 0·237 g. Similarly with the mutual precipitation of positive and negative sols, the ratio of the amounts which produce complete precipitation is a function of the time over which the addition is extended. This "acclimatisation" is an important objection to explanations of the phenomena on the basis of chemical combination, or of chemical equilibrium, for even when the latter requires appreciable time for equilibrium to be established, the equilibrium itself is independent of the time. Bredig noticed too that the manner in which hydrocyanic acid and hydrogen peroxide were added to platinum sol made very great differences in the result (p. 307). He also states that an old gold sol is much less sensitive to

[1] Freundlich, *Zeitsch. physikal. Chem.*, 1903, **44**, 143.

[2] Höber and Gordon, *Beitr. chem. Physiol. Path.*, 1904, **5**, 436.

ammonia than a freshly prepared one, and that the addition of such old insensitive sols to new very sensitive ones confers on the mixture "immunity" against ammonia.[1] There are thus many colloid analogies with the Danysz effect.

Several investigations of the electrical behaviour of toxins and antitoxins have been made with a view to explaining their action on each other, but with no very definite result. Diphtheria toxin and antitoxin were found by Field and Teague [2] to migrate distinctly. Bechhold also found that diphtheria toxin was slightly weakened at the anode, while the antitoxin migrated to the kathode. In a mixture containing an excess of toxin, the excess migrated to the kathode, provided that the experiment was performed immediately after mixing the toxin and antitoxin.[3]

The main question here, as in agglutination, is whether the reaction is due to chemical combination or to an adsorption. The chemical reaction which naturally is at once suggested, is the neutralisation of acid and base. Against this is not only the fact that, as stated above, the proportion of the two necessary for neutralisation varies with the manner in which the addition is made, but also the further fact that as the amount of antitoxin to a fixed amount of toxin increases, the amount of free toxin diminishes, but never entirely disappears. The corresponding chemical reaction is the equilibrium between a weak acid and a weak base, such as ammonia and boric acid, in which case too there will always be free boric acid (or ammonia), however great an excess of ammonia (or boric acid) is added. It is chemical reactions of this type on which Arrhenius has based the chemical

[1] Bredig, *Anorganische Fermente*, p. 28.
[2] *Journal of Experimental Medicine*, **9**, p. 86.
[3] Bechhold, *Koll. Zeitsch.*, 1907, **2**, 184, abstract.

theory of the reaction. The equilibrium equation for the above case of a weak acid and weak base in aqueous solution is—

$$c_1 c_2 = k\, c^2$$

in which c_1 is the concentration of free acid,

c_2 ,, ,, free base,

c ,, ,, combined acid,

and k is a constant.

The following table shows how closely the above equation holds for the reaction between toxin and antitoxin. In it c_1, c_2, and c are the amounts of free tetanus lysin, of antilysin, and of bound lysin respectively. The value of k is 0·115; n in the first column is the amount of antilysin added to 1 of lysin, the second column contains the amount of free lysin as determined by experiment, and the third column the amount calculated from the above equation:—

Tetanus Lysin and Antilysin.

n	c_1 (obs.).	c_1 (calc.).
0	100	100
0·05	82	82
0·1	70	66
0·15	52	52
0·2	36	38
0·3	22	23
0·4	14·2	13·9
0·5	10·1	10·4
0·7	6·1	6·3
1·0	4·0	4·0
1·3	2·7	2·9
1·6	2·0	2·5
2·0	1·8	1·9

Biltz was the first to suggest that the reaction might be an adsorption, and in support of this view showed that the results are in agreement with the adsorption formula.

The following table, calculated by Biltz [1] from Madsen's results [2] on the reaction between diphtheria toxin and antitoxins shows how closely the experimental results are expressed by the adsorption formula :—

Diphtheria Toxin and Antitoxin.

Free toxin in solution.	Toxin bound to the antitoxin.	
	obs.	calc.
1·2	197	180
5·6	210	210
11·1	222	230
17·2	237	240
28·0	240	255
32·2	270	260
49·8	251	270
57·6	283	275
72·8	272	280
74·4	(511)	283

The calculated results in the third column are obtained from the adsorption formula—

$$\frac{x}{m} = ac^{\frac{1}{n}}$$

in which $a = 177$, and $\frac{1}{n} = 0{\cdot}102$.

A comparison of the two tables shows that both the adsorption formula and the equation for the equilibrium between a weak acid and a weak base express the experimental results very closely, when the uncertainties of the experimental data are borne in mind; on the whole, the adsorption formula is in closer agreement. There is, however, the same difficulty here as in the case of agglutination, namely, the *specific* nature of the reaction. The fact is that diphtheria antitoxin is the only one which can

[1] Biltz, *loc. cit.*, p. 312.

[2] Madsen, *Arrhenius' Immunochemie*, p. 131.

neutralise diphtheria toxin, though it has not yet been made clear how this is to be explained by chemical action of the type of neutralisation of acid and base, which is certainly a general and not a specific reaction.

Osmotic Pressure and Semipermeability, Membrane Hydrolysis

The earlier determinations of the osmotic pressure exerted by biologically important colloids gave conflicting results, partly on account of inadequate methods, and partly because of unsuitable treatment of the substances. Recent work has shown that very considerable osmotic pressures are attained in some cases. Owing to the colloid character of the substances, there is usually no trouble in securing a membrane which is sufficiently impermeable by the colloid, while allowing water and crystalloids to pass freely. Parchment paper and collodion films (p. 27) are found most generally useful. As they are readily permeable by salts, any permanent osmotic pressure recorded cannot be ascribed to electrolytes or other crystalloid impurities.

