

# THEORY OF THE STABILITY OF LYOPHOBIC COLLOIDS

THE INTERACTION OF SOL PARTICLES  
HAVING AN ELECTRIC DOUBLE LAYER

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## PREFACE

The present work is the result of theoretical investigations and calculations which were performed, with some interruptions, in the years 1940—1944. As conditions during the occupation of our country prevented earlier publication, and as a description of the collected results seemed to exceed the limits set to articles in periodicals we decided to present them in book form after the war.

The science of colloids appears to be entering upon a new stage, which is less empirical, and where the experimental study of better defined objects will be guided rather by more quantitative theories than by qualitative "rules" or "working hypotheses". The theory of the stability of lyophobic colloids, as developed in this book, may serve as an example of this development. This stability problem has been placed on a firmer physical basis by the introduction of the concept of Van der Waals—London dispersion forces together with the theory of the electrolytic or electro-chemical double layer. In the present work, too, these theories form the starting points of our considerations.

For the main part this book gives an account of our own work on the interaction of colloidal particles. It has not been written, however, on the assumption that the whole of the relevant literature is known to the reader. Accordingly we have added a number of chapters which may serve as an introduction to the main problem of the book. These chapters contain, for instance, a brief survey of some aspects of lyophobic colloids, a concise summary of the theory of the double layer, and a short introduction to the subject of Van der Waals—London forces.

At the time of writing this work (1944/45) the literature which has appeared during the war in the countries fighting on the side of the Allies was not at our disposal. To some of the Chapters a few paragraphs were added later on (1947) in order to bring the text in accordance with recent developments.

We desire to acknowledge the assistance we received, in a considerable part of the numerical calculations, from Mr K. van Nes, chem. docts., now once again of the laboratory of the Bataafsche Petroleum Maatschappij, Amsterdam, to whom we are also indebted for valuable contributions in the final presentation of the results of the theory of Part II.

Eindhoven, June 1947.

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## SUMMARY

The purpose of this book is to explain the stability of hydrophobic colloids and suspensions and to develop as far as possible a quantitative theory of this stability.

The basic concepts of this theory were the mutual repulsion consequent upon the interaction of two electro-chemical double layers, and the attraction by the London-Van der Waals forces. The principal facts of stability could be explained by combining these two forces. Among other things, a quantitative explanation of the rule of Schulze and Hardy has been given. For this purpose it was essential to use the unapproximated Gouy-Chapman equations for the double layer. The approximation of Debye and Hückel, however useful in the theory of electrolytes, appears to have only a very limited applicability in colloid chemistry.

The introduction of several refinements was necessary to explain various details. The quantitative agreement between theory and experiment, and the deviations from the rule of Schulze and Hardy (lyotropic effects) made it necessary to reckon explicitly with dimensions and the specific adsorbility of the ions. To this end, Stern's theory has been introduced.

Repeptization phenomena cannot be understood without the introduction of the Born repulsion, which, however, apart from this, is of very minor influence on the stability properties.

The London theory also needed a certain rectification in the form of a relativistic correction, because the uncorrected theory led to conflicts with the experiments in the case of coarse suspensions.

Part I deals with the single double layer, Part II with the interaction of two flat plates, and here most of the fundamental results of the theory already come to the fore. Part III gives a treatment of the interaction of spherical particles, which serves to clarify various details, especially the influence of particle dimensions and of the kinetics of flocculation.

In an introductory chapter I, a survey is given of the known facts and of the fundamentals of the theories to be applied. The stability rules and the mechanical properties of sols and suspensions, as far as they are related to stability, are stated fairly extensively. Chapter II gives the mathematical treatment

of the electro-chemical double layer. In Chapter the free energy of the double layer is dealt with at length, because it served as a basis for the theory of interaction. There have been some controversies in the literature on this point, but we believe we have cleared up the difficulties, especially by the consistent separation of the chemical and the electrical contributions to the free energy. Cf. also the Appendix on pp.

In Chapter IV and V the charge, the potential, and the interaction energy of two parallel flat double layers are represented. The interaction is proved to be fundamentally a repulsion for all distances between the plates.

Chapter VI gives a short treatment of London-Van der Waals forces and its application to flat plates. In this chapter the relativistic correction mentioned above is also dealt with.

In Chapter VII, as a further extension of the general considerations of J. H. De Boer and more especially Hamaker, the stability of colloids is discussed on account of potential curves, which are formed by a combination of the London-Van der Waals attraction and the double layer repulsion. A criterion is given for distinguishing potential curves as belonging to either stable or flocculated systems, and we investigate the way in which the transition from the stable to the flocculated state is influenced by the potential of the particles, the concentration and valency of the ions, and the attraction constant. All these quantities are shown to influence the stability. In order to get a good accord with experiments the attraction constant must be taken at about  $1$  or  $2 \cdot 10^{-12}$ , in good agreement with other theoretical and experimental values.

The influence of the valency and the concentration of the electrolytes agrees with experimental data as expressed by the rule of Schulze and Hardy. As a first approximation following from the theory we find that the flocculation values for monovalent, bivalent and trivalent electrolytes are in the proportion

$$c_1 : c_2 : c_3 = \frac{1}{1^6} : \frac{1}{2^6} : \frac{1}{3^6}.$$

The deviating stability conditions of emulsions are dealt with in a separate section. The basis of this treatment is laid in a number of sections in the preceding chapters, where the double layer at the interface of two liquids is considered.

The ground plan of Part III (Chapters VIII-XII, spherical particles) resembles that of Part II. All concepts used in Part II return in Part III. The treatment of the stability conditions (Chapter XII) deviates in so far as the Brownian motion of the particles is here explicitly incorporated in the theory. For a good understanding of stability it was necessary

to give a thorough treatment of the kinetics of coagulation, especially of slow coagulation.

The results of Part III agree in most respects with those of Part II. Quantitative agreement with experimental evidence is also satisfactory. Different effects known from experiment, as there are: instability of very small particles, the increase of stability during the flocculation process, and the influence of the concentration of electrolytes on the rate of coagulation, can be explained without the introduction of new hypotheses.

Finally, the Appendix gives a critical survey of the work of other investigators in this field.

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PART I  
Theory of a single double layer

I. INTRODUCTION

§ 1. *Lyophobic and lyophilic colloids.*

Colloid science is generally understood to be the study of systems containing kinetic units which are large in comparison with atomic dimensions. Such systems may be systems in which the particles are free to move in all directions, or they may be derived systems (as a coagulum, a gel, etc.) in which the particles have lost their mobility either partially or entirely, but have maintained their individuality.

It is customary to distinguish two classes of colloids whose general behaviour is entirely different. These classes are generally called *lyophobic* and *lyophilic* colloids, respectively; hence it is assumed that in the colloids of the second kind there is a strong affinity between the particles and the molecules of the dispersion medium which, in the colloids of the first kind, is either weak or absent. This assumption is expressed, for instance, by the concept of Kruyt, according to which the stability of lyophobic colloids is governed by only one factor (the electric charge of the particles) and that of lyophilic colloids by two factors (charge and solvation). Examples of lyophobic colloids are: a gold sol, a silver iodide sol, a quartz suspension (in water or in an organic liquid), and strictly speaking also the emulsions (although the stability conditions of this group are apparently different). An example of a lyophilic colloid is the gelatin sol. Typical for lyophilic colloids are, for instance, the swelling phenomena illustrating the great affinity between the gelatin and the water molecules (hydration).

The kinetic units mentioned above in lyophobic colloids are rigid particles (either amorphous or crystalline) or small liquid droplets. The crystalline nature of the particles of a gold sol, for example, may easily be proved by investigating a coagulum with the aid of X-rays: it is seen that the particles are very small crystals of the same crystal structure as the metal itself.

A clear notion of the nature of the kinetic units in lyophilic colloids has been lacking for a long time. Modern investigations, however, especially in the fields of cellulose and protein chemistry, have revealed that the "particles" consist either of a single large molecule or of a cluster of such molecules dissolved

in the dispersion medium. This "macromolecule" may be either an extremely long threadmolecule, or a molecule of a more complicated form, with long side-chains, etc., and the molecules may either be more or less stretched, or rolled up to a complicated clew, or folded together. But a common property of the "particles" will be that they are entirely open to the dispersion medium in that each "link" or atom group of the chain system is in contact with the solvent molecules. Moreover, each link of the molecular threads or chains is subject to thermal motion, so that the spatial configuration of the dissolved macro-molecule or molecular cluster varies continually. The "hydration" of a hydrophilic colloid is therefore partially a direct adsorption of watermolecules at the polar groups throughout the entire macro-molecule (accompanied by a gain in energy) and partially an imbibition or enclosure of water due to the thermal expansion of the macro-molecule (accompanied by a gain in entropy).

This peculiar difference between the structure of the kinetic units in lyophobic and lyophilic colloids yields a second criterion used to distinguish between the two classes of colloids, namely the contrast: *irreversible* and *reversible* colloids. A protein "crystal" or dry gelatin, when brought into contact with water, is converted spontaneously into an apparently homogeneous gel, or, if the amount of water is sufficient and the temperature is not too low, into a stable sol. A gold crystal brought into contact with water, however, is a system with a much lower free energy than a gold sol, and the former will never generate the latter spontaneously. A lyophobic colloid is therefore never stable in the sense of thermodynamics; the subdivision of the gold crystal into small particles can be performed only by supplying a considerable amount of work. The total free energy of the gold/water interface is a positive quantity. The small gain in entropy accompanying the formation of more kinetic units is negligible (even a colloidal particle still contains a large number of gold atoms).

There is a third and important difference between the two classes of colloids. Lyophobic colloids may be *flocculated* or *coagulated* by comparatively small amounts of electrolyte added to the system, and the effective amounts depend characteristically on the valency type and the nature of the electrolyte. What we observe when a lyophobic sol is coagulated is that the at first apparently homogeneous liquid becomes turbid and distinctly non-homogeneous. On examination with the microscope or ultramicroscope it appears that before the flocculation each individual particle is subject to thermal motion (Brownian movement), but that afterwards the particles cluster together and form larger agglomerates. In the coagulum the particles have maintained their individuality in that they hold together

at a few points only (at any rate immediately after coagulation) by comparatively weak forces. Sometimes, by removing the electrolyte from the system, the coagulum may easily be peptized again, i.e., the regular distribution of the particles through the dispersion medium, as present in the original stable sol or suspension, may be re-established.

Because of this sensitivity of the stability of lyophobic colloids towards electrolytes (stability with respect to coagulation) Freundlich used the term of *electrocratic* colloids for this class of colloids.

Actually, lyophilic colloids do not, as a rule, show the phenomenon of flocculation under the influence of small amounts of electrolytes in a way analogous to the behaviour of lyophobic colloids. In special cases, however, very similar phenomena may be observed, for instance in an aqueous gelatin sol to which a sufficient amount of alcohol has been added; and the work of Kruyt and Bungenberg de Jong<sup>1</sup> has given a great many examples of lyophilic colloids in which the physical properties (though not always the stability with respect to flocculation) are influenced by electrolytes in much the same way as is typical for lyophobic colloids. One of the oldest examples is the electro-viscous effect shown by many lyophilic colloids: a considerable decrease in viscosity, effected by the addition of small amounts of electrolyte. This effect suggests that the electrolyte greatly influences the spatial configuration of the dissolved macro-molecules. It may even be said that the influence of electrolytes upon lyophilic colloids is more or less analogous to that upon lyophobic colloids. For, as will be argued in the following sections, an electrolyte added to a lyophobic colloid destroys the potential barrier existing between the particles, thus enabling their mutual approach and final agglomeration. In the case of the lyophilic colloid the electrolyte obviously has a similar effect with respect to different parts of the same macro-molecule or molecules of the same cluster, again allowing their mutual approach, and, therefore, a folding together or curling up of the molecule to a less stretched form.

In the present treatise we will confine ourselves to the study of the stability of lyophobic colloids and a number of kindred problems relating to this type of colloids; only occasionally shall we refer to analogous points in the behaviour of lyophilic colloids. The above considerations may suffice, however, to show that a treatment of the fundamental aspects of the stability of lyophobic colloids must also be important for a better under-

<sup>1</sup> H. R. Kruyt and H. G. Bungenberg de Jong, *Kolloidchem. Beihefte*, 28 (1928) 1 and other papers by Kruyt and coworkers in the same journal under the title „Zur Kenntnis der lyophilen Kolloide".

standing of the rather complex set of phenomena in the field of lyophilic and bio-colloids.

### § 2. The electric double layer surrounding the particles

From several phenomena observed in colloidal systems it has been inferred that the dispersed particles carry an electric charge. Since the system as a whole is electrically neutral, the dispersion medium must contain an equivalent charge of the opposite sign. These charges are carried by ions, i.e., by an excess of ions of one sign at the particle surface and an excess of ions of the opposite sign in the solution. We will consider, as a fairly simple example, the AgI sol<sup>1</sup> in which the nature and magnitude of these charges have been extensively investigated. In a dialysed AgI sol the particles carry a negative charge. It is possible to determine this charge analytically. The particles are small AgI crystals of about  $50 m\mu$  (or  $5 \cdot 10^{-6} cm$ ), containing about  $10^6$  AgI "molecules", and carry a charge of the order of  $10^3$  elementary charges per particle. This particle charge is caused by an excess of I<sup>-</sup> ions in the crystal faces of the particles; each particle, therefore, contains, per 1000 AgI "molecules", about one I<sup>-</sup> ion in excess. In a well dialysed AgI sol the negative ions in the intermicellar liquid are almost entirely removed, and, especially if the sol is not too diluted, the aqueous solution phase contains practically none but positive H<sup>+</sup> ions; these ions (or, more exactly, the excess of H<sup>+</sup> ions over the negative ions still present in the liquid) are therefore responsible for the positive charge neutralizing the negative charge of the particles.

The positive charge carried by the H<sup>+</sup> ions in the dialysed AgI sol is not distributed uniformly through the intermicellar solution, as the H<sup>+</sup> ions are strongly attracted by the negatively charged AgI particles. Conversely, however, the H<sup>+</sup> ions will not be adsorbed all on the surface of the AgI particles, as the electrical attraction is counteracted by the thermal motion of these ions. The result is that these ions, or at least part of them, are still "free" ions, being dissolved in the solution and subject, individually, to progressive thermal motion; but on the other hand they are forced by the electric attraction to remain in the neighbourhood of the particles, so that each particle charge is screened off by an equivalent swarm of H<sup>+</sup> ions surrounding the particle.

Hence, if we consider one particle separately, immersed in the liquid, it is surrounded by an *electric double layer*.

<sup>1</sup> E. J. W. Verwey and H. R. Kruyt, *Z. physik. Chem.*, A 167 (1933) 137, 149, 312.

E. J. W. Verwey, *Chem. Rev.*, 16 (1935) 363.

One layer of this double layer is formed by the charge in the surface of the particles. (Strictly speaking this assumption of a surface charge is only more or less justified if the particles are crystalline or amorphous; in the case of liquid droplets things may be different). Though in reality it is a charge consisting of point charges, it is customary to consider it, as a first approximation, as a homogeneous surface charge spread over the surface of the particles. This may be rather a rough approximation, as it seems possible that the excess of I<sup>-</sup> ions present in the AgI surface of a negative AgI particle will be concentrated around certain active spots, edges, and corners of the crystal faces, etc. In many problems, however, we are interested in the action of the surface charge at some distance from the particle surface, where its detailed structure is much less influential; often moreover, only its time average is material. We must also bear in mind that an excess of one elementary charge is generally carried by a group of surface ions, as it is often impossible to point to the ion which may be called the excess-ion (except in the case of an I<sup>-</sup> ion adsorbed upon a complete crystal plane; rather an improbable case). For all these reasons, and in default of preciser data, we shall, in the following considerations, generally assume the surface charge to be homogeneous.

The second layer of the electric double layer (the outer layer) is formed by the excess of oppositely charged ions in the solution; hence, in the case of the AgI sol, by the H<sup>+</sup> ions (more general: by the counter-ions of the colloid). In consequence of their thermal motion the electric charge carried by this layer (or at least part of it) extends over a certain distance from the particle surface, and dies out gradually with increasing ionic distance (diffuse layer). Though again carried by discrete ionic charges, this charge may very often be approximated by regarding it as a continuous space charge, since, in many problems, we are again interested only in its time average. The "thickness" of this diffuse layer appears to be of colloidal dimensions; in very diluted electrolytic solutions it may be of the order of  $10^{-5}$  to  $10^{-4} cm$ ; in more concentrated solutions (especially if the counter ions are polyvalent) the extension is much less. In a dialysed AgI sol the particles are therefore smaller than the thickness of the double layer; in suspensions, especially when some electrolyte is present, the double layer extension is generally small in comparison with the size of the particles.

### § 3. The stability of lyophobic colloids

After this introduction into the properties of the electric double layer surrounding colloid particles we may now return to the problem of the stability of lyophobic colloids.

In section 1 it has been mentioned that one of the typical aspects of lyophobic colloids is the sensitivity of their stability towards electrolytes added to the sol medium. As a matter of fact, in the development of the chemistry of lyophobic colloids, the stability has been the central problem during the last half century.

According to section 2 stable lyophobic colloid systems (including suspensions) may be considered as systems containing a great number of particles each surrounded by an electric double layer. In section 2 we only considered one separate particle with the double layer surrounding it. In actual sols or suspensions, however, we are facing with an additional problem, namely that of the interaction of two or more double layers. This problem arises in the first place in concentrated systems, in which the average distance of the particles is of the same order of magnitude as the "thickness" of the double layer, or even smaller. But also in more diluted systems (sol or suspension) particles meet continually, and the stability of the colloid depends entirely on the physical result of such an encounter. This interaction problem will therefore be one of the basic problems in a theory of colloid stability.

As will be evident from the brief survey of the main experimental facts relating to the stability of lyophobic colloids, to be given in the present section, this opinion is in complete accordance with colloid chemical evidence.

In discussing colloid stability, it is necessary to distinguish between two different factors influencing this stability<sup>1</sup>.

1. A sol or suspension primarily acquires stability by the formation of a double layer of sufficient strength to prevent agglomeration. This process is called peptization and depends on the presence of small amounts of specific ions in the system.

2. Secondarily, the stability of the sol or suspension once formed can be affected and eventually completely destroyed (coagulation or flocculation) by the addition of all kinds of electrolytes to the system.

Some colloids peptize spontaneously when a finely divided substance and a liquid are brought together under suitable conditions. A stable suspension of quartz, for instance, in water, ethanol, acetone (in general: in liquids of a sufficiently electrolytic dissociating power) may be prepared by simply shaking the pure powder with one of these liquids. Some precipitates, such as  $V_2O_5$ , or a number of insoluble metal sulphides, may be brought to peptization by washing them thoroughly with pure water. In other cases, however, we know that small quan-

tities of specific electrolytes are necessary for peptization. In the case of the  $AgI$  sol, a small excess of either  $Ag^+$  or  $I^-$  is necessary to obtain stable sols; sulphides need a small excess of  $S^{2-}$  or  $SH^-$  to build up the double layer, which sometimes has to be added deliberately to the system for peptization; oxides and metals may often be peptized by  $H^+$  or  $OH^-$ . This stabilizing rôle is strictly reserved for very special ions; if these ions are not formed by the materials themselves (in the case of spontaneous peptization this occurs to such an extent that the resulting double layer is already sufficient for stability), they are, at any rate, closely related to the materials of the particles.

The inverse process, too, may occur; i.e., a sol can sometimes be coagulated by depeptization. Thus, unlike a negative  $AgI$  sol (where the peptizing  $I^-$  can be withdrawn from the sol as far as this is possible by dialysis without affecting the stability), a positively charged  $AgI$  sol can easily be brought to flocculation by dialysing the sol. Several other sols show the same behaviour. To this class of phenomena must also be reckoned the flocculation occurring when a diluted solution of  $AgNO_3$  is added to a negative  $AgI$  sol. In this case the small excess of  $I^-$  ions building up the double layer is neutralized and precipitated by the  $Ag^+$  ions added to the sol. (An excess of  $AgNO_3$ , if mixed sufficiently rapidly with the sol, would convert the negative sol into the stable positive sol, without coagulation).

In the phenomena discussed in the preceding paragraph the flocculation is actually effected by reducing the particle charge.

Usually, however, coagulation is obtained by quite different methods, in which the concentration of the peptizing or stabilizing ions is not — at any rate not purposely — changed. Indeed, coagulation in lyophobic systems is mostly effected under the influence of "indifferent" electrolytes added to the systems. On determining the amount of electrolyte necessary to bring about a practically complete coagulation under specified conditions, adapted to the type of sol under consideration, the following values were found for different sols (see p. 8 and p. 9). The corresponding concentration is called the limiting or flocculation value.

The flocculation values united in Tables I and II clearly demonstrate the well-known rule of Schulze and Hardy stating that the flocculation value is first of all determined by the valency of the ions which are oppositely charged to the particles of the sol, whereas the specific nature of these ions is far less important. The influence of the valency and the nature of the ions bearing the same charge as the particles is of subordinate importance.

For the  $AgI$ -sol, for instance, the monovalent cations flocculate at a concentration of about 140 millimols/liter, the bi-

<sup>1</sup> E. J. W. Verwey, *Chem. Rev.*, 16 (1935) 391.

TABLE I

FLOCCULATION VALUES IN MILLIMOLS/LITER FOR NEGATIVELY CHARGED SOLS

Electrolyte	As <sub>2</sub> S <sub>3</sub> -sol *	Au-sol **	AgI-sol †
LiCl	58	—	—
LiNO <sub>3</sub>	—	—	165
NaCl	51	24	—
NaNO <sub>3</sub>	—	—	140
KCl	49.5	—	—
KNO <sub>3</sub>	—	25	136
1/2 K <sub>2</sub> SO <sub>4</sub>	65.5	23	—
RbNO <sub>3</sub>	—	—	126
MgCl <sub>2</sub>	0.72	—	—
Mg(NO <sub>3</sub> ) <sub>2</sub>	—	—	2.53
MgSO <sub>4</sub>	0.81	—	—
CaCl <sub>2</sub>	0.65	0.41	—
Ca(NO <sub>3</sub> ) <sub>2</sub>	—	—	2.38
SrCl <sub>2</sub>	0.635	—	—
Sr(NO <sub>3</sub> ) <sub>2</sub>	—	—	2.33
BaCl <sub>2</sub>	0.69	0.35	—
Ba(NO <sub>3</sub> ) <sub>2</sub>	—	—	2.20
ZnCl <sub>2</sub>	0.685	—	—
Zn(NO <sub>3</sub> ) <sub>2</sub>	—	—	2.50
UO <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub>	0.64	2.8	3.15
AlCl <sub>3</sub>	0.093	—	—
Al(NO <sub>3</sub> ) <sub>3</sub>	0.095	—	0.067
1/2 Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	0.096	0.009	—
La(NO <sub>3</sub> ) <sub>3</sub>	—	—	0.069
Ce(NO <sub>3</sub> ) <sub>3</sub>	0.080	0.003	0.069
Th(NO <sub>3</sub> ) <sub>4</sub>	—	—	0.013

\* H. Freundlich, *Z. physik. Chem.*, 44 (1903) 129; 73 (1910) 385.\*\* H. Freundlich and G. Von Elissafoff, *Z. physik. Chem.*, 79 (1912) 385.  
H. Morawitz, *Kolloidchem. Beihefte*, 1 (1910) 301.† H. R. Kruyt and M. A. M. Klompe, *Kolloidchem. Beihefte*, 54 (1942) 484.

valent cations at about 2.3 millimols/liter and the trivalent cations at about 0.07 millimols/liter.

The differences between electrolytes of the same valency type are comparatively small. Generally a negative sol is flocculated by large cations at a somewhat smaller concentration than by small cations of the same valency.

Organic ions often have an exceptional position in as much as they cause flocculation in a concentration which is much lower than would correspond to

TABLE II

FLOCCULATION VALUES IN MILLIMOLS/LITER FOR POSITIVELY CHARGED SOLS

Electrolyte	Fe <sub>2</sub> O <sub>3</sub> -sol *	Al <sub>2</sub> O <sub>3</sub> -sol **
NaCl	9.25	43.5
KCl	9.0	46
1/2 BaCl <sub>2</sub>	9.65	—
KNO <sub>3</sub>	12	60
1/2 Ba(NO <sub>3</sub> ) <sub>2</sub>	14	—
K <sub>2</sub> SO <sub>4</sub>	0.205	0.30
MgSO <sub>4</sub>	0.22	—
K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub>	0.195	0.63
K <sub>3</sub> Fe(CN) <sub>6</sub>	—	0.080
K <sub>4</sub> Fe(CN) <sub>6</sub>	—	0.053

\* H. Freundlich, *Z. physik. Chem.*, 44 (1903) 151.\*\* N. Ishizaka, *Z. physik. Chem.*, 83 (1913) 97.

their valency. This exceptional behaviour is evidently connected with the abnormal adsorbability of these ions. We have mentioned this point for completeness, but in the following we will mainly consider the normal inorganic ions.

It was originally assumed that the flocculating action of these electrolytes should be explained by an adsorption of the oppositely charged ions (Freundlich's adsorption theory). This theory was a direct result of the fact that in the more primitive stage of colloid chemistry one was satisfied with the picture of the agglomeration of the particles being prevented in stable sols or suspensions by the mutual repulsion of the particle charges. Later on it was recognized, however, that in reality we are not dealing with a pure Coulomb repulsion, but with the rather different and more complicated problem of the interaction of double layers. Moreover, Freundlich's adsorption theory, and therefore the simple conception that the coagulation by electrolytes is a matter of reduction of the particle charges, could not be affirmed by exact analytical measurements<sup>1</sup>. There were even a number of experimental indications that the effect of an increase of the electrolyte concentration is generally

<sup>1</sup> H. Freundlich, K. Joachimsohn and G. Ettisch, *Z. physik. Chem.*, 141 (1929) 249.  
E. J. W. Verwey and H. R. Kruyt, *Z. physik. Chem.*, A 167 (1934) 312.

an increase instead of a decrease of the double layer charge. About ten years ago, therefore, the above naive picture of colloid stability was completely abandoned by most colloid chemists. The adsorption theory may retain part of its value in a number of exceptional cases only (for instance that of strongly adsorbable organic ions).

Summarizing this section, we may state that small amounts of specific (peptizing) electrolytes, creating the double layer, are necessary for stability. Arbitrary electrolytes bring about a flocculation of the sol; the flocculating concentration is roughly determined by the valency rule. The potential barrier preventing agglomeration of the particles is directly connected with the double layers surrounding them. Stability and coagulation, however, can only be understood on the basis of a more detailed study of the changes occurring in these double layers when the ionic spheres of the particles interpenetrate.

#### § 4. Gelation and thixotropy

The question why an electrical double layer of sufficient strength prevents the agglomeration of lyophobic particles, and the influence of electrolyte concentration upon this phenomenon, i.e., the stability problem of lyophobic colloids in the proper sense, is not the only aspect of colloid chemistry in which the problem of the interaction of two double layers plays a predominant part. Although this stability will be the main problem to be dealt with in our efforts towards a more quantitative treatment of colloid chemical questions we will also give some considerations showing that the double layer interaction is equally important for a better understanding of a number of other phenomena of considerable interest. Among them are such phenomena as gelation and thixotropy of lyophobic colloid systems, the mechanical and rheological behaviour of suspensions, and related phenomena. Some experimental facts concerning these phenomena will therefore be treated shortly in the present and the next section.

A remarkable rheological behaviour of certain colloid systems is gelation. By gelation we mean solidification of the whole colloidal system into an apparently homogeneous jelly. Gelation, therefore, differs from flocculation in that, in flocculation, the system is macroscopically separated into two phases, whereas in gelation the system remains homogeneous. One of the most striking examples of gelation is the solidification of a gelatin sol upon cooling. On the whole the phenomenon of gelation is best known for lyophilic systems, but there also exist a number of hydrophobic systems showing gelation.

In these cases gelation may be brought about by the addition

of electrolyte; and by the fact that the concentrations of electrolytes again follow the rule of Schulze and Hardy we may infer that gelation is a specific form of coagulation, or, more exactly, an intermediate stage to coagulation. Cf Table III.

TABLE III  
CONCENTRATIONS OF ELECTROLYTE IN MILLIMOLS/LITER REQUIRED TO BRING ABOUT GELATION

Electrolyte	CeO <sub>2</sub> -sol * Positively charged	Electrolyte	SiO <sub>2</sub> -sol ** Negatively charged
NaBr	5	NaCl	100
NaClO <sub>4</sub>	5	1/2 Na <sub>2</sub> SO <sub>4</sub>	100
NaCl	3.5	BaCl <sub>2</sub>	15
Na <sub>2</sub> SO <sub>4</sub>	0.15		
Na <sub>2</sub> HPO <sub>4</sub>	0.16		

\* H. R. Kruyt and Miss J. E. M. van der Made, *Rec. trav. chim.*, 42 (1923) 277.

\*\* H. R. Kruyt and J. Postma, *ibid.*, 44 (1925) 765.

These hydrophobic gels often show the phenomenon called thixotropy. In this case the system behaves like a solid for weak shearing stresses; if stirred rapidly, however, the mass turns fluid, and flows as a liquid with low viscosity; when brought to rest again viscosity increases more or less rapidly, and after some time the mass is again converted into a stiff paste or jelly.

That the formation of a thixotropic gel is an intermediate stage between stability and flocculation will be clear from the following table, which shows the concentration of electrolyte necessary for thixotropic gelation and for flocculation of an Al<sub>2</sub>O<sub>3</sub>-sol<sup>1</sup>.

TABLE IV  
CONCENTRATIONS OF ELECTROLYTE IN MILLIMOLS/LITER, NECESSARY TO OBTAIN THIXOTROPIC GELATION RESP. FLOCCULATION OF AN Al<sub>2</sub>O<sub>3</sub>-SOL (POSITIVELY CHARGED)

Electrolyte	Optimal thixotropic gelation	Flocculation
KCl	330	400
Na <sub>2</sub> SO <sub>4</sub>	3.5	5
K <sub>3</sub> Fe(CN) <sub>6</sub>	1.5	2.5
K <sub>4</sub> Fe(CN) <sub>6</sub>	1.0	2.5

<sup>1</sup> M. Aschenbrenner, *Z. physik. Chem.*, 127 (1927) 415.

Furthermore it appears that the thixotropic state can best (or perhaps only) be obtained with sols containing disc-shaped or rod-shaped particles, such as bentonite (a colloidal clay), ferric oxide, vanadium pentoxide, etc.

From these facts and from other observations it has been inferred<sup>1</sup> that a gel is a loose network of colloidal particles interconnected only at a few points, in which the dispersion medium is immobilized, because it is enclosed in the network. The fact that this very loose structure does not entirely collapse must be attributed to repulsive forces between other parts of the particles. These repulsive forces are obviously of the same nature as the forces preventing the agglomeration in the stable sol.

A completely different picture<sup>2</sup> of gelation is also conceivable. In this conception it is assumed that the particles in the gel are fixed in a more or less regular structure by long range forces, thus having no material contact at all. The large quantity of dispersion medium contained in the gel then is an immediate consequence of the long range of the forces between the particles. Although this may be the right explanation of gelation in concentrated systems of elongated particles as e.g., in concentrated suspensions of bentonite or tobacco mosaic virus (*vide infra*), it is felt that this picture when applied to more dilute systems would involve interaction at very large distances, which is unlikely.

It is possible, however, to apply a combination<sup>3</sup> of the two pictures given above to the gelation of dilute systems in assuming a local orientation and fixation of the particles by long range forces. The structures formed in this way, however, do not extend throughout the whole system, but they form a network in which the major part of the dispersion medium is enclosed. This last conception seems to be especially well suited for an explanation of the relatively weak gel forming forces in thixotropic gels.

In several cases phenomena are observed, in some respects resembling flocculation, but in which the particles retain their individual freedom, as demonstrated by their Brownian motion. The outward appearance of the systems considered here may be completely homogeneous, but an examination under the microscope or ultramicroscope reveals the existence of small spindle-shaped regions of higher concentration where the particles, which may be either small disks or thin rods, are oriented

<sup>1</sup> H. R. Kruyt, *Chimie et Industrie*, **42**, October 1939; C. F. Goodeve, *Trans. Faraday Soc.*, **35** (1939) 342.

<sup>2</sup> E. A. Hauser, *Kolloid-Z.*, **48** (1929) 57.

<sup>3</sup> W. Heller, *J. Phys. Chem.*, **45** (1941) 1203; W. Heller and G. Quimfe, *J. Phys. Chem.*, **46** (1942) 765.

J. D. Bernal and I. Fankuchen, *J. Gen. Physiology*, **25** (1941) 111.

parallel to each other. These spindle-shaped regions have been called tactoids<sup>1</sup>. In favourable cases the tactoids may coalesce to form a separate anisotropic phase of high concentration.

A very remarkable example of this behaviour is the tobacco mosaic virus sol<sup>2</sup>. Upon sedimentation this sol separates into two layers; the toplayer is a diluted sol showing streaming birefringence; in the bottomlayer X-ray investigation shows that the threadshaped protein molecules (diameter 150 Å, length 1500 Å) are arranged in a two-dimensional hexagonal close packing of parallel rods. The distance between the particles varies from zero up to 300 Å and more, depending upon the concentration of protein in the bottom layer. This distance depends also on the concentration of electrolyte in the system, and decreases with increasing concentration of electrolyte.

Distances between particles of the same order of magnitude and an analogous influence of electrolytes have been found in lipide systems<sup>3</sup>. It seems tempting to put the formation of lamellar micelles<sup>4</sup> in soap solutions in the same class of phenomena.

Similar phenomena<sup>5</sup> were observed in sols of iron oxide or tungstic acid with pronounced disk-shaped particles; optical observations show parallel orientation of the disks with a uniform spacing up to 8000 Å<sup>6</sup>.

It will be clear that in all these phenomena the interaction of the double layers surrounding the particles or protein molecules plays an important part. Obviously the particles, which have parallel orientation, are kept apart by the repulsive forces mentioned above.

### § 5. Suspensions

In most text-books on colloid chemistry not much attention is paid to the properties of suspensions. It appears, however,

<sup>1</sup> H. Zocher, *Z. anorg. allgem. Chem.*, **147** (1925) 91; H. Freundlich, *Kapillarchemie II*, 55, Leipzig 1932.

<sup>2</sup> J. D. Bernal and I. Fankuchen, *Nature*, **139** (1937) 923.

<sup>3</sup> J. D. Bernal and I. Fankuchen, *J. Gen. Physiology*, **25** (1941) 111.

<sup>4</sup> R. S. Bear, K. J. Palmer and F. O. Schmitt, *J. Cellular Comp. Physiol.*, **17** (1941) 355.

<sup>5</sup> K. J. Palmer and F. O. Schmitt, *J. Cell. Comp. Physiol.*, **17** (1941) 385.

<sup>6</sup> K. Hess and J. Gundermann, *Ber.*, **70** (1937) 1808; K. Hess, H. Kiessig, W. Philippoff, *Naturwissenschaften*, **26** (1938) 184, **27** (1939) 593, *Kolloid-Z.*, **88** (1939) 40.

J. Stauff, *Kolloid-Z.*, **89** (1939) 224.

<sup>5</sup> H. Zocher and K. Jacobsohn, *Kolloidchem. Beihefte*, **28** (1929) 167; *Kolloid-Z.*, **41** (1927) 220.

<sup>6</sup> H. Zocher *et al.*, W. Heller, *Compt. rend.*, **201** (1935) 831.

P. Bergmann, P. Löw-Beer and H. Zocher, *Z. physik. Chem.*, A **181** (1938) 301.

that the interaction of the double layers of their particles plays an important part in a number of very characteristic phenomena shown by suspensions.

Fundamentally there is no difference between sols and suspensions. The principal difference is to be found in the dimensions of the particles forming the dispersed phase. A system is called a suspension when the individual particles settle down within a few hours, whereas in a colloidal solution they may remain in suspension for days, or when the particles are small enough, practically indefinitely. Roughly the limit between suspensions and colloids is given by a particle dimension of about  $1\text{ }\mu$ . So the difference is only one of degree and not of quality, and we may expect to find the same phenomena in suspensions as are found in sols.

In the field of stability, however, suspensions do not show such a marked difference between stable and flocculated systems as do sols, for the simple reason that even the individual particles of a "stable" suspension settle down in a comparatively short time.

Nevertheless, on closer examination there appear to be very clear differences between "stable" suspensions (in which the particles retain their individual independence) and "flocculated" systems (in which the particles adhere to one another)<sup>1</sup>. These differences are shown, among other things, in the mechanical properties of concentrated suspensions and the sediments formed from them.

A highly concentrated stable suspension such as an aqueous suspension of finely ground quartz powder shows the phenomenon called dilatancy<sup>2</sup>. A dilatant system behaves like a liquid and flows easily under weak stresses; for rapid changes of its shape or large shearing stresses, however, the system hardens and offers strong resistance to deformation. On releasing the stress the system recovers its original fluid properties more or less rapidly. The same happens in many other extremely stable suspensions of the proper, very high, concentration, such as a suspension of starch in water, of  $\text{Al}_2\text{O}_3$  in methanol, etc.

On the other hand, "flocculated" systems, which may be in the flocculated state either by the addition of electrolyte or by the use of a dispersion medium unsuited to create stability (e.g., quartz in benzene), show a very marked plasticity. Against weak stresses they offer a relatively strong resistance and

<sup>1</sup> See, for example, E. J. W. Verwey, *Rec. trav. chim.*, **60** (1941) 618.

<sup>2</sup> H. Freundlich and H. L. Röder, *Trans. Faraday Soc.*, **34** (1938) 308.  
E. J. W. Verwey and J. H. de Boer, *Rec. trav. chim.*, **57** (1938) 383.

behave more or less like a solid, whereas under greater stress they can be made to flow.

Obviously in the case of dilatancy the electric double layer creates a strong repulsion between the particles upon their close approach, so that the particles are prevented from being pressed against one another, and easily slip past each other owing to the presence of the thin layer of liquid between them. Hence the system flows easily, provided the stresses are sufficiently weak to allow the liquid to flow through the capillary spaces between the particles. But when it is tried to deform the dilatant system too quickly, the liquid, flowing in the narrow capillary canals between the particles, cannot follow these movements, so that further displacements are inhibited, and the system behaves more or less like a solid.

This explanation is corroborated by the fact that the electric double layer may be substituted by a thin lubricating film<sup>1</sup>. Thus, for instance, a mixture of iron powder and a non-polar liquid, forming a dry, stiff, plastic paste, is liquefied by a trace of oleic acid, forming a strongly dilatant fluid.

In a plastic sediment the particles adhere to each other, forming a solid framework which resists weak stresses. But when greater stresses are applied to the system, the bonds between the particles are broken and the system flows as a liquid.

There is a direct connection between the properties of dilatancy and plasticity, and the density of the sediment of the suspension. The higher the stability, the smaller the volume of the sediment formed when the particles are allowed to settle. In an unstable suspension the particles stick together and form an irregular and loose building in which the formation of a close packing is prevented by the adhesion of the particles. In a stable suspension, however, the particles settle individually and form a dense sediment, because the short distance repulsion permits the easy sliding of the particles against each other. The same effect can be obtained by a lubricating film; the sedimentation volume of, e.g., finely divided iron in non-polar liquid is greatly reduced by the addition of a very small amount of oleic acid. In accordance with these volume relationships we find that the sediment from a stable suspension adheres firmly to the bottom of the vessel; that from an unstable suspension, however, can be easily redispersed by shaking.

These phenomena play an important part in many technical applications of colloidal systems, especially of suspensions, in the properties of the soil, etc.

As an example we mention, for instance, the various methods

<sup>1</sup> E. J. W. Verwey and J. H. de Boer, *Rec. trav. chim.*, **57** (1938) 383.

used in the ceramic industry to give the objects to be baked the desired shape.

According to classical ceramic methods the finely powdered material is mixed with the proper amount of liquid to form a plastic paste of appreciable mechanical strength but easily deformed; it is given the desired shape by pressing, moulding, etc. Very often the ceramic mass consists for a considerable part of clay, or, if other materials are required, contains a small amount of clay as a binder. Highly plastic clays appear to consist of extremely fine, blade-shaped, particles. Under suitable conditions such a particle form is known to favour a rigid network, as mentioned in the preceding section when we discussed the gel formation. It is found that the plasticity of these masses is decreased by the addition of such ions (for instance  $\text{OH}^-$ ) as increase the stability of the negatively charged clay particles, showing that a certain degree of flocculation and aggregation is actually responsible for the lasting deformability and the coherence of the plastic paste.

Another ceramic process starts from a suspension containing considerably larger amounts of liquid. A rather concentrated, mostly aqueous, suspension of the powdered material is poured into porous forms of absorbent material such as plaster; the porous wall rapidly absorbs the water, so that after a short time a stiff layer of the dispersed particles is formed on the inside of the form; this layer remains in the form when the rest of the suspension is quickly poured out of it. The layer is then removed from the porous form without losing its shape, and after drying it can be baked. By this method all sorts of objects (crucibles, etc.) can be made from all sorts of materials, such as clay or porcelain, but also from simple oxydic materials as aluminium oxide, zirconium oxide, etc. The suspensions used must satisfy special — in each case different — conditions with respect to particle concentration,  $p_{\text{H}}$  of the medium, electrolyte content, etc., in order to ensure all phases of the process to be successful. These require a sufficient degree of fluidity, which, for the clay suspensions, means a certain degree of stabilization. On the other hand the compilation of the particles in the whole mass must be sufficiently loose, so that the liquid can be readily sucked away from the outer layers of the fluid into the pores of the plaster form; the oxydic materials must accordingly be applied in concentrated, rather unstable suspensions. Similar conditions are required for a sufficient shrinkage, which facilitates detaching the object from the mould.

An industrial application of suspensions which is of a more recent date is the formation of a deposit on a conducting substratum by electrophoresis. This process is used, for instance, in the preparation of thin emitter layers or thin ceramic

insulating layers as applied in various types of electric discharge tubes, radio valves, etc. Other examples are the electro-deposition of rubber latex or synthetic resins; sometimes with the aim of removing the metallic form afterwards. Especially when it is necessary that the coating adheres firmly to the substratum, a depolarizer should be present in order to prevent gas formation at the electrode. This condition can often be satisfied by using an organic liquid of sufficient electrolytic dissociating power, as a dispersion medium<sup>1</sup>. It has been found that the degree of colloid chemical stability of the suspensions plays an important part in determining the conditions required for a satisfactory coating. For the formation of a deposit it is necessary, as a rule, to use stable suspensions. Although in a coagulating suspension the particles will still move towards one electrode, they are not deposited on it. Hence there is a close resemblance between the formation of a sediment by gravitation and that of a deposit by an electric field. Obviously it is essential that the particles should move individually towards the surface to be coated; in consequence of the repulsive forces acting between the particles, concentration will first be increased there up to a certain limit, the electrode being surrounded by a layer of a concentrated suspension from which the particles are finally deposited systematically on to the adherent layer on the surface. The presence of such a concentrated layer is proved by the fact that a vertical, downward flow of particles due to the higher specific gravity of this more concentrated suspension is sometimes observed just below the electrode. Since the particles are thus prevented as long as possible from agglomerating, a rather compact deposit is formed showing much greater mechanical strength than that from an unstable suspension, and adhering to the electrode when the latter is removed from the suspension<sup>2</sup>.

In the coating of the glass surface of fluorescent lamps and cathode-ray tubes with fluorescent powder this is usually applied from a suspension. In this case, too, due regard should be paid to stability conditions.

In agriculture, the density relations discussed in the above play an important part in the determination of the drainage properties of the soil. In order to promote the growth of plants the soil needs an open structure, so that water and air can circulate freely. A loose structure is maintained if the colloids of the soil are in a flocculated state. Normally the salts, especially

<sup>1</sup> J. H. de Boer, H. C. Hamaker, and E. J. W. Verwey, *Rec. trav. chim.*, 58 (1939) 662.

<sup>2</sup> H. C. Hamaker and E. J. W. Verwey, *Trans. Faraday Soc.*, 36 (1940) 180.

the bivalent  $\text{Ca}^{++}$  ion, present in the soil, keep the system flocculated. One of the great dangers of inundation by sea-water is that these salts are replaced by  $\text{NaCl}$ . As long as the high concentration of sodium chloride present in sea-water is maintained, the flocculated state is preserved and no permanent harm is done. But after reclaiming of the flooded country the sodium chloride is washed out by the rain and the colloids in the soil turn stable. Consequently they will form a dense sediment, unsuitable for plant-growth and very hard to regenerate, so that the soil is ruined for many years to come. The facts have been known for ages, but they are now understood by colloid science, and a method has been developed which considerably shortens the period of restoration. It consists in a timely addition of  $\text{Ca}^{++}$  ions (in the form of gypsum) to these soils on the basis of the prior analytical determination of the  $\text{Cl}^-$  content.

### § 6. Emulsions

In the foregoing sections we have tacitly assumed that the dispersed particles are in the crystalline or the amorphous state, and have excluded from our considerations the case where the dispersed material is a liquid, as in emulsions. The reason is a fundamental difference between the primary stability conditions of emulsions and of "suspensoids". We have seen that many insoluble or slightly soluble substances can be peptized in the proper liquids, either spontaneously or with the aid of small amounts of special electrolytes. Under such conditions, however, it is impossible to obtain a stable emulsion (with the exception of the mercury sol, but here we are dealing with a very special case owing to the metallic properties of the dispersed phase). The preparation of an emulsion necessitates the addition of an emulsifier<sup>1</sup>. Various organic electrolytes containing highly adsorbable ions (salts of the higher fatty acids, the naphthenic acids, etc., or lyophilic colloids), or all sorts of finely divided solids (graphite,  $\text{Fe}_2\text{O}_3$ , etc.), may function as such.

This behaviour of emulsions and the effect of these emulsifying agents has been explained in terms of the very special properties of the electric double layer at the interface of two liquids. We return to this point later on when discussing the theory of the double layer.

The stability of an emulsion, once formed, towards electrolytes added to the system shows close resemblance to that of sols or suspensions of solid particles. In this respect emulsions may be compared with normal lyophobic colloids. Accordingly

<sup>1</sup> The very dilute oil-in-water hydrosols, obtained by pouring an alcoholic solution of the oil into the water, are sometimes more or less stable; it is probable that these sols are peptized by a capillary-active impurity ion.

in many cases considerations given for the latter may be applied equally to the case of emulsions.

### § 7. Van der Waals-London attraction forces

From the various phenomena discussed in the preceding section we may conclude that the forces acting between the particles owing to the interaction of their double layers are not the only forces to be considered in order to understand the physical aspects of colloids and suspensions. Several phenomena suggest the presence of long-range attractive forces, and the agglomeration of the particles in a rapidly coagulating sol indicates that under some conditions there are attracting forces prevailing for all particle-distances.

In 1932 London<sup>1</sup> gave a quantum-mechanical explanation of the non-polar Van der Waals forces, the weak attracting forces acting between all molecules and responsible for at least part of the deviations from the ideal gas laws. These universal attracting forces are explained, according to a first approximation of this theory, as second order forces between neutral atoms, the attraction being due to the polarization of one atom by the fluctuations of the charge distribution in a second atom, and *vice versa*. The theory shows that these forces may be assumed, as a further approximation, to be purely additive, i.e., each atom attracts all other atoms, and is attracted by all. Hence it is assumed that these forces act independently of the presence of other atoms, and are therefore not influenced by the medium through which they are transmitted<sup>2</sup>. Because of this additive character of these forces the attraction between two colloidal particles containing millions of atoms will be appreciable, although the attracting force between two atoms is rather weak. According to the theory the force between two atoms decreases with the seventh power of their mutual distance, and therefore has rather a short range. In consequence of the collaboration of all atoms of one particle, however, the attracting force between two particles decreases much more slowly with the particle distance. Long-range attractive forces, which under

<sup>1</sup> F. London, *Z. f. Physik*, 63 (1930) 245.

<sup>2</sup> It has been urged by I. Langmuir, *J. chem. phys.*, 6 (1938) 893, in a paper with which we will be dealing extensively later on, that this assumption is very improbable. It may be stated, however, that it cannot be far from the truth. If the two atoms or molecules considered are far away from each other, and many other molecules between them, the mutual polarization can be considered to act through a continuum with a definite dielectric constant. As the fluctuating dipoles are due to rapid electronic motion we need only to consider the electronic polarization of the medium. Hence in a condensed phase, with a refractive index of about 1.4, the attracting forces are maximally reduced by a factor 2 in consequence of the presence of other molecules or atoms. As the theory so far gives only the order of magnitude of these forces, it is hardly necessary to dwell upon this correction.

favourable conditions may outweigh the effect of repulsive forces, may therefore very well be explained on the basis of these Van der Waals-London forces<sup>1</sup>.

### § 8. The interaction of colloidal particles

A few years after the paper of London, the opinion was formed that a complete picture of the force action between colloidal particles must be obtainable on the basis of the double layer interaction combined with the Van der Waals-London interaction (Kallmann and Willstätter<sup>2</sup>, J. H. de Boer<sup>3</sup>). This problem, and, more particularly, that of the interaction of two particles, have been thoroughly investigated by Hamaker<sup>4</sup>. Following de Boer, Hamaker tried to describe all colloid chemical phenomena in terms of potential curves, i.e., curves giving the potential energy of two particles with respect to each other (as a function of their distance). This potential energy consists of two parts: (a) a negative one due to the Van der Waals-London potential, and (b) a contribution derived from the interaction of the two double layers, which may obviously be positive since the corresponding repulsion is sufficient under favourable conditions to exceed the Van der Waals-London attraction and prevent the agglomeration. Hamaker showed that the total potential and a repulsive potential are, at any rate qualitatively, explanatory of various colloid chemical aspects. He also gave quantitative calculations for the Van der Waals-London attraction between two spherical particles, between two parallel plates, etc., investigated the Van der Waals-London potential of two such particles immersed in a medium, and particles consist of the same material. As to the potential due to the double layer interaction, however, he confined himself to very simple assumptions which are, at best, rather rough approximations.

Some years later (about 1939) the problem of the interaction of colloidal particles was again investigated independently

<sup>1</sup> With the restriction that the London-theory should not be applied up to very large distances, as for these distances deviations from the inverse seventh power law occur. It will be explained in Chapter VI that it is necessary to apply a relativistic correction to the theory of London resulting in a comparatively rapid dying out of the London-van der Waals attraction when the distance between the particles becomes of the order of  $10^{-6}$  cm.

<sup>2</sup> H. Kallmann and M. Willstätter, *Naturwissenschaften*, **20** (1932) 952.

<sup>3</sup> J. H. de Boer, *Trans. Faraday Soc.*, **32** (1936) 21.

<sup>4</sup> H. C. Hamaker, *Rec. trav. chim.*, **55** (1936) 1015; **56** (1937) 3, 727.

by several authors using very different ways of treatment. We only mention here the work of Bergmann, Löw-Ber and Zocher<sup>1</sup>, of Derjaguin,<sup>2</sup> of Levine and Dube<sup>3</sup> and of Corkill and Rosenhead,<sup>4</sup> all of whom studied, as Hamaker had done, the problem of two particles screened off by their double layers. In the paper by Langmuir<sup>5</sup>, mentioned earlier, this problem of two particles is only considered as a limiting case, and the theoretical discussion centres more upon the whole of the charges (particle charges and ionic charges in the intermediate liquid) forming together the colloidal system.

The results of these authors are conflicting on some essential points, even on the important question, of whether the double layer interaction produces attraction or repulsion. A discussion has been started in the communications to the Symposium on the Electrical Double Layer, which the Faraday Society had intended to hold at Cambridge in September 1939. But this discussion has not removed the contradictions.

We have investigated the same problem extensively and believe that these difficulties are removed to a large extent by the considerations given in the following chapters. The discussion of the papers of the authors mentioned above has been concentrated in an Appendix, in which it is shown in greater detail how the difficulties may be solved and the divergent treatments and results made to conform with one another.

The publication of our work was prevented by war conditions, except for a few preliminary papers, partly in the Dutch language<sup>6,7</sup>.

<sup>1</sup> P. Bergmann, P. Löw-Ber and H. Zocher, *Z. physik. Chem.*, A **181** (1938) 301.

<sup>2</sup> B. Derjaguin and M. Kussakow, *Acta physicochim. U.S.S.R.*, **10** (1939) 25, 153.

B. Derjaguin, *ibid.*, **10** (1939) 333.

B. Derjaguin, *Trans. Faraday Soc.*, **36** (1940) 203.

<sup>3</sup> S. Levine, *Proc. Roy. Soc.*, A **170** (1939) 145, 165; *J. Chem. Phys.*, **7** (1939) 831.

S. Levine and G. P. Dube, *Compt. rend.*, **208** (1939) 1812; *Trans. Faraday Soc.*, **35** (1939) 1125, 1141; **36** (1940) 215; *Philos. Mag.*, (7) **29** (1940) 105; *J. Phys. Chem.*, **46** (1942) 239.

<sup>4</sup> A. J. Corkill and L. Rosenhead, *Proc. Roy. Soc.*, A **172** (1939) 410.

<sup>5</sup> I. Langmuir, *J. Chem. Phys.*, **6** (1938) 893.

<sup>6</sup> E. J. W. Verwey, *Trans. Faraday Soc.*, **36** (1940) 192; *Chem. Weekblad*, **39** (1942) 563; *Contribution to a symposium held at Utrecht by the Nederlandsche Chemische Vereeniging on July 3rd and 4th 1944*. See also *Philips Research Reports*, **1** (1945) 33.

<sup>7</sup> (Note added in proof) Meanwhile part of the work has been reviewed in: E. J. W. Verwey, *J. Phys. and Colloid Chem.*, **51** (1947) 631; E. J. W. Verwey and J. Th. G. Overbeek, *Trans. Faraday Soc.*, **43** (1947) (in press).

We now apply Poisson's equation, stating that in every point of the space charge. ( $\psi$  = electrical potential;  $\rho$  = charge density;  $\epsilon$  = dielectric constant of the medium;  $\Delta$  = Laplace operator)  $\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$

$$\Delta \psi = -\frac{4\pi\rho}{\epsilon} \quad (1)$$

where both  $\psi$  and  $\rho$  are a function of the coordinates  $x$ ,  $y$  and  $z$ .

This space charge is formed, if the surface charge is thought of as positive, by an excess of negative ions, as the negative ions are attracted by the surface charge and accumulated in the neighbourhood of the particle wall, while inversely, the positive ions, are repelled and pushed away from the wall.

The effect of these electric forces is counteracted by the thermal motion of the ions, which gives the liquid charge layer its spatial extension ("diffuse" layer). In order to take this thermal equilibrium into account the theory makes the implicit assumption that the average concentration of these ions at a given point can be calculated from the average value of the electric potential at the same point with the aid of Boltzmann's theorem:

$$\left. \begin{aligned} n_- &= n \cdot \exp(v_- e \psi / kT) \\ n_+ &= n \cdot \exp(-v_+ e \psi / kT) \end{aligned} \right\} \quad (2)$$

( $n$  is the number of ions per  $\text{cm}^3$  far from the surface, where  $\psi = 0$ ,  $e$  is the elementary charge or minus the charge of the electron and  $v_+$  and  $v_-$  are the valencies of the positive and negative ions). This method of determining  $n_-(x, y, z)$  and  $n_+(x, y, z)$  from  $\psi(x, y, z)$  is correct only for such small values of the electric potential  $\psi(x, y, z)$  that it is permissible to develop the exponential form according to a Mac Laurin series and to break off after the linear term. For in that case there is a linear relation between  $\psi$  and  $\rho$ . For larger values of the electric potential the latter is no longer true, and the determination of the mean value of  $n(x, y, z)$  from  $\psi(x, y, z)$  as indicated is then, strictly speaking, not allowed (Kirkwood<sup>1</sup>). It can be proved, that for the double layer of large particles bearing many elementary charges the error made thereby is not large, providing that, in the close neighbourhood of the surface, ionic concentration does not rise to values at which the deviations from the Debye-Hückel limiting laws become considerable (Casimir<sup>2</sup>). In most colloidal systems this condition

## II. DISTRIBUTION OF THE ELECTRIC CHARGE AND POTENTIAL IN THE ELECTRO-CHEMICAL DOUBLE LAYER

### § 1. Fundamentals

The theory of the electric or electro-chemical double layer, generally present at a phase boundary if one of the phases is a solution containing free ions, was developed already many years ago.

As considered in more detail in § 5 of this chapter, the double layer is a result of an unequal distribution of positive and negative ions between both phases. Nevertheless, as stated in Chapter I, § 2, the ionic nature of both charge layers is generally neglected to some extent by basing the theory on the simplifying assumption of continuous charges in both layers. In most colloid systems we have to do with solid particles. In that case it is customary to assume that one charge layer is a homogeneous surface charge; an approximation which will be better in the case of metallic particles than in that of polar crystals. The case of an emulsion, where both charge layers are present in a liquid phase, needs separate consideration. Furthermore, the solid particle is generally assumed to have either a plane surface or a spherical surface. The charge in the solution surrounding the particle extends, as we have seen, some distance into the liquid phase, as it is carried by dissolved ions. It is equally thought of as distributed homogeneously in a direction tangential to the particle surface. Hence it is assumed to be only a function of the normal coordinate, as a continuous space charge gradually decreasing in the direction of the normal on the surface.

A first approximative theory for the electro-chemical double layer was given by Gouy<sup>1</sup>, Chapman<sup>2</sup>, and Debye and Hückel<sup>3</sup>. In this theory the average charge distribution and the corresponding electric potential function have been computed on the basis of a number of further simplifying assumptions, one of which is that the ions are point charges of negligible dimensions. Hence, if we suppose the surface charge to be in the plane  $x = 0$  (or for spherical particles with radius  $a$  in the sphere  $r = a$ ), the space charge extends between  $x = 0$  (or  $r = a$ ) and infinity.

<sup>1</sup> G. Gouy, *J. physique*, (4) 9 (1910) 457; *Ann. d. phys.*, (9) 7 (1917) 129.

<sup>2</sup> D. L. Chapman, *Philos. Mag.*, (6) 25 (1913) 475.

<sup>3</sup> P. Debye and E. Hückel, *Physik. Z.*, 24 (1923) 185; 25 (1924) 97.

<sup>1</sup> J. G. Kirkwood, *J. Chem. Phys.*, 2 (1934) 767.

<sup>2</sup> H. B. G. Casimir, *Contribution to a symposium held at Utrecht by the Nederlandsche Chemische Vereeniging on July 3d and 4th 1944*.

will approximately be satisfied; in some cases, however, it should be borne in mind that eq. (2) has only a limited validity.

The value of  $\varphi(x, y, z)$  may be obtained directly from eq. (2), as it is given by the local excess of ions of one sign. In order to simplify the formulae we will here introduce the restriction of considering only solutions containing ions of one valency, the ions being assumed to have originated in a symmetrical electrolyte (or a mixture of electrolytes of the same valency type), and we therefore write  $v_+ = v_- = v$ . This restriction is justified by the circumstance that both the theory for a single double layer (see at the end of § 2) and the colloid chemical facts prove the minor importance of the ions having the same charge as the colloid particles, and it has the advantage of considerably reducing the mathematical difficulties when we proceed to the case of two interacting double layers. Eq. (2) may then be written:<sup>1</sup>

$$\rho = ve(n_+ - n_-) = -2nve \sinh(v\psi/kT) \quad (2a)$$

If the electric potential is so small that  $ve\psi/kT \ll 1$ , and  $\exp(v\psi/kT)$  may be replaced by  $1 + ve\psi/kT$ :

$$\rho = -2ne^2v^2\psi/kT \quad (2b)$$

The latter expression is the linear relation referred to above, existing between  $\rho$  and  $\psi$  for small values of  $\psi$ .

Hence we now have an expression for the charge density which may be inserted into eq. (1), when we obtain the fundamental differential equation:

$$\Delta\psi = \frac{8\pi n ve}{\epsilon} \sinh(v\psi/kT) \quad (3)$$

For small values of  $\psi$  this equation simplifies to

$$\Delta\psi = \frac{8\pi n e^2 v^2 \psi}{\epsilon k T} = \kappa^2 \psi \quad \left. \begin{array}{l} \\ \text{with: } \kappa^2 = \frac{8\pi n e^2 v^2}{\epsilon k T} \end{array} \right\} \quad (4)$$

Equation (4) is the well known starting point in the theory of Debye and Hückel for strong electrolytes (calculation of the electric potential in the ionic atmosphere around an ion). However, in the close neighbourhood of a colloid particle, where  $ve\psi/kT$  may be of the order  $5v$  or  $10v$ , eq. (4) is a very poor

<sup>1</sup>  $\sinh a = \frac{e^a - e^{-a}}{2}$ ;  $\cosh a = \frac{e^a + e^{-a}}{2}$ ;  $\tanh a = \frac{e^a - e^{-a}}{e^a + e^{-a}}$ .

approximation. For the double layer in colloid systems therefore we should preferably apply the complete differential equation (3).

It may seem rather surprising that eq. (4) has, nevertheless, often been used as a starting point in colloid chemical problems. We may observe, however, that one was more or less forced to use the simple equation for the double layer surrounding a spherical particle, because of the mathematical difficulties involved in the application of (3) to this case. And these difficulties grow into nearly unsurmountable obstacles when we proceed to the interaction of two such double layers. Fortunately, the application of eq. (4) proves to give the smallest deviations in the case where the spherical double layer theory has its best side, i.e. that of a small particle imbedded in an extensive, strongly diffuse, double layer. We shall return to this point later on. Inversely, it means that the use of eq. (4) meets with the strongest objections for a plane double layer. A serious drawback of this equation is that it contains both positive and negative ions in a symmetrical way, and cannot therefore explain the outstanding colloid chemical fact of the predominating influence of oppositely charged ions upon the double layer.

## § 2. Theory of the flat double layer

For a flat double layer,  $\psi$  is only a function of  $x$  (the normal co-ordinate), and  $\Delta\psi$  may be replaced by  $d^2\psi/dx^2$ . By introducing the substitutions:

$$y = ve\psi/kT \quad z = ve\psi_0/kT \quad \kappa^2 = \frac{8\pi n e^2 v^2}{\epsilon k T} \quad \text{and} \quad \xi = zx$$

the fundamental differential equation (3) is brought into the simple form<sup>1</sup>

$$\frac{d^2y}{d\xi^2} = \sinh y, \quad (3')$$

from which, considering the boundary conditions ( $y = 0$  and  $dy/d\xi = 0$  for  $\xi = \infty$ ), we obtain, after integrating once:

$$\frac{dy}{d\xi} = -\sqrt{2} \cosh y - 2 = -2 \sinh \left( \frac{y}{2} \right) \quad (5)$$

<sup>1</sup> We here follow a paper by E. J. W. Verwey and K. F. Niessen, *Philos. Mag.*, (7) 28 (1939) 435. A similar derivation has been given by A. J. Rutgers and Ed. Verlende, *Proc. Acad. Sci. Amsterdam*, 42 (1939) 71.

and after integrating a second time (boundary condition  $\psi = \psi_0$  or  $y = z$  for  $\xi = 0$ ):

$$e^{y/2} = \frac{e^{z/2} + 1 + (e^{z/2} - 1)e^{-\xi}}{e^{z/2} + 1 - (e^{z/2} - 1)e^{-\xi}} \quad (6)$$

In order to obtain these solutions we first write the differential equation (3')

$$2 \frac{d^2y}{d\xi^2} = e^y - e^{-y} \quad \text{or} \quad 2 \frac{dy}{d\xi} \cdot \frac{d^2y}{d\xi^2} = (e^y - e^{-y}) \cdot \frac{dy}{d\xi}$$

whence:  $\left(\frac{dy}{d\xi}\right)^2 = e^y + e^{-y} + C_1$

The constant  $C_1$  is obviously, for one single double layer (for  $\xi = \infty$  and therefore  $y = 0$  we have  $dy/d\xi = 0$ ):

$$C_1 = -2,$$

and we find (with the minus sign before the square root, since for positive values of  $y$  the derivative  $dy/d\xi$  is negative (cf. Fig. 1) if  $x$  and  $\xi$  are counted positive from the surface into the bulk of the solution):

$$\frac{dy}{d\xi} = -\sqrt{e^y + e^{-y} - 2} = -(e^{y/2} - e^{-y/2})$$

or:

$$\frac{dy}{e^{y/2} - e^{-y/2}} = -d\xi$$

or substituting  $a = e^{y/2}$ :

$$\frac{2da}{a^2 - 1} = \frac{da}{a - 1} - \frac{da}{a + 1} = d \ln(a - 1) - d \ln(a + 1)$$

Hence the integration yields:

$$\ln \frac{e^{y/2} - 1}{e^{y/2} + 1} = -\xi + C_2$$

The boundary condition  $y = z$  for  $\xi = 0$ , determines the value of  $C_2$

$$C_2 = \ln \frac{e^{z/2} - 1}{e^{z/2} + 1}$$

Inserting this value of  $C_2$  we obtain eq. (6).

Equation (6), giving the electric potential in the solution as a function of the distance from the plane surface, though at first sight rather complicated, has roughly a simple exponential form, falling from  $y = z$ , or  $\psi = \psi_0$  at the surface to  $\psi = 0$  for  $x = \infty$ . The character of (6) may be seen more clearly by considering a few approximations; it may be simplified for a number of special cases.

(a)  $z \ll 1$  (at room temperature, in aqueous solution, identical with  $v\psi_0 \ll 25$  millivolts); in this case we simply have (also obtainable directly from eq. (4)):

$$y = ze^{-\xi} \quad \text{or} \quad \psi = \psi_0 \cdot e^{-\kappa x} \quad (7)$$

For such small values of  $z$ , the quantity  $1/z$ , therefore, obviously has the significance that for this distance ( $\kappa x = 1$ ) the electric potential, falling off purely exponentially in this case, has reached the  $1/e$  fraction of its value at the wall. The centre of gravity of the space charge also coincides in this simple case with the plane  $\kappa x = 1$  or  $x = 1/\kappa$ , and the characteristic length of Debye ( $= 1/\kappa$ ) may then be called the "thickness" of the diffuse layer.

(b)  $z \gg 1$ . In this case the initial slope of the potential curve may be read from the approximation valid for small values of  $\xi$ :

$$y = z - e^{z/2} \cdot \xi \quad (8)$$

from which we see that this slope increases rapidly with increasing values of  $z$ .

A very useful approximative equation is obtained for large values of  $x$  ( $\xi \gg 1$ ); in that case (6) can be simplified to:

$$y = 4 \cdot e^{-\xi} \quad \text{or} \quad \psi = \frac{4kT}{ve} e^{-\kappa x} \quad (9)$$

Hence the outer part of the electrical potential curve again has a purely exponential form (just as, in case (a), where  $z \ll 1$ , for every value of  $x$ ), and it is noteworthy that this exponential "tail" appears to be, for these large values of  $z$ , independent of  $z$ . If extrapolated towards  $x = 0$ , this exponential part of the curve appears to start at  $z = 4$ ; hence for monovalent ions in the solution the curve seems to come from the point  $\psi_0 = 100$  millivolts; for bivalent ions, from  $\psi_0 = 50$  millivolts, etc.; for equal values of  $\kappa x$  the electric potential in the tail is therefore, at all points in the second case, half the value for the first case, etc.

(c)  $z$  arbitrary;  $\xi \gg 1$ . A somewhat better approximation, demonstrating simultaneously the transition between case (a) and case (b), may be derived for arbitrary values of  $z$  and great distances. Eq. (6) may also be written:

$$y = 2 \ln \frac{1 + \gamma \cdot e^{-\xi}}{1 - \gamma \cdot e^{-\xi}} \quad \text{with: } \gamma = \frac{e^{z/2} - 1}{e^{z/2} + 1},$$

and may therefore be simplified for  $\xi \gg 1$  to

$$y \approx 2 \ln(1 + 2\gamma \cdot e^{-\xi}) \approx 4\gamma e^{-\xi}, \quad (10)$$

an expression which, for small values of  $z$ , again gives eq. (7), for great values of  $z$ , eq. (9). This equation is especially useful as in colloid chemical problems  $z$  is generally greater than 1, but rarely very great; in that case the quantity  $\gamma$  will be slightly smaller than 1, so that the outer exponential part is only slightly dependent on the value of  $z$ .

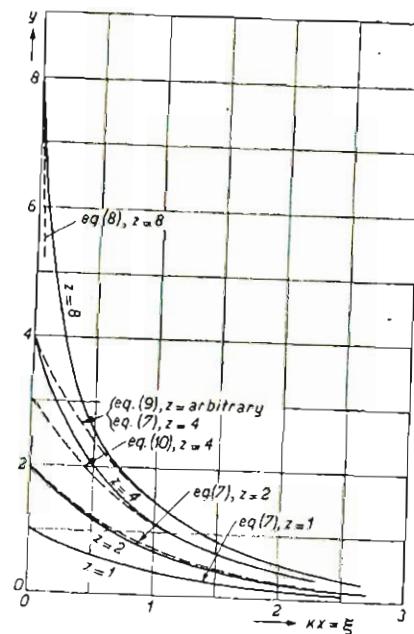


Fig. 1. Electric potential function,  $y(\xi)$ , in a diffuse charge layer of an electrochemical double layer according to the theory of Gouy-Chapman. Curves are given for  $z = 8$ ,  $z = 4$ ,  $z = 2$  and  $z = 1$  ( $z = ve \psi_0/kT$ ;  $y = ve \psi/kT$ ;  $\xi = xx$ ). Dotted lines: approximative equations for  $z \ll 1$  (eq. (7));  $z \gg 1$  and  $\xi \ll 1$  (eq. (8));  $z \gg 1$  and  $\xi \gg 1$  (eq. (9)); and  $z$  arbitrary and  $\xi \gg 1$  (eq. (10)).

Fig. 1 gives a survey of the electric potential function for a number of  $z$  values. At the same time it contains (dotted lines) curves corresponding to the approximations (7), (8), (9) and (10). We see that the simple formula (9) is applicable, for most practical purposes, to  $z \geq 8$  and  $\xi \geq 1$ . For smaller values of  $z$  (e.g.,  $z = 4$ ) it is preferable to resort to eq. (10), which appears to be an equally good approximation in the region  $\xi \geq 1$ .

The approximation for small values of  $z$  which is still very good for  $z = 1$  shows marked deviations for  $z > 2$ .

As expressed in eq. (10), the tail of the electric potential curve approaches asymptotically, with increasing values of  $z$ , the simple curve corresponding to eq. (9).

The influence of the valency of the ions upon the electric potential curve should be considered in some detail. Fig. 1 holds for

$$\psi_0 = \frac{25.6}{v} \cdot z \text{ millivolts}$$

(corresponding to  $T = 298^\circ \text{ K}$ ); hence the curve  $z = 8$  holds, for monovalent ions, for  $\psi_0 = 205$  millivolts; for bivalent ions, for  $\psi_0 = 102.5$  millivolts, etc. Furthermore, the quantity  $z$  is proportional to the valency  $v$ . Hence for bivalent ions the exponential tail decreases twice as rapidly with the distance as for monovalent ions. From this we see that substitution of monovalent ions by the same molar amount of bivalent ions in the solution lowers the electric potential at a given distance from the surface, for two reasons. If, for instance, the surface potential is 205 millivolts, the transition to  $v = 2$  implies that we must now use the curve  $z = 16$  instead of  $z = 8$ , which lowers the electric potential for equal, large values of  $z$  by a factor 2. For equal values of  $x$  the increase of  $z$  gives another decrease of the electric potential (in the outer part of the curve by a factor  $e^{zx}$ ). It should be noted that this is true only for large values of  $z$ ; the equation for  $z \ll 1$  gives, in the same case, only a decrease of the potential due to the increase of  $z$  in the exponent. In fact, as stated before, the approximation for small values, if used outside of its validity region, accounts insufficiently for the effect of valency.

The influence of the electrolyte concentration is expressed entirely by the corresponding variation of  $z$ ; this quantity is proportional to  $\sqrt{n}$ . In consequence of an increase in ionic concentration by a factor 10, the  $\psi(x)$  curve is concentrated more closely to the wall by a factor  $\sqrt{10}$  (the same value of the potential is now reached at a distance  $\sqrt{10}$  times smaller). The extension of the electric double layer for various ionic concentrations is shown in table V (c expressed in moles/liter):

TABLE V  
EXTENSION OF THE DOUBLE LAYER FOR DIFFERENT CONCENTRATIONS  
AND VALENCIES

c	monovalent ions		bivalent ions	
	1/z	1/z	1/z	1/z
$10^{-5}$	$10^{-5} \text{ cm.}$		$0.5 \times 10^{-5} \text{ cm.}$	
$10^{-3}$	$10^{-6} \text{ cm.}$		$0.5 \times 10^{-6} \text{ cm.}$	
$10^{-1}$	$10^{-7} \text{ cm.}$		$0.5 \times 10^{-7} \text{ cm.}$	

For moderate and large values of  $z$ , it is true, the centre of gravity of the diffuse charge is nearer to the surface than the plane  $x = 1/z$ ; but, as may be seen from Fig. 1, the quantity  $1/z$  is still a rough measure of the "thickness" of the double layer.

It may be stated conclusively that an increase in the valency of the ions and an increase in their concentration have a similar effect upon the "diffuse" layer, viz., a more rapid decay of the electric potential, and, therefore, a contraction of the diffuse layer, so that the two charge layers come more closely together and the charge in the solution becomes less diffuse.

We are here faced with the question of the distribution of the charges, which will now be considered in more detail. Quantitatively, the electric potential  $\psi$  and the charge density  $\rho$  are directly connected according to eq. (2), and more especially eq. (2a). Since the sinus hyperbolicus increases, for moderate and large values of  $y$ , almost exponentially with increasing  $y$ , we see that the charge density in the diffuse layer falls off still more rapidly with increasing distance from the surface than the electric potential. This is illustrated in fig. 2, on a modest scale, for the still rather low value  $z = 3$ . We also give the local ionic concentrations  $n_-$  and  $n_+$  as a function of  $x$ , showing that, already for this rather low value of  $z$ , the space charge (proportional to  $n_- - n_+$ ) is almost entirely a result of the accumulation of the negative ions in the neighbourhood of the wall. This means that there is already a considerable difference from the state of affairs which would be obtained by using the approximative equations for small values of  $z$ . For in that case there would be a linear relation between  $\psi$  and  $\rho$ , and the increase of  $n_-$  would equal the decrease of  $n_+$ . This throws a fresh light upon the origin of the inadequacy of the approximative equations for small potential as soon as  $z$  exceeds the value 1; these equations do not account for the great discongruity existing, even for moderate values of the potential between the parts played by the positive and the negative ions, respectively.

The total charge of the double layer (i.e., the surface charge per  $cm^2$ ,  $\sigma$ , or minus the charge of 1  $cm^2$  diffuse layer) may be obtained direct from the potential function. To this end we make use of the general equation

$$\sigma = - \int_0^\infty \rho dx = \frac{\epsilon}{4\pi} \int_0^\infty \frac{d^2\psi}{dx^2} dx = - \frac{\epsilon}{4\pi} \left( \frac{d\psi}{dx} \right)_{x=0} \quad (11)$$

from which we see that  $\sigma$  is proportional to the initial slope of the electric potential in the diffuse layer. The latter quan-

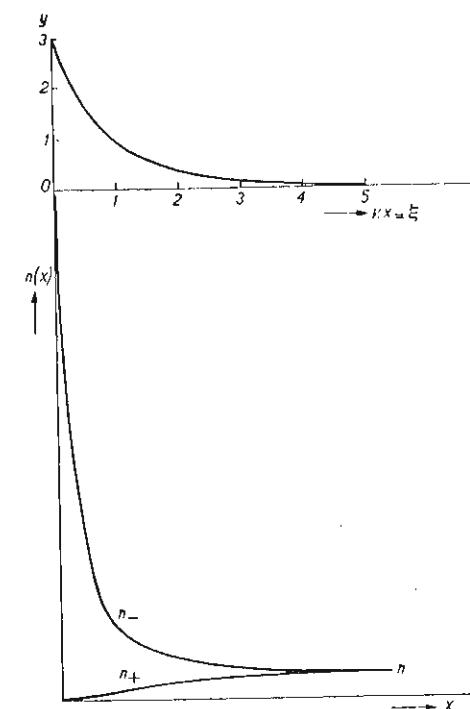


Fig. 2. Electric potential function,  $y(\xi)$ , and local concentrations of positive and negative ions,  $n_+(x)$  and  $n_-(x)$ , in the neighbourhood of a positively charged surface, for a double layer potential  $\psi_0 = \frac{76.8}{v}$  millivolts ( $z = 3$ ).

tity may be read from eq. (5) by rewriting this relation:

$$\begin{aligned} \frac{d\psi}{dx} &= - \frac{xkT}{ve} \sqrt{2 \cosh y - 2} = \\ &= - \sqrt{\frac{8\pi nkT}{\epsilon}} \cdot \sqrt{2 \cosh y - 2} = - \sqrt{\frac{32\pi nkT}{\epsilon}} \cdot \sinh \left( \frac{y}{2} \right) \end{aligned} \quad (5a)$$

and therefore

$$\begin{aligned} \left( \frac{d\psi}{dx} \right)_0 &= - \sqrt{\frac{8\pi nkT}{\epsilon}} \cdot \sqrt{2 \cosh z - 2} = \\ &= - \sqrt{\frac{32\pi nkT}{\epsilon}} \cdot \sinh \left( \frac{z}{2} \right) \end{aligned} \quad (5b)$$

and accordingly we find, by inserting this into eq. (11),

$$\sigma = \sqrt{\frac{n\varepsilon kT}{2\pi}} \sqrt{2 \cosh z - 2} = \sqrt{\frac{2n\varepsilon kT}{\pi}} \cdot \sinh\left(\frac{z}{2}\right) \quad (12)$$

This last equation simplifies, for small values of  $z = ve\psi_0/kT$ , to

$$\sigma = \frac{\varepsilon z}{4\pi} \cdot \psi_0 = \sqrt{\frac{n\varepsilon}{2\pi kT} \cdot ve\psi_0} \quad (13)$$

For small double layer potentials, therefore, the double layer behaves as an electric condenser ("plate distance"  $1/z$ ) with a constant capacity (i.e., independent of the potential). For larger  $z$  values, however, we find (in accordance with what was said above about the distribution of positive and negative ions in the neighbourhood of the surface) that the relation between  $\sigma$  and  $\psi_0$  is no longer a linear one, but that  $\sigma$  increases more rapidly with the double layer potential  $\psi_0$ . The capacity of the double layer therefore, according to eq. (12), increases considerably with increasing double layer potential, because of an increasing accumulation of the diffuse charge in the neighbourhood of the wall.

Similar changes in the charge distribution occur if we increase ionic concentration or the ionic charge. From (12) we read that, for a given value of the double layer potential, the charge is proportional to  $\sqrt{n}$ . An increase of the ionic charge, on the other hand, gives a considerable increase of the double layer charge: going from  $v = 1$  to  $v = 2$  the charge is increased by a factor 2 for small values of  $\psi_0$ , and by a much larger factor for larger values of  $\psi_0$ .

We have investigated thus extensively, the properties of the double layer according to the Gouy-Chapman equations, because this theory will be our starting point in the following chapters. We have paid special attention to the fallacies of the approximation for small potentials in this case, for the reason that it has often been used in treating colloid chemical problems. The work of Derjaguin, mentioned earlier, on the interaction of two flat double layers, for instance, is based on these simple equations. From what has been said about this approximative theory of the double layer it follows that it cannot give any satisfactory results.

A rectification of the theory, allowing for the individual properties of the ions, including their finite dimensions, will be treated of in § 5.

In the equations derived in sections 1 and 2 we have simplified by assuming that the electrolyte is a symmetrical one ( $v_+ = v_- = v$ ). This was justified by the remark that the valency of the ion carrying the same charge as the surface

has only a minor influence upon the distribution of the charge and the potential in the double layer. This can be proved in the following way:

In the general case that  $v_+ \neq v_-$ , eq. (2a) reads:

$$\rho = e(v_+ n_+ - v_- n_-)$$

It is now convenient to introduce the equivalent concentration  $c$ , the number of ion equivalents per  $\text{cm}^3$ :

$$v_+ n_+ = N c_+ \quad \text{and} \quad v_- n_- = N c_-$$

in which  $N$  is the Avogadro number, as for  $x = \infty$   $c_+$  and  $c_-$  are identical ( $= c$ ), which is no longer true in this case for the ionic concentrations. Applying again Boltzmann's theorem (but now to the equivalent concentrations) we obtain:

$$\rho = N c (\exp(-v_+ e\psi/kT) - \exp(v_- e\psi/kT)) \quad (2a')$$

If  $\psi$  is negative, and  $\rho$  therefore positive, we see that as soon as the absolute value of  $v_- e\psi/kT$  is larger than 2 the influence of the second term containing the valency of the negative ions becomes considerably smaller than that of the first term.

This may be illustrated by the relation between the charge of the double layer,  $\sigma$ , and the surface potential,  $\psi_0$ , which now becomes

$$\sigma = \sqrt{\frac{N c k T}{2\pi}} \cdot \sqrt{\frac{1}{v_+} (\exp(-v_+ e\psi_0/kT) - 1) - \frac{1}{v_-} (\exp(v_- e\psi_0/kT) - 1)} \quad (12')$$

To this end we consider, for instance, a double layer for which  $\psi_0 = -51.2$  millivolts, and calculate, with the last equation for different values of  $v_+$  and  $v_-$ , the equivalent concentrations leading to the same value of  $\sigma$  (or the same value of the double layer capacity). Choosing arbitrarily the concentration for I-1 valent electrolytes to be 50 millieq. per l, we readily find the values for other types of electrolytes from

$$c \left\{ \frac{1}{v_+} e^{2v_+} + \frac{1}{v_-} e^{-2v_-} - \frac{v_+ + v_-}{v_+ v_-} \right\} = \text{constant.}$$

These values are summarized in the following table.

TABLE VI  
CONCENTRATIONS OF ELECTROLYTES OF DIFFERENT VALENCIES LEADING TO  
THE SAME CAPACITY OF THE DOUBLE LAYER  
( $\psi_0$  IS SUPPOSED TO BE -51.2 mV).

$v_-$	$v_+ = 1$	$v_+ = 2$	$v_+ = 3$	$v_+ = 4$
1	50	10.7	2.06	0.38
2	47	10.5	2.06	0.38
3	46	10.4	2.06	0.38
4	46	10.4	2.06	0.38

Hence we see that the capacity of the double layer is actually almost completely determined by the valency of the positive ions, with a charge opposite

to that or the surface. The influence of the negative ions is especially small if the valency of the positive ion is large. For larger values of the surface potential the influence of the negative ions becomes entirely negligible, even in the case  $v_+ = 1$ .

### § 3. The double layer at the interface of two liquid phases

The theory described above may easily be extended to the case of a double layer present at the interface of two liquid phases.<sup>1</sup> Such a system has often served as a model for the electric conditions at interfaces supposed to be present in the living tissue of biologic objects. Furthermore, the problem has a bearing on the properties of emulsions.

It will be seen that this case differs from the foregoing one in that we are now dealing with a double layer consisting of two diffuse charge layers; in each of these layers the electrical potential function is given by equations completely analogous

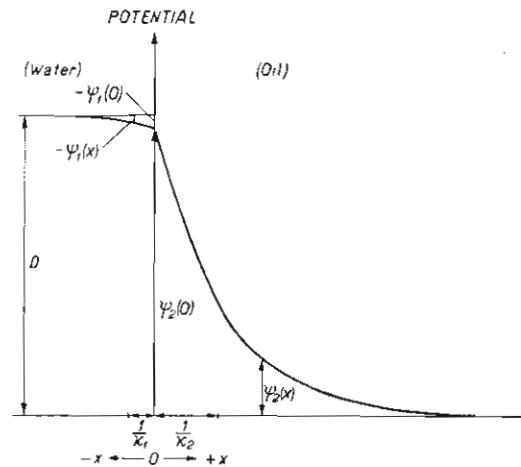


Fig. 3. Distribution of the potential at the interface of two liquid phases for small values of the total double layer potential  $D$ .

$$\epsilon_1 \approx 9 \epsilon_2 \quad n_1 = 81 n_2$$

Consequently  $\kappa_1 = 3 \kappa_2$  and  $\psi_2(0) = -27 \psi_1(0)$ .

to those valid for the liquid layer of the double layer at the phase boundary solid/liquid considered above. Accordingly the double layer potential (which will now be called  $D$ ) will be divided between both liquid phases and the corresponding potential drop will now occur partially in phase 1, and partially in phase 2. This is illustrated by Fig. 3, showing the electric potential function calculated for a special case. (Only the

<sup>1</sup> E. J. W. Verwey and K. F. Niessen, *Philos. Mag.*, (7) 28 (1939) 435.

potential due to free charges has been given; a possible boundary potential  $\Delta\phi_{\text{top}}$  due to orientated dipoles etc. in the interface has been put arbitrarily equal to zero). The corresponding distribution of the space charges is shown in Fig. 4. In

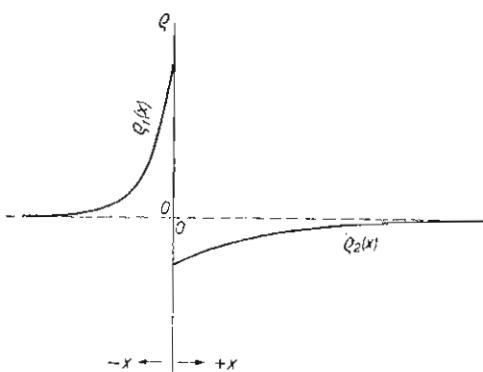


Fig. 4. Distribution of the space charges, corresponding to Fig. 3.

order to obtain more symmetrical equations, the electric potentials  $\psi_1$  and  $\psi_2$  in both phases are measured from different levels. In the state of equilibrium the electrolyte will generally be divided unequally between both phases; the case illustrated by Fig. 3 is one where, for  $\epsilon_1 > \epsilon_2$ , also  $n_1 > n_2$ , which is actually the most reasonable assumption, since the solubility of electrolytes in the liquid with lowest dielectric constant will generally be considerably smaller (so that even  $n_1 \gg n_2$ ).

The double layer as a whole is electrically neutral. Hence

$$\int_{-\infty}^0 \rho_1(x) dx + \int_0^{\infty} \rho_2(x) dx = 0$$

from which we find

$$\epsilon_1 \left( \frac{d\psi_1}{dx} \right)_0 = \epsilon_2 \left( \frac{d\psi_2}{dx} \right)_0$$

showing that the discontinuity in the derivative of the potential at the interface is entirely determined by the different dielectric constants.

These equations also give us the division of the double layer potential between both layers, as we can make use of (11) and (12), derived for the diffuse layer. By substitution we find directly

$$\sqrt{n_1 \epsilon_1} \cdot \sinh \left( \frac{z_1}{2} \right) + \sqrt{n_2 \epsilon_2} \cdot \sinh \left( \frac{z_2}{2} \right) = 0 \quad (14)$$

in which

$$-z_1 + z_2 = \Delta = \frac{veD}{kT},$$

showing that this partition is a function of the quantity

$$\alpha = \sqrt{\frac{n_1 \epsilon_1}{n_2 \epsilon_2}},$$

and of the total potential drop. As

$$\frac{z_1}{z_2} = \sqrt{\frac{n_1 \epsilon_2}{n_2 \epsilon_1}}$$

in which some compensation may occur as a consequence of a certain parallelism between  $n$  and  $\epsilon$ , we find that a very unequal distribution of the potential drop does not necessarily imply that the "thicknesses" of the diffuse layers or the densities of the charge on both sides of the interface differ very much.

The division of the total potential drop, due to the double layer, between both phases is illustrated by Fig. 5, giving the

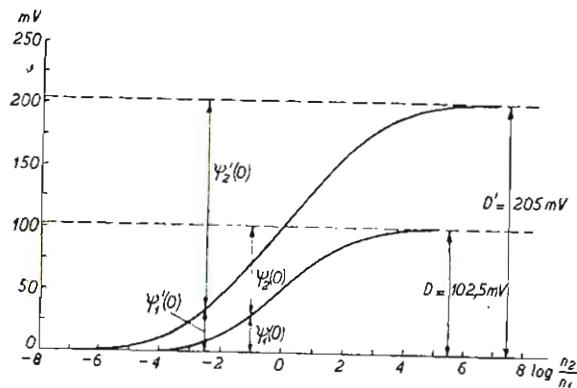


Fig. 5. Distribution of a total potential drop  $D$  resp.  $D'$  of 102.5 resp. 205 mV over two phases as a function of  $\log(n_2 \epsilon_2 / n_1 \epsilon_1) = \log \alpha^2$ .

fractions  $\psi_1(0)$  and  $\psi_2(0)$  for different values of  $D$  as a function of  $\alpha$ . Especially when the total potential drop is not very large and the valency of the ions has a low value, we find that the potential drop occurs almost completely in the phase with the lowest dielectric constant (and, therefore, generally, the lowest ionic concentration) as soon as the value of  $\alpha$  differs appreciably from 1. Hence, in the system oil/water, where especially the ionic concentrations may differ in order of magnitude, the potential drop will mainly occur in the oil phase. For large values of  $\Delta$ , however, this unequal distribution is counteracted

by the presence of the sinh terms in (14), which may then begin to predominate, so that for equal values of  $\alpha$  the division of the potential becomes less unequal, though the greater part of  $D$  is still found in the phase where the product  $n\epsilon$  has the lowest value.

#### § 4. The double layer around a spherical particle

Still neglecting the finite dimensions of the ions, we will now study the theory of a spherical double layer.

Working with spherical coordinates, the electric potential is in this case only a function of  $r$ , the distance from the centre of the particle. The fundamental differential equation can then be solved explicitly only for the approximation (4), and we shall therefore consider this approximative Debye-Hückel theory first.

Accounting for the proper boundary conditions, the solution of (4), giving the electric potential at a point outside the particle surface (radius  $a$ ) as a function of  $r$ , is

$$\psi = \psi_a \cdot \frac{a}{r} \cdot e^{\alpha(a-r)}, \quad (15)$$

and the corresponding relation for the particle charge  $Q$  is:

$$Q = a \cdot \epsilon (1 + \alpha a) \cdot \psi_a \quad (16)$$

These equations are easily derived in the following way. For a field of spherical symmetry we have

$$\Delta \psi = \frac{1}{r^2} \cdot \frac{d}{dr} \left( r^2 \cdot \frac{d\psi}{dr} \right) = \alpha^2 \psi,$$

and the solution satisfying the condition that  $\psi = 0$  and  $\frac{d\psi}{dr} = 0$  for  $r = \infty$ , reads:

$$\psi = \frac{A \cdot e^{-\alpha r}}{\alpha r},$$

as may easily be verified by introducing this value of  $\psi$  into the differential equation. The constant  $A$  is found by using the boundary condition  $\psi = \psi_a$  for  $r = a$ :

$$\psi_a = \frac{A \cdot e^{-\alpha a}}{\alpha a} \quad \text{or} \quad A = \alpha a \cdot e^{\alpha a} \cdot \psi_a,$$

and we immediately find eq. (15):

$$\psi = \psi_a \cdot \frac{a}{r} \cdot e^{\alpha(a-r)} \quad (15)$$

Differentiating with respect to  $r$

$$\frac{d\psi}{dr} = -\psi_a \cdot a \cdot e^{xa} \cdot \frac{(1+xa)e^{-xr}}{r^2},$$

and allowing for the demand:

$$\left(\frac{d\psi}{dr}\right)_{r=a} = -\frac{4\pi\sigma}{\epsilon} = -\frac{Q}{ra^2} = -\psi_0 \cdot \frac{1+xa}{a^2},$$

we find for the particle charge

$$Q = a\epsilon(1+xa)\psi_a \quad (16)$$

If desired, we can also express the potential into the particle charge, by combining (15) and (16):

$$\psi = \frac{Q}{sr} \cdot \frac{e^{x(a-r)}}{1+xa}.$$

For large particles, for which the double layer thickness is small in comparison to the particle radius, these equations must approach the corresponding equations (7) and (13) for small potentials for the flat double layer. Actually, if  $a$  is very large, in the diffuse layer the quotient  $a/r$  will be almost 1, and  $xa \gg 1$ , so that eq. (16) will pass into the form

$$Q = 4\pi a^2 \cdot \sigma = a^2 \cdot \kappa\epsilon\psi_a \quad \text{or} \quad \sigma = \frac{\kappa\epsilon}{4\pi} \cdot \psi_a.$$

For small particles, however, we see that the factor  $1/r$  causes the electric potential to fall off more rapidly than the purely exponential expression found for the flat double layer. If indeed, the particle is small in comparison to the thickness of the double layer, then the charge in the surrounding ionic atmosphere, going from the particle surface to the bulk of the solution, must be distributed among spherical shells of increasing volume. This explains the characteristic difference between spherical and flat double layers, and shows that the equations for the spherical double layer are especially important if  $xa \ll 1$ .

It seems, therefore, worth while also to consider the electric potential function around spherical particles for larger values of the potential, i.e. outside the validity region of the approximative Debye-Hückel equations. This has been done by Hans Müller<sup>1</sup>. This author has integrated numerically eq. (3) for the spherical case, and summarized his results in a number of tables.

<sup>1</sup> H. Müller, *Kolloidchem. Beihefte*, 26 (1928) 257.

The starting point of Müller's procedure was that the outer part of the potential curve, where  $\psi$  is still small, will again approach the general Debye-Hückel solution:

$$\psi = \frac{A \cdot e^{-xr}}{xr}.$$

The constant  $A$ , however, is now undetermined, and no longer equal to the value found from the boundary condition  $r = a$ , as in this region the solution is no longer valid.

Müller therefore chose a number of arbitrary values for this constant. In this way, starting from a given outer part of the electric potential function, he calculated numerically the curve in the direction of the particle by determining successively and proceeding in small steps the derivative along the whole curve with the aid of the complete differential equation (3).

Comparing the results of Müller with those corresponding to the Debye-Hückel equations, we find that the differences are not very large, though it should be considered that Müller's tables do not go to very high values of the potential where the deviations will certainly be higher.

If we choose the particle radius in such a way that  $xa = 0.2$ , we find in a definite case the following values of  $y$ , compared with the values for the Debye-Hückel curve with the same outer part.

TABLE VII

ILLUSTRATING THE DIFFERENCE BETWEEN THE APPROXIMATION OF DEBYE AND HÜCKEL AND THE THEORY OF MÜLLER FOR SPHERICAL PARTICLES.

$xr$	$z(r-a)$	$y = \frac{ve\psi}{kT}$	
		Müller	D.H.
0.2	0.0	2.83	2.78
0.5	0.3	0.82 <sup>6</sup>	0.82 <sup>5</sup>
1.0	0.8	0.25	0.25

In the foregoing section we have seen that the deviations (even for these rather low values of  $z$ ) are much larger in the case of a flat double layer. This may be shown, in addition, by the following table, containing a comparison of eq. (6) with eq. (7); for eq. (7) we gave  $z$  the value 2.78 again, and for eq. (6),  $z$  was chosen so as to make both curves coincide in their outer parts.

TABLE VIII

DIFFERENCE BETWEEN THE LINEAR APPROXIMATION (EQ. 7) AND THE EXACT EQ. (6) IN THE CASE OF A FLAT DOUBLE LAYER.

$\alpha a$	$y = \frac{ve\psi}{kT}$	
	eq. (6)	eq. (7)
0.0	3.44	2.78
0.3	2.28	2.06
0.8	1.30	1.25
1.5	0.62	0.61
3.0	0.14	0.14

A comparison of both tables is also instructive, as it reveals the fact, referred to earlier, that the potential decays much more rapidly in the spherical case than for a flat double layer.

That the Debye-Hückel approximation is so much better in the case of a spherical particle, for the same value of the double layer potential, especially when the particle is small in comparison to the thickness of the double layer, is easy to understand. The potential decays rapidly with increasing distance from the particle, and accordingly reaches high values only in the comparatively small volume close around the particles. Hence this part of the potential curve will have rather a small influence upon the form of the curve in the entire diffuse layer, as it comprises only a small part of the total space charge.

In a similar way we may understand another remarkable point to be derived from Müller's tables. For a flat double layer we found that the form of the electric potential curve is radically changed by an increase in the ionic charge. Müller's data however, show, that for a spherical particle (with  $\alpha a \ll 1$ ) the valency of the ions in the solution has only a minor influence upon the decline of the electric potential in the diffuse layer. Hence, also in this respect the Debye-Hückel theory is a much better approximation for the spherical double layer field than for the flat double layer, once we wish to apply this theory to cases where the potential is no longer small.

Summarizing, we may state that the application of the Debye-Hückel equations is only feasible for spherical particles when their dimensions and the electrolyte concentrations are small enough to satisfy the relation  $\alpha a \ll 1$ ; in that case it will give reasonable results, even when the potential is no longer small. For larger particles and (or) larger ionic concentrations, however, except for the rare cases in which the

double layer potential is actually very low, these equations become practically worthless. As soon as  $\alpha a$  is large in comparison with unity it will be necessary to account for the deviations from the approximated theory, either by Müller's method or by reverting to the equations for plane surfaces, derived on the basis of the complete differential equation. For a theory of coagulation, or similar cases where appreciable amounts of electrolyte are always present in the system,  $\alpha a$  is usually larger than 1. As a basis of such a theory the D.H. equations will accordingly be of practically no importance.

### § 5. Stern's theory for a flat double layer

In the following chapters the theory of the interaction of two double layers will be built up in the first place on the basis of the plane surface theory, for the reasons discussed in the preceding section. Before doing so, however, we must consider Stern's attempt to improve the theory of a single flat double layer.