The effect of electrolytes on the osmotic pressure of sols has also been investigated; these, especially in the case of albumin, are of interest from the biological point of view. As a rule, the osmotic pressure of sols is lower if salts are present, but in a few cases the pressure is increased, although the membranes are readily permeable by these salts. The cause of this is found in the change of dispersity of the disperse phase.

Moore and Parker[1] determined the osmotic pressure of soap solutions, and obtained fairly large values. They

[1] *Amer. J. Physiol.*, 1902, 7, 262.

concluded that soap is not dissolved as single molecules, but as "solution aggregates." (For a general account of the soaps, see p. 269.)

Particular interest attaches to Bayliss's[1] recent work on the osmotic pressure of Congo red, which is the sodium salt of a disulphonic acid, the theoretical molar weight of which is 696. The apparatus used was of the Moore and Roaf[2] type, in which a parchment paper septum is clamped between two metal chambers provided with flanges, the septum being supported by a rigid metal grid. The values obtained were slightly below those for a solution containing single molecules, and this behaviour was confirmed by vapour-pressure determinations, which gave normal values. Notwithstanding this, Congo red is a colloid, for it does not diffuse or dialyse, migrates in an electric field to the anode, and is precipitated by kations in accordance with the valency rule; at the same time, it is a good electrolyte, and in dilute solution is largely ionised, up to 80 per cent. at a dilution of 500 litres, from which the osmotic pressure should be from 1·5 to 3 times the calculated value. Similar results have been obtained by Biltz,[1] the osmotic pressure of Congo red corresponding to a molar weight of 602, when the osmometer was immersed in pure water. When the outer liquid was a solution containing the products of dialysis, concentrated until its electric conductivity was the same as that of the contents of the osmometer, the osmotic pressure fell, and then gave a molar weight of 2333.

The conditions obtaining in the dialysis of the salts of the nature of Congo red, say NaR, have been investigated

[1] **Bayliss**, *Proc. Roy. Soc.*, 1909, B. **81**, 209; 1911, B. **84**, 229; *Koll. Zeitsch.*, 1910, **6**, 23.

[2] *Biochem. J.*, 1906, **2**, 34; or Philip, *Physical Chemistry: its Bearing on Biology and Medicine*, p. 182.

[3] *Zeitsch. physikal. Chem.*, 1909, **68**, 357; 1910, **73**, 481; 1911, **77**, 91.

by Donnan.[1] He shows that if a salt NaR, like Congo red, is dissolved in water and separated from pure water by a semipermeable membrane like parchment paper, a large amount of hydrolysis may take place. Qualitatively at least this is readily deduced. The membrane is permeable by $Na^{\cdot}$ and not by R', nor by the unionised NaR; it is also permeable by $H^{\cdot}$ and OH', and also by H_2O; consequently it will be permeable by NaOH and not by HR. This being so, the salt which in water may not be hydrolysed at all, can be largely decomposed in water when separated from pure water by the membrane, and especially will this be possible where, as is the case with Congo red, the acid is more colloid than the salt. An aqueous solution of the blue acid of Congo red shows submicrons in the ultramicroscope, and the osmotic pressure corresponds to a molar weight about 20 times that for single molecules.

The same kind of thing will also occur with substances like aluminium chloride, and with simpler salts in the case of membranes like aluminium hydroxide which are permeable by various ions to very different extents. As experiments on the electric conductivity of salts across precipitation films showed, an aluminium hydroxide membrane is readily permeable by $H^{\cdot}$, $K^{\cdot}$, $Na^{\cdot}$, Cl', but not by SO_4''; from which it follows that an aqueous solution of say sodium sulphate, which is not hydrolysed to a measurable extent, can be separated by dialysis through such a film into sodium hydroxide and sulphuric acid. Similarly a weak acid like carbonic acid may be enabled to decompose a salt of a much stronger acid, if the latter is able to dialyse across the membrane much more rapidly than the other substances.

[1] *Zeitsch. Elektrochem.*, 1911, 71, 572; *Chem. Soc. Journ.*, 1911, 99, 1554.

At the same time electrical potential differences may also be established at such a membrane. With Congo red on one side of the film, sodium chloride is distributed unequally on the two sides of the film, being higher on the side opposite the Congo red. According to Donnan, these inequalities of concentration render fallacious any calculations of molar weight from the osmotic pressures observed in such cases.

Casein and sodium hydroxide give rise to a similar condition of matters,[1] for the sodium hydroxide crosses over to the casein against the osmotic pressure. Until the casein is almost saturated no alkali will remain on the outside of the osmometer. Alkali, therefore, moves against the osmotic pressure to the colloid side in order to unite with the casein.

Moore attributes the osmotic pressure to this union, and assigns to the membrane the purely mechanical *rôle* of holding together the aggregates; he maintains the impermeability of the membrane to be a fiction, stating that free ions pass through the membrane readily, while ions anchored to the colloid are retained on the colloid side of the membrane and exert pressure. With living cells the different concentrations of sodium, potassium, chloride and phosphate ions inside and outside the cell are regarded as expressions of the specific affinities of the definite colloid of each type of cell for these ions, and do not imply that there is a membrane acting as a "closed gate" to these ions. Moore and Roaf[2] are apparently not in favour of selective permeability of membranes, preferring on the whole selective adsorption by protoplasm.

[1] Moore, Roaf and Webster, *Biochem. J.*, 1911, **6**, 110.

[2] See further, Höber, *Arch. ges. Physiol.*, 1913, **150**, 15; and Moore and Roaf, *Koll. Zeitsch.*, 1913, **13**, 133.

The question arises whether there is any real difference between the two. Selectively adsorbing protoplasm in the cell would probably act as a selectively permeable membrane, if it was spread out as a film between the two phases.

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