As a matter of fact, the Gouy-Chapman theory, discussed in section 2 of this chapter, has a rather serious defect, which is for the main part a consequence of the neglection of the finite dimensions of the ions. In diluted solutions, where the extension of the diffuse layer is considerable, this neglection is in some degree permissible; but in more concentrated electrolyte solutions the picture according to the Gouy-Chapman equations becomes incorrect in essential details. If the double layer potential has rather a high value, for instance 300 millivolts, it is clear that, for a  $10^{-3}$  normal solution ( $v = 1$ ), we get into difficulties. According to eq. (2) we should find, in this case, that the concentration of counter-ions near the surface would be given by  $c_- = c \exp(ve\psi/kT) = 10^{-3} \cdot e^{12} = 160$  normal, which is clearly an absurdly high concentration in view of the finite dimensions of the ions.

The difficulty obviously originates from the assumption that the ions are point charges and can approach the surface charge without any limit. The theory will consequently become insufficient as soon as a considerable part of the space charge should be present, according to the theory, within a distance of, say,  $5 \times 10^{-8}$  cm from the surface.

Stern<sup>1</sup> has therefore altered the model underlying the double layer theory for a solid wall by dividing the liquid charge into two parts. One part is thought of as a layer of ions adsorbed to the wall, and is represented in the theory by a surface charge concentrated in a plane at a small distance  $\delta$

<sup>1</sup> O. Stern, Z. Elektrochem., 30 (1924) 508.

from the surface charge on the wall. This distance  $\delta$  is assumed to be of the order of magnitude of several times  $10^{-8} \text{ cm}$ . The second part of the liquid charge is then taken to be a diffuse space charge, as in the old theory, extending from the plane  $x = \delta$  to infinity. The decline of the electric potential in a double layer according to this model is represented schematically in Fig. 6. Between  $x = 0$  (the surface charge on

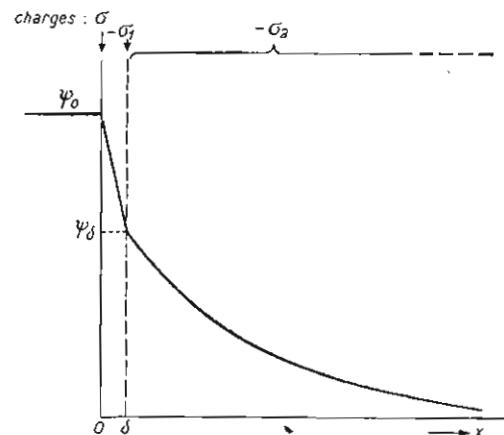


Fig. 6. Schematic representation of the double layer according to the theory of Stern.

the wall) and  $x = \delta$  (the adsorbed layer), the electric potential declines linearly, as in the dielectricum of a plate condenser. (The relation between the potential  $\psi_\delta$ , the potential drop in the diffuse layer, and the so-called  $\xi$ -potential known from colloid chemical work, will be considered in the following section).

Assuming that such a double layer could exist at absolute zero temperature the liquid charge would be found entirely in the adsorbed layer; at higher temperatures a more or less considerable part of the adsorbed counter-ions will have "evaporated" from the wall as a consequence of thermal motion, and will be transferred into the diffuse part of the liquid charge.

In order to calculate this distribution equilibrium of the liquid charge between the two layers (which may be called the Stern-layer and the Gouy-layer, respectively), Stern proceeds in a way somewhat analogous to the derivation of the "adsorption isotherm" of Langmuir.<sup>1</sup> We will simplify Stern's equations by considering only the counter-ions, i.e.

<sup>1</sup> I. Langmuir, *J. Am. Chem. Soc.*, 38 (1916) 2221; 39 (1917) 1885; 40 (1918) 1361.

by neglecting the contribution to the Stern layer of the ions with the same charge as the charge at the wall, as we have seen that the latter play a rôle of no importance in the formation of the liquid charge. In that case the Stern equation, giving the surface charge associated with the adsorbed ionic layer, reads:

$$\sigma_1 = \frac{N_1 \cdot ve}{1 + \frac{N}{M \cdot n} e^{-\frac{ve\psi_\delta + \varphi}{kT}}} \quad (17)$$

where  $N_1$  = the number of adsorption spots on  $1 \text{ cm}^2$  of the wall,  $N$  = the number of Avogadro,  $M$  = molecular weight of the solvent, and  $\varphi$  is the specific chemical adsorption potential of the counter-ion adsorbed to the wall.

Stern's derivation of this equation might easily be improved upon by the methods of statistical mechanics, and the equation itself will be liable to minor corrections by a more critical treatment. We have worked, however, with the original equation, because we only needed its general properties, and a more precise one hardly seems needed in view of the simplifications and defects still involved in Stern's picture.

The derivation of his equation runs as follows. If the number of adsorbed ions per  $\text{cm}^2$  is  $n_1$ , the number of available adsorption spots per  $\text{cm}^2$  of the wall is  $N_1 - n_1$ . The number of available positions in the solution is a less easily definable quantity, and is taken by Stern to be  $N/M$  per  $\text{cm}^3$ . Hence, applying Boltzmann's theorem, the thermal distribution equilibrium about the adsorbed layer and the solution is determined by:

$$\frac{n_1}{n} = \frac{N_1 - n_1}{N/M} \cdot e^{-\frac{ve\psi_\delta + \varphi}{kT}}$$

Considering further that

$$\sigma_1 = n_1 ve$$

and combining both equations we directly find eq. (17).

A complete set of equations to determine the distribution of the charges and the electrical potential function in the entire double layer may then be obtained in the following way.

In the first place the discontinuous change in the derivative of the electric potential must again be proportional to the surface charge at the wall, whence

$$\tau = \frac{\epsilon'}{4\pi\delta} \cdot (\psi_0 - \psi_\delta) \quad (18)$$

in which the prime denotes that the dielectric "constant" in the "inmedium" of the condenser of atomic dimensions between the surface charge and the adsorbed layer will be different from (probably considerably less than) that of the solvent. Both  $\epsilon'$  and  $\delta$  are unknown quantities, it is true; but the value of

the capacity ( $\epsilon'/4\pi\delta$ ) of the atomic condenser may be derived from other information; for instance from the work of Gouy on the electro-capillary curve.

The charge of the diffuse or Gouy layer is of course given by the Gouy equation given earlier:

$$\sigma_2 = \frac{1}{2\pi} \epsilon' k T n \sinh \left( \frac{ve\psi_d}{2kT} \right) \quad (19)$$

As a fourth equation we have:

$$\tau = \sigma_1 + \sigma_2, \quad (20)$$

so that the four unknown quantities (if  $\psi_0$  is given)  $\sigma$ ,  $\sigma_1$ ,  $\sigma_2$  and  $\psi_d$  can now be calculated from the combination of (17), (18), (19) and (20).

For diluted electrolyte solutions the product  $M.n$  is considerably smaller than  $N$ ; for instance in  $10^{-3}$  molar solutions is  $n = 10^{-6}.N$ . Hence, provided that  $\psi_d$  and  $\varphi$  are not too large (e.g. the exponent smaller than 8) the exponential form in eq. (17) is large with respect to unity, and we obtain

$$\sigma_1 = \frac{N_1 ve M n}{N} \cdot e^{\frac{ve\psi_d + \varphi}{kT}} \quad (21)$$

i.e., a more simple equation, which may be used in many cases instead of eq. (17).

Fig. 7 gives, for a double layer potential  $\psi_0 = 200$  millivolts, and for 1-1 valent electrolyte in water, a graphic representation of corresponding values of  $\sigma_1/\sigma$ ,  $\psi_d$  and  $n$  for a number of values of the adsorption potential  $\varphi$  (the latter counted positive if work is gained by the adsorption). In the calculations the "capacity" of the condenser of atomic dimensions was assumed to be

$$K = \frac{\epsilon'}{4\pi\delta} = 10^7 \text{ cm},$$

in accordance with measurements of the electro-capillary curve in concentrated electrolyte solutions (where practically the whole liquid charge is present in the Stern layer); for  $\delta = 5 \times 10^{-6}$  cm this capacity value corresponds to  $\epsilon' = 6.5$ . For the number of adsorption spots on the wall per  $\text{cm}^2$  the value  $N_1 = 5 \cdot 10^{14}$  has been taken. The value of  $\sigma$  is constant along the curves  $\psi_d = \text{constant}$ , and may easily be calculated from eq. (18).

From fig. 7 we see that, for more diluted electrolyte solutions, and for small values of the adsorption potential  $\varphi$ , only a small part of the total potential drop occurs in the Stern layer. At the same time, the fraction of the counter-ions adsorbed to the wall is unimportant; accordingly for this case the Stern picture

of the double layer approaches that of Gouy. In more concentrated solutions, however, we find a large potential drop in the Stern layer.

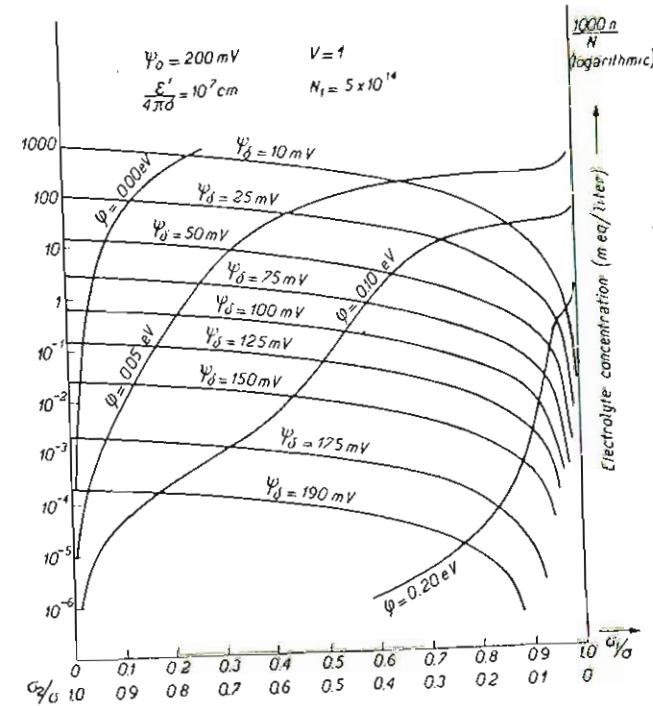


Fig. 7. Corresponding values of  $\frac{\sigma_1}{\sigma}$ ,  $\psi_d$ , and  $n$  for different values of the adsorption potential ( $\varphi = 0.00$ :  $\varphi = 0.05$ :  $\varphi = 0.10$  and  $\varphi = 0.20$  eV), for 1-1 valent electrolytes and a double layer potential  $\psi_0 = 200$  mV.

It is actually this division of the potential drop between the two layers which necessitates the application of Stern's theory. Fig. 7 shows that  $\psi_d$  is determined mainly by the concentration (and the valency) of the electrolyte and only secondarily by the adsorption potential  $\varphi$ . The corresponding partition of the charges may still vary to a large extent, dependent on the value of  $\varphi$ .

In diluted solutions  $\sigma_1$  may be large, if only  $\varphi$  is large enough, but the course of the potential nevertheless resembles very much that of the pure Gouy picture. This may be readily understood in view of the large extension and, therefore, the small capacity of the diffuse layer.

In concentrated solutions, however, even for small values of  $\varphi$  (and small  $\sigma_1$ ) the potential drop occurs for the main part in

the Stern layer. Obviously the diffuse layer is then "compressed" by the increased ionic concentration to such an extent that its capacity (owing also to its high dielectric constant, more than ten times that of the Stern-condenser) exceeds that of the Stern layer. However, there may be some doubt as to whether the model underlying this theory is applicable to such concentrated solutions.

Stern's theory may be considered as an improvement upon the Gouy-Chapman theory in two respects. In the first place it explains that for large electrolyte concentrations the double layer capacity does not rise above the value of about  $10\mu\text{F}/\text{cm}^2$ ; according to Gouy's equations it would rise indefinitely to values more than ten times the experimental ones. In the second place it distinguishes between the total double layer potential  $\psi_0$  and the Gouy potential  $\psi_s$ . As has been shown by recent work on the AgI sol, originating from the laboratory of Kruyt, both these quantities are accessible experimentally by combined analytical and electro-chemical measurements<sup>1</sup>, although all difficulties, especially with respect to the determination of  $\psi_s$ , have not yet been solved. Thus far the data available are insufficient for a quantitative test of the theory. They show, however, that  $\psi_0$  will often have values of several hundreds of millivolts (in negative AgI sols, for instance, it is usually — 250 to — 300 millivolts), for which Gouy's theory would give rise to difficulties. As a consequence of the presence of the Stern layer, in practical cases the potential in the Gouy layer, according to Fig. 7, will rarely exceed 100 or 150 millivolts; the values found experimentally, are indeed, of the same order of magnitude. Using Stern's theory we will, therefore, always be able to work with a diffuse layer for which the Gouy-Chapman equations may be more confidently applied.

#### § 6. The value of the surface potential and the significance of potential determining ions. The zeta-potential

In most colloid systems and suspensions the electro-chemical double layer has its origin in a distribution equilibrium of "potential determining" ions between the particle surface and the sol medium. This has been proved extensively by the work done on the AgI sol<sup>1</sup>, and it has been made plausible for many other systems (e.g. for suspensions of extremely insoluble oxides in water and other media).<sup>2</sup>

<sup>1</sup> E. J. W. Verwey and H. R. Kruyt, *Z. physik. Chem.*, A 167 (1933) 137, 149, 312.

H. De Bruyn, *Rec. trav. chim.*, 61 (1942) 5, 12, 21, 189, 193.

<sup>2</sup> E. J. W. Verwey, *Rec. trav. chim.*, 60 (1941) 625.

We may consider, for instance, the system AgI/water in some detail. In this case the double layer potential appears to be determined by the concentration of the silver- or iodide ions, respectively, in the solution. When AgI particles, as present in an AgI sol, are in equilibrium with an aqueous solution containing  $10^{-6}$  eq.  $\text{Ag}^+$  ions per litre (and therefore  $10^{-10}$  eq.  $\text{I}^-$  ions, as the solubility product of AgI is about  $10^{-16}$  eq./l at room temperature), the AgI is just about uncharged, hence no double layer is present ( $\psi_0 = 0$ ). When the  $\text{Ag}^+$  ions are brought to ten times this concentration (and accordingly the  $\text{I}^-$  to one-tenth their original concentration), the distribution equilibrium of the  $\text{Ag}^+$  ions about the particle surface and the solution is shifted in the direction of more  $\text{Ag}^+$  at the surface. Hence, when equilibrium has been newly established, we will find that the particle surface no longer contains equivalent amounts of  $\text{Ag}^+$  and  $\text{I}^-$  ions, but a small excess of the former.

The result is that the AgI particles are positively charged, and the particles are now surrounded by an electro-chemical double layer. The corresponding double layer potential will have such a magnitude that the electrical work  $e\psi_0$  outweighs the change of the chemical potential difference,  $\Delta\mu$ .

At the particle surface the concentration of the  $\text{Ag}^+$  ions has not perceptibly altered, as the excess of  $\text{Ag}^+$  carrying the positive particle charge is only a very small excess in comparison to the amount of  $\text{Ag}^+$  normally present at the crystal face. These excess ions are, moreover, in principle indistinguishable from the original  $\text{Ag}^+$  ions of the crystal surface, and bound there in exactly the same way. The thermodynamic potential of the  $\text{Ag}^+$  ions at the particle surface may therefore be considered, as a first approximation, to be a constant independently of the double layer potential.

The thermodynamic potential of the  $\text{Ag}^+$  ions in the solution, however, has been increased by an amount  $kT \ln 10$ , as a consequence of the increase in concentration by a factor 10. This increase must equal the product  $e\psi_0$ , and the resulting double layer potential is therefore  $\psi_0 = (kT/e) \ln 10 = 2.3(kT/e) = 57$  millivolts. More generally we have

$$\psi_0 = \frac{kT}{e} \ln \frac{c}{c_0}$$

in which  $c_0$  is the concentration of the potential determining ions (here the  $\text{Ag}^+$  ions) at the zero point of the charge. For a given system, where  $c_0$  is determined by its physical properties, the double layer potential is therefore entirely determined by the concentration of these ions in the solution,

i.e. the concentration at a point outside the double layers where the electrical potential is zero.

The important point in this equilibrium of potential determining ions is that by its existence the total potential difference in the double layer is completely determined, and consequently, in all problems of colloid chemistry, we have to consider the potential of the double layer as a given quantity, to be influenced only by the concentration of one species of ions. The charge and structure of the double layer adapt themselves to the variable properties of the system, such as concentration of indifferent (non-potential determining) electrolytes, dimensions and specific adsorption of the counter ions, form and dimensions of the particles, etc.

This total surface potential  $\psi_0$  may be of the order of several hundreds of millivolts. Indeed, every factor 10, by which the concentration of potential determining ions differs from that at the zero-point of charge, causes a shift in the potential of 57 millivolts, and concentration differences by a factor  $10^6$  or  $10^5$  are by no means inconceivable.

In a normal, well dialysed AgI sol, for instance, the concentration of  $I^-$  ions is usually about  $10^{-5}$  normal, whereas the zero point of charge is situated at  $10^{-10}$  n.l.<sup>1</sup>. Consequently in such an AgI sol the potential  $\psi_0$  is nearly — 300 millivolts.

We will try to realize now what is the connection between the surface potential discussed above and the  $\zeta$ -potential, which has been investigated so frequently in colloid chemistry. This  $\zeta$ -potential is a quantity not determined directly by potential measurements, but it is derived from experiments on electro-kinetics, such as electro-endosmosis, streaming-potentials and electrophoresis. All these experiments have this in common, that they involve tangential displacements of the liquid along the wall (or the reverse), and according to the theory of these phenomena it is possible to calculate from them the value of the potential in the plane where the liquid can move perceptibly with respect to the wall (slipping-plane). This potential is called  $\zeta$ .

It has long been recognized that the  $\zeta$ -potential has quite a different character from that of the potential  $\psi_0$  (the total potential difference of the double layer).  $\zeta$  is usually considerably smaller than  $\psi_0$ ; it reacts strongly to the addition of indifferent electrolytes, which leave  $\psi_0$  unaltered. Although  $\zeta$  is perhaps not identical with the potential  $\psi_s$  (the potential in the diffuse layer according to Stern's picture), it is felt that  $\zeta$  will resemble  $\psi_s$  much more than  $\psi_0$ .<sup>1</sup>

<sup>1</sup> This would mean that the slipping plane mentioned earlier coincides more or less exactly with the first layer of adsorbed ions.

On the other hand, investigations of later years made it pretty clear that the evaluation of the  $\zeta$ -potential from electro-kinetic phenomena presents more difficulties than was originally supposed. There are practically no cases standing the test of even moderate criticism in which determinations of  $\zeta$  for one system with different methods give concordant results.\* This may be explained partly by the difficulties of getting really comparable surfaces for the different experiments, partly by the difficulties in the interpretation of electro-kinetic phenomena.<sup>1</sup> And in all interpretations of electrokinetics we always retain the fundamental difficulty that even if  $\zeta$  could be calculated exactly, the place of the slipping plane is by no means self-evident, so that farther-reaching conclusions remain open to doubt.

It is no exaggeration to state that at this moment practically none of the values of  $\zeta$ -potentials, as found in the literature, can be relied upon to give fundamental information on the double layer.\*

In view of the latest investigations in this field, it may be hoped that in a few years time the situation will somewhat improve, but in the mean time we think it better to forgo the use of  $\zeta$ -potentials for our purposes, the dangers of misinterpretation being too great.

This seemed to us all the more justified because, as will become clear from the following chapters, we were able to give a fairly consistent theory of the stability of colloids, with only very rough notions about the exact values of the potentials involved. Nevertheless we found it impossible to pass over in complete silence a quantity which has played such a widespread rôle in colloid chemistry.

We would finally make a few remarks on the double layer at the interface of two liquids. Except when at least one of the liquids is non-polar, and the solubility or electrolytic dissociation of electrolytes, accordingly, zero, electrolytes added to the system, even in very small amounts, will each act there as

\* Note added in proof. In the meantime De Smet (*Versl. Kon. Vlaamsche Acad. v. Wetensch.*, VII (1945) no 5) has published an investigation on the streaming potential and electro-endosmosis of glass in which both methods give the same reliable value for the  $\zeta$ -potential. P. W. O. Wijsga obtained analogous results in his thesis (Utrecht, 1946).

<sup>1</sup> Cf. Rutgers and coworkers on streaming potential and electro-endosmosis, and Overbeek on electro-phoresis.

A. J. Rutgers, *Trans. Faraday Soc.*, 36 (1940) 69.  
M. De Smet, *Versl. Kon. Vlaamsche Acad. v. Wetensch.*, III (1941) no 12, no 14.

A. J. Rutgers, E. Verlende and M. Moorkens, *Proc. Acad. Sci. Amsterdam*, 41 (1938) 763; 42 (1939) 71, 764.

J. Th. G. Overbeek, *Kolloidchem. Beihefte*, 54 (1943) 287.

a potential determining electrolyte. These electrolytes, apart from being generally distributed unequally about both phases, build up the electric double layer at the interface because of the unequal distribution coefficients of the positive and negative ions. As a matter of fact this represents the most simple case of a double layer caused by a distribution equilibrium of potential determining ions, as already considered by Nernst and van Laar. Each electrolyte gives rise to a different potential drop, depending on the properties of the ions. The distribution coefficient (for a 1-1 valent electrolyte) and the corresponding potential difference are, according to well known thermodynamical considerations,

$$2kT \ln(n_1/n_2) = (\mu_2^+ - \mu_1^+) + (\mu_2^- - \mu_1^-)$$

$$2e(\Phi_1 - \Phi_2) = (\mu_2^+ - \mu_1^+) - (\mu_2^- - \mu_1^-),$$

in which  $\Phi_1$  and  $\Phi_2$  are the electric potentials in the interior of the phases,  $\mu_i^+$  the partial chemical potential of the positive ions (for instance in the standard state) in phase 1, etc., and  $n_1$  and  $n_2$  the ionic concentrations (which may be different from the electrolyte concentrations because of incomplete dissociation). By using, for the quantities  $\mu$ , which may be called the free energies of solvation, Born's equation

$$\mu = (e^2/2r)(1 - 1/\epsilon),$$

in which  $r$  is the ionic radius, it has been tried to derive general rules concerning the sign of the potential difference<sup>1</sup>. Such attempts, however, can never be quite successful, as theoretical calculations show that these solvation energies are not solely determined by the dimensions of the ions, but also depend, for instance, on the structure of the molecules of the liquid, etc.<sup>2</sup> The main difficulty, however, is that in this way we find the value of the potential difference between the interior of the phases (which is not accessible experimentally), and not the double layer potential (which differs from the former, as there is generally the unknown contact potential difference at the phase boundary, caused by oriented dipoles, polarisation effects, etc.).

<sup>1</sup> E. J. W. Verwey, *Thesis*, Utrecht 1934, page 61.

A. J. Rutgers, *Physica*, 5 (1938) 54.

E. J. W. Verwey, *Trans. Faraday Soc.*, 36 (1940) 192.

E. J. W. Verwey, *Rec. trav. chim.*, 61 (1942) 127.

### III. THE FREE ENERGY OF A DOUBLE LAYER SYSTEM

#### § 1. Introduction

As was pointed out in Chapter I, our aim is to obtain a quantitative expression for the total potential energy curve of two particles (or plates), including the van der Waals-London attraction and the interaction of the double layers. The potential energy of the two particles with respect to each other, as far as the interaction of the double layers is concerned, can be obtained, in principle, in two different ways. In the first place one may try to find an expression for the force between the particles or plates as a function of their distance; the potential energy is then found by integration with respect to the distance. In the second place one may determine the free energy of the system of two double layers as a function of the distance i.e., the difference between the free energies of the entire system with and without the double layers at the interfaces. As this free energy is identical with the amount of work associated with some isothermal and reversible process of building up the double layers, the variation of the free energy with the particle distance directly equals the variation of the potential energy of the two particles with respect to each other. Hence the free energy would give us directly the potential curve for the double layer interaction.

Both methods have their advantages and drawbacks. It appears comparatively easy to derive an expression for the force acting between two plates; for two spherical particles the problem is considerably more difficult. Serious difficulties arise, however, in the subsequent integration of the force with respect to the distance, even in the case of two flat double layers. For, the expression for the force in the latter case is not a simple function of the plate distance; its integration must therefore be carried out either numerically or graphically.

In view of these difficulties we have investigated the second, more straightforward, way: the determination of the free energy. General expressions for this thermodynamic quantity can be derived, and applied to different cases. We therefore followed usually this second way, which immediately led to the desired potential curve.

To this end we shall consider, in the present chapter, the general problem of the free energy of a double layer system.

This problem deserves special attention, because it was the main source of the difficulties and discrepancies in the literature, as mentioned in Chapter I.

As stated above, the free energy is the amount of work to be performed in building up, by some reversible and isothermal process, the double layers of the system. The formation of these double layers occurs spontaneously when the wall and the solution are brought into contact. Hence we can state, *a priori*, that the free energy of a double layer system must be a negative quantity (work is gained by the formation).

The determination of the free energy of a system of double layers may follow a number of different ways. We shall here consider two methods.

1. In the first place it is possible to consider a process in which the double layer is built up (or removed, if we wish to consider the inverse process) by a transfer of ions from one phase to another. A similar method was already proposed by Derjaguin,<sup>1</sup> in his discussion with Levine; the charging process will be carried out here in a somewhat different way.

2. Secondly, one may apply what may be called an extension of the method of Debye and Hückel in their theory of electrolytes, consisting in a consideration of the total work associated with a gradual decrease of all ionic charges of the system.

## § 2. First method

We imagine the particles (or plates, etc.) to be brought into contact with an infinitely large amount of the solution, ionic equilibrium at the interfaces, however, not yet established. Starting from this system, where the charges at the surfaces and in the solution are still absent, the double layer is now thought to be formed, isothermally, in the following way. Potential determining ions are allowed to be transported by infinitesimally small quantities from the bulk of the solution towards the surfaces; after each step the secondary rearrangement of the charges in the solution is allowed to occur, until, as far as the solution is concerned, ionic equilibrium has been reestablished. For instance, in the case of a negative AgI sol, we may represent the formation of the double layers by letting the AgI particles adsorb I<sup>-</sup> ions step by step from a diluted HI solution, and allowing the equivalent amount of H<sup>+</sup> ions to diffuse, after each step, to the neighbourhood of the particles. When the final state, complete ionic equilibrium being established, has been reached, the total amount of work

associated with the ionic transport will give us the free energy of the double layer system. This amount of work consists of two parts:

a. The origin of the double layer is an unequal distribution of positive and negative, potential determining ions about the surface and the solution. If in the final equilibrium state there is an excess of one of the ion species in the surface, there is obviously a chemical preference of these ions for the surface above the solution. Hence, if the ions go from one medium to another, in each step of the process considered above a constant amount of free energy is gained, corresponding to the chemical free energy difference,  $\Delta\mu$  per ion (chemical part of the partial free energy). In the final state this free energy difference  $\Delta\mu$  exactly outweighs the electric potential difference due to the double layer<sup>1</sup>, and therefore equals  $-e\psi_0$ . The chemical part of the free energy of the double layer is therefore  $-e\psi_0$  per ion, or  $-\sigma\psi_0$  per cm<sup>2</sup> surface, in which  $\sigma$  is the charge density of the surface.

b. During the charging process an electric double layer is gradually built up; calling the surface potential at an arbitrary stage of the charging process  $\psi_0'$ , we observe that  $\psi_0'$  increases gradually from 0 to  $\psi_0$ , and the electrical charge,  $\sigma'$ , at 1 cm<sup>2</sup> surface in an analogous way from 0 to  $\sigma$ . This potential  $\psi_0'$  counteracts the ionic transport from the bulk of the solution (where the electrical potential is zero) to the particle surface. Hence, a gradually increasing amount of electric work has to be done,  $\psi_0'd\sigma'$  for each step, and for the whole charging process we find the purely electrical work quantity

$$F_e = \int_0^\sigma \psi_0' d\sigma' \quad (22)$$

which may be called the electric part of the free energy of the double layer. This free energy, associated with the setting up of the charges, is clearly a positive contribution to the total free energy, like the free energy of a charged condenser (energy is needed for charging it).

A third work quantity which might be considered here is the energy gained in the secondary rearrangement of the charges in the solution. This rearrangement, occurring after each step, is responsible for the formation of the liquid charge layer. It is clear, however, that this formation of the liquid charge does

<sup>1</sup> This follows directly from the condition that the partial free energy (including electric work) per ion must have the same value in both phases, or  $\Delta\mu + e\psi_0 = 0$ .

not contribute to the free energy of the double layer. These ions are accumulated in the neighbourhood of the surfaces as a consequence of the equilibrium between the electric attraction by the surface charge and the thermal motion tending to distribute the ions over the entire solution. Hence the electric energy gained by these ions (accumulating in a region where the electric potential has an opposite sign) is spent again in favour of counteracting thermal motion. Each ion, reaching a point ( $x$ ) where the electric potential is  $\psi'(x)$ , gains an amount of (electric) energy  $v e \psi'(x)$ ; simultaneously it is brought to a point where the concentration has been raised from  $n$  to  $n_+(x)$ , and accordingly its entropy has been decreased by an amount  $k \ln(n_+(x)/n)$ . In accordance with the circumstance that in the diffuse layer thermodynamic equilibrium is constantly maintained, these two contributions to the partial free energy counterbalance each other exactly. Or, from a more kinetic point of view: as the whole charging process is an isothermal one, the electric work gained by the ions is transferred to the other ions and to the water molecules as kinetic energy, and finally flows in the form of heat out of the system.

Hence, the total free energy of the double layer (for  $1 \text{ cm}^2$  surface) amounts to:

$$F = -\sigma \psi_0 + \int_0^\sigma \psi'_0 d\sigma,$$

in which, obviously, the first (chemical) term is always larger than the second (electrical) term. By partial integration both terms can be summarized into one single term, so that we finally obtain

$$F = - \int_0^{\psi_0} \sigma' d\psi'_0 \quad (23)$$

Hence the free energy is always negative, in accordance with what initially has been said about this quantity.

If the electric surface potential is small, so that the linear approximation can be applied, eq. (23) simplifies to

$$F = -\frac{1}{2} \sigma \psi_0, \quad (23')$$

as in that case the charge and the potential increase proportionally during the charging process. Hence, in that case the electric work to be done is exactly half the chemical work gained in this process. For larger values of the potential the charge increases rapidly with increasing potential (for a single double layer it

increases, roughly, according to  $\exp(z/2)$ , see eq. (12)), and accordingly the electric work is now between the limits

$$\frac{1}{2} \sigma \psi_0 < F_e < \sigma \psi_0.$$

The absolute value of the free energy of the double layer system, therefore, is generally less than  $\frac{1}{2} \sigma \psi_0$ , and only in the limiting case of very small potentials equal to  $\frac{1}{2} \sigma \psi_0$ .

Several other derivations of (23) are possible. A fairly simple derivation, of a more thermodynamic nature, may be given in connection with the theory of the electrocapillary curve. In that case we must introduce a new set of variables. We start from the well known Lippmann equation

$$\left( \frac{\partial \gamma}{\partial \psi_0} \right)_{\omega, T} = - \left( \frac{\partial q}{\partial \omega} \right)_{\psi_0, T} = -\sigma, \quad (24)$$

giving a relation between the interfacial tension  $\gamma$  of a phase (in electrocapillary work usually a mercury surface) in contact with an electrolytic solution and the electric properties of the double layer at the interface.

This equation can be found in the following way.

If  $q$  be the charge of the double layer, the free energy change corresponding to an isothermal increase of the interface by  $d\omega \text{ cm}^2$  is

$$dF = \gamma d\omega + \psi_0 dq.$$

We now introduce a new function,  $L = F - \psi_0 q$ , which is completely defined by the state of the system; whence

$$dL = \gamma d\omega - q d\psi_0.$$

As  $dL$  is a total differential, we find from this directly eq. (24).

According to eq. (24) the surface tension shows a maximum for  $\sigma = 0$ ; at both sides of this zero point of the charge, i.e. both for positive and negative values of  $\sigma$ ,  $\gamma$  is lowered by an amount  $\gamma_0 - \gamma$  by the presence of the double layer.  $\gamma_0$ , the surface tension for the case that no double layer is present, is the amount of work performed against the intermolecular forces when the uncharged surface is increased by  $1 \text{ cm}^2$ . Hence  $\gamma - \gamma_0$ , actually a negative quantity, is identical with the free energy of  $1 \text{ cm}^2$  double layer. This holds equally for a single double layer and for a system of double layers, as, for instance, two interacting double layers. Hence, integrating equation (24), we have again

$$F = \gamma - \gamma_0 = \int_0^{\psi_0} \left( \frac{\partial \gamma}{\partial \psi_0} \right)_\omega d\psi_0 = \int_0^{\psi_0} -\sigma d\psi_0. \quad (23)$$

We have now obtained a simple expression (eq. (23)) for the free energy of a double layer system, which, for the sake of convenience, has been given in a form valid only for a single double layer, or for two parallel flat double layers, where the surface charge is constant throughout the entire system. It may easily be extended to more complicated cases, for instance for two interacting particles of arbitrary form, where the surface charge density is a function of the coordinates on the surfaces. In that case we have, in addition, an integration over all surfaces:

$$F = - \int_S dS \int_0^{\psi_0} q'd\psi' \quad (25)$$

if  $q'dS$  is the charge of a surface element  $dS$ .

In spite of its simplicity, the integration of eq. (23) entails considerable difficulties because of the complicated relation between  $\sigma'$  and  $\psi_0'$  as soon as we leave the region of potentials, where the linear approximation may be applied. (cf. eq. (12)). These difficulties are especially great in the case of double layer interaction. For our computations of the potential curve due to the interaction, therefore, we did not make use of eq. (23), but of the general expression obtained according to the second method. Only in those cases where the linear Debye-Hückel approximation is applied, is it advantageous to make use of eq. (23) or a related expression.

### § 3. Second method

Because of the difficulties encountered in the application of eq. (23) we approached the problem of the free energy of a double layer system in a way analogous to the method used by Debye and Hückel in their theory of strong electrolytes. In this theory the free energy of the arrangement of the ions under the influence of the electrostatic forces between the ions plays an important part. Each ion in turn is surrounded by an ionic atmosphere composed by all other ions. The theory is here concerned with the amount of work necessary to remove the ions from their ionic atmosphere by some reversible and isothermal process. In order to calculate this work quantity it is imagined that the ionic solution is converted gradually into a solution of neutral particles of the same concentration. To this end we imagine, that the charge of the ions is transported in infinitesimal small steps  $dq$  from one ionic species to another, and calculate the total amount of work to be done in this process by integrating over all steps. The total amount of work

will then be  $\int 2\psi'dq$  per ionic pair (in which  $\psi'$  is the electric potential at a given ion due to its atmosphere at some moment during the discharging process), because the charge  $dq$  must be brought from a point where the potential is  $+\psi'$  to a point where it is  $-\psi'$ . The total amount of work thus obtained is not identical with the total electrostatic energy of the ionic arrangement, which is equal to  $q_0\psi_0$  for each pair of ions ( $q_0$  is the charge of an ion,  $\psi_0$  the potential due to its atmosphere). During the discharging process the charge of all ions gradually decreases, and the ionic atmosphere accordingly becomes more and more diffuse and finally disappears entirely. In the Debye-Hückel theory the free binding energy of the ions in their atmosphere is consequently smaller than the electrostatic energy. (Actually it proves to be two thirds of it).

In the case of the electrochemical double layer, or a system of double layers, things are somewhat different, because here the element of reciprocity is lacking. In an electrolytic solution all ions are simultaneously captured in an atmosphere, and each contributes to the atmospheres of all surrounding ions. Hence we only need to calculate the work needed to discharge reversibly a single ion. In the case of a double layer system we must make the double layers vanish everywhere. We must therefore discharge all surface charges and simultaneously remove the charge from every point of the space in the solution. In mathematical language: for the calculation of the total work in this reversible process we must integrate twice: over the discharging process, and over the entire space occupied by the double layer system.

There is, however, a second important difference. In the electrolyte theory the charges of the ions are given quantities, and complete dissociation is supposed. In the double layer case the charge is caused by potential determining ions being „adsorbed” on the particle surfaces. The corresponding distribution equilibrium cannot be left out of consideration in the reversible and isothermal discharging process. In addition to the electric work the chemical work must be taken into account, exactly as we have done in our first discharging method.

We proceed in the following way. We imagine that all ions (the ions which are present in excess on the surfaces, and all ions in the solution) are gradually discharged by transporting their charge in small steps,  $+$  or  $-ved\lambda$ , to infinity. After each step the system is allowed to re-establish thermal equilibrium, and the system is connected with a large reservoir of constant temperature. The degree of discharge is measured by the variable  $\lambda$ , decreasing gradually from 1 to 0.

It is advantageous to imagine this discharging process to be

carried out under such conditions that the surface potential  $\psi_0$  remains a constant all the time. With regard to the equilibrium condition  $\lambda e\psi_0 + \Delta\mu = 0$ , we must imagine the chemical potential difference  $\Delta\mu$ , to be reduced at the same rate as the ionic charges. In this way we obtain that, for each degree of the discharging, i.e. we have  $-\lambda e\psi_0 = \lambda \Delta\mu$ , so that  $\psi_0$  remains unchanged. In the opposite case the mathematical difficulties in the following calculations would be considerably increased; if, for instance,  $\Delta\mu$  would be left unchanged during the discharging process, the electric potential  $\psi_0'$  would increase to infinity because of the equilibrium condition  $-\lambda e\psi_0' = \Delta\mu$ .

Accordingly, in each step an amount of chemical work  $\Delta\mu d\lambda$  per surface ion must be performed. Simultaneously, an amount of electric work  $e\psi_0 d\lambda$  is gained in decreasing the charge of this surface ion by an amount  $ed\lambda$ . Hence electric and chemical work associated with the surface charge compensate each other in each step. The very simple result is that we find the total free energy of the double layer if only we calculate the electric work necessary to discharge stepwise all ions of the solution. As we include in this way both the chemical and the electric effects, the expression found for the free energy will be valid for the case of true equilibrium in the double layers.

A further simplification is that we need only to consider those ions which are present in excess in the solution and carry the liquid charge of the double layer, since for the mutual neutralization of all other ions, present in equivalent amounts in each point of the space, the net work is zero. The neglection of the mutual Debye-Hückel energy of the ions seems justified, because this energy either bears no relation to the surface (for the ions in the bulk of the solution) or is only a second order effect (for the ions in the double layer).

For the determination of the free energy for a given system of double layers, we denote with  $\rho'$  and  $\psi'$  the charge density and the electric potential corresponding to an ionic charge  $\lambda e$ ; the primes distinguish these quantities again from  $\rho$  and  $\psi$  before the discharging process. The number of excess ions in a volume element  $dx dy dz$  is given by  $(\rho'/\lambda \cdot v \cdot e) dx dy dz$ ; the amount of work to decrease the charge of these ions by a fraction  $d\lambda$  is, therefore,  $\rho' \psi' (d\lambda/\lambda) dx dy dz$ , and the work associated with the entire process:

$$F = \int_0^1 \frac{d\lambda}{\lambda} \iiint \psi'(x, y, z) \rho'(x, y, z) dx dy dz, \quad (26)$$

in which the threefold integration must be carried out over the entire space in the solution.

It is of some interest to consider, as we have done for the

first method, the nature of the thermal effect occurring in this process. After each step there will again be a rearrangement of the charges. More particularly, if we consider a single flat double layer, because of the gradually decreasing ionic charge the liquid charge layer becomes more and more diffuse. This is expressed by the decrease of the quantity  $\nu'$ , which is proportional to  $\lambda$ . Here we have, therefore, something analogous to the first method, where the formation of the liquid charge had to be performed by a secondary diffusion towards the neighbourhood of the surface. During the discharging process considered here the counter ions must diffuse more and more back into the solution. This diffusion occurs against the electric forces. Hence, in the rearrangement of the ions occurring after each step, the ions in the liquid layer lose a certain amount of (electric) energy. Simultaneously, however, the local concentration of these ions is lowered as a result of the extension of the liquid charge layer over an increasing part of the solution. It may easily be seen, as in the case of the first method, that the corresponding increase of entropy ( $T \Delta S$ ) exactly outweighs the increase of the internal energy ( $\Delta U$ ), so that the net change in the free energy is again zero. The energy needed to raise the electric energy of these ions must be taken up from the surrounding ions and molecules, and is delivered as kinetic energy from the thermal motion of the latter. As the whole discharging process occurs isothermally, a corresponding amount of heat will flow from the reservoir into the solution.

It may seem somewhat surprising that, according to this second derivation of the free energy, the negative value appears to be a result of the action of the counter ions, extending over a certain region in the solution where the space charge and the electric potential have opposite signs (the product  $\rho' \psi'$  in (25) is therefore always negative). This suggests a contradiction to the first method, where the counter ions did not contribute to the free energy, and its negative value was caused by the chemical free energy of the surface charge ions. It should be clear, however, that there is, at least qualitatively, complete accordance between the results obtained by both methods. There are three different forms of free energy to be considered, viz. the chemical and the electric free energy of the surface charges, and the electric free energy of the charges in the diffuse double layer. The first method appears to be a way of calculating the work necessary to suppress, primarily, the surface charges; the second method gives the work required to disperse, primarily, the liquid charge from the diffuse double layer towards the bulk of the solution; in both cases the method has been chosen in such a way that the removal of the second layer occurs secondarily and automatically.

Although in this way it may be argued, physically, that the two general expressions (25) and (26) may very well lead to the same result, the general proof that both expressions are quantitatively equivalent is desirable. For special cases it can be shown more or less easily that both expressions give identical results. This is, for instance, the case for a flat double layer, or for two parallel double layers, on the basis of the Gouy-Chapman theory. The identity of both expressions is made quite plausible by these results.

For a general proof, given in the Appendix added to this chapter, we are indebted to Prof. Dr H. B. G. Casimir of this laboratory. As the first expression comprises an integration over the surface charge, and the second over the charge in the solution, the general proof appeared to be possible by the application of Green's theorem known from the theory of electricity. This proof shows that the conversion of one expression into another is a complicated procedure. This is one of the reasons why we derived, in the present section, both expressions separately. A second reason was that we have worked with the second expression (25) in the following considerations, whereas the calculation of the free energy according to a method analogous to the first one is already to be found in the literature. The consideration of both methods of determining the free energy may therefore be useful in a discussion of the differences in the results of other authors, to be given in the Appendix at the end of this book, while it may also further a better understanding of the nature of the phenomena investigated here.

#### § 4. On double layer interaction

Starting from the image of the free energy of the double layer, as developed in this chapter, it is not difficult to trace in broad outline the consequences of the interaction of two or more double layers.

If two surfaces are brought so close together that their double layers overlap sensibly, these double layers cannot develop to the full extent, and the double layer charge will become smaller, as may be seen most clearly by imagining two parallel flat surfaces, where the double layers may be completely made to disappear by bringing the plates into contact. As a result of this interaction of double layers the free energy becomes less negative; therefore work must have been performed on the system, or in other words: *the interaction of double layers gives rise to a repulsion between the surfaces bearing them.* It has been explained in § 2 of this chapter that the free energy is composed of a — negative — chemical part and a — positive —

electric part, the negative value of the total free energy arising from the greater absolute value of the chemical part. Putting it somewhat schematically we may say that the repulsion between double layers is a result of the chemical contribution to the free energy, i.e. of the difference in partial free energy of the potential determining ions in the two phases. It has been tacitly assumed in the foregoing that the double layer potential is independent of the distance of the surfaces. In view of what was stated in § 6, chapter II, concerning the equilibrium of potential determining ions, this corresponds to the assumption of thermodynamic equilibrium everywhere in the double layer.

The existence of thermodynamic equilibrium may even be assumed during the rapidly passing moment of the encounter of two colloidal particles, both subject to their thermal (Brownian) movement. If two particles approach each other, it follows from the above that the double layer charge at the particle surfaces facing each other decreases, and a number of ions must accordingly diffuse temporarily from the particle surface into the solution. Hence, thermodynamic equilibrium will exist, if this adjusting of the charge in the region between two encountering particles occurs sufficiently rapidly, so that at each moment the charge distribution corresponds to the particle distance. It may be assumed that this condition will generally be fulfilled, because the Brownian motion of the comparatively heavy colloid particles is much slower than the thermal diffusion of the ions.

In exceptional cases it might be possible that the transition of ions from the surface to the solution or in the inverse direction needs an activation energy. That such a barrier at the interface of two phases may sometimes be present is suggested by certain phenomena (overvoltage, etc.) observed in electrolytic processes. In that case adjustment of the charge would occur slowly, and the assumption that the double layer charge is a constant, independent of the particle distance, would then be a more suitable approximation<sup>1</sup>. In a case like that of AgI, behaving as a perfectly reversible electrode, and in many other systems, the assumption  $\psi_0 = \text{constant}$  will be more correct.

In the following chapters, therefore, we have based our general considerations on the assumption  $\psi_0 = \text{constant}$ , and only incidentally studied the second case,  $\sigma = \text{constant}$ . In this second case the main effect of the interaction, instead of being a reduction of the charge, is an increase of the surface potential  $\psi_0$ .

It might seem that this increase of the potential would result in a reversal of the sign of the interaction, compared to the case  $\psi_0 = \text{constant}$ . We should not forget, however, that in the

<sup>1</sup> Also in some cases of organic (hydrophilic) colloids like gum arabic where the charge is determined by the dissociation of discrete ionogenic groups in the molecule, the supposition of constant charge may be nearer the truth than that of constant potential.

case of constant charge there is no thermodynamic equilibrium in the double layer, while no ionic transport from one phase to another occurs when the distance of the surfaces is varied. We have only to deal, therefore, with the *electric* part of the free energy,

$$F_e = \int_0^\sigma \psi'_0 d\sigma' \quad (22)$$

As  $\psi'_0$  increases with increasing interaction, we also find an increase of  $F_e$ , and the result of the interaction is again, as in the case of constant potential, a repulsion.

It should be noted that, for a given configuration of the system, the force acting between the surfaces must be independent of the choice of the parameter to be held constant in a subsequent variation of their distances. Hence differentiation of  $F$  as expressed by (23) with respect to  $d$  (a parameter expressing the distance between the surfaces)

$$\left( \frac{\partial}{\partial d} \right)_{\psi'_0} \left\{ -\sigma \psi'_0 + \int_0^\sigma \psi'_0 d\sigma' \right\}$$

will lead to the same result as differentiation of  $F_e$  (eq. 22) for  $\sigma = \text{constant}$ :

$$\left( \frac{\partial}{\partial d} \right)_\sigma \int_0^\sigma \psi'_0 d\sigma'$$

It can easily be shown that both expressions are identical and equal to

$$-p = \int_0^\sigma \frac{\partial \psi'_0}{\partial d} d\sigma'$$

For the second expression this is at once clear, the limits of integration being kept constant during the differentiation.

In differentiating the first expression it should be borne in mind that  $\sigma$  is a function of  $d$ , and  $\psi'_0$  a function of  $\sigma'$  and  $d$ . Hence,

$$\begin{aligned} \left( \frac{\partial}{\partial d} \right)_{\psi'_0} \left\{ -\sigma \psi'_0 + \int_0^\sigma \psi'_0 d\sigma' \right\} &= \\ -\psi'_0 \left( \frac{\partial \sigma}{\partial d} \right)_{\psi'_0} + \left\{ \frac{\partial}{\partial \sigma} \int_0^\sigma \psi'_0 d\sigma' \right\} \left( \frac{\partial \sigma}{\partial d} \right)_{\psi'_0} + \int_0^\sigma \frac{\partial \psi'_0}{\partial d} d\sigma' &= \\ -\psi'_0 \left( \frac{\partial \sigma}{\partial d} \right)_{\psi'_0} + \psi'_0 \left( \frac{\partial \sigma}{\partial d} \right)_{\psi'_0} + \int_0^\sigma \frac{\partial \psi'_0}{\partial d} d\sigma' &= \int_0^\sigma \frac{\partial \psi'_0}{\partial d} d\sigma' = -p, \end{aligned}$$

so that we get exactly the same expression for the repulsive force in both cases.

In order to obtain further quantitative data on the interaction, we shall, in parts II and III, deal especially with the cases of interaction of two flat parallel plates and of two spheres respectively. These examples are comparatively easy to handle, and also constitute suitable approximations of cases occurring frequently in the reality of colloid chemistry.

For crystalline particles which are large in comparison with the double layer extension, the effect of the interaction will practically be restricted to the crystal faces which are brought in opposite positions during a particle encounter. The effect upon crystal faces not facing each other may be neglected as a first approximation.

This means that the conclusions drawn from the model of flat plates will probably hold to a large extent for crystalline particles, provided the double layer is sufficiently compressed.

On the other hand, when the particles are small in comparison with the double layer extension, so that, in a particle encounter, one particle may be enclosed by the double layer of the second and vice versa, the model of interacting spheres is more adequate. Moreover, the influence of the particle dimensions can be gathered more easily from the case of spheres than from the infinitely large flat plates, where particle dimensions have to be introduced in a more or less arbitrary way.

## APPENDIX

### § 5. On the equivalence of the two methods

We want to show the identity of the two expressions for the free energy, *viz.*,

$$F_1 = - \iint_{S_i} dS \int_0^\infty q' d\psi'_0 \quad (25)$$

and

$$F_2 = + \int \frac{dk}{k} \iiint \psi'(\lambda; x, y, z) \rho'(\lambda; x, y, z) dx dy dz \quad (26)$$

where  $\psi'$  satisfies, everywhere outside a number of closed surfaces  $S_1, S_2, \dots$ , the equation

$$\Delta \psi' = -\frac{4\pi\rho'}{\epsilon},$$

with the boundary conditions  $\psi' \rightarrow 0$  at infinity and  $\psi' = \psi'_0$  on  $S_i$ . Between the charge-density  $\rho'$  and the potential  $\psi'$  there exists a relation of the form

$$-\frac{4\pi\rho'}{\epsilon} = \lambda f(\lambda \psi'); \quad (27)$$

it will not be necessary to specify the function  $f$ , and our proof remains valid even if  $f$  depends explicitly on the coordinates  $x, y, z$ . Let us denote by  $\zeta$  the constant value  $\psi_0'$  which  $\psi'$  assumes on the surfaces  $S_i$ , and let us introduce a function  $\chi$  defined by

$$\chi = \psi'/\zeta.$$

This function satisfies the equation

$$\Delta\chi = \frac{1}{\zeta} f(\lambda\zeta\chi), \quad (28)$$

with the boundary conditions  $\chi \rightarrow 0$  at infinity and  $\chi = 1$  on  $S_i$ . The expression (25) becomes:

$$\frac{4\pi}{\epsilon} F_1 = - \int_0^1 d\lambda \iint_{S_i} \zeta \frac{\partial\chi(\lambda\zeta\chi)}{\partial n} dS d\zeta, \quad (29a)$$

where the surface integral is taken over all the surfaces  $S_i$ :  $\partial/\partial n$  denotes the derivative in the direction of the outward normal and  $dS$  is a surface element on  $S_i$ .

$$\frac{4\pi}{\epsilon} F_2 = - \int_0^1 \frac{d\lambda}{\lambda} \iint \zeta \chi(\lambda, \zeta; x, y, z) f(\lambda\zeta\chi) dx dy dz \quad (29b)$$

We differentiate both expressions with respect to  $\psi_0$ , which for (29b) is identical with a differentiation with respect to  $\zeta$ , as in the second method, the surface potential is considered as remaining constant:

$$\frac{4\pi}{\epsilon} \frac{\partial F_1}{\partial \psi_0} = \iint_{S_i} \zeta \frac{\partial\chi}{\partial n} dS \quad (30a)$$

$$\frac{4\pi}{\epsilon} \frac{\partial F_2}{\partial \psi_0} = - \int_0^1 d\lambda \iint [(\chi + \zeta\chi_\zeta) f + (\lambda\zeta\chi^2 + \lambda\zeta^2\chi\chi_\zeta) f'] dx dy dz \quad (30b)$$

where  $\chi_\zeta$  is the derivative of  $\chi$  with respect to  $\zeta$ . In order to transform the volume integral in (30b) we try to express it in such a form that Green's theorem can be applied. Differentiating (28) with respect to  $\lambda$  and  $\zeta$ , we find:

$$\Delta\chi_\lambda = \frac{1}{\zeta} f + \frac{\lambda}{\zeta} (\zeta\chi + \lambda\zeta\chi_\lambda) f'$$

$$\Delta\chi_\zeta = -\frac{\lambda}{\zeta^2} f + \frac{\lambda}{\zeta} (\lambda\chi + \lambda\zeta\chi_\lambda) f'.$$

whence

$$\zeta^2 (\chi_\zeta \Delta\chi_\lambda - \chi_\lambda \Delta\chi_\zeta) = (\zeta\chi_\zeta + \lambda\chi_\lambda) f + (\lambda\zeta^2\chi\chi_\zeta - \lambda^2\zeta\chi\chi_\lambda) f',$$

$$\zeta (\chi \Delta\chi_\lambda - \chi_\lambda \Delta\chi) = (\chi - \lambda\chi_\lambda) f + (\lambda\zeta\chi^2 + \lambda^2\zeta\chi\chi_\lambda) f'.$$

It follows that

$$\begin{aligned} \frac{4\pi}{\epsilon} \frac{\partial F_2}{\partial \psi_0} &= - \int_0^1 d\lambda \iint \left[ \zeta^2 \{ \chi_\zeta \Delta\chi_\lambda - \chi_\lambda \Delta\chi_\zeta \} + \right. \\ &\quad \left. + \zeta \{ \chi \Delta\chi_\lambda - \chi_\lambda \Delta\chi \} \right] dx dy dz. \end{aligned}$$

Applying Green's theorem and observing that the outward normal to the region of integration is the inward normal to the surfaces  $S_i$ , we obtain:

$$\begin{aligned} \frac{4\pi}{\epsilon} \frac{\partial F_2}{\partial \psi_0} &= + \int_0^1 d\lambda \iint_{S_i} \left[ \zeta^2 \left\{ \frac{\partial\chi_\lambda}{\partial n} \cdot \chi_\zeta - \frac{\partial\chi_\zeta}{\partial n} \cdot \chi_\lambda \right\} + \right. \\ &\quad \left. + \zeta \left\{ \frac{\partial\chi_\lambda}{\partial n} \chi - \frac{\partial\chi}{\partial n} \cdot \chi_\lambda \right\} \right] dS. \end{aligned}$$

But because of the boundary condition,  $\chi = 1$  on  $S_i$ ,  $\chi_\lambda$  and  $\chi_\zeta$  vanish, so that

$$\frac{4\pi}{\epsilon} \frac{\partial F_2}{\partial \psi_0} = + \int_0^1 d\lambda \iint_{S_i} \zeta \frac{\partial\chi_\lambda}{\partial n} dS = \iint_{S_i} \zeta \frac{\partial\chi(\lambda=1)}{\partial n} dS.$$

for  $\partial\chi(\lambda=0)/\partial n = 0$ . Thus we have proved that

$$\frac{\partial F_1}{\partial \psi_0} = \frac{\partial F_2}{\partial \psi_0}$$

Since for  $\psi_0 = 0$  both  $F_1$  and  $F_2$  reduce to zero, this establishes the required result.

Starting again from the "complete" differential equation (3'):

$$\frac{d^2y}{d\xi^2} = \sinh y, \quad (3')$$

we have to find its solution satisfying the boundary conditions:

$$y = u = \frac{ve\psi_d}{kT} \quad \text{and} \quad \frac{dy}{d\xi} = 0 \quad \text{for } x = d.$$

In Chapter II, § 2, we saw that the general solution of this differential equation, after integrating once, reads:

$$\left( \frac{dy}{d\xi} \right)^2 = 2 \cosh y + C.$$

In the central plane in which  $x = d$ ,  $y = u$  and  $dy/d\xi = 0$ , whence

$$0 = 2 \cosh u + C \\ \text{or } C = -2 \cosh u.$$

For the solution we obtain<sup>1</sup>:

$$\frac{dy}{d\xi} = -\sqrt{2 \cosh y - 2 \cosh u} \quad (31)$$

In order to find the electric potential function we have to integrate eq. (31) a second time; this will give us, if the integration is carried out between the limits  $x = 0$  and  $x = d$  (or between  $y = z$  and  $y = u$ ), the desired expression giving us the potential midway between the plates ( $u$ ) as a function of the plate distance ( $2d$ ). Hence

$$\int_z^u \frac{dy}{\sqrt{2(\cosh y - \cosh u)}} = - \int_0^{xd} d\xi = -xd \quad (32)$$

This integral leads to an elliptic integral of the first kind, for which tables are available; it can therefore be solved numerically. The results are given in Table IX. Here, for a number of values of  $z$ , from  $z = 0.5$  up to  $z = 10$  (i.e., for monovalent ions, up to  $\psi_0 = 256$  millivolts), we give the values of  $xd$  for a series of values of  $u$ . From these data a graphic representation of  $u$  as a function of the plate distance, for a given value of  $z$ , may easily be obtained.

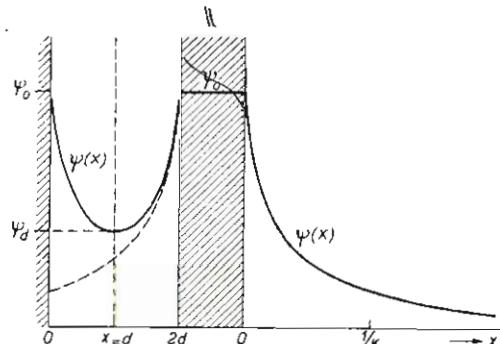


Fig. 8. Schematic representation of the electric potential between two plates, in comparison with that for a single double layer

each other. The first question to be answered is then the static problem of the distribution of the charges and the electric potential function in the liquid layer between the two plates. Mathematically this problem differs from that considered in Chapter II, Section 2, because of the different limiting conditions. In view of the symmetry of the problem we shall only consider the liquid layer between the left wall and the central plane between the two plates, i.e., if the plate distance is  $2d$ , the system between  $x = 0$  and  $x = d$ . (See Fig. 8).

<sup>1</sup> A similar equation was already derived by Corkill and Rosenhead, Proc. Roy. Soc., A 172 (1939) 410.

In order to carry out the integration we bring the integral into the general form (annotation of Jahnke-Emde<sup>1</sup>)

$$F(k, q) = \int_0^q \frac{d\psi}{\sqrt{1 - k^2 \sin^2 \psi}} = \int_0^q \frac{d\psi}{\sqrt{1 - \sin^2 u \sin^2 \psi}}$$

For this purpose we put

$$e^{-u} = k = \sin u \quad \text{and} \quad e^{-y} = \sin u \sin^2 \psi.$$

Differentiating the latter form we have

$$e^{-y} dy = -2 \sin u \sin \psi \cos \psi d\psi = \sin u \sin^2 \psi dy.$$

or:

$$dy = -\frac{2 d\psi}{\operatorname{tg} \psi}$$

Further on we have the limiting conditions:

$$y = u \text{ corresponds to } \sin^2 \psi = 1, \text{ or } \psi = \pi/2,$$

and for  $y = z$  we have  $\sin^2 \psi = \exp \{- (z - u)\}$  or

$$\psi = \arcsin \exp \{- (z - u)/2\},$$

whence:

$$\begin{aligned} zd &= \int_u^z \frac{dy}{\sqrt{2 \cosh y - 2 \cosh u}} \\ &= \int_{\arcsin e^{-\frac{z-u}{2}}}^{\pi/2} \operatorname{tg} \psi \left\{ \frac{1}{\sin u} \left( \frac{1}{\sin^2 \psi} - 1 \right) + \sin u (\sin^2 \psi - 1) \right\}^{1/2} - 2 d\psi \\ &= \int_{\arcsin e^{-\frac{z-u}{2}}}^{\pi/2} \frac{2 d\psi}{\frac{1}{\sqrt{\sin u}} \sqrt{1 - \sin^2 u \sin^2 \psi}} = \\ &= 2 e^{-\frac{u}{2}} \int_{\arcsin e^{-\frac{z-u}{2}}}^{\pi/2} \frac{d\psi}{\sqrt{1 - \sin^2 u \sin^2 \psi}} = \\ &= zd = 2 \exp(-u/2) [F(\exp(-u), \pi/2) - \\ &\quad - F(\exp(-u), \arcsin \exp\{- (z - u)/2\})]. \end{aligned}$$

Accordingly (32) is found from the difference of two functions  $F(k, q)$  which may both be read directly from the tables of Jahnke-Emde.

<sup>1</sup> E. Jahnke and F. Emde, *Tables of functions* 2nd ed., Teubner, Leipzig, Berlin 1933, p. 124 et. seq.

	$z-u=0,1$	$z-u=0,3$	$z-u=0,6$	$u=9$	$u=8$	7	6	5	4	3	2	1	0,4	0,25	0,1
$z = 10$	0,00434	0,00836	0,01337	0,02042	0,04374	0,08128	0,1429	0,2444	0,4117	0,68795	1,148	1,962	2,721	3,440	4,366
9	0,007324	0,01379	0,02208		0,03367	0,07211	0,1340	0,2356	0,4030	0,6792	1,139	1,953	2,712	3,431	4,357
8	0,01208	0,02273	0,03642		0,05551	0,1189	0,2210	0,3885	0,66475	1,1245	1,939	2,698	3,417	4,343	
7	0,0199	0,03748	0,06005		0,09154	0,1961	0,3644	0,6407	1,101	1,915	2,674	3,393	4,318		
6	0,03275	0,06179	0,09900		0,1509	0,3232	0,6010	1,061	1,876	2,635	3,354	4,280			
5	0,05410	0,10185	0,1632		0,2488	0,5333	0,9955	1,811	2,570	3,290	4,215				
4	0,08915	0,1680	0,2692		0,4105	0,8837	1,702	2,462	3,181	4,107					
3	0,1471	0,2774	0,4455		0,6813	1,518	2,280	2,998	3,924						
2	0,2435	0,4643	0,7513		1,178	1,958	2,680	3,608							
1	0,4353	0,8551	1,537		1,283	2,035	2,971								
0,5	0,8706	1,558			1,309	2,241									

TABLE IX  
 $zd$  AS A FUNCTION OF  $z$  AND  $u$  ACCORDING TO EQ. (32)

$$z = \frac{v e^{\frac{u}{kT}}}{kT} \quad u = \frac{v c^{\frac{z}{kT}}}{kT}$$

Before investigating the properties of (32) more closely, we shall consider two approximations. Both for small and for strong interaction it appears possible to derive explicit expressions approximating (32), and the former case especially leads to a simple expression for  $u$  as a function of  $zd$ , which proves to be very useful.

If the interaction is small, the electric potential due to one double layer will be negligible at the surface of the second plate, and inversely. As a first approximation we may therefore assume that the electric potential in the neighbourhood of the central

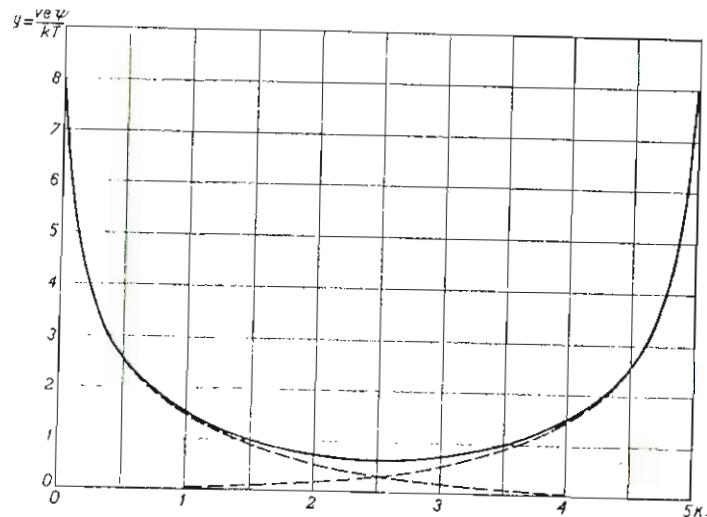


Fig. 9. Electric potential function between two plates ( $z = 8$ ) for small interaction ( $zd = 2.5$ ). Approximately, the potential can be built up additively from the electric potential functions of the two single double layers separately (dotted lines).

plane is simply built up additively from the electric potential functions due to the two unperturbed double layers separately. (Cf. fig. 9). Hence we put

$$u = 2y_d'$$

in which  $y_d' = ve\psi_d'/kT$  measures the electric potential for a single double layer at a distance  $d$  from the surface.

As the interaction is small the plate distance is necessarily large, so that  $zd \gg 1$ , and eq. (10) can be applied:

$$y_d' = 4\gamma \cdot e^{-zd}, \quad \text{with } \gamma = \frac{e^{z/2} - 1}{e^{z/2} + 1};$$

and accordingly we obtain

$$u = 8\gamma \cdot e^{-zd} \quad (33)$$

Hence we see that, for small interaction, for a given value of the electric potential at the surface of the plates (and therefore a given value of  $\gamma$ ), the potential midway between the plates decreases exponentially with increasing plate distance.

In order to show the validity region of this approximation we compare, for two values of  $z$ , the values calculated with the aid of (33) to those of Table IX;

TABLE X  
VALUES OF  $zd$  ACCORDING TO (33) AS COMPARED WITH THOSE OF TABLE IX

$u$	$z = 6, \gamma = 0.905$					$z = 8, \gamma = 0.964$				
	0.1	0.25	0.50	1.0	2.0	0.1	0.25	0.50	1.0	2.0
$zd$ (eq. 33)	4.28	3.365	2.67	1.98	1.29	4.35	3.43	2.73	2.04	1.35
$zd$ (table IX)	4.280	3.354	2.635	1.876	1.061	4.343	3.417	2.698	1.939	1.124

This comparison shows that the deviations become appreciable in the neighbourhood of  $zd = 1$ ; according to the approximation the value of  $u$  has there been computed somewhat too high.

As  $u$  is proportional to  $\gamma$ , which (if the double layer potential is not very small) is only slightly dependent on  $z$ , we see that, if the interaction remains small, neither is  $u$  very sensitive to variations of  $z$ .

The approximative equation for strong interaction, referred to above, is obtained when the electric potential between the two plates is everywhere large, hence  $u \gg 1$ . The formula is less interesting than eq. (33), because it is not so simple; moreover, for the stability problem investigated further on, the electric potential function for small plate distances ( $zd \ll 1$ ) proves to be of minor importance.

If  $u \gg 1$ , eq. (32) can be simplified to

$$zd \approx \int_u^z \frac{dy}{V e^y - e^u},$$

with neglection of  $e^{-y}$  and  $e^{-u}$ . This enables the integration to be executed:

$$\int_u^z \frac{dy}{V e^y - e^u} = e^{-u/2} \int_u^z \frac{e^{-y/2} dy}{V e^{-u} - e^{-y}} = -2e^{-u/2} \int \frac{de^{-y/2}}{V e^{-u} - e^{-y}} =$$

$$\begin{aligned} & \cdot 2e^{-u/2} \left[ \arcsin \exp \left( -\frac{y-u}{2} \right) \right]_u^z \\ & \cdot 2e^{-u/2} \left[ \arcsin \exp \left( -\frac{z-u}{2} \right) - \frac{\pi}{2} \right] \\ & 2e^{-u/2} \arccos \exp \left( -\frac{z-u}{2} \right). \end{aligned}$$

Hence we get <sup>1</sup>

$$\begin{aligned} zd = & 2e^{-u/2} \arccos \exp \left( -\frac{z-u}{2} \right) \\ \exp \left( -\frac{z-u}{2} \right) = & \cos \left\{ \frac{zd}{2} \cdot e^{u/2} \right\} \end{aligned} \quad (33a)$$

The values of  $u$  as a function of  $zd$ , have been represented graphically in Figs. 10 and 11. In fig. 10 curves are given for

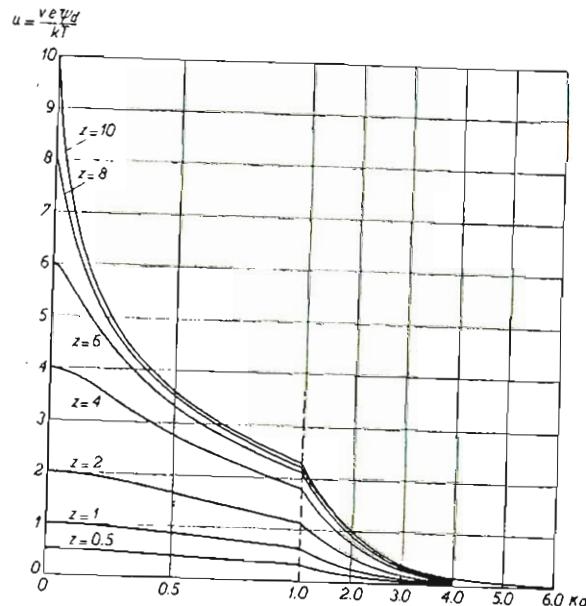


Fig. 10. Potential ( $\psi_d$ ) half-way between the plates as a function of the plate distance ( $2d$ ) for different values of the surface potential ( $\psi_0$ ). In the figure the values of  $u = \frac{ve\psi_d}{kT}$ ,  $zd$ , and  $z = \frac{ve\psi_0}{kT}$  are given.

a number of  $z$  values. In fig. 11 (holding for  $z = 8$ ) the full line refers to the data of Table IX, the dotted lines refer to

<sup>1</sup> E. J. W. Verwey, *Trans. Faraday Soc.*, 36 (1940) 192.

the approximative equations (33) and (33a). With increasing interaction the potential midway between the plates increases continually from 0 ( $d = \infty$ ) to  $u = z$  (for  $d = 0$ ). All curves show an inflexion point, so that the strongest increase of  $u$  always occurs for finite values of  $d$ .

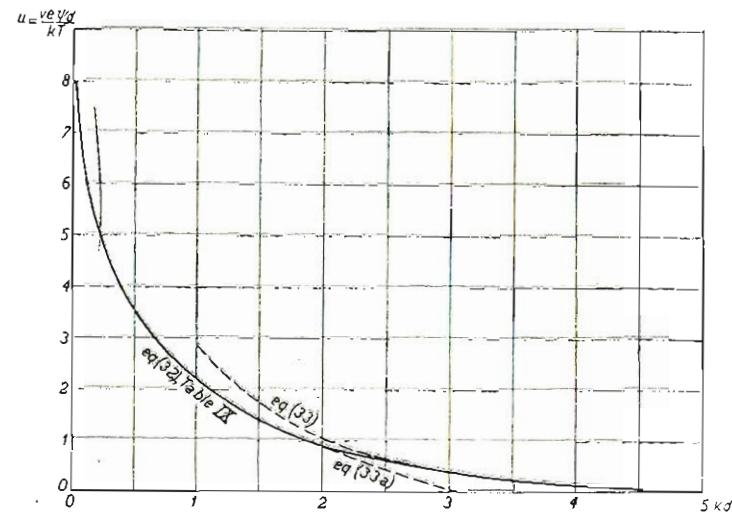


Fig. 11. Potential ( $\psi_d$ ) half-way between the plates as a function of the plate distance ( $2d$ ) for  $\psi_0 = 204.8$  mV ( $z = 8$ ).  
Dotted lines: approximative for strong (eq. (33a)) and small (eq. (33)) interaction.

If the value of  $u$  is known, the whole electric potential function between the plates may now be derived with the aid of eq. (31), giving the derivative in every point. Again, the value of  $d\psi/dx$  for  $x = 0$  will be especially interesting. From (31) we find directly

$$\left( \frac{d\psi}{dx} \right)_0 = \left( \frac{dy}{d\xi} \right)_0 \cdot \frac{xkT}{ve} = - \frac{xkT}{ve} \sqrt{2 \cosh z - 2 \cosh u}, \quad (31a)$$

showing that, for constant values of  $z$ , the initial slope of  $\psi(x)$  decreases with increasing  $u$ , and, accordingly, with decreasing plate distance. For  $d = \infty$  or  $u = 0$ ,  $\cosh u = 1$  and eq. (31a) reduces again to the corresponding eq. (5b) for a single double layer.

The electric potential as a function of the distance between the plates, for a number of plate distances, is given schematically in Fig. 12.

As the charge of the double layer is directly proportional

to  $(d\psi/dx)_0$ , the above remark about the initial slope of the potential will hold invariably for the charge  $\sigma$ :

$$\sigma = - \int_0^d \epsilon \frac{d\psi}{dx} dx = - \frac{\epsilon}{4\pi} \left( \frac{d\psi}{dx} \right)_0 = \frac{n\kappa kT}{2\pi} \sqrt{2\cosh z - 2\cosh u}. \quad (34)$$

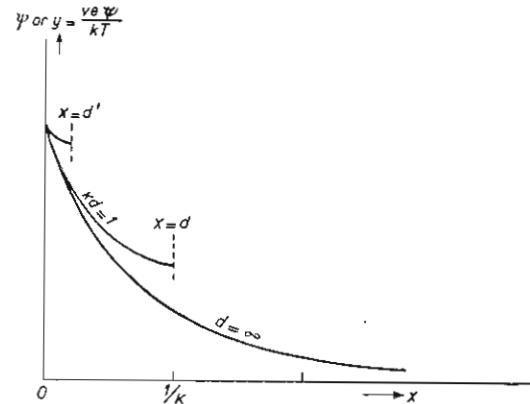


Fig. 12. Electric potential function (left hand part) between two parallel plates (schematically) for different plate distances. With increasing interaction the potential midway between the plates increases, and the initial slope  $(d\psi/dx)$  for  $x=0$  decreases.

The decrease of the double layer charge with increasing interaction, for a constant value of the double layer potential, is illustrated in Fig. 13. It shows that the double layer charge

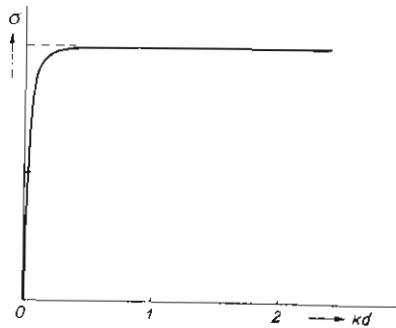


Fig. 13. Surface charge,  $\sigma$ , as a function of the plate distance for  $z = 8$ .

is only slightly affected as long as the interaction is small (For  $z = 8$ , for instance, the charge for  $zd = 1$  is still 99.7 % of the charge for  $d = \infty$ ). Neither will the electric potential

function in the close neighbourhood of the wall be sensibly changed by the interaction, even for moderate plate distances. Considerable changes of charge and potential function only occur if  $zd < 0.5$ , i.e., if the plates are brought rather closely together (their distance being smaller than the characteristic length of Debye,  $1/z$ ).

We already mentioned in § 4 of Chapter III that this decrease of the double layer charge may well be considered to be the most important feature in the interaction of two double layers. It follows from equation (23) that the free energy of the double layer increases (becomes less negative) with decreasing charge. Now an increase of the free energy is equivalent to a repulsion between the plates, so this decrease of the charge is the primary cause of the repulsion between two double layers. This point is dealt with in more detail in Chapter V.

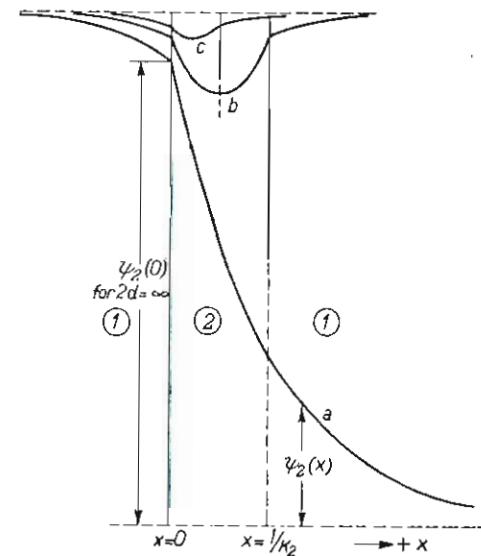


Fig. 14. The interaction of two double layers at the interface liquid/liquid. The electric potential for small values of  $D$  when the liquid with the smallest dielectric constant, phase 2, is not infinitely large but present as a thin layer (thickness  $2d$ ) between two phases 1. Curve (a):  $2d = \infty$ ; curve (b):  $2d = 1/z_2$ ; curve (c):  $2d = 1/2z_2$ . In the drawing it is assumed that  $n_1 \epsilon_1 / n_2 \epsilon_2 = 100$  and  $z_1/z_2 = 2$ . For  $2d = 1/z_2$  the partial potential in phase 1 is 0.44 times that for  $2d = \infty$ ; for  $2d = 1/2z_2$  it is 0.25 times that for  $2d = \infty$ .

## § 2. Interaction of two double diffuse double layers

It is instructive to consider finally the case where two double diffuse double layers interact; i.e., the double layer interaction

occurring when two equal liquid phases are separated by a thin layer of a second liquid<sup>1</sup>. This case is illustrated by Fig. 14, the parallel of Fig. 8, showing the electric potential function for different thicknesses of the central liquid layer. The partition of the electric double layer potential  $D = -\psi_1(0) + \psi_2(0)$  about the two liquid layers on both sides of the interface (we use here the same annotation as in Fig. 3, showing the double layer at the interface of two liquids) is now influenced by the interpenetration of the two diffuse layers in phase 2. The circumstance that in this case not only the potential in the intermediate phase 2 but also that in phase 1 is altered, expresses very clearly the incomplete development of the electric double layer as a result of the interaction.

The partition of the electric potential may again be calculated from the condition that the charge in phase 1 and that in phase 2 between  $x = 0$  and  $x = d$  compensate each other; hence, according to eq. (14) and eq. (31), we have

$$\sqrt{n_1 \epsilon_1} \sqrt{2 \cosh z_1 - 2} = \sqrt{n_2 \epsilon_2} \sqrt{2 \cosh z_2 - 2 \cosh u}$$

with

$$-z_1 + z_2 = \Delta = \frac{veD}{kT}.$$

Together with the relation (32) between  $u$  and  $d$  we can calculate, for a given value of  $D$ , corresponding values of  $z_2$ ,  $u$  and  $d$ . For small values of  $D$  the equations may be further simplified.

<sup>1</sup> E. J. W. Verwey, *Trans. Faraday Soc.*, 36 (1940) 192.

## V. THE POTENTIAL ENERGY DUE TO THE INTERACTION OF TWO FLAT DOUBLE LAYERS.

### § 1. Introduction

We shall now pass to the calculation of the potential energy, for a system of two flat double layers, as a function of the distance of the plates. These calculations will be given for two double layers according to the Gouy-Chapman model, and are therefore based on the complete differential equation (3). We shall therefore make use of the equations derived in the preceding chapter for the distribution of the charges and the electric potential function for this case.

We shall follow two different ways. In the first place we calculate, with the aid of the general expression (26) on page 58, the free energy of such a double layer system. The potential energy due to the interaction may then be derived immediately from this quantity. By this method we shall be able to give a complete numerical evaluation of the potential energy for arbitrary plate distance. For, the integration leads to an elliptic integral of the second kind, and can therefore be computed numerically with the aid of the well known tables. — In the second place we shall derive, by integrating the force between the plates with respect to the distance, an approximate explicit expression for the potential energy; this expression has only a limited validity, but proves to be useful in special cases.

### § 2. Potential energy via the free energy

We start from the general expression (26) for the free energy, and make use of the expressions derived in chapter IV between  $\psi$ ,  $\rho$  and  $d$ . The integration, a somewhat tedious one, leads to the following expression for the free energy of 1 cm<sup>2</sup> double layer (between  $x = 0$  and  $x = d$ ):

$$F = -\frac{2nkT}{\pi} \left\{ \frac{xd}{2} (3e^u - 2 - e^{-u}) + \right. \\ \left. + 2\sqrt{2 \cosh z - 2 \cosh u} + 2 \int_u^z \frac{e^{-y} - e^u}{\sqrt{2 \cosh y - 2 \cosh u}} dy \right\} \quad (35)$$

The integral in this expression may be converted into an

elliptic integral of the second kind, for which tables are available. Combining this expression with

$$xd = \int_{-u}^z \frac{dy}{\sqrt{2 \cosh y - 2 \cosh u}}, \quad (32)$$

which is computed numerically in Chapter IV (Table IX), we can evaluate  $F$  (for a given value of  $z$ ) as a function of  $d$ .

For  $d = \infty$ , i.e. for a single double layer, the free energy may be found either by integrating eq. (26) on the basis of the equations of Gouy and Chapman discussed in § 2 of Chapter II, or by specialising eq. (35) to the case  $d = \infty$ . In both cases we find the explicit expression:

$$F_\infty = -\frac{2nkT}{\pi} \left\{ 4 \cosh \frac{z}{2} - 4 \right\} \quad (36)$$

In these two expressions, eq. (35) and eq. (36), we dispose of the necessary equations for the calculation of the variation of the free energy of the double layer system as a consequence of the interaction.

The conversion of the general expression (26) to the special cases (35) and (36) can be effected in the following way.

Introducing the variable  $\lambda; \psi'$  we make the following substitutions for  $\psi'$  and  $\rho'$  in eq. (26):

$$\psi' d\lambda = \frac{\partial(\lambda\psi')}{\partial\lambda} d\lambda = \lambda \cdot \frac{\partial\psi'}{\partial\lambda} d\lambda$$

and

$$\rho' = -\frac{\epsilon}{4\pi} \cdot \frac{\partial^2\psi'}{\partial x^2} = -2ne \lambda \cdot \sinh \frac{\lambda e\psi'}{kT}$$

and obtain, by specializing (26) to the case considered here, i.e. to  $1 \text{ cm}^2$  surface,

$$F = \int_0^1 \int_0^d \rho' \psi' dx d\lambda = - \int_0^1 \int_0^d 2ne \sinh \frac{\lambda e\psi'}{kT} \cdot \frac{\partial(\lambda\psi')}{\partial\lambda} dx d\lambda + \\ + \int_0^1 \int_0^d \frac{\epsilon}{4\pi} \cdot \frac{\partial\psi'}{\partial\lambda} \cdot \frac{\partial^2\psi'}{\partial x^2} dx d\lambda = I_1 + I_2.$$

In the first of these integrals the integration with respect to  $\lambda$  may be carried out immediately.

$$I_1 = - \int_0^1 \int_0^d 2n kT \sinh \left( \frac{\lambda e\psi'}{kT} \right) \frac{d}{dx} \left( \frac{\lambda e\psi'}{kT} \right) dx \\ = - \int_0^d 2n kT \left( \cosh \frac{e\psi}{kT} - 1 \right) dx,$$

in which  $\psi$  denotes the potential, when the double layer is fully charged ( $\lambda = 1$ ). The second integral may be written:

$$I_2 = \frac{\epsilon}{4\pi} \int_0^1 \int_0^d \left\{ \frac{\partial}{\partial x} \left( \frac{\partial\psi'}{\partial x} \cdot \frac{\partial\psi'}{\partial\lambda} \right)_\lambda - \left( \frac{\partial\psi'}{\partial x} \right)_\lambda \cdot \frac{\partial^2\psi'}{\partial x \cdot \partial\lambda} \right\} dx d\lambda,$$

the first half of which may be integrated immediately with respect to  $x$ , and is zero, as:

for  $x = 0$ :  $\left( \frac{\partial\psi'}{\partial\lambda} \right)_x = 0$ , because eq. (26) is derived on the assumption that  $\psi'_0$  is kept constant during the charging process,

for  $x = d$ :  $\left( \frac{\partial\psi'}{\partial x} \right)_\lambda = 0$ , because of the minimum in the potential midway between the plates.

The remaining part of  $I_2$  may then be written:

$$I_2 = -\frac{\epsilon}{8\pi} \int_0^1 \int_0^d \frac{\partial}{\partial\lambda} \cdot \left( \frac{\partial\psi'}{\partial x} \right)^2 dx d\lambda,$$

and be integrated with respect to  $\lambda$  (in which  $\frac{\partial\psi'}{\partial x} = 0$  for  $\lambda = 0$ ):

$$I_2 = -\frac{\epsilon}{8\pi} \int_0^d \left( \frac{\partial\psi'}{\partial x} \right)^2 dx.$$

Hence the complete expression for  $F$  runs

$$F = -2n kT \int_0^d \left( \cosh \frac{e\psi}{kT} - 1 \right) dx - \frac{\epsilon}{8\pi} \int_0^d \left( \frac{\partial\psi}{\partial x} \right)^2 dx \quad (37a)$$

It is now convenient to introduce again  $y, u$  and  $\xi$  as variables, then to take  $+2nkT \cosh u$  under the first integrand, and transform the expression  $\cosh y - \cosh u$  with the aid of equation (31):

$$\begin{aligned}
 F = & -2n kT \int_0^d (\cosh u - 1) dx - 2n kT \int_0^d (\cosh y - \cosh u) dx + \\
 & - \frac{\varepsilon z^2 k^2 T^2}{8\pi e^2} \int_0^d \left( \frac{dy}{dx} \right)^2 dx = \\
 = & -2n kT d (\cosh u - 1) - n kT \int_0^d \left( \frac{dy}{dx} \right)^2 dx - \frac{\varepsilon z^2 k^2 T^2}{8\pi e^2} \int_0^d \left( \frac{dy}{dx} \right)^2 dx.
 \end{aligned}$$

The integrals (which are equal) may then be transformed into an integration over  $y$ :

$$F = -2n kT d (\cosh u - 1) + \frac{2n kT}{z} \int_z^u \sqrt{2 \cosh y - 2 \cosh u} dy \quad (37b)$$

The integral contained in this expression may be transformed into an elliptic integral of the second kind. To this end it is written and transformed in the following way:

$$\begin{aligned}
 I_3 = & \int_z^u \sqrt{2 \cosh y - 2 \cosh u} dy = \int_z^u \frac{e^y + e^{-y} - e^u - e^{-u}}{\sqrt{2 \cosh y - 2 \cosh u}} dy = \\
 = & \int_z^u \frac{e^y - e^{-y} + e^u - e^{-u} + 2e^{-y} - 2e^u}{\sqrt{2 \cosh y - 2 \cosh u}} dy = \\
 = & - \int_u^z \frac{2 \sinh y}{\sqrt{2 \cosh y - 2 \cosh u}} dy - 2 \sinh u \int_u^z \frac{dy}{\sqrt{2 \cosh y - 2 \cosh u}} - \\
 & - 2 \int_u^z \frac{e^{-y} - e^{+u}}{\sqrt{2 \cosh y - 2 \cosh u}} dy = \\
 = & -2 \sqrt{2 \cosh z - 2 \cosh u} - 2 zd \sinh u - 2 I_1,
 \end{aligned}$$

in which eq. (32) is used for the introduction of  $zd$ .

Substituting again  $e^{-u} = \sin \alpha$  and  $e^{-y} = \sin \alpha \cdot \sin^2 q$ , the integral  $I_1$  may be written (notation of Jahnke-Emde)

$$\begin{aligned}
 I_1 = & -2e^{\frac{u}{2}} \int_{\arcsin \exp(-\frac{z-u}{2})}^{\pi} \sqrt{1 - \sin^2 \alpha \sin^2 q} dq = \\
 = & -2e^{\frac{u}{2}} \left\{ E \left( e^{-u}, \frac{\pi}{2} \right) - E \left( e^{-u}, \arcsin \exp \left( -\frac{z-u}{2} \right) \right) \right\} \quad (38)
 \end{aligned}$$

and we obtain for  $F$  the final expression:

$$\begin{aligned}
 F = & -2n kT d (\cosh u - 1) + \frac{2n kT}{z} I_3 = \\
 = & -\frac{2n kT}{z} \left( \frac{zd}{2} (3e^u - 2 - e^{-u}) + 2 \sqrt{2 \cosh z - 2 \cosh u} + 2I_1 \right)
 \end{aligned}$$

This equation enables us to calculate the free energy for any given value of the surface potential ( $z$ ) and the plate distance ( $zd$ ).

For  $zd = \infty$  it can easily be shown that the first term between the brackets is zero ( $u$  approaches to zero as  $e^{-zd}$ ) and we find for

$$\begin{aligned}
 F_{d=\infty} = & -\frac{2n kT}{z} [2 \sqrt{2 \cosh z - 2} - 4 \int_{\arcsin \exp(-z/2)}^{\pi/2} \cos q dq] \\
 = & -\frac{2n kT}{z} [2 \sqrt{2 \cosh z - 2} - 4 \{1 - \exp(-z/2)\}] \\
 = & -\frac{2n kT}{z} [4 \cosh \frac{z}{2} - 4]
 \end{aligned} \quad (36)$$

which is, therefore, the free energy of a single double layer.

The quantity we are chiefly interested in is the amount of work needed to bring the plates from infinity to a distance  $2d$  (i.e., the repulsive potential). As the free energies  $F$  and  $F_{\infty}$  are related to the double layer of  $1 \text{ cm}^2$  of one plate only, this repulsive potential per  $\text{cm}^2$ ,  $V_R$ , is:

$$V_R = 2(F - F_{\infty}). \quad (39)$$

Hence, passing now to a reproduction of the results of the numerical computation of (35), we shall give these data by tabulating (Table XI) directly the values of  $V_R$  obtained by combining eq. (35) and (36).

Inspecting (35) and (36) we note that this quantity  $V_R$  may be written  $V_R = (z/v^2) f(u, z)$ ; the form between brackets contains only  $u$  and  $z$  as variables ( $zd$  is, itself, a function of

$u$  and  $z$ ), and the factor  $n/z$  is proportional to  $n^1/v$ , or to  $z/v^2$ .

$$(z = \sqrt{\frac{8\pi n}{\epsilon kT}} ve)$$

For given values of  $u$  and  $z$  (and, therefore, for given values of  $zd$ ) the value of  $V_R$  still depends on the valency and the concentration of the ions, in such a way that it is proportional to  $z/v^2$ . We have therefore given, in Table XI, the quantity

$$(v^2/\kappa) V_R = f(u, z) \quad (40)$$

in  $10^{-4}$  dynes. (The temperature is supposed to be 25° C. the dielectric constant 78.55). Hence, if, for instance,  $v = 1$  and  $\kappa = 10^5 \text{ cm}^{-1}$  (i.e. an ionic concentration of about

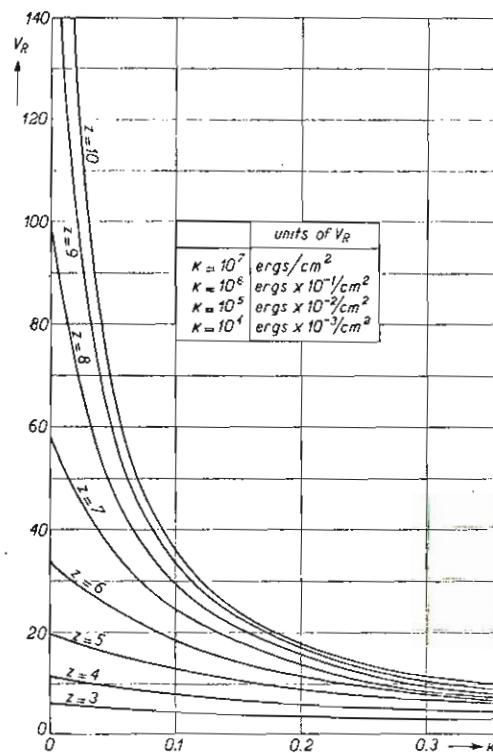


Fig. 15. Repulsive potential for 1-1 valent electrolytes as a function of  $zd$ , for strong interaction (small  $zd$ ).

$10^{-5} \text{ mol/liter}$ ) we find, in the table,  $V_R$  in  $10^{-2} \text{ ergs/cm}^2$ , but for  $v = 3$ , and the same value of  $\kappa$ , the value derived from Table XI must be divided by 9 in order to obtain  $V_R$  expressed in the same unit, etc. The value of  $d$  corresponding to each set of

TABLE XI  
 $f(u, z) = (v^2/\kappa) V_R$  in  $10^{-7}$  dynes, and corresponding values of  $zd$ , for different values of  $z = ve\psi_0/kT$

( $u = ve\psi_0/kT$ ;  $V_R$  = repulsive potential due to the double layer interaction for two parallel plates per  $\text{cm}^2$  plate surface).

The numbers given have been computed for a temperature of 25° C and a dielectric constant of 78.55.

	$u = z$	$u = z - 0.1$	$u = z - 0.3$	$u = z - 0.6$	$u = 9$	$u = 8$	$u = 7$	$u = 6$	$u = 5$	$u = 4$	$u = 3$	$u = 2$	$u = 1$	$u = 0.5$	$u = 0.25$	$u = 0.1$	
$z = 10$	$f(u, z)$ $\kappa d$	268.3 .0000	228.2 .00434	192.6 .00836	160.0 .0134	127.1 .0204	75.4 .0437	44.1 .0813	25.4 .143	14.1 .244	7.36 .412	3.42 .690	1.26 .148	.26 .962	.06 .2721	.015 .3440	.0023 4.366
$z = 9$	$f(u, z)$ $\kappa d$	161.5 .0000	135.2 .0073	115.2 .0138	95.6 .0221	76.3 .0337	44.3 .0721	25.4 .134	14.1 .236	7.36 .403	3.42 .679	1.26 .139	.26 .953	.06 .2712	.015 .3431	.0023 4.357	
$z = 8$	$f(u, z)$ $\kappa d$	96.52 .0000	80.56 .0121	68.56 .0227	56.60 .0364			44.8 .0555	25.4 .119	14.1 .221	7.36 .388	3.42 .665	1.26 .124	.26 .939	.06 .2698	.015 .3417	.0023 4.343
$z = 7$	$f(u, z)$ $\kappa d$	57.13 .0000	47.46 .0199	40.18 .0375	32.89 .0600				25.8 .0915	14.17 .196	7.36 .364	3.42 .641	1.26 .1101	.26 .915	.06 .2674	.015 .3393	.0023 4.318
$z = 6$	$f(u, z)$ $\kappa d$	33.27 .0000	27.47 .0327	23.04 .0618	18.66 .0990					14.17 .1509	7.36 .323	3.42 .601	1.26 .1061	.26 .876	.06 .2635	.015 .3354	.0023 4.280
$z = 5$	$f(u, z)$ $\kappa d$	18.83 .0000	15.32 .0541	12.69 .1018	10.07 .1632					7.52 .2488	3.43 .533	1.26 .995	.26 .811	.06 .2570	.015 .3290	.0023 4.215	
$z = 4$	$f(u, z)$ $\kappa d$	10.13 .0000	8.07 .0891	6.51 .1680	4.97 .2692						3.50 .4105	1.26 .884	.26 .702	.06 .2462	.015 .3181	.0023 4.107	
$z = 3$	$f(u, z)$ $\kappa d$	4.962 .0000	3.793 .1471	2.913 .2774	2.061 .4455						1.291 .681	.26 .518	.26 .280	.06 .2998	.015 .3924	.0023 3.924	
$z = 2$	$f(u, z)$ $\kappa d$	1.993 .0000	1.413 .2435	.966 .4643	.584 .751							.265 .1.178	.06 .915	.06 .2.680	.015 .3.608	.0023 3.608	
$z = 1$	$f(u, z)$ $\kappa d$	.4575 .0000	.280 .4353	.135 .855	.0348 .1.537								.063 .1.283	.015 .2.035	.015 .2.971	.0023 2.971	

combinations of  $z$  and  $u$  is obtained from Table IX, but, for the sake of convenience, it has been repeated in Table XI so that  $V_R$  as a function of  $kd$  may be read directly from the table. As in Table XI we give the dimensionless quantity  $zd$ , we find  $d$  for  $z = 10^i$  cm<sup>-1</sup> in 10<sup>-i</sup> cm, etc.

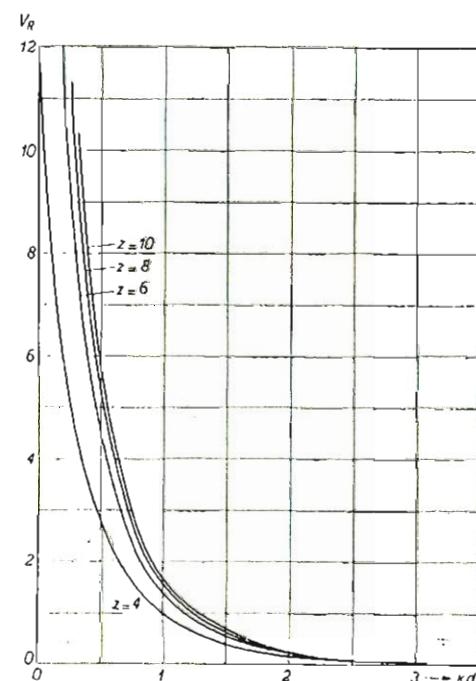


Fig. 16. As fig. 15, showing especially the  $V_R$  curve for large values of  $zd$ .

Scale of  $zd$ : 0.1  $\times$  that of fig. 15.

Scale of  $V_R$ : 10  $\times$  that of fig. 15.

In Fig. 15 and 16 the repulsive potential for 1-1 valent electrolytes is shown as a function of  $zd$ . Fig. 15 especially gives  $V_R$  for small values of  $zd$ , showing a considerable spread according to the value of  $z$ . Fig. 16 shows the outer part of the curves, for large values of  $zd$ , where the interaction is small. Both sets of curves show that the influence of  $z$  upon  $V_R$  decreases with increasing value of  $z$ .

The general character of these  $V_R$  curves is much more strikingly revealed by Fig. 17, containing  $\log V_R$  as a function of  $zd$  (full curves). We see that for  $zd > 1$  the  $V_R$ -curves approximately show a simple exponential decay with increasing plate distance since  $\log V_R$  varies linearly with  $zd$ . For strong interaction the curves show deviations from this simple behaviour. If  $z$  is small ( $z < 3$ ) the repulsive potential increases

less rapidly with decreasing distance than the exponential curve, for larger values of  $z$  ( $z > 3$ ) the repulsive potential increases even more rapidly. It is remarkable that all  $\log V_R$  curves run parallel for large values of  $zd$ . This purely exponential part of the curves shows distinctly that the influence of  $z$  upon the repulsive potential is chiefly perceptible if  $z$  is still small; for large values of  $z$  the parallel logarithmic curves for successive, increasing  $z$  values approach each other more and more.

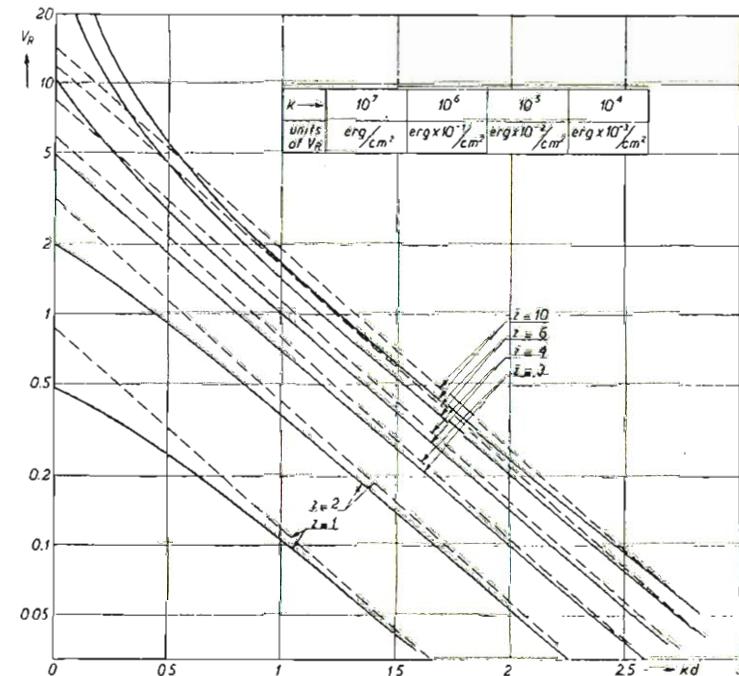


Fig. 17. Repulsive potential on a logarithmic scale against the distance separating the plates.

Full curves: exact according to Table XI.

Dotted curves: approximated equation (43) *vide infra*.

Of course this behaviour must be closely connected with the fact mentioned earlier, that according to the Gouy-Chapman theory the electric potential function in the outer part of the double layer is only slightly affected by the value of the surface potential as soon as  $z$  reaches higher values.

The exponential behaviour of the repulsion curves may be deduced from equation (35) or more easily from considerations on the repulsive force which will be dealt with in the next section.

The curves in Figs. 15, 16 and 17, giving  $V_R$  or  $\log V_R$  as a function of  $zd$ , are applicable for arbitrary values of  $z$ , if

only the potential energy is measured in the proper units along the ordinate. Thus, as indicated in the small tables accompanying Fig. 15 and 17, the energy scale represents ergs per  $\text{cm}^2$  for  $z = 10^4$ , tenths of ergs per  $\text{cm}^2$  for  $z = 10^6$ , etc., and intermediate energy units for intermediate values of  $z$ . This is obviously a direct consequence of the circumstance, mentioned above, that  $v^2/z \cdot V_R = f(u, z)$ , and therefore, for a given value of  $z$ , a function of  $zd$  only.

The influence of the concentration of the electrolyte in the solution upon the repulsive potential between the two plates is entirely expressed by the quantity  $z$ . As  $z$  is proportional to  $n^{\frac{1}{2}}$ , the value of  $f(u, z)$ , as read from the table, must be

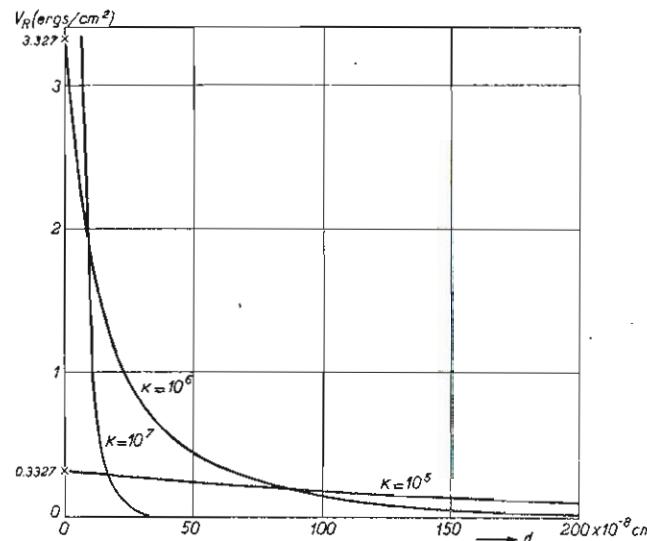


Fig. 18. Repulsive potential for 1-1 valent electrolytes, assuming that  $\psi_0 = 153.6 \text{ mV}$  ( $z = 6$ ) for different concentrations.

multiplied by a factor which increases according to the square root of the ionic concentration. Hence, for equal values of  $f(u, z)$ , i.e., for equal values of  $zd$ , the repulsion potential increases with increasing ionic concentration. Thus, for instance, for  $zd = 0$  the value of  $V_R$  is proportional to  $n^{\frac{1}{2}}$  (provided that the surface potential  $\psi_0$  is not altered by the change in ionic concentration, as will be fulfilled when indifferent electrolyte is added to a diluted sol or suspension). Hence we infer that for small plate distances the repulsion is increased by an increase in ionic concentration. This increased repulsion may readily be explained by the fact that the total charge of the double layer is increased by more electrolyte in the solution (with increasing concentration the double layer

is less diffuse, and has therefore a larger "capacity"). In the previous chapter we have seen that the decrease of the surface charge, which accompanies the drawing together of the plates, is the fundamental factor governing the repulsion. If, by the interaction of the double layers, more charge must be removed from between the plates, more work must be done in bringing the two plates completely together.

Generally, however, we are not interested in  $V_R$  as a function of  $zd$ , but as a function of  $d$ . Accordingly, when the ionic

$$V_R(\text{ergs/cm}^2)$$

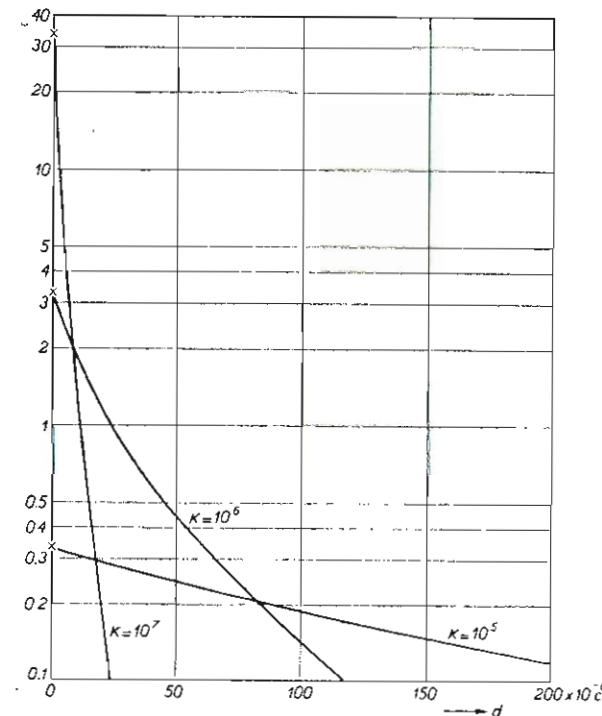


Fig. 19. The same as Fig. 18, with a logarithmic scale of  $V_R$ .

concentration, and therefore  $z$ , is increased the repulsion potential decays more rapidly with increasing plate distance. This more rapid decay (like the quantity  $z$  proportional to  $n^{\frac{1}{2}}$ ) is obviously a consequence of the reduced double layer extension by the increased electrolyte concentration.

The total result of an increase in ionic concentration, therefore, is a reduced repulsion for great distances, but an increased repulsion for small plate distances. This influence of the concentration is illustrated in Fig. 18 and Fig. 19, for 1-1 valent electrolytes, and  $\psi_0 = 154 \text{ mV}$ . ( $z = 6$ ).

The influence of the valency is rather complicated. In the first place the valency  $v$  of the ions enters into  $V_R$  in a way analogous to the concentration  $n$ : the quantity  $z$  is directly proportional to the valency. According to this factor an increase of the ionic valency influences  $V_R$  as a function of  $d$  in much the same way as an increase of  $n$  does. For larger ionic charges the liquid charge is concentrated closer to the surface; the corresponding increase of the double layer capacity again implies a larger repulsion for small plate distances; the corresponding contraction of the double layer, however, will again have the result that the repulsive potential decays more rapidly with increasing distance, and will accordingly be diminished for greater plate distances.

In addition to this there are two other factors influencing  $V_R$  when the ionic valency is altered. To discuss these two factors, we shall compare solutions of a 1-1 valent and a 3-3 valent electrolyte at such concentrations that  $x$  has the same value for both solutions. It then follows from the definition of  $x$  that the molar concentration of the trivalent electrolyte is one-ninth of that of the monovalent electrolyte. The effect of the valency upon the  $V_R$  curve is then twofold.

We again assume the electrical potential on the plates to be the same in both cases. Hence we must consider that  $z = ve\psi_0/kT$ , and that  $z$  is increased by a factor 3 if we pass from  $v = 1$  to  $v = 3$ . If the surface potential has already a large value, this increase of  $z$  has only a minor influence upon the  $V_R$  curve, especially in the outer part of these curves. If the surfaces potential is small, however, the repulsive potential is still rather sensitive to changes of  $z$ , and  $V_R$  is raised appreciably by the corresponding transition to a curve with the threefold value of  $z$ .

In the second place the influence of the valency is present in the factor  $x/v^2$ . According to this effect the whole curve is lowered by a factor 9 (i.e., a constant amount,  $\log 9$ , has to be subtracted from the  $\log V_R$  curve) if we pass from  $v = 1$  to  $v = 3$ .

Accordingly the two effects considered here work in opposite directions. This is illustrated, in the logarithmic scale, in fig. 20. Passing from a system for which  $\psi_0 = 25.6$  millivolts, containing 1-1 valent electrolytes, to a system with 3-3 valent electrolytes and the same value of  $x$  is equivalent, in Fig. 20, to a transition from the curve  $v = 1, z = 1$  to the curve  $v = 3, z = 3$ . It will be seen that, as a result of these two effects, the repulsion is increased for very small values of  $zd$ , but decreased for moderate and large values of  $zd$ . For larger values of the electric surface potential  $\psi_0$  we find an analogous result, as is shown by a comparison of the curves

$v = 1, z = 2$  and  $v = 3, z = 6$  ( $\psi_0 = 51.2$  mV) or the curves  $v = 1, z = 3$  and  $v = 3, z = 9$  ( $\psi_0 = 76.8$  mV). The differences, on both sides of the intersection point of each set of curves, are here larger than for small  $\psi_0$  values, where both curves almost coincide. This is rather important, as we shall see later

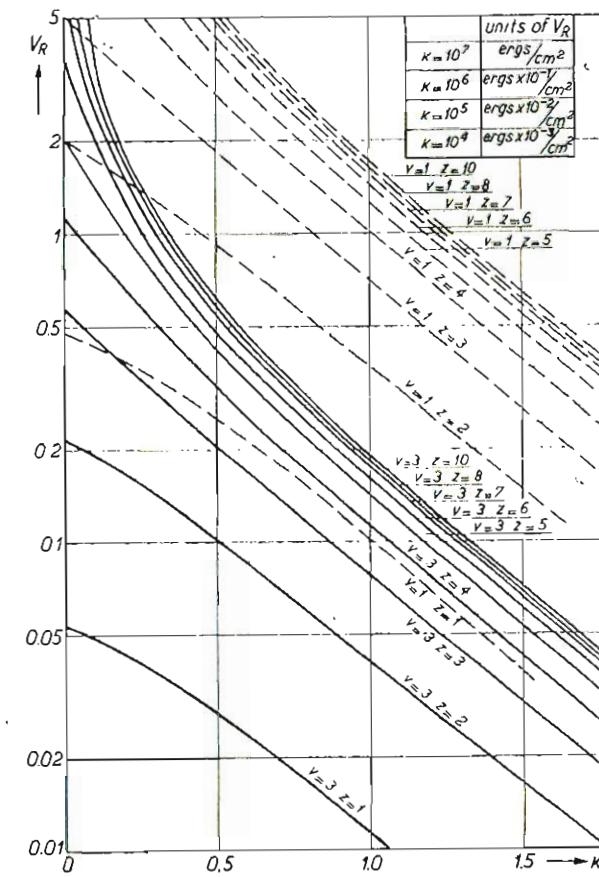


Fig. 20. Repulsive potential (logarithmic scale) as a function of  $zd$ , for different valencies of the electrolyte ( $v = 1$  and  $v = 3$ ).

that, for our purpose, the most important part of the  $V_R$  curves is situated in the neighbourhood of  $zd = 1$ . For this value of  $zd$  we see therefore that the repulsion is diminished by an increase in the ionic charge, especially for larger values of  $\psi_0$ .

The considerations given here refer to a comparison of two solutions with equal values of  $x$ . If we want to compare solutions of equal ionic concentrations (mol/l.) we must ac-

count for the corresponding increase of  $z$ . From what has been said above about the influence of  $z$  it follows that this gives an additional decrease of the repulsion for larger values of the plate distance.

The final result of the effect of the valency of the ions upon the repulsive curve is summarized in Fig. 21. In order to avoid too large a spread of the various curves, we have here made the comparison of an 1-1 valent and a 2-2 valent electrolyte ( $\psi_0 = 102.4$  millivolts).

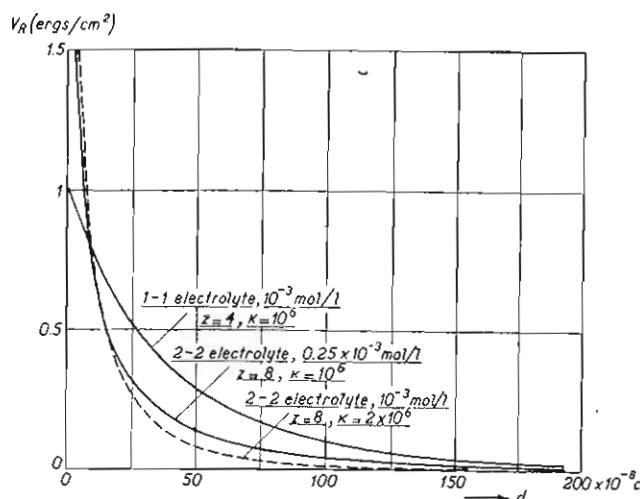


Fig. 21. Repulsive potential as a function of the plate distance ( $2d$ ) for comparable concentrations of an 1-1 and a 2-2 valent electrolyte. ( $\psi_0 = 102.4$  mV;  $z = 4$  resp.  $z = 8$ ).

### § 3. Potential energy via the force

An expression for the force acting between the two plates and due to the interaction of the double layers has been derived, in the second part of his paper, by Langmuir<sup>1</sup>, while Derjaguin<sup>2</sup> also gives an expression for the force, but only for the case of very small surface potentials<sup>3</sup>. The considerations

<sup>1</sup> I. Langmuir, *J. chem. phys.*, 6 (1938) 893.

<sup>2</sup> B. Derjaguin, *Trans. Faraday Soc.*, 36 (1940) 203.

<sup>3</sup> Bergmann, Löw-Beer and Zocher, *Z. physik. Chem.*, A 181 (1938) 301, gave a theory of so-called "Schiller-layers", based upon the repulsion between two flat double layers. Their derivations, although correct, are too much specialized on the case of Schiller-layers, i.e., a case of very small interaction and large distances, to be able to serve us as a useful starting point for a general theory of the stability of colloids where large interactions and small distances are involved.

of Langmuir and Derjaguin appear at first sight to deviate considerably, but it can be proved that they are essentially equivalent. Actually, Derjaguin's equation is only a special case of that of Langmuir; in view of the approximation involved in the former (development of the exponential from and breaking off after the linear term) and the objections raised earlier in this work against the application of this approximation to actual colloid systems, we shall here only consider Langmuir's equation.

This equation for the force acting between the two plates per  $\text{cm}^2$  reads:

$$p = 2n kT (\cosh u - 1) \quad (41)$$

This equation may be derived in various different ways. In the first place, it is obtainable directly from the expressions for the free energy by differentiation. Eq. (41) may be obtained for instance, by differentiating eq. (37) with respect to  $d$ .

Starting from (37b) we find

$$p = - \left( \frac{\partial F}{\partial d} \right)_z = 2n kT (\cosh u - 1) + 2n kT \cdot d \cdot \frac{\partial}{\partial d} (\cosh u) + \frac{2n kT}{z} \cdot \frac{\partial I_3}{\partial d},$$

$$\text{in which, again, } I_3 = \int_z^u \sqrt{2 \cosh y - 2 \cosh u} \cdot dy.$$

$$\begin{aligned} \frac{\partial I_3}{\partial d} &= \int_z^u \frac{\frac{\partial}{\partial d} (-2 \cosh u)}{2 \sqrt{2 \cosh y - 2 \cosh u}} \cdot dy = \int_z^u \frac{-\sinh u \cdot \frac{\partial u}{\partial d}}{\sqrt{2 \cosh y - 2 \cosh u}} \cdot dy = \\ &= -zd \sinh u \cdot \frac{\partial u}{\partial d} \end{aligned}$$

Hence we find

$$\begin{aligned} p &= 2n kT (\cosh u - 1) + 2n kT d \cdot \sinh u \cdot \frac{\partial u}{\partial d} - 2n kT \cdot d \cdot \sinh u \cdot \frac{\partial u}{\partial d} = \\ &= 2n kT (\cosh u - 1). \end{aligned}$$

It is also possible to derive eq. (41) without making use of the expressions respecting the free energy. Langmuir works with the osmotic pressure of the counter-ions between the plates, Derjaguin (as well as Bergmann, Löw-Beer and Zocher) considers the electric force acting on the surface charges. A common point in their derivations is that they calculate the force on both sides of one plate and by subtraction find the resultant force driving the plates apart. In this procedure it may seem essential that on both sides the plate is in contact with the same liquid. It has already been pointed out

by Levine and Dube<sup>1</sup> that this must be a superfluous complication, as the double layer is a system in equilibrium, so that no force can be exerted on the outer side facing infinity. This complication is not involved in the derivation we will give below. Moreover, the latter avoids a number of other difficulties associated with the considerations of the authors mentioned above. The introduction of osmotic pressure, for instance, in such derivations of physical chemical laws always gives them a somewhat artificial character (cf. the well-known critical considerations of Van Laar<sup>2</sup> on this subject). The consideration of the electric force acting on the surface charges also creates certain difficulties.

If we consider two infinitely large parallel plates with liquid between them, but confined on the outside by a neutral substance (e.g., air) we must add a reservoir, containing an infinitely large amount of liquid in order to balance the change of volume when the distance of the plates is altered. This reservoir is imagined to be beyond the field of the double layers, and consequently contains the solution at a concentration of  $n$  mols/cm<sup>3</sup> at an electric potential zero and at a hydrostatic pressure which we shall call  $P_\infty$ .

Now the equilibrium of the system requires that at every point of the solution phase the gradient of the hydrostatic pressure and the force on the space charge balance each other:

$$dP + \rho d\psi = 0 \quad (42a)$$

Using Poisson's equation and specializing to the problem between the two plates this equation may also be written

$$\frac{dP}{dx} - \frac{\epsilon}{4\pi} \cdot \frac{d^2\psi}{dx^2} \cdot \frac{d\psi}{dx} = 0$$

$$\frac{d}{dx} \left[ P - \frac{\epsilon}{8\pi} \cdot \left( \frac{d\psi}{dx} \right)^2 \right] = 0$$

or:

$$P - \frac{\epsilon}{8\pi} \cdot \left( \frac{d\psi}{dx} \right)^2 = \text{constant}; \quad (42b)$$

thus we see that the difference between the hydrostatic pressure and Maxwell's stresses has everywhere a constant value. As, midway between the plates  $d\psi/dx = 0$ , this difference is equal to  $P_d$  the hydrostatic pressure for  $x = d$ . Hence the force which drives the plates apart in excess of the hydrostatic pres-

<sup>1</sup> S. Levine and G. P. Dube, *Trans. Faraday Soc.*, 36 (1940) 215.

<sup>2</sup> J. J. van Laar, *Sechs Vorträge über das thermodynamische Potential*, Vieweg Braunschweig 1906.

sure of the reservoir, or the force acting on 1 cm<sup>2</sup> of the phase boundary of one plate due to the double layer interaction, is simply identical with  $p = P_d - P_\infty$ .

In order to evaluate  $P_d - P_\infty$ , we have to integrate (42a) between the middle of the plates and a point in the reservoir, or between  $\psi = \psi_d$  and  $\psi = 0$ .

So

$$P_d - P_\infty = \int_{-\infty}^{\psi_d} dP = - \int_0^{\psi_d} \rho d\psi$$

With  $\rho$  as found in eq. (2a)

$$\rho = -2nve \sinh \frac{ve\psi}{kT}$$

we find

$$-\int_0^{\psi_d} \rho d\psi = \int_0^{\psi_d} 2nve \sinh \frac{ve\psi}{kT} d\psi = 2nkT (\cosh \frac{ve\psi_d}{kT} - 1),$$

$$\text{or } p = 2nkT (\cosh u - 1).$$

In this way, therefore, we arrive at the same expression as that given by Langmuir, and we should have found exactly the same result if we had applied Derjaguin's method on the basis of the complete Gouy-Chapman picture. Actually, all three derivations are essentially identical.

Langmuir's derivation makes use of the osmotic pressure caused by the excess of ions present between the plates. This excess is a result of the fact that the oppositely charged ions (hence for positive  $\psi_d$  the negative ions) are accumulated there. The increase of the negative ions (for  $x = d$  proportional to  $e^u - 1$ ) is always larger than the corresponding decrease of the local concentration of the positive ions (for  $x = d$  proportional to  $1 - e^{-u}$ ). Hence the total increase of the concentration of ions at the central plane, where the electrical field is zero, will be equal to

$$n \{ (e^u - 1) + (e^{-u} - 1) \} = 2n (\cosh u - 1).$$

The difference between the osmotic pressures midway between the plates and at a point outside the fields of the double layers, and therefore the force acting between the plates, will be

$$p = 2nkT (\cosh u - 1).$$

Derjaguin's argument, too, is connected with the derivation given here. It may be reproduced in the following way. The electric force, pressing the space charge of the double layer into the direction of the surface charge, is, according to the theory of electricity (cf. also our eq. (42a) and (42b)) equal to

$$\frac{\epsilon}{8\pi} \left( \frac{d\psi}{dx} \right)^2$$

Considering the system of two plane double layers in interaction, this force gradually increases from zero (in the central plane, where  $d\psi/dx = 0$ ) to its final value

$$\frac{\epsilon}{8\pi} \left( \frac{d\psi}{dx} \right)_0^2$$

in the thin liquid layer adjacent to the plate surface ( $x = 0$ ). An equal force, but working in the opposite direction, will accordingly be exerted on the electric surface charge, under the influence of the space charge in the solution.

As  $(d\psi/dx)_0$  is a function of the plate distance, and decreases with increasing interaction, this force acting on the surface charges, and pointing into the direction of the solution, will also vary with the plate distance. It reaches its maximal value for  $d = \infty$ , and this is therefore at the same time the force acting at the back of the plates facing infinity (thought to be in contact with the same solution).

Hence, comparing the forces acting on both sides of each plate, Derjaguin finds for the repulsive force the expression

$$p = \frac{\epsilon}{8\pi} \left[ \left\{ \left( \frac{d\psi}{dx} \right)_0 \right\}_\infty - \left\{ \left( \frac{d\psi}{dx} \right)_0 \right\}_d \right].$$

Applying now the expressions derived in chapters II and IV for the derivative of the electric potential for one and two double layers, eq. (5b) and eq. (31a):

$$\begin{aligned} \left\{ \left( \frac{d\psi}{dx} \right)_0 \right\}_\infty &= \sqrt{\frac{8\pi n kT}{\epsilon}} \cdot \sqrt{2 \cosh z - 2} \\ \left\{ \left( \frac{d\psi}{dx} \right)_0 \right\}_d &= \sqrt{\frac{8\pi n kT}{\epsilon}} \cdot \sqrt{2 \cosh z - 2 \cosh u}. \end{aligned}$$

we again find Langmuir's equation:

$$p = 2 n k T (\cosh u - 1).$$

Considering the three derivations given here we may say that their equivalence is a direct result of the circumstance that they are all based on a double layer theory involving the equilibrium between the electric and "osmotic" (thermal diffusion) forces acting on the ions in the solution.

The equation for the force acting between the plates owing to the interaction of the double layers has a very simple form. It is noteworthy that it applies equally well to a system with constant electric surface potential (with varying plate distance) as to one with constant surface charges. This does not mean that the force varies with varying  $d$  in the same way. In Chapter IV we saw that the quotient  $\sigma/\psi_0$  decreases with decreasing plate distance. The electric potential midway between the plates is increased by the interaction, but it is evident that in the first mentioned case ( $\psi_0 = \text{constant}$ ) it will increase less than in the second case ( $\sigma = \text{constant}$ , and therefore  $\psi_0$  increases). Hence, in the latter case the repulsive force will increase more rapidly with decreasing plate distance than in the case of ionic equilibrium ( $\psi_0 = \text{constant}$ ).

A remarkable point about eq. (41) is that it contains neither the electric surface potential ( $\psi_0$  or  $z$ ) nor the plate distance  $2d$ , but only the electric potential midway between the plates ( $\psi_d$  or  $u$ ). But the relation between  $z$ ,  $u$ , and  $d$  being rather complicated (cf. Chapter IV), it is impossible to integrate eq. (41), for a given value of  $\psi_0$ , with respect to the distance. Hence there is no advantage in using this force equation to evaluate the repulsive potential  $V_R$ , for a system of two plane double layers, on the basis of the complete differential equation (3).

However, as we have seen in Chapter IV, an explicit relation between  $d$  and  $u$  may be obtained in a special case, namely in the case of small interaction. For this case we found the approximate equation (33):

$$u = 8\gamma \cdot e^{-zd}$$

$$\text{with } \gamma = \frac{e^{z/2} - 1}{e^{z/2} + 1}.$$

The consequent application of this relation in the force equation then leads to the following approximative equation for the repulsive potential

$$V_R = \frac{64 n k T}{z} \cdot \gamma^2 \cdot e^{-2zd} \quad (43)$$

As

$$p = -\frac{\partial F}{\partial d},$$

we have for the repulsive potential:

$$V_R = 2(F - F_\infty) = -2 \int_{\infty}^d p dd.$$

As the interaction is small, the electric potential midway between the plates will also be small, so that  $u < 1$ . For that case eq. (41) simplifies to

$$p = 2 n k T \left\{ \frac{1 + u + \frac{u^2}{2} + 1 - u + \frac{u^2}{2} - 2}{2} \right\} = n k T \cdot u^2 \quad (41')$$

Inserting then the value of  $u$  given by eq. (33) we find for the repulsive force:

$$p = 64 n k T \cdot \gamma^2 \cdot e^{-zd},$$

and accordingly for the repulsive potential:

$$\begin{aligned} V_R &= 64 n k T \cdot \gamma^2 \cdot 2 \int_d^\infty e^{-2zd} dd = \\ &= \frac{64 n k T}{z} \cdot \gamma^2 \cdot e^{-2zd} \left( = \frac{8 \epsilon k^2 T^2 z}{\pi (ye)^2} \cdot \gamma^2 \cdot e^{-2zd} \right). \end{aligned}$$

According to Chapter IV, Table IX,  $zd$  is slightly less than 2 for  $\nu = 1$  (except for very small values of  $z$ , where it becomes appreciably smaller than 2). The validity region of eq. (43) may therefore be said to be, according to its derivation,  $zd > 2$ .

Inspecting eq. (43) we see that it expresses that, for small interaction, the repulsive potential decays purely exponentially, and the rate of decay is independent of the value of the surface potential: it is entirely determined by the quantity  $z$ . This is exactly what was found in the foregoing section for the  $V_R$  derived via the free energy. There we saw that the  $\log V_R$  curves become, for larger values of  $zd$ , straight lines, which prove to run parallel to each other for all values of  $z$ .

Fig. 17, giving  $\log V_R$  as a function of  $zd$  for a number of values also contains (dotted lines)  $\log V_R$  according to the approximate equation (43). Comparison of both sets of curves yields the following facts:

a. In all cases, except those of very strong interaction at a large value of  $z$ , the approximate curves are a little higher than the exact ones.

This may be explained by considering another approximation, viz. the Debye-Hückel approximation. For that case, where the potential is everywhere small, we find

$$V_R = \frac{2 nkT}{z} z^2 (1 - \tanh zd) = \frac{4 nkT}{z} z^2 \frac{e^{-zd}}{1 + e^{-2zd}} \quad (44)$$

This equation is easily found by considering that, for  $z < 1$  (and  $y < 1$ ),

$$zd = \int_u^z \frac{dy}{\sqrt{2 \cosh y - 2 \cosh u}} = \int_u^z \frac{dy}{\sqrt{y^2 - u^2}} = \ln \frac{z + \sqrt{z^2 - u^2}}{u}$$

This expression for  $zd$  may be rewritten and leads to:

$$\frac{z}{u} = \cosh zd.$$

Now  $V_R$  is found by integrating  $p$  (eq. 41') with respect to  $d$ , which leads to

$$V_R = \int_d^\infty p dd = \int_d^\infty n kT \frac{z^2}{\cosh^2 zd} dd = \frac{2 nkT}{z} z^2 (1 - \tanh zd).$$

When  $z$  is small and  $zd$  is large, (43) and (44) give identical results as for  $z < 1$ ,  $y^2 = z^2/16$  but when  $z$  is smaller, (44) shows that the repulsive potential energy will increase less steeply than should follow from eq. (43). The additional  $\exp(-2zd)$  in the denominator of (44) explains the trend for a negative deviation from the approximated curves in figure 13.

By combining eq. (43) and (44), we may find an expression

for the repulsion satisfying in all cases when the interaction is not very strong:

$$V_R = \frac{64 nkT}{z} \gamma^2 \frac{e^{-2zd}}{1 + e^{-2zd}} = \frac{32 nkT}{z} \gamma^2 (1 - \tanh zd) \quad (46)$$

b. The steep increase of the repulsion for strong interaction and large values of  $z$  has to be explained by the great accumulation of ions at very small distances from the wall when the surface potential is large. At these small distances the electric potential of the double layer goes much steeper than the simple exponential expression ( $\exp(-zd)$ ) would demand, causing at the same time a steeper repulsive energy curve.

c. Although eq. (43) has been derived for the case of small interaction, its approximate validity appears to extend to a considerably larger region.

The combination of the two deviations from the approximate eq. (43), one diminishing and the other increasing the energy of interaction, is the cause that the exact curve and the approximated one run nearly parallel over such considerable distances.

## VI. THE VAN DER WAALS-LONDON ATTRACTIVE FORCES

### § 1. The attraction between two atoms

As stated earlier we shall assume that the attractive potential between the particles of a colloid system is mainly due to Van Der Waals-London attractive forces. When the particles come into contact forces of a different origin will also have to be considered, for instance attractive forces caused by residual chemical valency fields. For the present, however, we are interested in comparatively long-range forces, for which the type mentioned above is the only type coming up for consideration.

The attractive forces acting between two neutral, chemically saturated molecules, postulated by Van Der Waals, may be partially understood from a classical electrical point of view. If the molecule carries a dipole moment the two molecules will mutually influence their spatial orientations in such a way that, on the average, attraction will result (Debye)<sup>1</sup>. Moreover, each molecule induces a dipole in the other molecule, and the attraction is reinforced by this mutual polarisation (Keesom)<sup>2</sup>. Between nonpolar molecules, too, however, attractive forces are active, as is shown by the liquefaction of helium, hydrogen, carbon disulfide, etc. These universal attractive forces, acting between all atoms, molecules, ions, etc., were explained by London on the basis of wave-mechanics<sup>3</sup>. They may be understood as being the result of the mutual influencing of the electronic motion in two atoms under consideration. The charge fluctuations in one atom cause, as a first approximation, a fluctuating electric dipole in the atom considered. This temporary dipole induces a dipole in the second atom, and the result is attraction. Inversely, the fluctuating dipole in the second atom induces a dipole in the first atom.

As the field of an electric dipole is proportional to the inverse third power of the distance from the dipole, the induced dipole moment will also show this dependence on the distance of both atoms. The attractive potential between two dipoles, on the other hand, is also proportional to  $r^{-3}$ ; the corresponding attractive forces decrease according to  $r^{-4}$ . Hence according to London's theory these universal Van Der Waals-forces

between two atoms will be proportional to  $r^{-7}$ , which means a rather rapid decay with increasing atomic distance; the corresponding attractive potential varies as  $r^{-6}$ . Accordingly:

$$V = -\frac{\lambda}{r^6} \quad (47)$$

in which  $\lambda$  is a constant depending on the properties of the atoms (or molecules) under consideration. Because of the reciprocal character of these forces this constant will be proportional (for two equal atoms) to  $\alpha^2$ ,  $\alpha$  being the polarisability of the atom (for two different atoms it will be proportional to  $\alpha_1 \alpha_2$ ).

It appears to be rather difficult to evaluate the constant  $\lambda$ , and to express it completely in terms of physical constants of the atoms. On this point the quantum-mechanical theory is still imperfect. More or less rough approximate equations have therefore been proposed. One of them is that given by London. For two equal atoms it reads:

$$\lambda = \frac{3}{4} \alpha^2 h \nu_0,$$

in which  $h \nu_0$  is a characteristic amount of energy corresponding to the chief specific frequency  $\nu_0$  taken from the dispersion equation of the atom considered. An alternative approximation formula was derived by Slater and Kirkwood<sup>1</sup>:

$$\lambda = 11.25 \cdot 10^{-24} n^{\frac{1}{2}} \alpha^{\frac{3}{2}},$$

in which  $n$  = the number of electrons in the outermost shell of the atom. The last mentioned equation gives higher results in some cases than the former, and has the further advantage that not much doubt exists in most cases about the choice of the quantity  $n$ . Finally, a third equation may be derived from a paper by Neugebauer<sup>2</sup>:

$$\lambda = -2 mc^2 \cdot \alpha \chi = -1.62 \times 10^{-6} \cdot \alpha \chi$$

in which  $\chi$  is the diamagnetic susceptibility of the atom under consideration. This equation sometimes gives still higher results, especially in the case of the negative ions, where the latter equation seems to be the better approximation (In this case the results may differ by a factor 2 or more).

A fundamental implication of the quantum-mechanical treatment of these forces as a result of second order perturbation theory is that these forces are additive. Hence, in an assembly

<sup>1</sup> P. Debye, *Physik. Z.*, **21** (1920) 178; **22** (1921) 302.

<sup>2</sup> W. H. Keesom, *Proc. Acad. Sci. Amsterdam*, **18** (1915) 636; **23** (1920) 939.

<sup>3</sup> F. London, *Z. Physik*, **63** (1930) 245.

<sup>1</sup> J. C. Slater and J. G. Kirkwood, *Phys. Rev.*, **37** (1931) 682.

<sup>2</sup> Th. Neugebauer, *Z. Physik*, **107** (1937) 785.

of atoms each atom attracts all other atoms, and this attraction is, as a first approximation, independent of the presence of the surrounding atoms. Only when the density of the surrounding atoms is very high, as in condensed systems, are the attractive forces slightly weakened by the dielectricum through which they are transmitted.

### § 2. The attraction between two flat plates

On the basis of this theory the attractive potential between two particles may then be calculated approximately by a summation of the attractive potentials for all atomic pairs formed by two atoms belonging to different particles. As a next approximation the summation may be replaced by an integration, which will be permissible for all cases where the atomic distance is great in comparison to atomic dimensions. This integration may easily be carried out for special cases, such as two infinitely large blocks with parallel plane surfaces facing each other (J. H. De Boer)<sup>1</sup>, and two spherical particles (Hamaker)<sup>2</sup>. The first case will give us approximate information as to the attractive potential between two cubic particles closely approaching each other, or for other particles with a low number of crystal faces. The second case will be a better approximation if the particles resemble spheres, or if the particle distance is great in comparison to particle dimensions. In the following we shall, moreover, consider the case of two infinitely large parallel planes with a thickness small in comparison to their distance. The latter approximation will be applicable in certain cases of blade-shaped particles.

All equations derived in this way have this in common, that the attractive potential between the particles decays more slowly with increasing particle distance, than the attractive potential between two atoms with increasing atomic distance (eq. (47)). This different behaviour is a direct result of the cooperation of all atoms of the two particles. In the case of two large blocks with parallel faces, for instance, an increase of the particle distance will only imply an increase of the atomic distance by the same factor for atomic pairs in the adjacent faces right opposite each other; for all other atomic pairs the atomic distance is increased by a smaller factor.

Following Hamaker we will introduce the quantity

$$A = \pi^2 q^2 \lambda,$$

<sup>1</sup> J. H. De Boer, *Trans. Faraday Soc.*, 32 (1936) 21.

<sup>2</sup> H. C. Hamaker, *Physica*, 4 (1937) 1058.

in which  $q$  is the number of atoms contained in 1 cm<sup>3</sup> of the substance building up the particles considered. If the substance contains more than one atomic species we will have a somewhat more complicated expression defining  $A$ ; in that case it contains also a summation over all these species.

The expression obtained by integration as indicated above for the case of two spherical particles is rather complicated. It will be given in Chapter XI of Part III. More simple expressions are obtained in the case of two large parallel plates, especially in the limiting cases that the plate distance is either large or small in comparison to the thickness of the plates. The attractive potential for two plates of thickness  $\delta$ , at a distance  $2d$  from each other, is found to be

$$V_A = -\frac{A}{48\pi} \left\{ \frac{1}{d^2} + \frac{1}{(d+\delta)^2} - \frac{2}{(d+\delta/2)^2} \right\}$$

with the following useful approximations:

$$\begin{aligned} (a) \quad d \gg \delta \quad V_A &= -\frac{\delta^2 A}{32\pi d^4} \\ (b) \quad d < \delta \quad V_A &= -\frac{A}{48\pi} \left\{ \frac{1}{d^2} - \frac{7}{\delta^2} \right\} \\ (c) \quad d \ll \delta \quad V_A &= -\frac{A}{48\pi d^2} \end{aligned} \quad (48)$$

These equations are found in the following way. We first consider an atom opposite to an infinitely large plate of thickness  $\delta$ . The distance from the atom to the surface plane of the plate will be  $R$ . The Van Der Waals-London attractive force is then found by adding together the components of all attractive forces exercised by the atoms of the plate substance, in a direction perpendicular to the surface plane.

Differentiating eq. (47) we find for the force

$$f = 6\lambda/r^2$$

and, therefore, for the force component (cf. fig. 22),

$$f = \frac{6\lambda}{r^2} \cos \varphi.$$

The volume of the ring with radius  $\rho$  is  $dx \cdot 2\pi\rho \cdot d\rho$ , and the number of atoms contained in this ring, therefore,  $2\pi q \cdot \rho d\rho \cdot dx$ . As  $\cos \varphi = x/r$ , and  $r^2 = (\rho^2 + x^2)$  we find, substituting the summation by an integration, for the total force

$$\begin{aligned} f &= 12\pi q \lambda \int_0^\infty \rho d\rho \int_R^{R+\delta} x dx \cdot \frac{1}{(\rho^2 + x^2)^2} \\ &= \frac{\pi q \lambda}{2} \left\{ \frac{1}{R^4} - \frac{1}{(R+\delta)^4} \right\} \end{aligned}$$

We now consider a row of atoms extending from the atom considered at a distance  $R$ , to a distance  $R + \delta$ , in a direction perpendicular to the plates. The total attraction force is then simply a superposition of the attraction forces exercised by all these rows. Hence, we find the total force from

$$\begin{aligned} f &= q \int_{1 \text{ cm}^2} dO \int_{R}^{R+\delta} \frac{\pi q^2}{2} \left\{ \frac{1}{R^3} - \frac{1}{(R+\delta)^3} \right\} dR = \\ &= \frac{\pi q^2 \lambda}{6} \left\{ \frac{1}{R^3} + \frac{1}{(R+2\delta)^3} - \frac{2}{(R+\delta)^3} \right\}. \end{aligned}$$

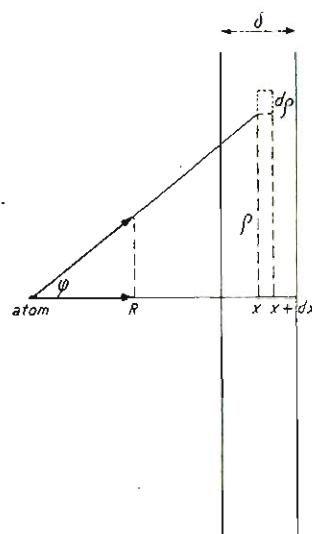


Fig. 22. Illustrating the London-Van der Waals forces between an atom and an infinitely large plate of thickness  $\delta$ .

The corresponding attraction potential is then found by final integration with respect to  $R$  between  $\infty$  and  $R$ :

$$V_A = -\frac{\pi q^2 \lambda}{12} \left\{ \frac{1}{R^2} + \frac{1}{(R+2\delta)^2} - \frac{2}{(R+\delta)^2} \right\}$$

From this the equations (48) can easily be derived.

It is clear that the quantity  $A$ , and the attractive potential  $V_A$ , are proportional to  $q^2$ . It is seen that the attractive potential between the two plates decays comparatively slowly with the plate distance, especially if the plate thickness is very large in comparison to the distance: in that case the potential decays according to  $d^{-2}$ .

A difficulty when operating with equation (48) is the infinitely large negative value of  $V_A$  when  $d = 0$ , i.e., when the plates

are in immediate contact. This, of course, cannot have any physical meaning. It is true, that the attractive energy reaches large negative values when the plates touch each other, but the value of equation (48) will be doubtful for distances smaller than an atomic diameter (say  $3 \cdot 10^{-8}$  cm). For these small distances yet another kind of forces should be introduced, viz. the Born-repulsion preventing the interpenetration of matter.

Moreover, a physical surface is never perfectly plane in the mathematical sense of the word. It always possesses a certain roughness much exceeding molecular dimensions. So if two surfaces touch each other, they are only in direct contact in a few protruding points, which diminishes the London-Van der Waals attraction and invalidates the equations (48) for small distances.

Fortunately when combining the London-Van der Waals attraction with the repulsion found in the foregoing chapters, the interesting region proves to be situated at (in most cases considerably) greater distances between the plates. Consequently the above complications form no serious hindrance in applying eq. (48) to the theory of the stability.

If the medium between the plates or particles is no longer a vacuum, but a second substance (e.g., water) we have to account for the fact that each plate or particle replaces an equal volume of water.  $A$  is then composed of a number of similar quantities  $A_{11}$ ,  $A_{12}$ ,  $A_{22}$ , in which the first refers to the interaction between the atoms of the plates or particles, the second to that between this substance and the water, and the third to that between the water molecules.

$$A = A_{11} + A_{22} - 2A_{12}.$$

It can be proved that this total  $A$  is always positive, so that between two particles of the same substance immersed in a second medium there is always an attraction<sup>1</sup>.

The influence of the medium through which the forces are transmitted may be roughly taken into account by dividing the constant  $A$  found in this way by the square of the refractive index, as the London-Van der Waals force is essentially of an electric nature. But as we are not fully informed as to the exact values of the London-Van der Waals constants, we shall leave this point out of the discussion for the present.

In view of the theoretical uncertainties and the various approximations involved in these considerations, there would be no sense in trying to calculate the value of  $A$  in special cases. In order to form an idea of the order of magnitude of this

<sup>1</sup> H. C. Hamaker, *Physica*, 4 (1937) 1058.

constant we shall compute  $A_{22}$ , i.e. the constant relevant to the interaction water-water, and the term returning in  $A$  for all aqueous colloid systems. Using the Slater-Kirkwood equation<sup>1</sup> we find, for this case, ( $n = 8$ ,  $\alpha = 1.43 \cdot 10^{-24}$ )

$$\lambda = 54 \cdot 10^{-60} \text{ and } A_{22} = \pi^2 q^2 \lambda = 0.6 \cdot 10^{-12}.$$

From this we infer that in most practical cases we may expect, according to the theory, that  $A$  is in the neighbourhood of  $10^{-12}$ .

### § 3. Relativity correction to the theory of London-Van Der Waals forces

In applying the theory of the attractive forces as developed in the preceding section to colloidal systems, we met with some difficulties, especially in the treatment of coarse suspensions, because the London theory as such is not relativistically invariant, and by working out this idea we found that precisely in the case of coarse particles a relativistic correction may well become important.

We have to consider the fact, that the London-forces, being of an electrical nature, need a certain time for their propagation. In the theory of London, this time is completely neglected, as it uses the non-relativistic Schrödinger equation. But for great distances a relativistic correction becomes necessary.

If we consider the picture of the London-Van Der Waals forces as given above, viz., as an attraction between the temporary dipole of one atom and the dipole induced by it of the second atom, the finite velocity of propagation of electromagnetic actions causes the induced dipole to be retarded against the inducing one by a time equal to  $rn/c$  (if  $r$  is the distance between the two atoms and  $n$  the refractive index of the medium for the frequency coupled with the temporary dipole). The reaction of the induced dipole on the first one again is retarded by the same time, and if in this total time-lag of  $2rn/c$  the direction of the first dipole is altered by  $90^\circ$ , the force exerted is exactly nullified, and by a change of  $180^\circ$  even reverted from an attraction into a repulsion.

<sup>1</sup> Using the Neugebauer equation we find (specific susceptibility  $= -0.72 \cdot 10^{-6}$ , hence  $\chi = -2.2 \cdot 10^{-24}$ )

$$\lambda = 51 \cdot 10^{-60}$$

whereas London's equation leads to the value (if we use for  $h\nu_0$  the ionisation potential, 13 eV.)

$$\lambda = 32 \cdot 10^{-60}.$$

If we call the frequency of the motion of electrons in the atom  $\nu$ , the wavelength connected with it  $\lambda$ , the first zero of the London-Van Der Waals force will be reached at a distance  $r = \frac{\lambda}{2}$ , time-lag, velocity  $= 1/8 \nu \cdot c/n = \lambda/8$ . If we assume that the frequency involved here is the same as the frequency in the London equation

$$V = -\frac{3/4 \alpha^2 h \nu}{r^6},$$

$\lambda$  is of the order of  $1000 \text{ \AA}$ , so  $r$  is of the order of  $10^{-6} \text{ cm}$ . This means that beyond this distance the London-Van Der Waals force is practically non-existent.

Of course the picture sketched here will have to be refined in different respects, viz. a sharper discussion of the value of  $\nu$ , an exact calculation of the decay of the London force for large distances, and the influence of the summation or integration over larger volumes on the effect mentioned.

We believe, however, that for the principal aspect of the question, and the determination of the order of magnitude, the above suffices. The consequences of this cutting off of the London-Van Der Waals forces are unimportant for small particles ( $\leq 10^{-6}$ ) where these forces do not, anyway, reach farther than  $10^{-6} \text{ cm}$ . The influence in the case of large particles ( $10^{-4}$  and larger) will be discussed in Chapter XII, § 5.

Very recently Casimir and Polder<sup>1</sup> succeeded in giving an exact quantum mechanical description of the influence of the retardation effects on the London-Van Der Waals-forces. They found, in fair accord with what was expected by the semi-classical reasoning given above, that a significant reduction of the London-Van Der Waals force between two atoms is felt for distances larger than  $2/3$ . When the distance is very large the London-energy is proportional to  $1/r^7$ , instead to  $1/r^6$  as is found when no account is taken of the retardation.

<sup>1</sup> H. B. G. Casimir and D. Polder, *Phys. Rev.*, 1948 (in press); cf. also preliminary comm. in *Nature*, 158 (1946) 787.

## VII. TOTAL POTENTIAL ENERGY (REPULSION + ATTRACTION) FOR TWO PLATES, AND APPLICATION TO COLLOID STABILITY.

### § 1. Examples of potential energy curves.

In Chapter V we derived the potential energy of a system of two parallel plates due to the interaction of the double layers (corresponding to a repulsion). In Chapter VI we considered the Van Der Waals-London potential for the same system (corresponding to an attraction). In the present chapter we shall study the result of both actions together: the total potential curve, being a superposition of the two separate potential energies as a function of the plate distance. We may expect to arrive in this way at a quantitative theory for the interaction of colloid particles for all colloid systems in which the particles are sufficiently large in comparison to the double layer extension, and accordingly an encounter of two particles may be approximated by a system of two large parallel plates.<sup>1</sup>

It depends on the shape of the particles what equation should be used for the attractive potential. We will assume for the present that the particles are cubic (or of another regular form). This case is approximated by two plates for which the plate thickness is considerable in comparison to the thickness of the double layer. As we are chiefly interested in plate distances of the same order of magnitude as the double layer thickness, we may use eq. (48c) for the attractive potential (See, however, § 4).

In Chapter V we found that the repulsive potential  $V_R$  decreases with increasing distance according to a more or less exponential decay. At any rate the curve starts with a finite value of  $V_R$  for zero distance (the free energy of the double

<sup>1</sup> Cases may be imagined, in which the attraction between colloidal particles is caused by other forces than the London-Van Der Waals forces. Such a case was dealt with by Bergmann, Löw-Beer and Zocher<sup>2</sup>, who explained the existence of the so-called "Schiller-layers" by an equilibrium between the double-layer repulsion and the gravitational forces pressing the plate-shaped particles to the bottom of the vessel, and thereby pressing them together. In the layers of particles originated in this way, the particles lie horizontally and parallel to each other. Their distance can be measured by observing the interference colours generated in them, and is found to be in reasonable accordance with the theoretical calculations of Bergmann et al.

<sup>2</sup> P. Bergmann, P. Löw-Beer and H. Zocher, *Z. physik. Chem.*, A 181 (1938) 301.

layer is finite), and the curve approaches a purely exponential one for moderate and large plate distances. The attractive potential, according to eq. (48c), decreases quadratically with increasing distance. Hence, on the basis of the unlimited validity of this equation we may infer that the absolute value of the attractive potential  $|V_A|$  will always be larger than  $V_R$  for two cases: for very large and for very small plate distances. Indeed, it is well known that an exponentially decreasing function goes to zero more rapidly than a function decreasing with a negative power. Accordingly, for great distances (though the absolute value of  $V_A$  may there be very small) the attractive potential according to eq. (48c) will always surpass the repulsive potential. For small distances  $V_A$  approaches the value  $-\infty$ , so that, for sufficiently small distances, the attractive potential will, again, always be larger than the repulsive potential.

In the intermediate distance region (i.e., distances of the order of magnitude of the "thickness" of the double layers, or distances around  $d = 1 \times$ ) there are, generally speaking, two possibilities. If the repulsive potential is sufficiently large in comparison to the attractive potential, the potential energy  $V_R + V_A$  may reach positive values over a certain region of distance; in that case the total potential curve will there show a maximum reaching beyond the horizontal axis. As illustrated in Fig. 23 we may therefore distinguish between two types of total potential curves:

a. Curves with a potential energy "barrier", corresponding to positive values of  $V_R + V_A$ . As with increasing distance this quantity again reaches negative values and finally approaches the abscissa asymptotically, these curves also show a weak minimum for moderately large plate distances.

b. Curves for which  $V_R + V_A$  is always negative or zero. As the minimum for greater distances is always very shallow, these curves will show at most a very low energy barrier; generally, however, the total potential energy will decrease continually with decreasing plate distance.

As the force between the plates is given by the (negative) derivative of the potential, we read from Fig. 23, for curves of the type (a), that with decreasing plate distance, a weak attraction between the plates is found at first, until the minimum is reached. For distances between the minimum and the maximum, work must be performed in bringing the plates together, and accordingly a repulsive force is active between the plates. For plate distances smaller than the maximum, again, we once more find attraction.

If, on the other hand, the total potential curve is of the

type (b) we shall generally find attraction prevailing for all plate distances; only in the intermediary case of curves showing a very small barrier touching, or almost touching, the horizontal axis will there be a small repulsive force again for intermediate plate distances.

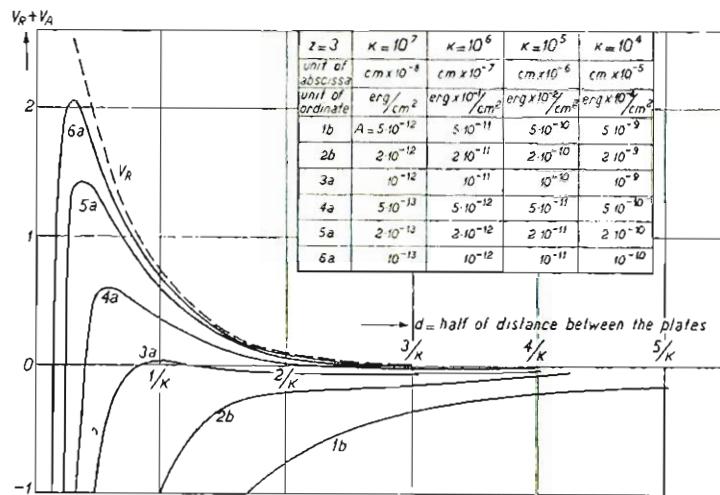


Fig. 23. Curves of total potential energy found as combinations of one repulsion curve (marked  $V_R$ ,  $v = 1$ ,  $z = 3$ ,  $\psi_0 = 76.8$  mV) with a series of different attraction curves, showing the different types of curves of total potential energy.

In applying these potential curves to the problem of the stability of hydrophobic colloids, we observe first of all that the particles in a sol or suspension are subject to Brownian movement. This implies that encounters take place continually between two (or more) particles. If the potential curve between two particles is of the type (a), the potential barrier will prevent lasting contact between the particles and after the encounter the two particles retain their independence. If, on the contrary, the potential curve is of type (b), the particles attract each other and if they are brought together by Brownian motion, they will yield to their mutual attraction and form a lasting combination — difficult to separate — so that after the encounter one double particle results instead of two single ones, which means that flocculation has set in.

Hence, as a first approximation, we will assume that type (a) represents stable systems, type (b) flocculated systems, and that the transition between stable and flocculated systems is represented by the potential curve with a weak potential barrier for which the top coincides with the horizontal axis  $V_R + V_A = 0$ .

In doing so we make a double neglection: (1) the influence of the kinetic energy of the particles due to thermal motion; and (2) the influence of the weak minimum. Hence we do not take into account the possibility that in the case of a potential curve with a low maximum a particle approaching another one may still be able to cross the potential barrier as a consequence of their relative thermal motion. Neither do we account for the fact that the potential curve corresponding to the intermediary case still contains a weak maximum as a consequence of the weak minimum at great distances. We return to both points separately in following sections; we shall see that the neglection of thermal motion is the more justified the larger the size of the particles, and that in reality the weak minimum is probably much less pronounced than is suggested by the simple London-theory. Moreover, both effects tend to cancel out each other. At any rate, an approximate theory involving both neglections will give us the general aspects of colloid stability.

Accordingly a study of stability conditions of a colloid system will then be equivalent to a study of the question for which values of the parameters of the system the transition case between (a) and (b) is found to exist.

Now for a system built up by given substances, the Van Der Waals-London constant  $A$  will be a given quantity; by a change in electrolyte concentration within the limits usual in colloid practice it will not be perceptibly altered. As a matter of fact a change in the properties of the system, for a given valency of the ions, can be entirely covered by a change in the two physical quantities  $\psi_0$  and  $z$ . The first is governed by a change in the concentration of the potential determining ions in the sol medium; the second by a change in the total electrolyte concentration of the ions. A third variation is introduced if the valency of the ions is also varied. We shall consider this case later on.

Accordingly, there are in essence two different ways to transfer potential curves of the type (a) into potential curves of the type (b); in the first place by a decrease of  $\psi_0$ , in the second place by an increase of  $z$ . We will discuss both these possibilities separately.

In considering the influence of  $\psi_0$  upon the form of the total potential curve we are still free to choose the quantities  $z$  and  $A$  arbitrarily; in order to obtain reasonable results they should be adjusted to experimental conditions. We will first consider the case of a colloid system containing such amounts of electrolyte in the dispersion medium, that flocculation has just about been effected. For the sake of simplicity we will assume that the electrolyte is 1-1 valent. The quantity  $z$  will then be of the order  $10^7$  (corresponding to a 1-0.1 molar solution).

As to the quantity  $A$ , we had already found that, theoretically, its magnitude is expected to be of the order  $10^{-12}$ , more or less dependent on the nature of the substances involved. We shall consider potential curves for a number of values of

A. Starting with the value  $5 \times 10^{-12}$  (a very large value indeed), we give, in Figs. 24–28, for 1–1 valent electrolytes, in each figure a set of potential curves for different values of  $z$ , where in each following graph the value of  $A$  has been decreased by a factor 2 or  $2\frac{1}{2}$ . We see that  $A = 5 \times 10^{-12}$  is actually such a high value of the Van Der Waals-London constant that, even for the largest values of  $z$  (i.e., for very high double layer potential), the total potential curve expresses attraction between the particles or plates (a hydrophobic colloid would accordingly not be stable). In the second graph, however, for which  $A = 2 \times 10^{-12}$ , positive values for  $V_R + V_A$  are reached for  $z = 6$  or higher, and in the following graphs the repulsive forces already predominate to such an extent that a low value of  $z$  is sufficient to prevent coagulation. As we considered a system containing as much as 100 milliequivalent of a univalent electrolyte per liter, on the verge of flocculation, for which we can only expect stability if the double layer potential is large, we may infer that graph 25 approaches experimental conditions better than the other graphs; hence  $A = 2 \times 10^{-12}$  seems to be the best value of  $A$ .

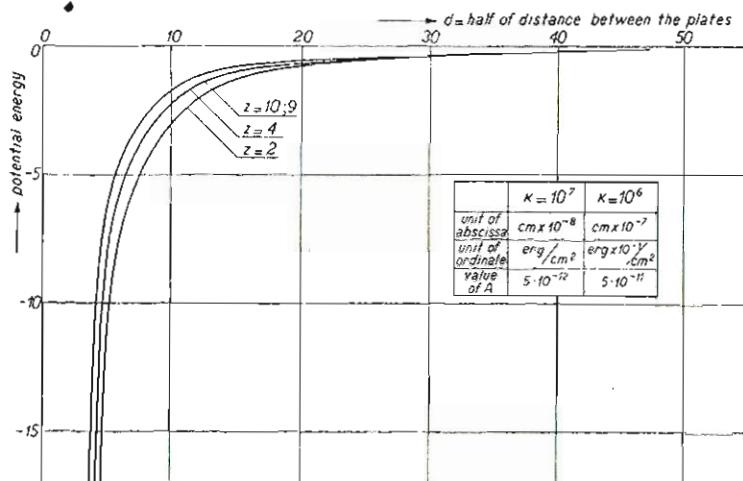


Fig. 24.

Fig. 24–28. Curves giving the total potential energy per  $cm^2$  against the separation of the plates. Potential of the plates  $\psi_0 = z \cdot 25.6$  m.V.

The electrolyte is supposed to be univalent.

For other units cf. the conversion tables inserted in each figure.

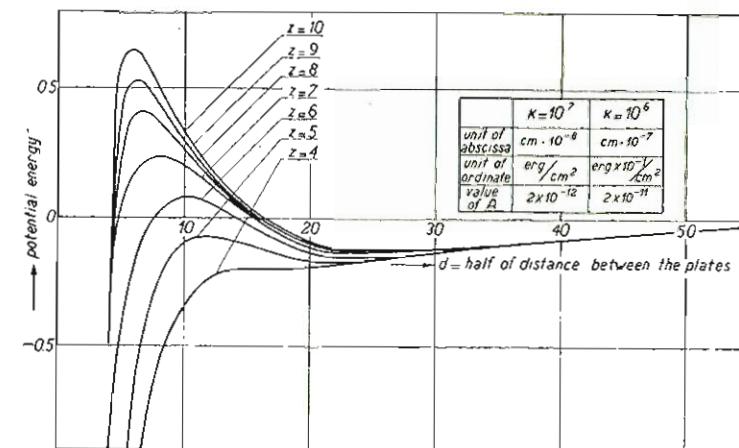


Fig. 25.

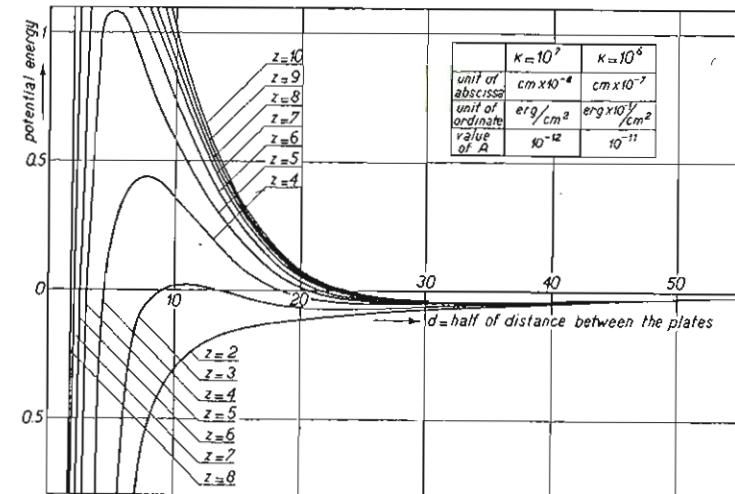


Fig. 26.

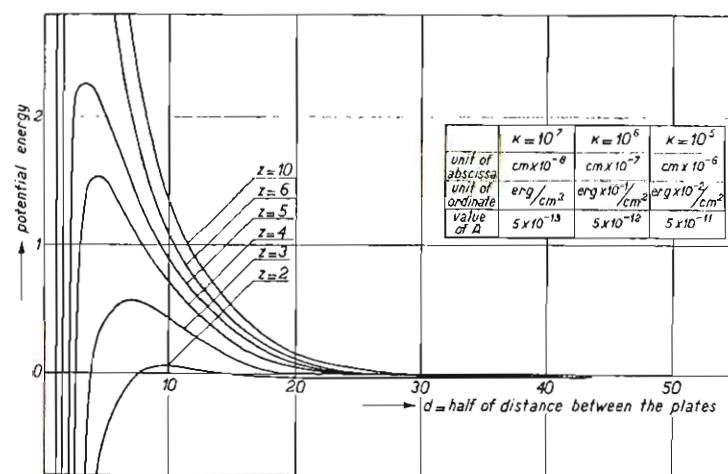


Fig. 27.

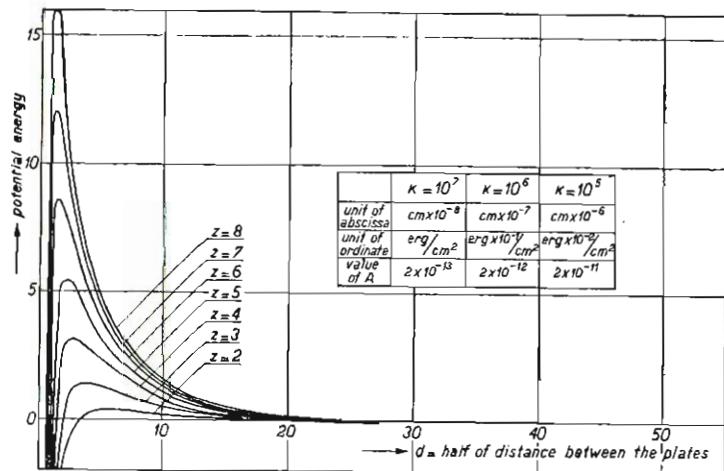


Fig. 28.

It is interesting to study in some detail the influence of the double layer potential on the potential energy curve, by inspecting Fig. 25 more closely. This graph very distinctly shows the increasing action of the double layer repulsion with increasing values of  $z$ . For  $z < 4$  the curves are purely attractive, i.e.  $dV/dd$  is everywhere negative. In the neighbourhood of  $z = 4$  the curve shows a point where  $dV/dd = 0$ , splitting, for still higher values of  $z$ , into a maximum and a minimum. Hence part of the curve here has a negative derivative, corresponding to a distance region where the force between the plates is a repulsive one. For  $z = 5$  the curve still has a maximum corresponding to a negative value of the total potential energy ( $V_A + V_R$ ). For  $z = 6$  the maximum has risen above the abscissa. It is noteworthy that for the intermediary case, between  $z = 5$  and  $z = 6$ , where the maximum touches the horizontal axis, the maximum is pretty neatly situated at  $zd = 1$ . For higher values of  $z$  the maximum rises well above this axis, at the same time shifting to lower values of  $zd$ .

For the reasons mentioned earlier we shall not here go into the question of the significance of the minimum; it should be clear that this minimum is lowest when the repulsion is just about sufficient to counteract the attraction. It shifts to greater distances when the repulsion is increased by increasing values of  $z$ .

Figs. 26, etc., show essentially the same behaviour as Fig. 25, though the minima are here less pronounced. Indeed, a rather low minimum will not occur when the repulsion predominates very greatly. Favourable conditions for a low minimum may obviously be expected, on the basis of an unrestricted validity of eq. (48c) for  $V_A$ , in those cases where strong repulsion and strong attraction are roughly of the same order of magnitude.

We shall now consider the case that the electrolyte concentration is 100 times smaller than in the case considered above. Hence the medium contains 0.001 mol/l of an 1-1 valent electrolyte, and  $\kappa = 10^6$  approximately. We observe that for this case we can make use of the same graphs as used above. In Chapter V, § 2 we have already stated that, for a given value of  $z$ ,

$$V_R/\kappa = f(\kappa d).$$

Hence, if  $\kappa$  is decreased by a factor 10 we obtain the same  $V_R$  curve when the energy units are decreased by a factor 10 and the distance units are increased by a factor 10. As  $V_A$  is proportional to  $d^{-2}$ , we have, again for a given value of  $z$ ,

$$V_A/\kappa = \kappa A \cdot g(\kappa d).$$

(where  $g(zd)$  is another function of  $zd$ ) and the transformation of units therefore leads to the result that we obtain a  $V_A$  curve with the same value of  $zA$ . Hence, if  $z$  is decreased by a factor 10, the value of  $A$  belonging to a given potential curve in one of the graphs 24—28 is simultaneously raised by a factor 10.

Accordingly, if we wish again to consider the graph for which the value of  $A$  is equal to that found above to be the most plausible value ( $A = 2 \times 10^{-12}$ ), we must pass to Fig. 28. Making then a comparison with Fig. 25, we note that by this decrease of the ionic concentration the minimum has almost been made to disappear, and has shifted to about 10 times greater distances. For  $z = 10^7$  the depth is of the order of 0.1—0.2 ergs/cm<sup>2</sup>; for  $z = 10^6$  it has decreased to less than 0.01 ergs/cm<sup>2</sup>. As to the influence of the double layer potential upon the potential energy curves, we again note a rapidly increasing stability maximum with increasing electric potential. The transition case between "stable" and "unstable" potential curves is now situated between  $z = 1$  and  $z = 2$ , which means that a double layer potential of a few tens of millivolts is sufficient to attain stability of the colloid system.

From the latter influence of ionic concentration upon the value of  $z$  corresponding to the transition case, it may already be seen that a second method to transfer potential energy curves of the type (a) into curves of the type (b) may be by increasing the quantity  $z$ . This is illustrated in more detail in Fig. 29, holding for 1—1 valent electrolyte as well, and for  $z = 4$ , being the value of the double layer potential. If the Van Der Waals constant  $A = 10^{-12}$ , the curves 1—5 belong to  $z$  values ranging from  $10^5$  to  $10^7$  (electrolyte concentrations varying from  $10^{-5}$  to  $10^{-1}$  molar approximately), and have a maximum above the horizontal axis. Only for the very large value  $z = 10^{7.5}$  (corresponding to about 1 molar solutions of electrolyte) does attraction prevail for all distances. Hence we find that, for these values of  $A$  and  $z$ , the transition between stable and flocculated systems is found in the concentration region where the theory reaches the limit of its quantitative applicability. The same graph may be used again for other values of the constant  $A$ , with the proper transformation of the units. For instance, for  $A = 10^{-11}$  the transition case between "stable" and "unstable" potential curves is found between the curves  $z = 10^6$  and  $10^{6.5}$  (i.e., roughly between  $10^{-3}$  and  $10^{-2}$  molar), and for intermediate values of  $A$  the transition is found somewhere between these two sets of  $z$  values.

Inspecting Fig. 29, we observe that for more diluted solutions (i.e., for decreasing values of  $z$ ) the height of the energy barriers goes through a maximum value and then decreases

again. The breadth of these energy barriers increases continually with decreasing ionic concentration, in accordance with the increasing extension of the diffuse layer of the double layer.

The question arises, however, whether the potential curves found for very low electrolyte concentrations have any significance, as the approximation of the flat plates here loses

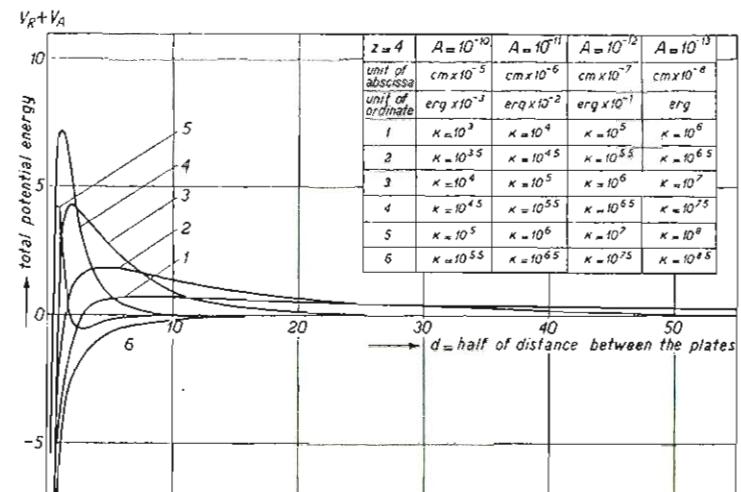


Fig. 29. Illustrating the influence of the concentration of electrolyte (expressed through  $z$ : cf. inserted table) on the potential energy curve.

its applicability for real colloids or even suspensions. Adequate treatment of this question, however, can only be given in Part III, where colloidal particles are approximated as spheres. We will find there, that the decrease in height of the potential barrier for low electrolyte concentrations is not confirmed by the theory for spherical particles.

## § 2. Graphic survey of the stability conditions

Although a discussion of graphs such as Figs 24—29 is rather instructive in discussing the balance of attractive and repulsive forces, it is difficult to obtain a complete survey of all possible potential curves. We shall therefore investigate, in the following pages, the problem of stability in yet another way.

The question of whether the total potential energy curve is a "stable" or an "unstable" potential curve for a given case (i.e., for a given valency of the ions, for given values of  $A$ ,

$z$  or  $\psi_0$ , and  $\kappa$ ) may be settled elegantly by plotting in one graph both  $\log V_R$  and  $\log (-V_A)$  against the plate distance.

If the  $\log (-V_A)$  curve and the  $\log V_R$  curve intersect twice, there will be a region in which  $V_R + V_A$  is positive, and we are accordingly dealing with a case where the total potential energy curve is of the type (a). If, on the other hand, both curves have no point in common, the  $\log (-V_A)$  curve will always be above the  $\log V_R$  curve, and the attraction accordingly prevails for all distances. The potential curve will then be of the type (b).

The two cases are illustrated in Fig. 30.

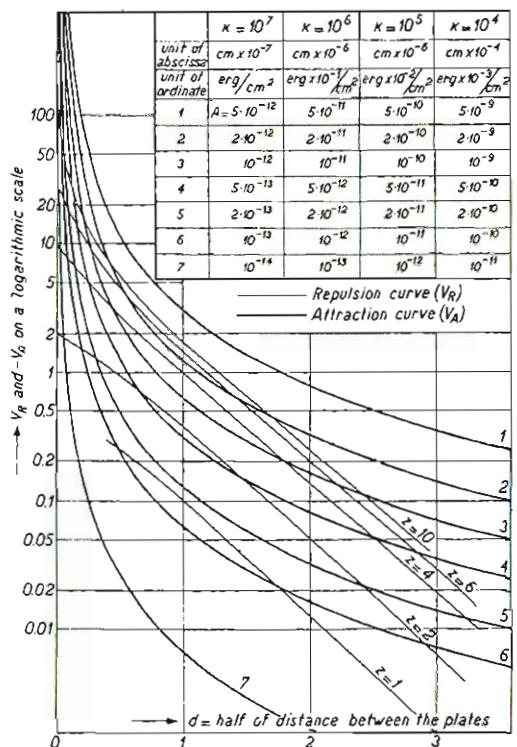


Fig. 30. Repulsion and attraction on a logarithmic scale against the separation of the plates.

We may consider, for instance, the two cases  $z = 4$  and  $z = 6$ , for  $A = 2 \times 10^{-12}$  and  $\kappa = 10^4$ . The  $\log (-V_A)$  curve corresponding to these values of  $A$  and  $\kappa$  is curve 2. From fig. 30 it is then seen at a glance that the first case leads to an "unstable" potential curve (type (b)), as  $\log V_R$  for  $z = 4$  and the  $\log (-V_A)$  curve considered do not intersect. The

second case, however, corresponds to a "stable" total potential energy curve (type (a)), as the attraction curve 2 cuts the  $\log V_R$  curve for  $z = 6$  twice. This is in complete accordance with Fig. 25 (in Fig. 30 the  $\log V_R$  curve for  $z = 5$  has been omitted for practical reasons).

A similar comparison can be made with Fig. 28, which was seen to hold for the same value of  $A$ , but for  $z = 10^6$ . The general picture of the set of potential curves given there may, again, be read directly from Fig. 30. The  $\log (-V_A)$  curve corresponding to these values of  $A$  and  $z$  is now curve 5. We see that this curve gives rise to a "stable" potential curve with the  $\log V_R$  curve for  $z = 2$ , but to an unstable one with the repulsive curve for  $z = 1$ , both again in accordance with Fig. 28.

The transition case is realized for those curves in which the  $\log V_R$  curve and the  $\log (-V_A)$  curve touch each other and have only one point in common. This transition case defines a relation between  $A$ ,  $\psi_0$  and  $z$ . This means that, for a given system or a given value of  $A$ , there exists a set of combinations of the double layer potential and the electrolyte concentration which will be just sufficient to convert a potential curve of the type (a) into one of the type (b). In the following the latter concentration will be called "flocculating concentration" of the electrolyte under consideration.

The evaluation of this "flocculating concentration" as a function of  $A$ ,  $\psi_0$  and  $z$  may be done (1) with the aid of an explicit relation, to be derived by using an approximate equation for  $V_R$ , or (2) graphically, with the aid of diagrams such as Fig. 30. These considerations may be easily extended to variations of  $v$ , so that we can now simultaneously introduce the valency of the ions as an additional variable, and turn to the important problem of the effect of ionic valency upon the flocculating concentration of electrolytes.

In Chapter V we found a simple expression (eq. 43), giving  $V_R$  as a function of  $zd$ . This equation was derived as an approximation for large values of  $zd$ ; but it appeared to be applicable more or less satisfactorily down to  $zd = 1$ . With the aid of this equation and of equation (48c), we can therefore derive an approximate explicit relation between the flocculating concentration and the physical properties of the system. For the transition case we obviously have the conditions:

$$\frac{dV_R}{dd} = \frac{d(-V_A)}{dd} \quad \text{and} \quad V_R = -V_A.$$

Applying equations (43) and (48c), we derive from these conditions:

$$zd = 1.$$

Hence, according to the approximation (43) (corresponding to a straight line for  $\log V_R$ , which means a purely exponential decay of  $V_R$ ) we should find that, for the transition case, the  $\log V_R$  and  $\log (-V_A)$  curves touch each other (i.e., the maximum in the potential curve touches the horizontal axis) exactly at  $zd = 1$ . As stated in the discussion of Fig. 25, the latter is actually very nearly the case. From this result we easily derive that for  $T = 298^\circ K$  and  $\epsilon = 78.55$  the flocculating concentration is

$$c = 8 \cdot 10^{-22} \cdot \frac{\gamma^4}{A^2 v^6}, \quad (49)$$

$c$  being expressed in millimols per liter.

Equation (43) reads

$$V_R = \frac{64\pi kT}{x} \cdot \gamma^2 \cdot e^{-2xd},$$

whence:

$$\frac{dV_R}{dx} = -2x V_R.$$

Combining this result with

$$V_A = \frac{A}{48\pi} \cdot \frac{1}{d^2} \quad \text{or} \quad -\frac{dV_A}{dd} = -V_A \cdot \frac{2}{d}$$

we easily find

$$zd = 1.$$

Applying again the equations for  $V_R$  and  $V_A$ , we have

$$\frac{64\pi kT}{x} \cdot \gamma^2 \cdot e^{-2} = \frac{A}{48\pi} \cdot z^2$$

in which

$$\gamma = \frac{e^{z/2} - 1}{e^{z/2} + 1} \quad \text{and} \quad z = \left( \frac{8\pi n}{\epsilon kT} \right)^{1/2} v \cdot e,$$

Hence,

$$n = \frac{107r^3 k^5 T^5 \gamma^4}{A^2 (v e)^6} \quad (49a)$$

From this we obtain, for room temperature, eq. (49).

Thus we find a rather simple relation between the flocculating concentration and the double layer potential. For low and moderate values of  $z$ , concentration increases with in-

creasing double layer potential; for large values of  $z$  (i.e., for large values of  $v$  or (and)  $\gamma_0$ ) concentration becomes rather insensitive to the values of the potential, and approaches a limiting value, since  $\gamma$  approaches unity for larger values of  $z$ .

As 1-1 valent electrolytes cause flocculation of most lyophobic colloids in a concentration of 100–200 millimol/liter, and as a stable sol or suspension has a comparatively large double layer potential (so that  $\gamma$  approaches the value 1) we can directly derive (using the highest values for  $c$  and  $\gamma^4$ ) that  $A$  will be about equal to

$$A = \sqrt{\frac{8 \cdot 10^{-22}}{200}} = 2 \cdot 10^{-12},$$

which is the same value as that found in § 1 from a study of the potential curves individually. This value is wholly within the limits set by the quantum-mechanical theory of Van Der Waals-London forces.

Still more interesting conclusions may be drawn from eq. (49), as to the effect of the valency of the ions upon the flocculating concentrations. Eq. (49) contains  $v$  both explicitly and in the quantity  $z$ , implicitly. If, however, the double layer potential is sufficiently large, so that even for univalent ions ( $v = 1$ ) the factor  $\gamma^4$  approaches 1, the value of  $\gamma^4$  will, a fortiori, be 1 for larger valencies, and therefore practically independent of  $v$ . (For  $z = 8$ ,  $\gamma = (e^4 - 1)/(e^4 + 1) = 0.964$  and  $\gamma^4 = 0.864$ ). In that case the concentration  $c$  is simply proportional to  $v^{-6}$ . Hence, under the conditions presumed in this chapter (involving in particular the assumption that the diffuse layer theory of Gouy and Chapman may be applied), eq. (49) leads to the very important result that we must expect the quantities of 1-1 valent, 2-2 valent and 3-3 valent electrolyte, needed to flocculate a lyophobic sol or suspension, to be in a ratio

$$1 : (\frac{1}{2})^6 : (\frac{1}{3})^6 \quad \text{or} \quad 100 : 1.6 : 0.13$$

This result of our theory is in very good agreement with colloid chemical experience.

Although eq. (49) appears to show all essential features to describe the flocculation phenomenon as a function of the system, and, as a first approximation, gives quite satisfactory results, most of our calculations have been done according to the second method, in which the approximate eq. (43) is substituted by the "exact" values of  $V_R$  as obtained from Table XI. To this end we applied the graphic method mentioned above. We determined graphically, for a given value of  $A$ , a number

of corresponding values of  $z$  and  $\alpha$ , for which the  $\log V_R$  curve touches the  $\log (-V_A)$  curve. This was done for all three valencies of the ions. In the discussion of Fig. 30 we saw that a change of  $\alpha$  from  $10^1$  to  $10^6$  is quite simply effected by a vertical shift over a logarithmic unit of the  $\log (-V_A)$  curve, if a transformation of units occurs simultaneously in such a way that the  $\log V_R$  curves hold for all values of  $\alpha$ . We have seen earlier that this correlation was made possible by the circumstance that  $v^2/\alpha \cdot V_R = f(\alpha d)$  and  $V_A/\alpha = \alpha A \cdot g(\alpha d)$ , so that the shift of the  $\log (-V_A)$  curve is determined by the condition that  $\alpha A$  must be kept constant. Hence, for constant value of  $A$ , the  $V_A$ , in the transformed scale, must be decreased by a factor 10 if  $\alpha$  is multiplied by this factor.

The graphic determination of the "flocculating"  $\alpha$  values for a number of  $z$  values may, therefore, easily be performed by accurately measuring the vertical shift necessary to bring the  $\log (-V_A)$  curve in touch with the  $\log V_R$  curve belonging to the value of  $z$  considered. This determination is made especially easy by the fact that the curves very nearly touch at  $\alpha d = 1$ .

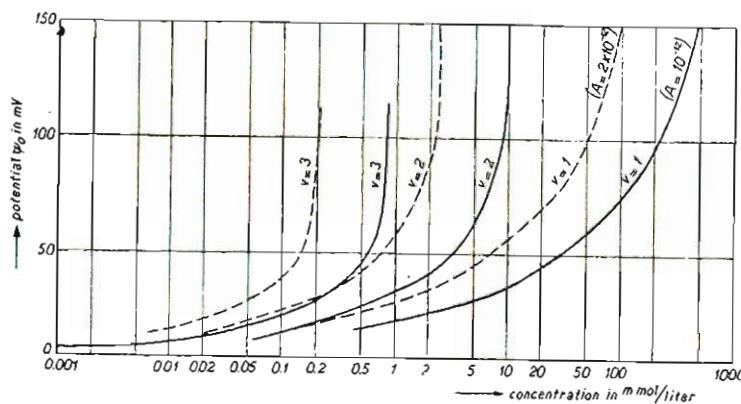


Fig. 31. Conditions of limiting stability (flocculation values) for two values of the London-Van Der Waals constant  $A$  and the valencies  $v = 1$ ,  $v = 2$  and  $v = 3$ .

Left and top = stable, right and bottom = unstable.

The result of this investigation is given in Fig. 31, where  $\log c$  is plotted against  $\psi_0$ . This graph therefore represents, for a number of values of  $A$ , and for  $v = 1, 2$  and  $3$ , the "flocculation curves", separating the  $\psi_0$ ,  $\log c$ -field into two regions.

The upper left-hand part of the  $\psi_0$ ,  $\log c$ -field, corresponding to the lowest values of the concentration and the highest values of the double layer potential, is the "stability region", where part of the total potential energy curves corresponds to positive values of  $V_R + V_A$ . In the remaining part of the  $\psi_0$ ,  $\log c$ -field  $V_R + V_A$  is everywhere negative; the combination of  $\psi_0$  and  $c$  indicated by a point in this "instability region" will accordingly be associated with a flocculated system\*.

The flocculating concentrations  $c$  found in this way according to the "exact" expression for  $V_R$  are, on the whole, in good agreement with those given by the approximate theory given above. The difference between both procedures is only quantitative and not very significant, especially in view of the many simplifying assumptions involved in the present "exact" theory. For a number of values of  $A$  and  $\psi_0$  we give in Table XII (p. 122) the flocculating concentrations  $c$ , as they may be read from Fig. 31. In order to obtain the best agreement with average experimental flocculation data, especially with respect to the influence of the valency of the flocculating ions, the Van Der Waals-London constant  $A$  must obviously be chosen as

$$A = 2 \times 10^{-12}.$$

As stated in Chapter VI this is the order of magnitude predicted by quantum-mechanical theory, considering the uncertainty inherent in the latter. The results obtained here even suggest that the "experimental" value of  $A$  is slightly larger than that found according to the usual approximate equations. If this conclusion should be allowed, the theory developed here would create the possibility to determine  $A$  from colloid chemical data with greater accuracy than that attained by the theory of atomic forces in its present stage.

\* Stability curves, representing systems on the verge of flocculation, have already been used by H. C. Hamaker, *Chem. Weekblad*, 35 (1938) 47: (Cf. also *Hydrophobic Colloids*, page 16, D. B. Centen's Uitg. Mij. N.V. Amsterdam 1938), with this difference that Hamaker used the particle charge as a variable instead of the double layer potential. Such curves proved very useful in discussing colloid phenomena. The general form tentatively proposed by this author for his flocculation curves in the  $\sigma$ ,  $c$  field appears to be in qualitative agreement with that derived here for the curves in the  $\psi_0$ ,  $\log c$  field on the basis of our theoretical considerations. As  $\sigma$  is a continuous function of  $\psi_0$  both representations are more or less comparable. The present theory (cf. Chapter III § 4) leads to the conclusion that  $\psi_0$  is a better parameter to characterize a lyophobic colloid.

TABLE XII  
STABILITY LIMITS READ FROM FIGURE 31

c in millimols/liter	$\frac{q}{\psi_0}$			100 mV			$\frac{\psi}{\psi_0}$			150 mV		
	A	$10^{-12}$	A	2	$10^{-12}$	A	$10^{-12}$	A	$2 \cdot 10^{-12}$	A	$10^{-12}$	
v = 1	260			50			410			100		
v = 2	9			2.2			10			2.2		
v = 3	0.85			0.21			0.85			0.21		

The theory as developed thus far, leading to Fig. 31 or the table given above, still contains a considerable number of simplifications. We have applied the concepts of the diffuse double layer, and more especially the equations valid for two parallel plates. The latter simplification means that our conclusions are valid only for sufficiently large particles, since only in that case does the main part of the interaction occur at the crystal faces of the particles facing each other in a particle encounter. It has been assumed here that during this encounter the particles will be orientated more or less in such a way that the opposite crystal faces of the two particles approach parallelism. In using the equations for parallel plates we have neglected the effect of the edges of the other crystal faces, and the quantitative importance of this effect cannot be estimated easily.

This simplification will be the less detrimental the larger the size of the particles. If we take (more or less arbitrarily), as the limit of applicability, that the edge length of the particles (imagined to be cubes)  $b$  must be at least  $5 \times$  the double layer "thickness" or the characteristic length  $1/\alpha$ , we find that for 1-1 valent electrolytes the present theory may be roughly applied if the particles are  $> 5 \cdot 10^{-7}$  cm, ("flocculating"  $z$ -value about  $10^7$ ). For 2-2 valent electrolytes we find in the same way a limit:  $b > 2 \cdot 10^{-6}$  cm, for 3-3 valent electrolytes  $b > 5 \cdot 10^{-6}$  cm.

In Part III, however, where we deal with the case of spherical particles, we find relatively unimportant deviations between spherical particles and flat surfaces. The reality will probably be found between those two extreme cases, and for the time being we may conclude that the model of flat plates already gives us a fairly accurate picture of the stability conditions in actual colloids and suspensions.

There is a second reason, apart from the geometric factor, however, why our simple theory needs to be corrected. This is that we have neglected the kinetic energy due to the thermal motion of the particles. We will consider the effect of this factor in the following section.

### § 3. Correction of the theory in respect of thermal motion of the particles

One of the simplifications used in the theory of colloid stability given above is that we have associated the flocculation limit more or less arbitrarily with a total potential energy curve for which the point  $V_R + V_A = 0$  coincides with the maximum of the curve. If we now drop this simplification we shall have to consider that the sol particles are able to pass over an energy barrier owing to their thermal motion.

It will be evident that the effect of thermal motion depends on the particle size. The potential curves given in § 1 of this chapter were expressed in energy units per  $\text{cm}^2$ . For a given physical system the energy to be supplied in surpassing a potential barrier will be proportional to the area of the crystal faces, hence proportional to the square of the particle dimensions.\* The amount of kinetic energy supplied by thermal motion, however, is independent of the particle size. For the same physical system, therefore, i.e. for the same protecting double layer, the potential barrier will be crossed more easily by thermal motion when the particles are smaller.

As a first approximation we assume that a potential barrier is sufficient to prevent coagulation only if its height is at least  $10 kT$  or  $4 \cdot 10^{-13}$  ergs. In that case, for a particle of  $10^{-6}$  cm, the total potential curve should show a maximum of at least  $0.4$  ergs/ $\text{cm}^2$ . For a particle of  $10^{-9}$  cm, however, an energy barrier higher than  $0.004$  ergs/ $\text{cm}^2$  would be sufficient to reach the same effect.

Considering a colloidal system containing only monovalent ions, where the flocculating concentration was seen to correspond to about  $\alpha = 10^4$ , we see from fig. 25 that an energy barrier of  $0.004$  ergs/ $\text{cm}^2$  as stability limit does not materially change the "critical" double layer potential; the distance between the maxima of  $z = 5$  and  $z = 6$ , for instance, is almost  $0.2$  ergs/ $\text{cm}^2$ . For the smaller particle, however, where the stability limit would correspond to an energy of  $0.4$  ergs/ $\text{cm}^2$ , the correction for thermal motion appears to be of considerable

\* It will be shown in Part III that for spherical particles this energy is proportional to the first power of the particle dimensions.

importance: setting the stability limit at  $V_R + V_A = 0.4 \text{ ergs/cm}^2$  instead of  $V_R + V_A = 0$  we would find for the critical value of  $z$  the value  $z = 8$  instead of the value  $z = 5$  or 6, found according to our primitive theory.

We may therefore infer that a serious influence of the particle dimensions will be found for particles of  $10^{-6} \text{ cm}$  and smaller, whereas for the larger ones the influence of thermal motion and particle dimensions will be less important. This conclusion will be fully confirmed by our considerations on the spherical particles (Chapter XII).

From the above considerations it may easily be inferred that in regard to this influence of the particle size the theory leads to the interesting conclusion that thermal motion has the effect of decreasing the stability of small particles. It is a well-known fact, indeed, given by colloid chemical experience, that it is generally much easier to prepare a stable colloid with larger particles or a suspension, than a system with a very high degree of dispersion (a gold sol, for instance). A similar effect is to be expected if we compare the small particles of a sol and the agglomerates present in the partially flocculated sol. As a result of the cooperation of the particles in one floc we may expect again that the agglomerates will be more stable than the individual particles. Hence, in a slowly coagulating sol, where the particles gradually join to form larger kinetic units, we might expect a gradually increasing stability, so that finally the flocculation may even come to a stop. This, again, was observed by several authors in the case of different colloid systems.

It is clear that the influence of the dimensions and the thermal motion of the particles will emerge more easily from a discussion on spherical particles, where particle dimensions are introduced quite naturally, than in the case of more or less cubic particles approximated by flat plates. We shall therefore postpone detailed discussion of these effects to Part III (Chapter XII).

#### § 4. The minimum in the potential curves for large distances between the plates

In our considerations on the potential energy curves we have so far neglected the minimum occurring at great distances between the plates, where the London-Van Der Waals forces again surpass the repulsion. This minimum, if low enough, will lead to a coagulation of the colloidal particles, although this coagulation will be of another character than the coagulation in the low minimum where the particles are in

immediate contact. This new form of coagulation is more reversible, both through the shallowness of the minimum and through the fact that there exists no potential barrier between the situation represented by this minimum and the complete separation of the plates.

An example of this sort of coagulation is probably given by the formation of tactoids in sols with plate-shaped or rod-shaped particles<sup>1</sup>, by the separation of an anisotropic phase from solutions of the tobacco-mosaic-virus<sup>2</sup> and by analogous phenomena<sup>3</sup>. In all these cases a phase containing a high concentration of the colloid is in equilibrium with a more dilute solution. X-ray investigation and optical phenomena have shown that in the concentrated phase the particles are orientated parallel to each other, the distances between the particles being of the order of 10–1000 Ångstroms.

The distance between the particles is very sensitive to the concentration of electrolytes in the system and in the case of the tobacco-mosaic virus to the  $p_H$  of the solution. In high concentrations of electrolyte or at a  $p_H$  near the iso-electric point of the protein, the distance is small, in good accord with the behaviour of the minimum in the potential curves which shifts to short distances for large values of  $\kappa$  and for small values of the surface potential  $\psi_0$ . C.f. figures 25, 26, 27.

Hamaker<sup>4,5</sup> considers a secondary minimum of this kind to be the cause of thixotropy i.e. an easily reversible form of gelation. The difference between thixotropic gelation and the formation of individual tactoids or the separation of a concentrated phase would then be that in the thixotropic gel the tactoids that have been primarily formed are interconnected by thin threads of the concentrated phase, according to an image put forward by Bernal and Fankuchen<sup>6</sup>, thus immobilizing the whole system by the formation of a network structure.

The fact that the thixotropic gelation can be abolished by simply shaking the system is easily explained by the shallowness of the minimum in the potential curve.

Also the phenomenon of rheopexy, discovered by Julius-

<sup>1</sup> C.f. H. Freundlich, *Kapillarchemie II*, 54, Leipzig 1932.

<sup>2</sup> J. D. Bernal and I. Fankuchen, *J. Gen. Physiol.*, 25 (1941) 111.

<sup>3</sup> C.f. Chapter I, § 4, p. 13.

<sup>4</sup> H. C. Hamaker, *Chem. Weekblad*, 35 (1938) 47. C.f. also *Hydrophobic Colloids*, page 16, D. B. Centen's Uitg. Mij. N.V., Amsterdam, 1938.

<sup>5</sup> H. C. Hamaker, *Rec. Trav. Chim.*, 56 (1937) 727.

<sup>6</sup> J. D. Bernal and I. Fankuchen, l.c. figure 11. W. Heller, *Compt. Rend.*, 202 (1936) 61; *J. Phys. Chem.*, 45 (1941) 1203.

burger<sup>1</sup> fits into this picture. Freundlich and Juliusburger observed that a liquefied thixotropic system sets to a gel in a short time if the system is subjected to a regular motion i.e. a rotation. Apparently this rotation favours the parallel orientation of the particles and therewith the formation of the tactoids and threads present in the gel structure.

There remains the question whether the depth of the minimum in the potential curve is of the right order of magnitude. It may be seen from figures 25 and 26 that this depth may be of the order or 0.1 erg/cm<sup>2</sup>, i.e. when the flat surface of the particles is more than 10<sup>-12</sup> cm<sup>2</sup> the minimum is deeper than  $kT$  and may manifest itself. It should be borne in mind, that the retardation<sup>2</sup> of the Van Der Waals-London force will diminish the value of the minimum but it will never make it disappear completely as even in the corrected theory the attraction goes with some reverse power of the distance, and thus for large distances is always more important than the repulsion which decays exponentially.

That the phenomena mentioned in this section are exclusively found with anisodimensional particles should be explained by the relatively enormous flat (or cylindrical) surface of these particles. When orientated parallel, cylindrical particles may be on the favourable distance of each other over their whole length, diskshaped particles even in two dimensions. Moreover with cylindrical particles a configuration can be formed in which each particle is surrounded by six other ones, thereby enhancing the interaction six-fold<sup>3</sup>.

In order to offer a same surface of interaction more nearly spherical particles would have to be large, i.e. in the range of very coarse colloidal systems or even of suspensions. For such particles the effects of gravity and of slight motions in the liquid are much larger than for elongated particles and would tend to destroy any structure based upon the flocculation in the secondary minimum. It is, however, worth while to apply refined techniques of observation to suspensions of nearly spherical particles in order to detect phenomena connected with the existence of this minimum of energy.

### § 5. Theory for two flat double layers on the basis of Stern's picture of the double layer

Our entire theory as developed thus far is based on the simple picture of the diffuse double layer, neglecting the

<sup>1</sup> H. Freundlich and F. Juliusburger, *Trans. Faraday Soc.*, **31** (1935) 920.

<sup>2</sup> C.f. Chapter VI, § 3, p. 104.

<sup>3</sup> C.f. E. J. W. Verwey and J. Th. G. Overbeek, *Trans. Faraday Soc.*, **44** (1948), in press.

finite dimensions of the ions. In § 5 of Chapter II we have seen that the correction, introduced by Stern<sup>1</sup>, had a number of advantages. It is worth while here to consider briefly the influence of this correction when it is applied to the theory for the interaction of two double layers.

The preliminary problem to be solved will then again be the problem of the distribution of the charge and the nature of the electric potential function for two Stern double layers in interaction. The next problem is the determination of  $V_R$ , for this case, as a function of the plate distance. For two diffuse double layers these problems are dealt with in Chapters IV and V.

In many respects we shall be able to make use of the considerations and equations given earlier, as what happens in the interaction of two Stern double layers is primarily an interpenetration of the diffuse Gouy layers of these double layers. As we need to consider only moderate and large plate distances, the Stern layers do not interfere directly, and will be altered only secondarily by the interaction. The difference from the theory given in Chapter V will be that the electric potential of the Gouy layer,  $\psi_s$ , will now be a function of the plate distance.

The distribution of the charges, and the electric potential function, in the two interacting Stern layers will be determined by the equations (17), (18) and (20), where eq. (19) must be replaced by eq. (34) with  $\tau = \tau_2$ ; moreover,  $u = ve\psi_s/kT$  is a function of  $d$  given by eq. (32), where the plate distance  $2d$  must now be measured from the beginning of the Gouy layer, i.e., from the point  $x = \delta$ . With the aid of this set of equations we can compute numerically in what way, for a constant value of  $\psi_0$ , the potential  $\psi_s$  and the charges  $\tau_1$ ,  $\tau_2$  depend on the plate distance.

It is obvious that such calculations, which prove to be rather laborious, may be carried out for a great variety of parameters, as apart from the double layer potential the capacity of the Stern layer, too, (which is determined for instance by the dimensions and the polarizability of the counter ions) and the adsorption potential of the ions (see § 5 of Chapter II) may be different for different systems. Furthermore, a new calculation has to be set up for each ionic concentration and for each value of the valency of the ions. A further difficulty is that especially the adsorption potentials of the ions, which depend on the properties of the ions and of the wall material, are entirely unknown quantities.

<sup>1</sup> O. Stern, *Z. Elektrochemie*, **30** (1924) 508.

For all these reasons the introduction of the Stern correction into our considerations will be valuable only as an illustration of the influence of the individual properties of the ions in a qualitative way, and not as a quantitative theory. We have therefore made a number of calculations for which the adsorption potentials of the ions have been more or less arbitrarily taken equal to zero. As a plausible average value of the capacity of 1 cm<sup>2</sup> of the Stern layer we used the same value as in the calculations of Chapter II, viz. 10<sup>7</sup> cm.

For a special case, i.e.  $\psi_0 = 200$  millivolts, and for a number of electrolyte concentrations, the results of the calculations are summarized in Fig. 32 and Table XIII.

TABLE XIII

THE POTENTIAL  $\psi_\delta$  OF THE STERN LAYER FOR DIFFERENT DISTANCES OF THE PLATES, WHEN THE TOTAL POTENTIAL  $\psi_0$  IS 200 m.V.

$xd$	$\psi_\delta$ in mV for		
	$x = 10^5$	$x = 10^6$	$x = 10^7$
$\infty$	160	93.5	22.5
2	160	93.5	23.5
1	160	95	27
0.5	160	98	33
0.3	161	105	41
0.0	197	153	55

Table XIII shows the variation of the potential  $\psi_\delta$  and Fig. 32 the variation of the charges in the double layer as a function of  $xd$ .

The graphs show that the result of the interaction is a decrease of the charge ( $\sigma_2$ ) in the diffuse Gouy layer. Simultaneously  $\sigma$  decreases but not to the same extent as  $\sigma_2$ , because the charge of the Stern layer ( $\sigma_1$ ) increases at the same time. Thus the interaction is accompanied by a notable transition of charge from the Gouy layer to the Stern layer. The decrease of the surface charge  $\sigma$  results in an increase of the potential  $\psi_\delta$  (cf. eq. 18),

$$\sigma = \frac{\epsilon'}{4\pi\delta} (\psi_0 - \psi_\delta) \quad (18)$$

but as the changes in  $\sigma$ , especially for slight and moderate interaction ( $xd > 0.5$ ), are rather unimportant,  $\psi_\delta$  changes only in a slight degree, as is clearly demonstrated in table V. A perceptible increase of  $\psi_\delta$  sets in only for  $xd < 0.5$ . The

increase is strongest for large values of  $x$  where  $\psi_\delta$  is only a small fraction of the total potential drop  $\psi_0$ .

A difference from the case of the interaction of two double layers according to the picture of Gouy-Chapman, dealt with in the foregoing sections, becomes apparent in the neighbourhood of  $d = 0$ . For it is seen that for  $d = 0$ , where the Gouy layers are completely pushed aside, the total charge has not decreased to zero, as in that case there is still a certain amount of charge left in the Stern layer; the latter amount is then equal to the total charge of the double layer ( $\sigma_1 = \sigma$ ).

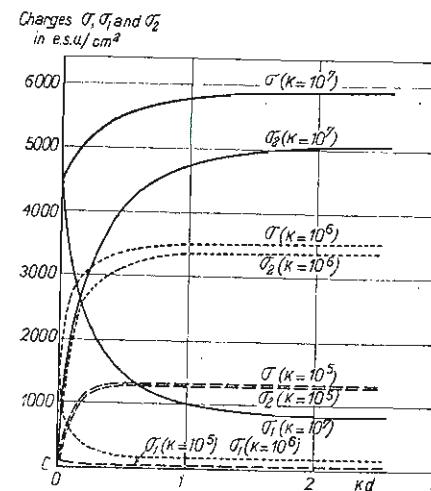


Fig. 32. Demonstrating the change of the charges in the combined Gouy-Stern layers as a function of the distance of the plates. The total double layer potential  $\psi_0$  is supposed to be 200 m.V.

$\sigma$  = total charge of the double layer =  $\sigma_1 + \sigma_2$ ,

$\sigma_1$  = charge of the Stern-layer.

$\sigma_2$  = charge of the diffuse Gouy-layer.

In considering the total potential energy of a system of parallel plates we have seen that the form of the potential curve is virtually determined by the contribution of  $V_R$  in the neighbourhood of  $xd = 1$  and for larger values of  $d$ ; the contribution of  $V_R$  for small distance has only a minor influence upon the  $V_R + V_A$  curve, because in this region the attractive potential  $V_A$  predominates anyway. Accordingly the relevant part of the potential energy curve may be determined, as a first approximation, with the aid of the assumption that  $\psi_0$  has everywhere the same value as for  $d = \infty$  (c.f. table XIII). Hence,

for the contribution of  $V_R$  for two Stern double layers to the total potential curve, we can make use of the  $V_R$  function derived earlier for two Gouy double layers with a surface potential equal to the potential  $\psi_s$  of the Stern double layer.

This is rather an important result. In the considerations of the foregoing sections, working with the model of two Gouy double layers, the repulsive potential was determined by the surface potential  $\psi_0$ . For diluted colloid systems, where the addition of indifferent electrolytes does not materially change the concentration of the potential determining ions, we could assume that this surface potential was independent of the electrolyte concentration, and the stability theory could be based on the assumption of a constant value of  $\psi_0$ . Introducing now the Stern correction, we find the repulsive potential is not determined by  $\psi_0$ , but, as a first approximation, by the potential  $\psi_s$ . The consequences thereof are twofold:

1. Comparing systems with the same value of  $\psi_0$  but with different electrolyte concentrations we must consider that  $\psi_s$  is a function of the ionic concentration and decreases notably with increasing concentration.

2. In systems containing no capillary active ions, i.e., in systems where the adsorption potentials have no excessively high values, the potential  $\psi_s$  is always smaller than the surface potential.

The first point implies a complication of the theory; the second point is in a certain respect an advantage, as it eliminates the very high potentials in the diffuse layer for which the theory becomes less reliable (application of the Boltzmann factor in eq. (2); *vide* the discussion of this equation in the introductory part of chapter II).

It may be observed that the application of the Stern correction to our theory results, in a way, in a compromise between our simple theory and older conceptions of the stability of colloids. A current working hypothesis in colloid chemistry is that the electrolyte coagulation of a lyophobic colloid is connected with the reduction of the potential drop in the outer diffuse part of the double layer; it was originally thought that this reduction of the electric potential was caused by a reduction of the charge by the electrolyte (adsorption theory; Freundlich<sup>1</sup>); later on it was recognized that such a reduction of the potential might also be understood on the basis of the double layer theory, as in the case of a constant charge, too, the contraction of the diffuse charge layer and, therefore,

the increase in the double layer capacity, must lead to a decrease of the potential (Müller<sup>1</sup>, Verwrey<sup>2</sup>). In the theory developed in the foregoing sections we have shown that coagulation may be understood entirely as a result of the contraction of the diffuse layer only, so that even for a constant value of the potential the repulsive forces do not extend far enough into the liquid layer surrounding the particles to prevent the agglomeration of the particles under the influence of the Van der Waals-London attraction. Introducing the Stern correction, however, we take into account again that, in addition to the compression of the diffuse charge, the potential in the diffuse layer is lowered by the addition of electrolyte.

There is yet another reason why the application of Stern's picture of the double layer may be called a correction of our theory in its most simple form in the direction of the ideas usually adopted in colloid chemistry. In our simple theory we used the total double layer potential  $\psi_0$  as a parameter determining stability. In colloid chemical research, however, stability is generally connected with the zeta potential (Chapter II, § 6), derived from electrokinetic data, which may be considered as a measure of the electric potential drop in the diffuse part of the double layer. Obviously the Stern correction inclines in the same direction, as it leads to the result that our theory may be improved by simply using the potential  $\psi_s$  instead of the double layer potential  $\psi_0$ . This relation to older conceptions in colloid chemistry, it is true, is still rather theoretical, as we have seen in Chapter II, § 6, that our knowledge of zeta-potentials is poor at present, and the experimental determination of the potential drop in the diffuse layer from electrophoretic data is still an incompletely solved problem.

Finally the Stern-correction is essential to an understanding of the differences between electrolytes of the same valency type. Although with hydrophobic substances these differences are not so outstanding as with hydrophilic colloids, they nevertheless exist, manifesting themselves in differences of flocculation values. In all cases the flocculation value is smaller with larger ions and with strongly adsorbable ions. On the base of Stern's theory this is just what might be expected, for large ions make the capacity of the Stern layer small and the fall of the potential in this layer large, as a result of which the potential in the diffuse double layer is smaller than with small ions. In the same way strongly adsorbed ions cause a large part of the total double layer

<sup>1</sup> H. Müller, *Kolloidchem. Beihefte*, 26 (1928) 274.

<sup>2</sup> E. J. W. Verwrey, *Chem. Reviews*, 16 (1935) 400.

<sup>1</sup> H. Freundlich, *Kapillarchemie*, Band II, 4. Auflage, 129 (Leipzig 1932).

potential to occur within the Stern layer, and leave only a small part of  $\psi_0$  as "effective" repulsive potential.

The quantitative effect of the use of Stern's concept of the double layer is illustrated in Fig. 33. This figure, again, contains a set of curves similar to those in Fig. 31, with the only difference that they now represent the combination of  $\psi_s$  and  $\log c$ , for which the maximum of the total potential energy curve ( $V_R + V_A$ ) exactly coincides with the horizontal

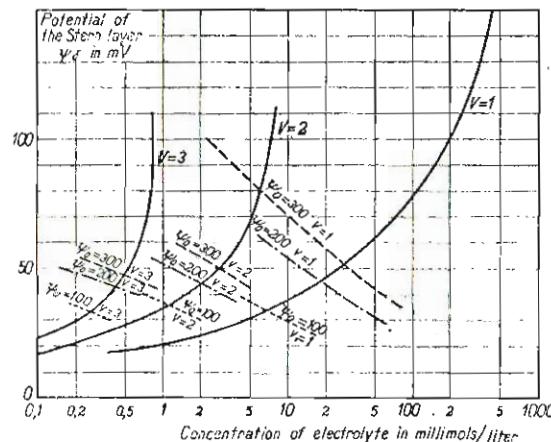


Fig. 33. Flocculation values according to the Stern theory.

The curves marked  $\nu = 1$ ,  $\nu = 2$ ,  $\nu = 3$  represent limits of stability for combinations of the electrolyte concentrations (abscissa) and the potential of the Stern-layer  $\psi_s$  (ordinate). The Van Der Waals constant  $A$  has been taken as  $10^{-12}$ . The curves marked  $\psi_0 = 300$ ,  $\psi_0 = 200$  etc. give the value of the potential  $\psi_s$  as a function of the electrolyte concentration for the specified value of the total potential  $\psi_0$ . The intersection points of the two sets of curves determine the concentration of electrolyte and the value of  $\psi_s$  in the limit of stability.

line of zero energy. In addition, the graph contains a set of curves giving, according to the Stern-theory, the potential  $\psi_s$  as a function of the concentration, for  $\psi_0 = 100$  mV.,  $\psi_0 = 200$  mV., and  $\psi_0 = 300$  mV., respectively. As in the foregoing, the adsorption potential of the ions has been taken equal to zero.

The intersection points in both sets of curves will now give the ionic concentrations corresponding to the flocculation limit for the three values of the double layer potential given above. The difference from the more simple theory is clearly illustrated. The values of the electric potential  $\psi_s$  in the different cases are appreciably lower than the double layer potential  $\psi_0$ . In comparison to our simpler theory, working with

the Gouy-Chapman picture of the double layer, we accordingly find much lower values of the flocculating concentrations. Consequently, we also find a smaller difference between the flocculating values for ions of different valency, although, for a given value of  $\psi_0$ , the polyvalent ions give a smaller value for the corresponding  $\psi_s$ . The difference between the flocculating values of 1-1, 2-2, and 3-3 valent electrolytes may be enlarged, and the flocculating concentrations of the electrolytes increased, by choosing a smaller value of the Van Der Waals constant,  $A$ . In this way we could again attain a better accordance with experimental values of the flocculating concentrations and with the value predicted by the quantum-mechanical theory for the attractive constant. Considering the many variables involved in the theory of Stern we have not investigated quantitatively cases any other than that used to illustrate the above.

In our opinion, however, further progress in our understanding of the stability of hydrophobic colloids can only be expected from a further development, experimental as well as theoretical, of the principle underlying Stern's theory.

### § 6. Stability of emulsions

We shall finally consider briefly the case of emulsions<sup>1</sup>. We have seen that a double layer is also formed at the interface of two liquids, and that every electrolyte can act as a potential determining electrolyte. Nevertheless in the presence of normal electrolytes it is impossible to prepare stable emulsions. The explanation of this must be sought in the special properties of the double layer at the interface of two liquids. We have seen that this double layer consists of two diffuse layers, and that the total potential drop is accordingly divided into two parts, one on either side of the interface. In an oil-in-water emulsion the potential drop in the aqueous phase will then be negligibly small, for two reasons. In the first place the potential drop was found to occur mainly in the phase with lowest dielectric constant and lowest ionic concentration, i.e., in the oil phase. Moreover, the oil droplets will generally be much smaller than the value  $1/\lambda$  in the oil phase, which will probably be of the order of  $10^{-3}$  cm, so that a considerable interaction of double layers occurs within the oil drop, and the double layer cannot develop completely, owing to lack of space in the small droplets. As is illustrated in Fig. 14, this leads to an additional decrease of the potential drop in the aqueous phase. If  $\psi_i(0)$  is small the double layer charge will *a fortiori* be small, as  $\sigma \propto \sinh(\nu e \psi_i(0)/2kT)$ ;

<sup>1</sup> E. J. W. Verwey, *Trans. Faraday Soc.*, 36 (1940) 192.

which means that the double layer has an extremely small capacity and accordingly an extremely small free energy. There will also be an equally small repulsive potential between the oil droplets, not sufficient to prevent the droplets from agglomerating and eventually coalescing.

The influence of the two kinds of emulsifiers mentioned in § 4, Chapter I, should now be clear, as both have the effect of giving to the liquid drops a double layer with the same properties as the double layer around solid particles, and of shifting the double layer potential drop again towards the outer phase.

When a salt with a highly adsorbable ion is used as an emulsifier, the double layer charge of the inner layer is present as a monomolecular layer of the active ions accumulated at the interface, thus re-establishing the case that the charge may be considered as a true surface charge. The double layer potential occurs in the phase with the highest solvating power for the counter ions.

As to the emulsifying action of finely divided solids, Van Der Minne<sup>1</sup> postulated that the emulsifying particles must be wetted more readily by the dispersion medium than by the dispersed phase; the particles trapped at the interface will therefore cover the outside of the liquid droplets. Furthermore, the colloidal solid alone must give a stable sol in the dispersion medium. The larger part of the surface of the solid particles in the emulsion is in contact with this dispersion medium, and has a double layer of the same structure and electrical properties, as in this sol; if a sufficient part of the surface of the droplets is covered with these solid particles, their double layer assumes the properties of a double layer of a solid substance, and the drops undergo the same repulsion as may be assumed for normal hydrophobic colloids. It is noteworthy in this respect that the emulsifying action of these finely divided solids needs the presence of a small amount of electrolyte, and optimal emulsification occurs for electrolyte concentrations somewhat below the flocculation of this electrolyte for the sol of the solid particles alone. This amount of electrolyte reduces the thickness of the outer layer of their double layer, and therefore reduces the mutual repulsion between these solid particles at the interface in such a way that they can be packed sufficiently densely on the surface of the droplets, and the properties of the liquid-liquid interface can be suppressed. The emulsifying action of finely dispersed solids, therefore, may also be easily understood along these lines.

<sup>1</sup> J. C. Van der Minne, *Thesis*, Utrecht, 1928. Cf. also *Hydrophobic colloids*, page 138, D. B. Centen's Uitg. Mij. N.V. Amsterdam 1938.

## PART III

### On the interaction of spherical colloidal particles

#### VIII. INTRODUCTION

In Part I the principles were discussed on which the interaction of colloidal particles may be understood, and by way of application the case of the interaction of two parallel flat plates was dealt with in Part II. Starting from this case it was possible to form a picture of the behaviour of colloidal particles and to come to an understanding of such fundamental properties as stability, flocculation value and the rule of Schulze and Hardy.

Nevertheless, in reality colloidal particles are not infinitely large flat plates, and it seems worth while to consider, as an other extreme case, the interaction of two spherical particles. In the first place the picture of two spherical particles will give a very good approximation of reality, irrespective of the shape of the particles, when they are far apart. Moreover, in the theory of spherical particles the influence of the size of the particles follows quite naturally, whereas in the theory of flat surfaces it has to be introduced afterwards in a more or less arbitrary way. Again, the border effects caused by the curvature of the particles, which have been completely neglected in Part II can now fully be taken into account. Finally, the interaction of spherical particles has already been treated of by other authors, and although the general principles underlying their work were erroneous, as will be expounded in the Appendix, details of their calculations may be used in our work.

In a series of papers Levine and Dube<sup>1</sup> treated of the interaction of spherical particles as an independent problem. They started from the distribution of field and charge around one spherical particle, using the approximation for small potentials. Introducing the changes in this distribution accompanying the interaction of two particles, they derived — unfortunately using a wrong method — equations for the potential energy of interaction.

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- <sup>1</sup> S. Levine, *Proc. Roy. Soc., London, A* **170** (1939) 145, 165.  
 S. Levine and G. P. Dube, *Compt. rend.*, **208** (1939) 1812.  
 " " " *Trans. Faraday Soc.*, **35** (1939) 1125, 1141;  
     " " " *ibid.* **36** (1940) 215.  
 S. Levine, *J. Chem. Phys.*, **7** (1939) 831.  
 S. Levine and G. P. Dube, *Phil. Mag.*, (7), **29** (1940) 105.  
 " " " *J. Phys. Chem.*, **46** (1942) 239.

On the other hand Derjaguin<sup>1</sup> showed that it is possible to calculate the interaction of spherical particles by simple integration, when the interaction of infinitely large flat surfaces is known, and used this method in investigating the stability of colloids. The method of Levine and Dube, when applied in a more justifiable way, gives the most reliable results when the thickness of the double layer is large as compared to the dimensions of the particles, whereas Derjaguin's method is more satisfactory with thin double layers and large particles. Both methods supplement each other, and together they enable us to survey the whole field of particle dimensions and electrolyte concentrations which interests us.

In one respect Derjaguin's method is superior to Levine and Dube's. It is possible to apply the principle of Derjaguin's method to the complete Gouy-Chapman equation, whereas in Levine's and Dube's treatment it is unavoidable to introduce the linear approximation of Debye and Hückel. The theory for large spherical particles, surrounded by a thin double layer may therefore be made almost as exact as that of flat plates, but in the case of small particles with an extended double layer the situation is less favourable.

Nevertheless this does not constitute a serious defect in the theory. As explained earlier (cf. Chapter II, § 4), precisely in the case of small particles with an extended double layer, the application of the linear approximation may be allowed and gives reliable results, even for relatively high potentials.

Applying the same principles as used in Part II we now have to calculate the change in free energy accompanying the approach of two colloidal particles. To this end we shall first consider the free energy of the double layer system for spherical particles, and add to it the free energy of the London-Van Der Waals attraction forces. From the curves of total free energy so constructed we shall derive the criteria for the stability of colloids.

<sup>1</sup> B. Derjaguin, *Kolloid-Z.*, 69 (1934) 155.  
*Acta Physicochimica URSS.*, 10 (1939) 333.  
*Trans. Faraday Soc.*, 36 (1940) 203.

## IX. THE POTENTIAL ENERGY OF INTERACTION FOR LARGE PARTICLES WITH A RELATIVELY THIN DOUBLE LAYER

### § 1. Introduction

In calculating the interaction of spherical particles we consider two spheres of radius  $a$ , with a distance between their centres ( $O_1$  and  $O_2$ ) equal to  $R$ . The smallest distance between the surfaces is called  $H_0$ , so

$$H_0 = R - 2a. \quad (50)$$

The extension of the double layer is of the order of  $1/\alpha$ . In this Chapter we consider large particles with a thin double layer, viz. the case that  $\alpha a \gg 1$ . It is advantageous to introduce the abbreviations

$$\alpha a = \tau \quad \text{and} \quad R/a = s. \quad (51)$$

### § 2. The repulsion for large $\alpha a$

Derjaguin<sup>1</sup> introduced a method by which it is possible to calculate the interaction of two spheres when the interaction of two infinitely large parallel planes of the same material is known. This method only may be applied when the range of the interaction is much smaller than the particle radius. This condition is satisfied when  $\alpha a$  is large.

The repulsive energy between two spheres is considered to be formed by the contributions of infinitesimal parallel rings, each pair of rings contributing to the potential energy an amount equal to

$$2\pi h \cdot 2(f_H - f_\infty) dh, \quad (52)$$

$2f_H$  being the free energy per  $cm^2$  of two parallel plates at a distance  $H$ ,  $h$  being the distance of the ring considered from the axis of symmetry (c.f. Figure 34).

This implies the supposition that the interaction is not influenced by the adjacent elements having either a larger or a smaller distance from each other, or in other words, it is supposed that the lines of force remain parallel to the axis of symmetry  $O_1O_2$ . In reality the lines of force will be curved out-

<sup>1</sup> B. Derjaguin, *Kolloid-Z.*, 69 (1934) 155.  
*Acta physicochimica URSS.*, 10 (1939) 333.

wards, the more so the greater the distance from the line  $O_1O_2$ . As the lines of force insert perpendicular to the surface of the spheres, their curvature will be negligible as long as the angle  $O_2O_1D$  is small.

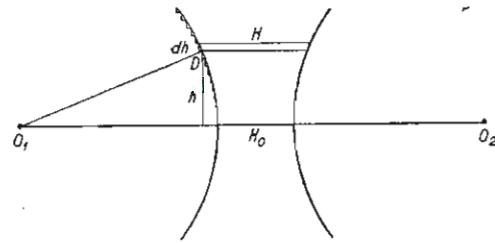


Fig. 34. Illustrating the building up of the repulsion between two spheres out of the repulsion between quasi-parallel layers.

The total repulsive energy is then found by integrating (52) over the whole surface of the spheres. As we started from the assumption that the range of the repulsion is much smaller than the dimensions of the spheres, the contributions of layers far from the axis are unimportant, and it is immaterial what upper limit of integration we take. The value  $\infty$  is chosen as it gives the most simple expression. This same assumption ensures that the layers giving important contributions shall be practically parallel, the curvature of the surface beginning to be felt only where the contribution to the repulsive energy is negligible.

Hence we find, for the repulsive energy  $V_R$ ,

$$V_R = \int_0^\infty 2\pi h \cdot 2(f_H - f_\infty) dh. \quad (53)$$

As  $\frac{H-H_0}{2} = a - \sqrt{a^2 - h^2}$ ,  $2h dh$  is equal to  $a \cdot dH \sqrt{1 - h^2/a^2}$ , and may be approximated by  $a \cdot dH$  for small values of  $h$  ( $a$  is the radius of the sphere). So the repulsive energy is found to be

$$V_R = 2\pi a \int_{H_0}^\infty (f_H - f_\infty) dH. \quad (54)$$

Introducing provisionally\* for  $f_H - f_\infty$ , the approximate value for small potentials (cf. eq. (44))

\* At the end of this chapter we introduce, instead of (44), the exact equation for the repulsion between flat plates and carry out the integration graphically.

$$2(f_H - f_\infty) = \frac{2n k T}{\kappa} z^2 \left(1 - \tanh \frac{\kappa H}{2}\right) = \frac{\epsilon a \psi_0^2}{4\pi} \left(1 - \tanh \frac{\kappa H}{2}\right) \quad (55)$$

equation (54) may be integrated, giving

$$V_R = \frac{\epsilon a \psi_0^2}{2} \int_{H_0}^\infty \left(1 - \tanh \frac{\kappa H}{2}\right) d \left(\frac{\kappa H}{2}\right) = \frac{\epsilon a \psi_0^2}{2} \ln (1 + e^{-\kappa H_0})$$

$$\frac{V_R}{\epsilon a \psi_0^2} = \frac{\ln (1 + e^{-\kappa H_0})}{2} \quad (56)$$

As  $H_0 = R - 2a$ ,  $\kappa H_0$  may be replaced by  $\kappa R - 2\kappa a = \tau(s - 2)$ , so that

$$\frac{V_R}{\epsilon a \psi_0^2} = \frac{1}{2} \ln (1 + e^{-\tau(s - 2)}). \quad (56)$$

In order to find out the minimum value of  $\tau$ , for which (56) may be applied with some accuracy, we observe that in the deduction of (56) two approximations are introduced, both of which tend to make the value of  $V_R$  too high.

Firstly the upper limit of integration is put equal to  $H = \infty$ , whereas the highest value having any physical sense should be  $H = 2a + H_0$ . This gives an error in the final expression for the repulsive energy equal to

$$2\pi a \int_{2a+H_0}^\infty (f_H - f_\infty) dH = \frac{\epsilon a \psi_0^2}{2} \int_{2a+H_0}^\infty \left(1 - \tanh \frac{\kappa H}{2}\right) d \frac{\kappa H}{2} =$$

$$= \frac{\epsilon a \psi_0^2}{2} \ln (1 + e^{-\kappa(H_0 + 2a)}) = \frac{\epsilon a \psi_0^2}{2} \ln (1 + e^{-\tau s}) \quad (57)$$

It is easy to verify that this error remains under one percent, when  $\tau s - 5 > \tau(s - 2)$  practically independent of the value of  $s$ , meaning that the expression (56) should not be used if  $\tau < 2.5$ .

In the second place the surfaces of the spheres are not parallel to each other, as was assumed in our deduction. This will certainly cause the repulsion to be smaller than it would have been if the surfaces were exactly parallel. For each ring the repulsive energy will be between  $4\pi h (f_H - f_\infty) dh$  as a minimum, and  $2\pi a (f_H - f_\infty) dH$  as a maximum value. In our calculation we used the upper limit (cf. equation 54). The amount of the error introduced by this approximation is not so easy to establish. As a maximum value, using  $4\pi h dh$  instead of  $2\pi a dH$ , we found the error for  $\tau = 10$  to be about

5%; for  $\tau = 5$  about 10% and for  $\tau = 2$  about 30%, but probably (see below) the actual errors are much smaller.

### § 3. Application of the complete Gouy-Chapman equations

If we wish to apply the complete Gouy-Chapman equations instead of the linear approximation, we have only to replace the value of  $(f_H - f_\infty)$  as it is given by equation (55) by the more exact value following from table XI, where  $f(u,z) = \frac{v^2}{\kappa} \cdot 2(f_H - f_\infty)$  may be read as a function of  $\frac{\kappa H}{2}$  ( $d = \frac{H}{2}$ ).

In doing this we lose the possibility of carrying out the integration in a closed form, but a graphic integration, although somewhat laborious, leads to the desired purpose.

Calling

$$\frac{v^2 V_R}{a} = G(\kappa H) = G(\tau(s-2)), \quad (58)$$

we find  $G$  by carrying out a graphic integration,<sup>1</sup> viz.:

$$G(\kappa H_0) = 2\pi \int_{H_0}^{\infty} f(u,z) d \frac{\kappa H}{2} \quad (59)$$

The function  $G$  as found by this integration is represented for a number of values of  $z$  in figure 35 and in table XIV<sup>2</sup>. The numbers given are correct to within a few percent of their value. In figure 35 we have also inserted a few curves following from the approximated equation (56). It will be seen that for  $z = 2$  the difference between the approximative and the exact curve is not very great, but for  $z = 3$  and higher values it becomes more and more important. The exact curves are always lower than the approximative ones. They are flatter at great

<sup>1</sup> In many cases it is an advantage to use approximate equations for  $f(u,z)$ , which may be integrated exactly, and to make the necessary corrections for the difference between the approximate and the true values of  $f(u,z)$  by graphic integration. This restricts the graphic integration to a relatively small part of the function and so increases the accuracy. For small interaction we used the approximative equation (43).

$$f(u,z) = v^2 \frac{64\pi kT}{\kappa^2} \gamma^2 e^{-\kappa H} = \frac{r}{2\pi} \frac{16k^2 T^2 \gamma^2}{e^2} e^{-\kappa H} = 1.471 \times 10^{-6} \gamma^2 e^{-\kappa H}$$

leading to the following approximative expression for  $G$ :

$$G_{app.}(\kappa H) = v^2 \frac{64\pi n kT}{\kappa^2} \gamma^2 e^{-\kappa H} = \frac{r}{2} \frac{16k^2 T^2 \gamma^2}{e^2} e^{-\kappa H} = 4.62 \times 10^{-6} \gamma^2 e^{-\kappa H}$$

<sup>2</sup> The potential  $\psi_0$  is equal to 25.6  $z$  millivolts.

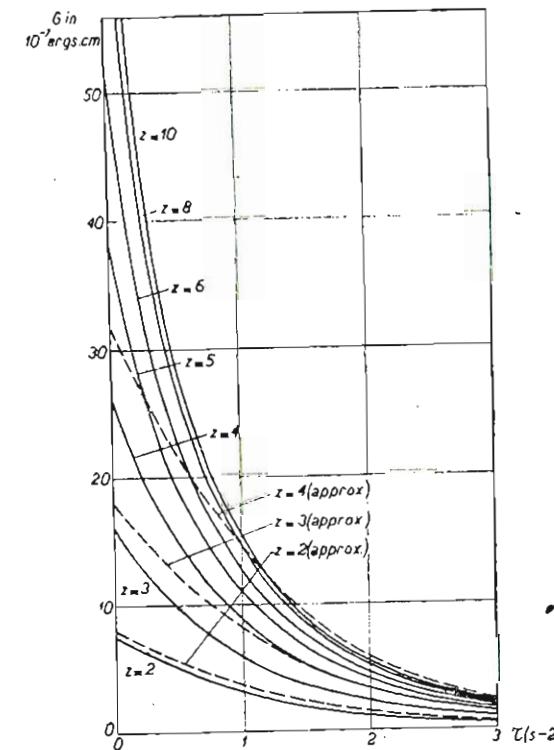


Fig. 35. The repulsive potential  $V_R$  between two spherical particles, when the exact expression for high potentials is applied.  
Dotted lines = repulsive potential according to the approximated equation (56).  $V_R = \frac{aG}{v^2}$ .

TABLE XIV  
Values of  $G \times 10^7$  as a function of  $z$  and  $z(s-2)$ .  $G$  being  $\frac{v^2}{a} V_R$

$z$	2	3	4	5	6	8	10
$z(s-2)$							
0	7.50	16.02	26.5	38.46	51.4	78.7	108.1
0.10	6.90	14.5	23.3	33.0 <sup>3</sup>	42.5	57.3	66.9
0.20	6.35	13.1	20.7 <sup>5</sup>	28.6	35.6	45.0	51.1
0.30	5.85	11.9	18.6 <sup>1</sup>	24.92	30.5	37.0	40.9
0.50	4.96	9.78	14.85 <sup>5</sup>	19.36	23.0	26.9 <sup>5</sup>	29.3
0.70	4.06	7.98	11.96	15.31	17.93	20.7	22.2
1.00	3.04	5.91	8.73	11.06	12.72	14.5	15.44
1.20	2.54	4.86	7.13	8.92	10.23	11.5	12.33
1.50	1.91 <sup>5</sup>	3.67	5.29	6.59	7.56 <sup>5</sup>	8.54	8.99
2.00	1.16 <sup>5</sup>	2.37	3.25	4.03	4.59	5.17	5.40
2.50	0.71	1.44	2.08	2.46	2.94	3.16	3.35
3.00	0.43	0.86 <sup>5</sup>	1.25	1.53	1.78	1.95	2.05 <sup>5</sup>

distances and steeper at small distances. This is a result of the difference between the exact and the approximated repulsion curves for flat plates, the interaction energy being lower according to the exact expression.

It may be remarked that for small interaction (large distances) the exact curves tend to come near to the approximative curve for  $z = 4$ , but that they always remain under this curve. That is just what might be expected, as the exact expression for  $G$  at large distances is\*

$$G = \pi \int_{H_0}^{\infty} f(u, z) d(z H) = \frac{\epsilon k^2 T^2}{2e^2} 16 \gamma^2 e^{-\gamma(s-2)},$$

which for large  $z$  is nearly equal to

$$G = \frac{\epsilon k^2 T^2}{2e^2} 16 e^{-\gamma(s-2)},$$

whereas the approximated value for  $z = 4$  and small interaction is

$$G_{app.} = \frac{\epsilon \psi^2}{2} \ln(1 + e^{-\gamma(s-2)}) \approx \frac{\epsilon k^2 T^2}{2e^2} (4)^2 e^{-\gamma(s-2)}.$$

Before combining the repulsion curves found here with the London-VanderWaals attraction, we will first deal with the interaction of the double layers for the case that  $\kappa a$  is not large.

\* Cf. first footnote on page 140.

## X. THE POTENTIAL ENERGY OF INTERACTION, WHEN $\kappa a$ IS SMALL (LINEAR APPROXIMATION)

### § 1. Principle of the method

Whereas, when  $\kappa a$  is large, we have at our disposal a direct transformation of the energy of interaction of two plates into that of two spheres, such a simple transformation does not exist when  $\kappa a$  is small. In that case we follow essentially the same method which we used to calculate the interaction of flat plates, viz. we first calculate the electric field in the double layer around the particles, and after that the free energy of the double layers. This method was used by Levine and Dube and we can use several parts of their calculations, although our conclusions differ from, and are in part even opposite to theirs.

According to Chapter III of part I the free energy of any given system of double layers may be written

$$F = - \int_{\text{surface}} dS \int_0^{\psi_0} q' d\psi'_0 \quad (60)$$

in which  $q'$  is the specific charge of a surface element  $dS'$ , the surface potential being  $\psi'_0$ . The integration has to be carried out over the whole interface of the system.

It is difficult to work out this integral exactly, because  $q'$  is rather an intricate function of  $\psi'_0$ . If, however, the problem is simplified by introducing the approximation of small potentials,  $q'$  is directly proportional to  $\psi'_0$  and the first integration now leads to the simple result

$$\int_0^{\psi_0} q' \cdot d\psi'_0 = \frac{1}{2} q_0 \psi_0. \quad (61)$$

As the potential of the surface is considered constant, the second integration is now equally simple, and the whole integral (60) transforms into

$$F = - \int dS \int q' d\psi'_0 = - \frac{1}{2} Q \psi_0, \quad (62)$$

in which  $Q$  represents the total charge of the interface in the configuration considered.

Considering two spherical particles, which approach each other from an infinitely great distance to a distance ( $l$ ) where the interaction is sensible, the potential energy of interaction  $V_R$ , which is equal to the change of the free energy, is given by

$$V_R = \Delta F = Q_\infty \psi_0 - Q_l \psi_0 = \psi_0 (Q_\infty - Q_l), \quad (63)$$

in which  $Q_\infty$  and  $Q_l$  are the charges of one particle when the particles are at infinitely great distance and at a distance  $l$  respectively, the factor  $1/2$  of equation (62) being just cancelled by the fact that we are considering two identical particles.

In the foregoing it has been tacitly assumed that during the whole process the potential  $\psi_0$  of the surface remains constant. If we wish to assume that not the potential but the charge of the particles remains constant,\* we have to use another equation instead of (63), giving the change in free energy, which in this case is equal to the change in electrical field energy. In this case the potential energy of interaction is equal to

$$V_R = \Delta F = Q \psi_l - Q \psi_\infty = Q (\psi_l - \psi_\infty), \quad (64)$$

$Q$  being the charge of one particle, now supposed to be constant, whereas the potential changes from  $\psi_\infty$  to  $\psi_l$ .

This expression (63) (or, if desired, (64)) forms the fundamental equation of our problem, and all we have to do is to find the relation between the charge  $Q$  and the potential  $\psi_0$ , as a function of the distance separating the particles.

## § 2. The distribution of the electric field and the relation between charge and potential of two interacting spherical particles

We consider two identical spherical particles of radius  $a$  at a distance  $R$  between their centres  $O_1$  and  $O_2$ , immersed in a solution of a simple electrolyte. In the approximation used here, the influence of the concentration and the valency of the electrolyte is completely expressed by the corresponding thickness

\* As we pointed out in § 4 of Chapter III, the assumption of constant potential is the most reasonable. We here introduce, as an alternative, the assumption of constant total charge of the particles, mainly because it has been used extensively by Levine and Dube; but this assumption is rather artificial. If the potential is not constant during the interaction, this means that equilibrium is not established. In that case it would seem more reasonable to suppose that the charge density at the surface, and not the total charge, is a constant. But this would imply that the potential has different values at different points of the surface, which makes the solution of equation (65) still more difficult. As, furthermore, as far as the energy of interaction is concerned, the difference between constant charge and constant potential is not very important, (see f.i. Table XV to XX in this chapter) we felt confident in confining ourselves to the case of constant potentials, and leaving the other possibilities practically out of discussion.

of the ionic atmosphere, i.e. by the value of  $1/\epsilon$ . Let the potential at the surface of the particles be  $\psi_0$ , and that of the liquid far away from the particles, zero. If we use the approximation for small potentials, the potential  $\psi$  at every point  $P$  in the liquid has to satisfy the differential equation (cf. eq. (4) of Chapter II Part I)

$$\Delta \psi = \epsilon^2 \psi. \quad (65)$$

In the solution of this equation we have to observe the boundary conditions that the potential  $\psi$  has the value  $\psi_0$  on the surface of the particles, and the value zero in the infinite.

Furthermore the charge of the particles may be determined by applying Gauss's theorem

$$Q = - \int \frac{\epsilon}{4\pi} \left( \frac{\partial \psi}{\partial r_1} \right)_{\substack{\psi_1 = \text{constant} \\ r_1 = a}} d\omega_1$$

the integration being carried out over the whole surface  $\omega_1$ , of the first particle.

In this way a relation may be found between the charge  $Q$  and the surface potential  $\psi_0$  of the particles expressed in the following equation

$$\psi_0 = \frac{Q \left[ 1 + \frac{e^{-r(s-2)}}{2s\tau} (1 - e^{-2\tau}) \left\{ 1 + \lambda_1 \left( 1 + \frac{1}{s\tau} \right) + \lambda_2 \left( 1 + \frac{3}{s\tau} + \frac{3}{(s\tau)^2} \right) \right\} \right]}{a \epsilon (1 + \tau) \left\{ 1 - \delta (1 + \alpha) \right\}}, \quad (79)$$

in which  $\lambda_1$  and  $\lambda_2$  are parameters which may be calculated from equations (71) and (72);  $\alpha$  and  $\delta$  are expressed by eq. (78). (See below).

Equation (79) may be derived in the following way.

The solution of eq. (65) can be expressed as an infinite series\*, from which the first three terms are given in equation (66).

\* The development may be understood as follows: The most general solution of eq. (65), showing the required symmetry around the axis  $O_1O_2$  may be written as an infinite series of spherical functions, each member being multiplied by a suitable function of  $r_1$ .

$$\psi = \sum_n P_n (\cos \vartheta_1) \cdot f_n (r_1).$$

In consequence of the orthogonality of the spherical functions each member of this series separately has to satisfy eq. (65). By this condition the functions  $f_n (r_1)$  are defined and may easily be determined. Apart from the symmetry around the axis  $O_1O_2$  the solution has to be symmetrical for the two particles. This is

$$\psi = A \left[ \frac{e^{-\kappa r_1}}{r_1} + \frac{e^{-\kappa r_2}}{r_2} + \right. \\ \left. + \lambda_1 \left\{ \cos \vartheta_1 \left( 1 + \frac{1}{\kappa r_1} \right) \frac{e^{-\kappa r_1}}{r_1} + \cos \vartheta_2 \left( 1 + \frac{1}{\kappa r_2} \right) \frac{e^{-\kappa r_2}}{r_2} \right\} + \right. \\ \left. + \frac{\lambda_2}{2} \left\{ (3 \cos^2 \vartheta_1 - 1) \left( 1 + \frac{3}{\kappa r_1} + \frac{3}{(\kappa r_1)^2} \right) \frac{e^{-\kappa r_1}}{r_1} + \right. \right. \\ \left. \left. + (3 \cos^2 \vartheta_2 - 1) \left( 1 + \frac{3}{\kappa r_2} + \frac{3}{(\kappa r_2)^2} \right) \frac{e^{-\kappa r_2}}{r_2} \right\} \right] + \dots \quad (66)$$

The significance of the symbols  $r_1$ ,  $r_2$ ,  $\vartheta_1$  and  $\vartheta_2$  may be seen from figure 36.  $A$ ,  $\lambda_1$  and  $\lambda_2$  are constants, which should be chosen in such a way as to make the potential equal to  $\psi_0$  at every point of the surface of both particles. Now this cannot be done exactly, when the series (66) is broken off after the third

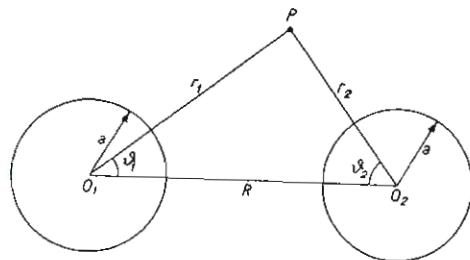


Fig. 36. Coordinates used in the calculation of the field around two spherical particles.

member. Levine and Dube propose a variety of methods, suitable to satisfy approximately the condition  $\psi_{\text{surface}} = \psi_0$ . We shall not discuss these methods in detail, as this was done amply in Levine and Dube's papers. For our use we shall adhere to the "Moment Method", requiring that the potential on the surface of each particle has no dipole or quadrupole moment, the lowest moment to occur being the octopole. This condition is fulfilled when the potential on the surface is developed after spherical functions, and the first two members of

obtained by simply adding, to the solution originating in the first particle, a similar series taking the centre of the second particle as origin.

Taking only the first three members of both series we arrive at eq. (66).

When the particles are far apart, the field around each particle is given by the term  $A \exp(-\kappa r)/r$ , and all following terms are zero. Now if the particles are drawn closer together, the two fields are superimposed on each other. This would cause (just as in the case of flat plates) an increase of the potential. So the charge has to be diminished, which is expressed by a lowering of the constant  $A$ . Moreover, when the particles come into each other's field, the fields lose their spherical symmetry, which is expressed by the correction terms with  $\lambda_1$  and  $\lambda_2$ .

the development made to disappear. Using again the properties of orthogonality of the spherical functions, these conditions may be written as

$$\int_0^\pi \cos \vartheta_1 \psi_{r_1} = a \sin \vartheta_1 d\vartheta_1 = 0 \quad (67)$$

and

$$\int_0^\pi (3 \cos^2 \vartheta_1 - 1) \psi_{r_1} = a \sin \vartheta_1 d\vartheta_1 = 0. \quad (68)$$

Evidently, for reasons of symmetry, if these conditions are satisfied for  $r_1 = a$  they will hold as well for the surface of the other particle ( $r_2 = a$ ).

The conditions (67) and (68) are sufficient to determine the values of  $\lambda_1$  and  $\lambda_2$ , the smallness of these coefficients (see below) being a justification for breaking off the series.

The constant  $A$  may then be determined from the condition

$$\bar{\psi}_{\text{surface}} = \psi_0 \quad (69)$$

expressing that, if the potential has not got the value  $\psi_0$  in every point of the surface, at least the average value  $\bar{\psi}$  is equal to  $\psi_0$ .

In order to obtain explicit expressions for  $\lambda_1$  and  $\lambda_2$  we have to substitute the value of  $\psi$  from equation (66) into the integrals (67) and (68), carrying out the integration for  $r_1 = a$ .

With the aid of the expressions

$$\cos \vartheta_1 = \frac{R^2 + a^2 - r_1^2}{2Ra}; \quad \cos \vartheta_2 = \frac{R^2 + r_2^2 - a^2}{2Rr_2}; \quad \left. \sin \vartheta_1 d\vartheta_1 = \frac{r_2 dr_2}{Ra} \right\} \quad (70)$$

the integration over  $\vartheta_1$  from  $0 \rightarrow \pi$  may be replaced where necessary by an integration over  $r_2$  from  $R - a$  unto  $R + a$ .

After a lengthy but elementary calculation the first condition (67) may be transformed into

$$0 = \frac{1}{3} \lambda_1 + \frac{e^{-\tau(s-2)}}{2s\tau} \left\{ \frac{\tau-1}{\tau+1} + e^{-2\tau} \right\} \left\{ \left( 1 + \frac{1}{s\tau} \right) + \right. \\ \left. + \lambda_1 \left( 1 + \frac{2}{s\tau} + \frac{2}{(s\tau)^2} \right) + \lambda_2 \left( 1 + \frac{4}{s\tau} + \frac{9}{(s\tau)^2} + \frac{9}{(s\tau)^3} \right) \right\}, \quad (71)$$

and the second condition (68) into

$$0 = \frac{1}{5} \lambda_2 + \frac{e^{-\tau(s-2)}}{2s\tau} \left\{ \frac{\tau^2 - 3\tau + 3}{\tau^2 + 3\tau + 3} - e^{-2\tau} \right\} \left\{ \left( 1 + \frac{3}{s\tau} + \frac{3}{(s\tau)^2} \right) + \right. \\ \left. + \lambda_1 \left( 1 + \frac{4}{s\tau} + \frac{9}{(s\tau)^2} + \frac{9}{(s\tau)^3} \right) + \lambda_2 \left( 1 + \frac{6}{s\tau} + \frac{24}{(s\tau)^2} + \frac{54}{(s\tau)^3} + \frac{54}{(s\tau)^4} \right) \right\}, \quad (72)$$

in which, for simplicity of notation the abbreviations introduced in eq. (51) have been used.

$$\alpha a = \tau \quad R/a = s \quad (51)$$

The equations (71) and (72) enable us to calculate the values of  $\lambda_1$  and  $\lambda_2$ , i.e., the form of the electric field, when the electrolytic concentration and the radius and distance of the particles are given. It is clear that the coefficient  $A$  does not figure in equations (71) and (72); for, as a result of the introduction of the approximation for small potentials, the whole problem is linear in the potential, and the form of the electric field is not influenced by the magnitude of the potential, which determines the value of  $A$ .

The condition (69), that the average value of the potential on the surface must be equal to  $\psi_0$  or

$$\bar{\psi} = \frac{1}{2} \int_0^\pi \psi_{r_1} = a \sin \theta_1 d\theta_1 = \psi_0 \quad (73)$$

will give the required condition for the constant  $A$ . After introducing  $\psi$  from equation (66) and carrying out the integration, using where necessary the expressions (70) we find

$$\psi_0 = A \frac{e^{-\tau}}{a} \left\{ 1 + \frac{e^{-\tau(s-2)}}{2s\tau} (1 - e^{-2\tau}) \times \right. \\ \left. \times \left( 1 + \lambda_1 \left( 1 + \frac{1}{s\tau} \right) + \lambda_2 \left( 1 + \frac{3}{s\tau} + \frac{3}{(s\tau)^2} \right) \right) \right\} \quad (74)$$

By the equations (71), (72) and (74), the field around the particles is completely determined.

It follows immediately from equations (63) and (64) that, in order to evaluate the free energy of the double layer system, it is necessary to express the charge of the particles as a function of the potential  $\psi_0$  and the geometric configuration. To this end the charge  $Q$  of one particle is expressed with the aid of Gauss's theorem, i.e.

$$Q = - \int \frac{1}{4\pi} \left( \frac{\partial \psi}{\partial r_1} \right)_{\theta_1 \text{ constant}} \frac{d\omega_1}{r_1 - a} \quad (75)$$

the integration being carried out over the whole surface,  $\omega_1$ , of the first particle or, explicitly using the symmetry of the problem around the axis  $O_1 O_2$ ,

$$Q = - \frac{\epsilon a^2}{2} \int_0^\pi \left( \frac{\partial \psi}{\partial r_1} \right)_{\theta_1} \sin \theta_1 d\theta_1. \quad (76)$$

The differentiation of  $\psi$  with respect to  $r_1$ , keeping  $\theta_1$  constant, is carried through in the following way.  $\psi$  is written as a function of  $r_1$ ,  $\theta_1$  and  $r_2$  eliminating  $\theta_2$  with the aid of equation (70). We may then write

$$\left( \frac{\partial \psi}{\partial r_1} \right)_{\theta_1} = \frac{\partial \psi}{\partial r_1} + \frac{\partial \psi}{\partial r_2} \left( \frac{\partial r_2}{\partial r_1} \right)_{\theta_1} = \frac{\partial \psi}{\partial r_1} + \frac{\partial \psi}{\partial r_2} \frac{r_1^2 + r_2^2 - R^2}{2r_1 r_2},$$

The integration of (76) is carried out in the usual way, using the expression (70), the result being

$$Q = A \epsilon (1 + \tau) e^{-\tau} \{ 1 - \delta (1 + \alpha) \}. \quad (77)$$

in which

$$\delta = \frac{e^{-\tau(s-2)}}{2s\tau} \left( \frac{\tau - 1}{\tau + 1} + e^{-2\tau} \right) \quad (78)$$

and

$$\alpha = \lambda_1 \left( 1 + \frac{1}{s\tau} \right) + \lambda_2 \left( 1 + \frac{3}{s\tau} + \frac{3}{(s\tau)^2} \right).$$

From eq. (74) and (77), eq. (79) may easily be derived by elimination of the constant  $A$ .

$$\psi_0 = \frac{Q \left[ 1 + \frac{e^{-\tau(s-2)}}{2s\tau} (1 - e^{-2\tau}) \left\{ 1 + \lambda_1 \left( 1 + \frac{1}{s\tau} \right) + \lambda_2 \left( 1 + \frac{3}{s\tau} + \frac{3}{(s\tau)^2} \right) \right\} \right]}{a \epsilon (1 + \tau) \{ 1 - \delta (1 + \alpha) \}} \quad (79)$$

### § 3. Potential energy of interaction of two spherical double layers.

Having thus obtained the necessary relation between charge and potential, we can proceed to calculate the energy of interaction.

Assuming that the potential of the surface remains constant, the potential energy of interaction at the approaching of the particles is given by equation (63)

$$V_{R, \psi_0 = \text{const.}} = \psi_0 (Q_\infty - Q_R). \quad (63)$$

Using equation (79) to eliminate  $Q$ , we find that the potential energy of interaction is given by

$$V_{R, \psi_0 = \text{const.}} = \psi_0^2 \epsilon a \frac{e^{-\tau(s-2)}}{s} \beta, \quad (80)$$

in which

$$\beta = \frac{1 + \alpha}{1 + \frac{e^{-\tau(s-2)}}{2s\tau} (1 - e^{-2\tau}) (1 + \alpha)}. \quad (81)$$

If, on the other hand, the charge is supposed to remain constant during the approach of the particles, the potential energy of interaction is found to be (cf. equation (54)).

$$V_R \underset{Q=\text{const.}}{=} Q(\psi_R - \psi_\infty) = \psi_0^2 \epsilon a \frac{e^{-\tau(s-2)}}{s} - \gamma \quad (82)$$

in which

$$\gamma = \frac{1 + \alpha}{1 - \frac{e^{-\tau(s-2)}}{2s\tau} \left( \frac{\tau-1}{\tau+1} + e^{-2\tau} \right) (1 + \alpha)} \quad (83)$$

The quantity  $\alpha$  occurring in these two equations for  $V_R$  has to be calculated according to (78) after the two equations (71) and (72) for  $\lambda_1$  and  $\lambda_2$  have been solved.

The potential energy of interaction is seen to be directly proportional to the radius of the particle (not to the square of it, as might be expected), to the square of the surface potential, and further to depend only on two ratio's, viz.  $s$ , the distance of the particles divided by their radius, and  $\tau$ , the ratio of the radius of the particles to the thickness of the double layer.

In order to make practical use of the equations (80) and (82), we constructed the tables XV to XX for six different values of  $\tau$ . Tabulated are the values of  $\lambda_1$  and  $\lambda_2$ , of  $1 + \alpha$ , of  $\beta$  and  $\gamma$ , and finally the values of  $\frac{V_R}{\epsilon a \psi_0^2}$ , from which the change in free energy may easily be calculated for different values of the potential and the radius of the particles. Table XXI gives approximate expressions which may be used when  $\tau$  is very small.

The repulsion curves for constant potentials are shown in figure 37.<sup>1</sup> The ordinate scale is the same for all curves. The abscissa, expressed as  $\tau(s-2)$  has a common scale for all curves, but of course different scales when the separation is expressed in  $s$ . We may remark that the quantity  $\tau(s-2)$  gives the distance between the surfaces of the two particles expressed in the thickness  $1/\alpha$  of the double layer as unity.

It is clearly demonstrated in figure 37 that the repulsion

<sup>1</sup> A figure of the repulsion curve for constant charge is not given, as we shall confine the discussion of the stability of colloids to the case of constant potentials. Our preference for constant potentials has been explained in § 4, Chapter III. Moreover, the difference between the two cases is not very important as may be gathered from Tables XV—XX.

is only important when the particles are closer together than a few times the thickness of the double layer.

The potential energy reached for immediate contact ( $s = 2$ ) is practically independent of the value of  $\alpha a$ . This is in striking contrast to the case of flat plates, where the limiting potential

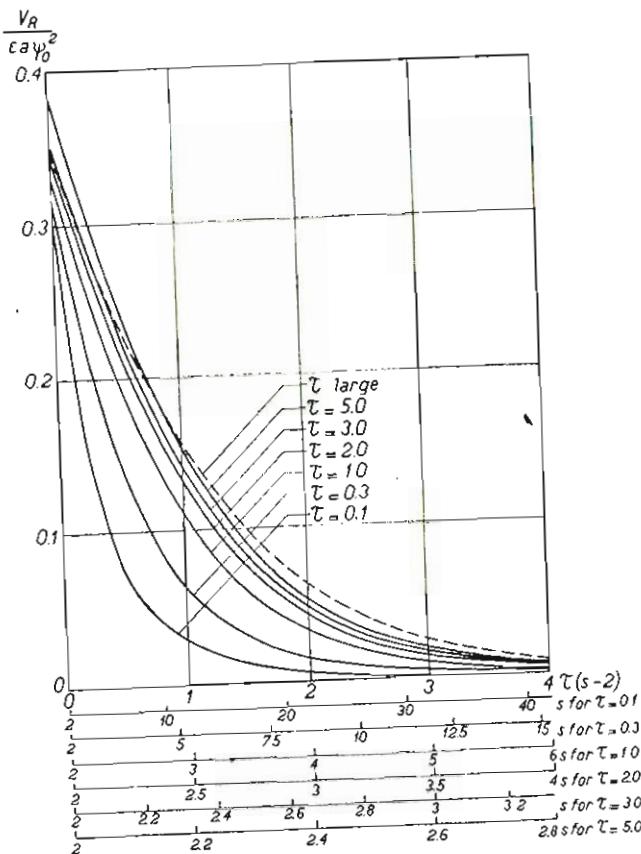


Fig. 37. Potential energy of repulsion between two spherical particles at constant surface potential.  $\tau = \alpha a$ ;  $s = R/a$ ;  $\tau(s-2) \propto (R-2a)$  measures the distance between the surfaces of the particles in the thickness of the double layer  $1/\alpha$  as a unit.

energy is found to be inversely proportional to the thickness of the double layer.

It may be seen from Figure 37 and from the tables XV—XXI that  $V_R$  (as in the case of two flat plates) always remains positive and diminishes monotonously with growing  $s$ . This means

that the force connected with this potential energy is always repulsive. The attraction at relatively great distances, found by Levine and Dubé, which they consider as an important feature in the behaviour of colloids, is a result of their using a fallacious expression for the potential energy. This matter is discussed in detail in the Appendix.

As  $\beta$  and  $\gamma$  are always between 0.60 and 1.00, we may neglect their influence on the repulsion in many cases where no great precision is required, and we find a useful and simple approximate expression for  $V_R$  in

$$V_R = \epsilon a \psi_0^2 \frac{e^{-\tau(s-2)}}{s} \quad (84)$$

Nevertheless, as in our case we want to combine the expression for the repulsion with that for the London-Van Der Waals attraction, we shall work henceforth with the more precise values of the Tables XV-XXI.

TABLE XV

REPULSION FOR  $\tau = 0.1$ 

$s$	$-\lambda_1$	$-\lambda_2$	$1 + \alpha$	$\beta$	$\gamma$	$V_R \frac{\psi_0}{\psi_0^2 \epsilon a} = \text{const.}$	$V_R \frac{\psi_0}{\psi_0^2 \epsilon a} = \text{const.}$
2	0.01839	0.00030	0.8624	0.6200	0.8634	0.310	0.432
3	0.00988	0.00013	0.9514	0.7550	0.9521	0.228	0.287
4	0.00570	0.00006	0.9785	0.8282	0.9790	0.170	0.200
5	0.00360	0.00003	0.9886	0.8727	0.9890	0.129	0.147
8	0.00127	0.00000	0.9971	0.9389	0.9973	0.064	0.068
12	0.00046	0.00000	0.9992	0.9722	0.9992	0.030	0.031
17	0.00017	0.00000	0.9997	0.9880	0.9998	0.013	0.013
22	0.00007	0.00000	0.9999	0.9944	0.9999	0.006	0.006
40	0.00001	0.00000	1.0000	0.9995	1.0000	0.001	0.001
70	0.00000	0.00000	1.0000	0.9999	1.0000	0.000	0.000

TABLE XVI

REPULSION FOR  $\tau = 0.3$ 

$s$	$-\lambda_1$	$-\lambda_2$	$1 + \alpha$	$\beta$	$\gamma$	$V_R \frac{\psi_0}{\psi_0^2 \epsilon a} = \text{const.}$	$V_R \frac{\psi_0}{\psi_0^2 \epsilon a} = \text{const.}$
2	0.05129	0.00223	0.8306	0.6330	0.8366	0.317	0.418
2.3	0.04156	0.00173	0.8780	0.6955	0.8833	0.276	0.351
2.6	0.03380	0.00130	0.9102	0.7461	0.9148	0.240	0.294
3	0.02514	0.00089	0.9398	0.8002	0.9436	0.198	0.233
4	0.01270	0.00038	0.9746	0.8859	0.9796	0.122	0.134
5	0.00694	0.00019	0.9876	0.9314	0.9890	0.076	0.080
7	0.00243	0.00006	0.9962	0.9730	0.9968	0.031	0.032
9	0.00097	0.00000	0.9987	0.9886	0.9989	0.013	0.014
15	0.00009	0.00000	0.9999	0.9990	0.9999	0.001	0.001
25	0.00000	0.00000	1.0000	1.0000	1.0000	0.000	0.000

TABLE XVII

REPULSION FOR  $\tau = 1.0$ 

$s$	$-\lambda_1$	$-\lambda_2$	$1 + \alpha$	$\beta$	$\gamma$	$V_R \frac{\psi_0}{\psi_0^2 \epsilon a} = \text{const.}$	$V_R \frac{\psi_0}{\psi_0^2 \epsilon a} = \text{const.}$
2	0.11106	0.02007	0.7682	0.6588	0.7886	0.329	0.394
2.1	0.09934	0.01714	0.8018	0.6976	0.8210	0.301	0.354
2.2	0.08789	0.01572	0.8253	0.7285	0.8428	0.271	0.314
2.4	0.06853	0.01197	0.8698	0.7871	0.8843	0.220	0.247
2.7	0.04645	0.00778	0.9167	0.8545	0.9273	0.157	0.171
3.0	0.03125	0.00510	0.9464	0.9012	0.9539	0.111	0.117
3.5	0.01618	0.00244	0.9741	0.9486	0.9782	0.060	0.062
4.0	0.00847	0.00121	0.9871	0.9730	0.9893	0.033	0.033
6.0	0.00072	0.00007	0.9904	0.9891	0.9906	0.003	0.003
9.0	0.00002	0.00000	1.0000	0.9999	1.0000	0.000	0.000

TABLE XVIII

REPULSION FOR  $\tau = 2.0$ 

$s$	$-\lambda_1$	$-\lambda_2$	$1+\alpha$	$\beta$	$\gamma$	$V_R \frac{\psi_0}{\psi_0^2 \epsilon a} = \text{const.}$	$V_R \frac{\psi_0}{\psi_0^2 \epsilon a} = \text{const.}$
						$\psi_0^2 \epsilon a$	$\psi_0^2 \epsilon a$
2	0.12114	0.04973	0.7522	0.6887	0.7779	0.344	0.389
2.02	0.11027	0.04522	0.7765	0.7162	0.8006	0.316	0.353
2.10	0.10007	0.04094	0.7990	0.7423	0.8215	0.289	0.320
2.20	0.08177	0.03324	0.8386	0.7891	0.8578	0.240	0.261
2.30	0.06623	0.02668	0.8715	0.8292	0.8896	0.198	0.212
2.50	0.04266	0.01676	0.9234	0.8936	0.9345	0.132	0.138
2.70	0.02708	0.01046	0.9506	0.9307	0.9579	0.085	0.088
3.00	0.01354	0.00507	0.9762	0.9679	0.9800	0.044	0.044
4.00	0.00136	0.00000	0.9985	0.9974	1.0000	0.005	0.005
5.50	0.00005	0.00000	1.0000	1.0000	1.0000	0.000	0.000

TABLE XIX

REPULSION FOR  $\tau = 3.0$ 

$s$	$-\lambda_1$	$-\lambda_2$	$1+\alpha$	$\beta$	$\gamma$	$V_R \frac{\psi_0}{\psi_0^2 \epsilon a} = \text{const.}$	$V_R \frac{\psi_0}{\psi_0^2 \epsilon a} = \text{const.}$
						$\psi_0^2 \epsilon a$	$\psi_0^2 \epsilon a$
2	0.1097	0.07180	0.7583	0.7133	0.7837	0.357	0.392
2.02	0.1041	0.06788	0.7717	0.7281	0.7956	0.339	0.371
2.05	0.09604	0.06212	0.7910	0.7496	0.8136	0.315	0.342
2.10	0.08356	0.05353	0.8201	0.7824	0.8404	0.276	0.296
2.20	0.06236	0.03925	0.8684	0.8381	0.8844	0.209	0.221
2.30	0.04622	0.02840	0.9133	0.8894	0.9258	0.157	0.164
2.40	0.03339	0.02052	0.9317	0.9139	0.9409	0.115	0.118
2.70	0.01251	0.00735	0.9755	0.9684	0.9791	0.044	0.0445
3.00	0.00461	0.00046	0.9942	0.9916	0.9957	0.0165	0.0165
3.50	0.00087	0.00003	0.9990	0.9985	0.9993	0.0032	0.0032

TABLE XX

REPULSION FOR  $\tau = 5.0$ 

$s$	$-\lambda_1$	$-\lambda_2$	$1+\alpha$	$\beta$	$\gamma$	$\frac{V_R \frac{\psi_0}{\psi_0^2 \epsilon a} = \text{const.}}{\psi_0^2 \epsilon a}$	$\frac{V_R \frac{\psi_0}{\psi_0^2 \epsilon a} = \text{const.}}{\psi_0^2 \epsilon a}$
2	0.08746	0.07923	0.7984	0.7678	0.8203	0.384	0.410
2.02	0.08004	0.07247	0.8159	0.7872	0.8363	0.353	0.375
2.05	0.06984	0.06317	0.8399	0.8139	0.8582	0.309	0.326
2.10	0.05504	0.05273	0.8702	0.8489	0.8851	0.245	0.256
2.20	0.03368	0.03017	0.9241	0.9100	0.9338	0.152	0.156
2.30	0.01968	0.01796	0.9551	0.9463	0.9611	0.092	0.093
2.40	0.01189	0.01054	0.9737	0.9684	0.9773	0.055	0.055
2.70	0.00239	0.00205	0.9949	0.9939	0.9957	0.011	0.011
3.00	0.00048	0.00042	0.9990	0.9988	0.9992	0.002	0.002
3.50	0.00033	0.00000	0.9996	0.9997	0.9997	0.000	0.000

TABLE XXI

REPULSION FOR SMALL VALUES OF  $\tau$ For small values of  $\tau$  the following approximate equations may be used.When  $\tau(s-2) \ll 1$ 

$$\lambda_1 = -\frac{s^6 + 3s}{s^8 + 2s^5 + 6s^3 + 3} \quad \lambda_2 = -\frac{\tau^2}{3} \frac{s^5 - s^2}{s^8 + 2s^5 + 6s^3 + 3}$$

$$\gamma = 1 + \alpha = \frac{s^8 + s^5 + 5s^3 + 1}{s^8 + 2s^5 + 6s^3 + 3} = \tau \frac{s^6 + s^4 + 2s}{s^8 + 2s^5 + 6s^3 + 3}$$

$$\beta = \frac{s^9 + s^6 + 5s^4 + s}{s^9 + s^8 + 2s^6 + s^5 + 6s^4 + 5s^3 + 3s + 1} + \tau \frac{s^{18} - s^{17} + \dots}{(s^9 + s^8 + 2s^6 + \dots)^2}$$

$$\frac{V_R \frac{\psi_0}{\psi_0^2 \epsilon a} = \text{const.}}{r a \psi_0^2} = \frac{e^{-\tau(s-2)}}{s} \quad \frac{V_R \frac{\psi_0}{\psi_0^2 \epsilon a} = \text{const.}}{r a \psi_0^2} = \frac{e^{-\tau(s-2)}}{s} \gamma$$

When  $\tau(s-2) \gg 1$ 

$$\lambda_1 = -\frac{\tau^2}{s} e^{-\tau(s-2)} \quad \lambda_2 = -\frac{\tau^4}{9s} e^{-\tau(s-2)}$$

$$\gamma = 1 + \alpha = 1$$

$$\beta = \frac{1}{1 + \frac{e^{-\tau(s-2)}}{s} (1 - \tau)}$$

$$\frac{V_R \frac{\psi_0}{\psi_0^2 \epsilon a} = \text{const.}}{r a \psi_0^2} = \frac{1}{s e^{\tau(s-2)} + 1 - \tau} \quad \frac{V_R \frac{\psi_0}{\psi_0^2 \epsilon a} = \text{const.}}{r a \psi_0^2} = \frac{1}{s e^{\tau(s-2)}}$$

#### § 4. Convergency and accuracy of the method used

In order to get an impression of the convergency of the method and of the accuracy attained by it, we made comparisions in a lower approximation by putting  $\lambda_1$ , or  $\lambda_1$  and  $\lambda_2$  equal to zero. The potential energy is again given by the expressions (80) and (82), but the values of  $\alpha$  and  $\beta$  were altered.

In Table XXII we find a comparison of the values of  $\beta$  in different approximations for a few important cases. It will be seen that for small values of  $\tau$  the correction for the second approximation is much smaller than that for the first, so that breaking off the series for  $\beta$  at its third term seems justified. But when  $\tau = 3$  or still more pronounced when  $\tau = 5$ , the second correction is nearly as large as the first, and there is no reason to expect that the contributions of the following terms will be much smaller. We conclude therefore that it is advisable to look for another method of approaching the problem for cases where  $\tau > 3$ . The influence of the distance separating the particles on the absolute value of the correction is large, but the convergency is hardly influenced by it.

Fortunately for large values of  $\tau$  we can approach the problem from the other angle, viz. starting from the interaction of flat surfaces.

TABLE XXII  
VALUES OF  $\beta$  IN DIFFERENT APPROXIMATIONS

$\tau$	$s$	$\beta$ 1st approx. $\lambda_1 = \lambda_2 = 0$	$\beta$ 2nd approx. $\lambda_2 = 0$	$\beta$ 3rd approx.	$\beta_1 - \beta_2$	$\beta_2 - \beta_3$	Estimated accuracy
0	2	0.6666	0.6207	0.6144 *	0.0459	0.0063	$< 1\%$
	very large	$1 - \frac{1}{se^{r(s-2)}}$	$1 - \frac{1 + r^2}{se^{r(s-2)}}$	$1 - \frac{1 + r^2 + \frac{1}{2}r^4}{se^{r(s-2)}}$	$\frac{r^2}{se^{r(s-2)}}$	$\frac{r^4}{9se^{r(s-2)}}$	$< \frac{r^4}{9se^{r(s-2)}}$
1	2	0.822	0.695	0.659	0.127	0.036	2 %
	3	0.949	0.912	0.901	0.037	0.011	1 "
	4	0.985	0.974	0.973	0.011	0.001	0.1 "
2	2	0.891	0.753	0.689	0.138	0.064	10 "
	2.50	0.965	0.915	0.894	0.050	0.021	2 "
	3.00	0.9889	0.9732	0.9678	0.0157	0.0054	0.5 "
3	2	0.923	0.797	0.713	0.126	0.084	20 "
	2.30	0.971	0.919	0.889	0.052	0.030	10 "
	3.00	0.9972	0.9921	0.9916	0.0051	0.0005	0.1 "
5	2	0.952	0.855	0.768	0.097	0.087	?
	2.20	0.984	0.945	0.910	0.039	0.035	?
	2.70	0.9989	0.9963	0.9939	0.0026	0.0024	?

\* The accurate value of  $\beta$  for this case may be calculated from pure electrostatics and proves to be  $2 - 2 \ln 2 = 0.6137$ .

#### § 5. Comparison of the equations for small and large values of $xa$ and evaluation of the repulsion for intermediate values of $xa$ .

As an alternative method for establishing the accuracy of the equations (56) (valid for small  $xa$  and large  $xa$ ) and (80) (valid for small  $xa$  and small  $xa$ ) we analysed both formulae graphically. In figure 38 the values of  $V_n$  for a series

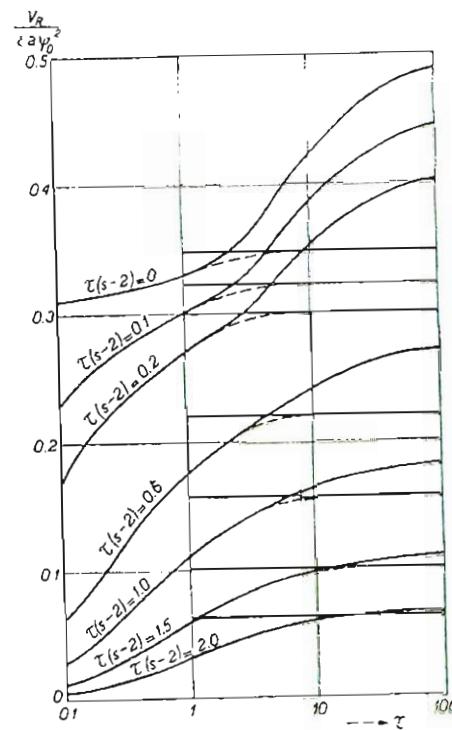


Fig. 38. Showing the regions of validity for the repulsion equations (56) and (80), and the transition between them. The horizontal lines represent eq. (56), the curved ones eq. (80), the dotted lines form the estimated transition.

of values of  $\tau(s-2)$  are plotted against the logarithm of  $xa$ . Since the first method gives the best results for large  $xa$ , and the second for small  $xa$ , and as both methods tend to give results which are too high, we may draw the connection between the two expressions in the intermediate region where both are too high.

Figure 38 clearly shows that the second method may safely be used up to  $\tau = 1$ , (for weak interaction even up to  $\tau = 10$ ),

and the first (Derjaguin's) method down to  $\tau = 10$ , whereas in the middle region we can connect the two graphically without becoming too much arbitrary. To give an impression of the correction involved, we drew in Fig. 39 the repulsion curves

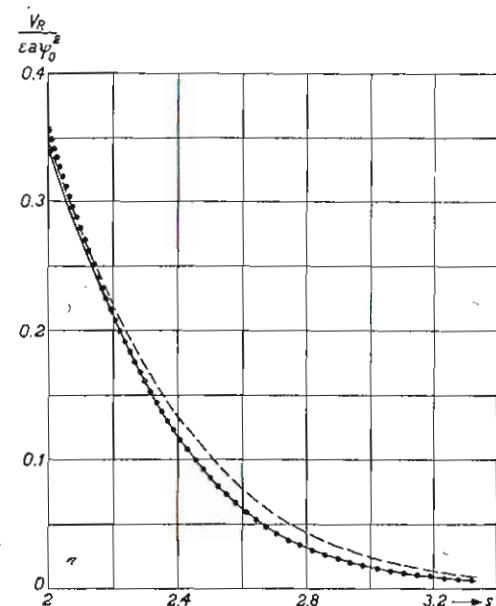


Fig. 39. Repulsion curves for  $\tau = 3$

- — — equation (56)
- ..... equation (80)
- Best curve, from Figure 38.

for  $\tau = 3$  according to equations (56) and (80), and interpolated from Fig. 38. Altogether we get a fairly accurate knowledge of the repulsion curves for any value of  $\tau$  and  $s$ .

Derjaguin combined the two equations (56)\* and (80) into one equation, valid for any  $s$  and  $\tau$ ; but this can only be done with loss of precision in the whole field. In his case it was nevertheless of advantage to use the combined equation from which he deduced a criterion of stability of colloids, assuming that the attraction between two particles acted only when the particles were in direct contact.

In the following sections, however, we shall introduce the farther-reaching London—Van Der Waals attraction, when it will be most important to have at our disposal an accurate repulsion curve, the advantage of a simpler equation being far less than in Derjaguin's case.

We now possess a good system of equations for the repulsion when the surface potential is low. But in the case of large

potentials we found a satisfactory solution only for large values of  $\kappa a$ , whereas the problem for small values of  $\kappa a$  has not yet been solved.

In combining the repulsion as found in this chapter with the London—Van der Waals attraction, the most important cases will prove to be those of either large potential and large  $\kappa a$ , or small potential combined with a small value of  $\kappa a$ , for which satisfactory solutions are now available. Nevertheless we shall be compelled in a few cases to use a repulsion equation for small  $\kappa a$  and large potentials. In these cases we will simply use equation (80). This seems very imprudent; but we shall show that in the cases concerned the uncertainty introduced by this neglection is unimportant.

\* He used equation (56) only in the first approximation, i.e. with  $\alpha = 0$ .

## XI. THE ATTRACTIVE FORCE AND THE TOTAL POTENTIAL ENERGY OF INTERACTION

As in part II, we shall assume also in this part that the attraction between colloidal particles is entirely based upon the London-Van der Waals forces. Hamaker<sup>1</sup> showed how the London-Van der Waals interaction between two spherical particles may be found from the interaction between the elements of these spheres. His expression for the energy of attraction ( $V_A$ ) runs, using our symbols,

$$V_A = -\frac{A}{6} \left( \frac{2}{s^2 - 4} + \frac{2}{s^2} + \ln \frac{s^2 - 4}{s^2} \right) \quad (85)$$

For the value of  $A$ , the reader is referred to p. 103 and 104.

It is worth while to consider how  $V_A$  behaves when the particles are very close together. Putting  $s = 2 + \frac{H}{a}$ , in which  $H$  is the shortest distance between the two spheres, and assuming that  $H \ll a$ ,  $V_A$  may be approximated by

$$V_A = -\frac{Aa}{12} \cdot \frac{1}{H} = -\frac{A}{12} \frac{1}{s-2} \quad (86)$$

So the free energy of attraction decays very slowly, viz. reciprocally with the distance, and even slower than it does in the case of flat plates, where it goes reciprocally with the square of the distance. (eq. 48c of Part II). At larger separations of the two spheres the decay is of course faster, as for very great distances the attraction must die out as  $1/H^6$ , but nevertheless the decay remains slower than  $1/H^2$  until  $s$  exceeds 2.4, as may be read from a double logarithmic plot of eq. (85).

This slow decay must be explained by the fact that, for  $H = 0$ , only small parts of the spheres are very close together. A small change of the distance between the spheres has a great effect only on the elements immediately surrounding the place of contact, whereas, for the greater part of the matter contributing to the attraction, the relative change of the distances and, with that, the change in attractive energy, are only small.

Combining the values of repulsive and attractive potential energy, as they were found in this and the preceding two Chapters, we find the total potential energy of interaction,

called  $V$ . On the whole it has the same characteristics as those found in the case of flat plates (cf. Chapter VII, of Part II); although of course there are differences in detail. The curves of free energy against the distance separating the particles all show a negative value at large separations, because the London-Van der Waals energy has a smaller slope ( $\sim \frac{1}{s^6}$ )

than the repulsive force ( $\sim \exp(-\tau s)$ ). At very small distances the London-Van der Waals energy is again most important, the energy reaching large negative values. At intermediate distances, i.e. when  $\tau(s-2)$  is of the order of unity, there may be a maximum of energy, if the conditions of  $\psi_0$ ,  $\chi$  and  $A$  are well chosen. The great number of parameters that can be varied makes it difficult to give a general survey of their influence on the interaction. We therefore show only a few examples of curves of total potential energy, in figures 40 and 41.

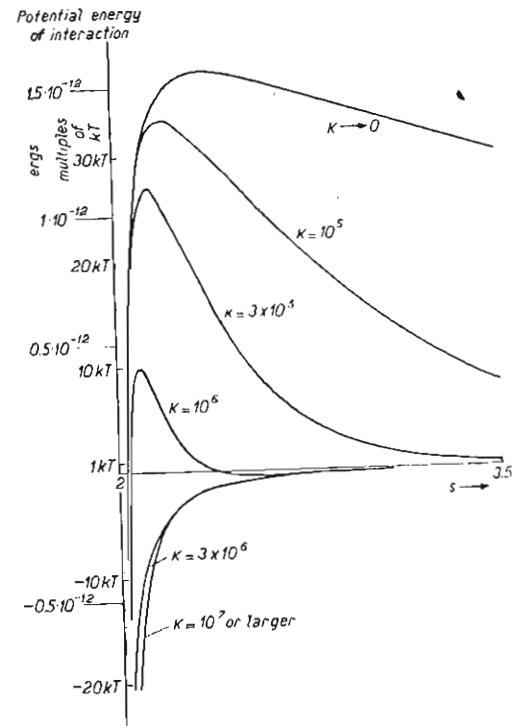


Fig. 40. Showing the influence of the concentration of electrolyte ( $\chi$ ) on the total potential energy of interaction.

$$a = 10^{-5} \text{ cm}; A = 10^{-12} \text{ ergs}; \psi_0 = 1 \text{ e.v.} \quad kT = 25.6 \text{ mV.}$$

<sup>1</sup> H. C. Hamaker, *Physica*, 4 (1937) 1058.

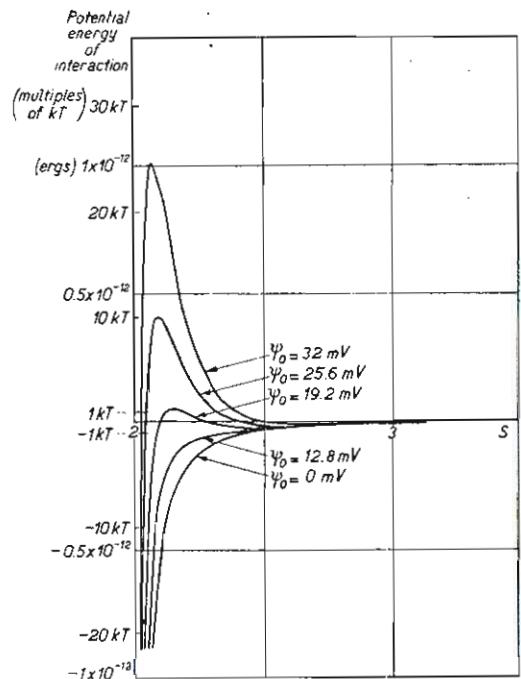


Fig. 41. Showing the influence of the surface potential ( $\psi_0$ ) on the total potential energy of interaction.

$$a = 10^{-5} \text{ cm}; A = 10^{-12} \text{ ergs}; x = 10^6 \text{ cm}^{-1}$$

In Figure 40, the radius of the particles, the attraction constant, and the potential  $\psi_0$  are all kept constant, (values  $a = 10^{-5} \text{ cm}$ ,  $A = 10^{-12} \text{ ergs}$ ,  $\psi_0 = 25.6 \text{ mV}$  ( $\frac{e\psi_0}{kT} = 1$ ) respectively). The different curves belong to different values of  $x$ , so this set of curves shows what happens when the concentration of the electrolyte is modified, all other factors being kept constant.\*

\* In the curve for  $x \rightarrow 0$  we find a distinct difference between the flat plates (cf. page 114, 115) and the spheres.

In the case of flat plates we found by decreasing  $x$  (i. e. decreasing the concentrations of electrolyte) a continuous increase of the breadth of the potential barrier, but at the same time a decrease of its height.

Now we find for spheres the same increase in breadth, but no decrease in height.

This is a direct result of the divergence of the lines of force in the case of spherical particles.

Infinitely large flat plates need only an infinitesimal small charge density to maintain a certain potential, because the lines of force do not diverge and the field strength, although very small, has the same value until the infinite ( $x \rightarrow 0$  means that we have only to reckon with the surface charge, whereas the diffused charge is in

In Figure 41,  $x$  is kept constant, but now the potential  $\psi_0$  has been varied.

In both figures the ordinate is expressed in ergs, with an alternative scale in multiples of  $kT$  ( $4.1 \times 10^{-14}$  ergs), which becomes of interest as soon as we have to discuss the stability of colloids.

It may be seen from figures 40 and 41 and it proves to be a general rule, that the maximum, if any, is always situated at about  $\tau (s - 2) \approx 1$ , shifting to somewhat smaller distances when the maximum is high, and to somewhat greater distances when  $\tau$  is small. In the case of flat plates an analogous rule was found to exist, the maximum being situated at about  $xd \approx 1$ . (Cf. Figures 24–28 and the discussion on this point in Chapter VII).

the infinite). Spheres, however, need a finite charge to reach the same potential, because the field strength around the sphere decays as  $1/r^2$  (for  $x \rightarrow 0$ ).

If two plates bearing practically no charge are brought together, there is practically no change of energy. But it costs quite an amount of energy to push two charged spheres together.

It is clear that we are dealing here with a case where spherical particles form a better image of real colloids than do flat plates, because the latter method of approach requires that the double layer thickness is small in comparison with the particle size, which for  $x \rightarrow 0$  is certainly not fulfilled.

## XII. STABILITY OF COLLOIDS

### § 1. Kinetics of coagulation

From the curves representing the total potential energy of interaction, mentioned in the preceding section, it is possible to derive a criterion for the stability of colloids. This may already be done in a qualitative way, by remarking that we can only expect stability if the curves show a maximum, which must be of the order of  $kT$  to prevent flocculation.

By a theory first developed by Fuchs<sup>1</sup> it is possible, however, to obtain a more quantitative formulation of this criterion of stability. In this theory, the probability of aggregation of colloidal particles is treated as a diffusion problem, just as in the well known theory of rapid coagulation by Von Smoluchowski<sup>2</sup>.

One might proceed in a simpler way to calculate the probability of agglomeration in a particle encounter and identify this quantity with the probability that a particle moving in the direction of a second particle carries a certain amount of kinetic energy and is therefore able to pass a potential barrier. But the amount of kinetic energy of the particle with respect to the second particle at a certain moment persists only during a time which is negligible in comparison to that needed to cover a distance of the order of the thickness of the double layer. This may easily be seen in the following way. We consider a particle with an initial velocity  $v_0$ , and calculate the retardation of this particle due to mechanical friction in the liquid. Applying the Stokes equation, and considering that the frictional force  $6\pi\eta av$  is the product of the mass  $m$  and the acceleration ( $-dv/dt$ ), we have

$$\frac{dv}{dt} = -\frac{6\pi\eta av}{m} \quad \text{or} \quad v = v_0 e^{-\frac{6\pi\eta a}{m} t}$$

Hence, if its original velocity is given by

$$p kT = \frac{1}{2} m v_0^2 \quad \text{or} \quad v_0 = \sqrt{\frac{2kT}{m}} p$$

we derive that the particle for purely mechanical reasons (leaving thermal motion out of consideration) has completely lost its velocity after travelling over a distance  $s$ :

$$s = v_0 \int_0^\infty e^{-\frac{6\pi\eta a}{m} t} dt = \frac{mv_0}{6\pi\eta a} = \frac{\sqrt{2p kT m}}{6\pi\eta a} = \frac{1}{3\eta} \sqrt{\frac{2p kT a d}{3\pi}}$$

<sup>1</sup> N. Fuchs, *Z. Physik.*, 89 (1934) 736.

<sup>2</sup> M. von Smoluchowski, *Physik. Z.*, 17 (1916) 557, 585; *Z. physik. Chem.*, 92 (1917) 129.

in which  $d$  = the density of the particle substance. With  $kT = 4 \times 10^{-14}$ ,  $d = 5$ , and  $\eta = 0.01$  we find

$$s = 0.7 \cdot 10^{-3} \sqrt{pa} \text{ cm.}$$

which means that, for  $p = 10$  and  $a = 10^{-5}$  cm, the distance  $s$  is only  $7 \times 10^{-8}$  cm, i.e., far less than the extension of the potential barrier. For smaller particles the distance will be still smaller. Hence a comparatively rapid particle (kinetic energy  $10 kT$ ) will lose this extreme velocity as a result of the liquid friction within a distance of a few Ångstrom units.

The probability of passing the potential barrier will therefore be determined by more factors than the height of the barrier and the kinetic energy of the particles alone; and it will be necessary to treat the encounter of two particles as a problem of diffusion in a field of force.

If one of the particles of the suspension is considered fixed, it may be asked how many other particles reach it in a second. The supposition is made that every collision leads to agglomeration, or, in mathematical terms, the concentration of particles at the surface of the fixed particle is zero. On the other hand, far away from this central particle the number of particles per unit of volume remains unaltered and is put equal\* to  $n_0$ . The movement of the particles with respect to this central one is treated as a diffusion problem, where in addition the interaction between the particles may be taken into account. This leads to a rather complicated differential equation, but it has been shown by Von Smoluchowski, that only an unimportant error is made if we neglect the very beginning of the flocculation process, when the concentration is  $n_0$ , throughout the whole system, except at the surface of the central particle, where it is zero. We have to consider only the stationary state, which is established after a very short time, and is characterized by the facts, (1) that at every point the concentration remains constant, and (2) that per unit of time a constant number ( $G$ ) of particles passes through every sphere surrounding the central particle, finally hitting upon, and fixing themselves to, the central particle. This number  $G$  is built up by two influences; the diffusion under the influence of concentration gradients, and the displacement caused by the interaction of two particles.

So  $G$  may be put equal to

$$G = 4\pi R^2 \left( D \frac{\partial n}{\partial R} + \frac{n}{\rho} \frac{\partial V}{\partial R} \right). \quad (87)$$

in which  $R$  is the distance from the centre of the fixed particle;  $D$  the diffusion constant;  $n$  the number of particles in  $1 \text{ cm}^3$ ;

\* Of course during flocculation the total number of particles diminishes, but for the evaluation of the distribution of the particles around the central one,  $n_0$  may be treated as a constant.

$\rho$  the friction constant ( $\sim 6\pi \eta a$ ), and  $V$  the energy of interaction of two particles at a distance  $R$ .

This equation must be solved with the boundary conditions

$$n = 0 \text{ when } R = 2a$$

expressing the fact that the minimal distance between the centres of two particles is twice their radius

$$\text{and } n = n_0 \text{ when } R = \infty.$$

According to a well-known theorem of Einstein,  $D$  is equal to  $kT/\rho$ . If, however, the central particle is no longer considered fixed, but also free to move, diffusion of two particles against each other is accelerated by a factor two, or  $D' = 2D$ . On the other hand, the relative displacement of the particles under the influence of the interaction force is doubled as well, or  $\rho' = \rho/2$ . So the Brownian movement of the central particle is fully taken into account by replacing, in eq. (87),  $D$  by  $2D$ , and  $\rho$  by  $kT/2D$ .

With  $V_\infty = 0$ , the solution of the modified (87) then runs

$$n = n_0 e^{-V/kT} + \frac{Ge^{-V/kT}}{8\pi D'} \int_{\infty}^R e^{V/kT} \frac{dR}{R^2} \quad (88)$$

To satisfy the condition for  $R = 2a$ ,  $G$  must have the value

$$G = \frac{4\pi D' n_0}{\int_{2a}^{\infty} e^{V/kT} \frac{dR}{R^2}} \quad (89)$$

This  $G$ , representing the number of collisions against one particle during one second, is a direct measure of the flocculation velocity. The value of  $G$  when  $V = 0$ , i.e., when there is no interaction between the particles, except a very steep attraction when the particles touch each other, is equal to

$$G_{V=0} = 8\pi a D' n_0,$$

and gives a measure for rapid coagulation.

The interaction  $V$  diminishes the velocity of coagulation by a factor

$$W = 2a \int_{2a}^{\infty} e^{V/kT} \frac{dR}{R^2} \quad \text{or} \quad W = 2 \int_2^{\infty} e^{V/kT} \frac{ds}{s^2}. \quad (90)$$

(84)

Now the time of coagulation of a rapidly coagulating sol is given by Von Smoluchowski's theory as<sup>1</sup>

$$t = \frac{1}{8\pi D a n_0}, \quad (91)$$

which equation has been fully confirmed by experiment (Kruyt and Van Arkel,<sup>2</sup> Westgren and Reitstötter<sup>3</sup>).

If we put  $D$  equal to  $kT/6\pi\eta a$ , the time of coagulation becomes equal to

$$t = \frac{3\eta}{4kT n_0}, \quad (92)$$

which, for water as a dispersion medium and  $T = 298^\circ$ , is equal to  $t \sim \frac{2 \times 10^{11}}{n_0}$ , and is seen to depend (at a given temperature and for a given dispersion medium) solely on the concentration of particles.

Even for the most concentrated sols, the value of  $n_0$  scarcely surpasses  $10^{14}$ , so that the shortest time of coagulation to be reckoned with is of the order of  $10^{-3}$  sec. For the more common examples investigated by the above authors the time of rapid coagulation is of the order of 10 sec.

Now a colloid may be termed stable when it does not flocculate, say, in a week or a month, which means that the time of flocculation should be longer than  $10^6$  sec. Consequently the ratio  $W$  between rapid and slow coagulation will have to surpass  $10^5$  for diluted and  $10^9$  for very concentrated sols, to give them a reasonable stability.

Our task is, therefore, to get a survey of the dependence of  $W$  on the several variables influencing the stability, as there are, radius of the particles, concentration and valency of the electrolyte (expressed by the value of  $\gamma$ ), surface potential  $\psi_0$ , and the value of the London-Van Der Waals constant  $A$ .

Derjaguin<sup>4</sup> used this same theory to establish a criterion of stability. The difference between his theory and the theory expounded here is found in the form of the total energy curve  $V(R)$ . Whereas Derjaguin used for the repulsion about the same expression as we did with this difference, that he confined

<sup>1</sup> It represents the time in which the number of particles is halved, taking into account not only the collisions between primary particles, giving rise to double particles, but as well collisions between secondary particles, giving rise to complexes of more than two particles.

<sup>2</sup> H. R. Kruyt and A. E. Van Arkel, *Rec. trav. chim.*, 39 (1920) 656; 40 (1921) 169.

<sup>3</sup> A. Westgren and J. Reitstötter, *Z. physik. Chem.*, 92 (1918) 750; *J. Phys. Chem.*, 26 (1922) 537.

<sup>4</sup> B. Derjaguin, *Trans. Faraday Soc.*, 36 (1940) 203.

himself to the linear approximation, he completely neglected the London-Van Der Waals attraction, retaining only an infinitely strong attraction when the particles make material contact.

By his method Derjaguin found that the stability of a colloid is practically determined by the quantity

$$n = \frac{\epsilon a \psi_0^2}{2kT},$$

$n$  having to be larger than 10, whereas we shall find a considerable influence of the London-Van Der Waals constant and of the concentration of electrolyte.

The quantity  $W$  has to be calculated by graphic integration for a considerable number of cases. In Figure 42 we give an

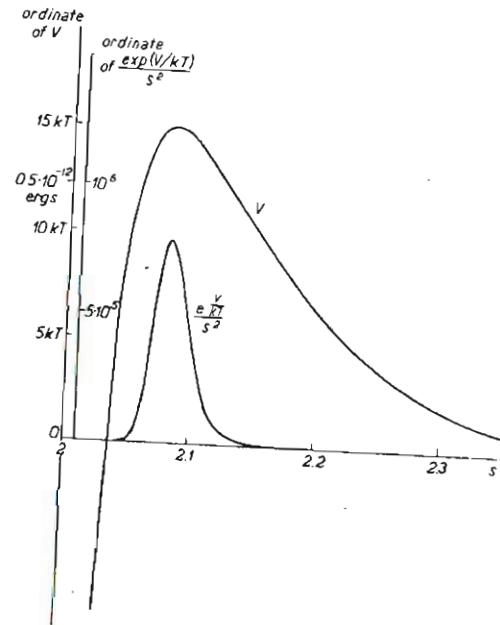


Fig. 42. Curves of potential energy of interaction ( $V$ ) and of the quantity  $\frac{\exp(-V/kT)}{s^2}$

$$\begin{aligned} a &= 10^{-5} \text{ cm}; \quad \alpha = 10^6 \text{ cm}^{-1}; \quad A = 10^{-12} \text{ ergs}; \\ \psi_0 &= 1.1 \times 25.6 \text{ mV} = 28.2 \text{ mV}. \end{aligned}$$

By graphic integration it is found that

$$W = 2 \int_2^\infty \frac{e^{-V/kT}}{s^2} ds = 5.4 \times 10^4$$

Hence this example is just under the threshold of stability where  $W = 10^5$ .

The potential has to be risen to 28.5 mV to reach  $W = 10^5$ .

example of the interaction curve and the curve of  $\exp(-V/kT)/s^2$  (cf. eq. 90) to match it. Integrating the second curve, one soon becomes convinced that the most important factor governing the value of  $W$  is the maximum of the  $V(s)$  curve, the detailed form of this curve being of little or no importance. This is easily understood by remarking that  $V$  enters into  $W$  as an exponential, in which a change of about 15% in  $V$  changes the integrand by a factor 10 (supposing  $V_{\max}$  to be about 15  $kT$ ). This change of 15% in  $V$  is accomplished by a change of less than 7.5% in  $\psi_0$ , as  $V$  is formed by the difference between the London-Van Der Waals attraction and the repulsion, which in the linear approximation is proportional to  $\psi_0$ .

If, however, we use the non-approximated repulsion equation for higher potentials, the influence of  $\psi_0$  proves to be of less primary importance.

Broadly speaking it may be said that  $V_{\max}$  has to be of the order of 15  $kT$  if  $W$  is to exceed  $10^5$ , and about 25  $kT$  if  $W$  is to exceed  $10^6$ , thereby ensuring a stability sufficient for all practical purposes.

### § 2. Application to the stability of colloids and related problems.

On the basis of a sufficient number of calculations of  $W$ , we constructed a series of curves giving the values of potential and concentration of 1 - 1 valent electrolyte (for a given London-Van der Waals constant), for which the stability-ratio  $W$  just reaches the value  $10^5$ , or in other words just sufficient to make a diluted sol passably stable. The figures 43 and 44 show for two values of  $A$ , ( $10^{-12}$  and  $2 \cdot 10^{-12}$ ),  $\psi_0$ -curves separating stability- from instability-regions.

In the construction of these figures we have chosen the repulsion curves as described on page 158, i.e. we used the complete Gouy-Chapman equations for large values of  $\alpha a$ , whereas, for small values of  $\alpha a$ , the method of chapter X using the linear approximation has been applied. For particles with a radius of  $10^{-6}$  cm or larger we get very satisfactory results, as in these cases the potential is small when  $\alpha a$  is small, so that the approximative method may be safely applied. For a particle radius of  $10^{-7}$  cm, however, the situation is less favourable, as in this case, small values of  $\alpha a$  are combined with large values of the potential. So for this very small particle radius the results are far from accurate. The dotted curves in figures 43 and 44 are drawn in such a way that the real curve would certainly be situated above the dotted one. Consequently the dotted curves represent the stability of  $a =$

$10^{-4}$  too favourably, which still enhances our argument following below.

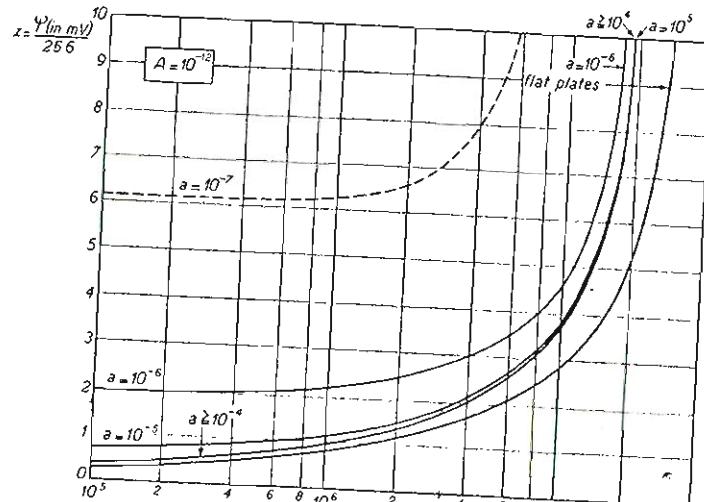


Fig. 43.

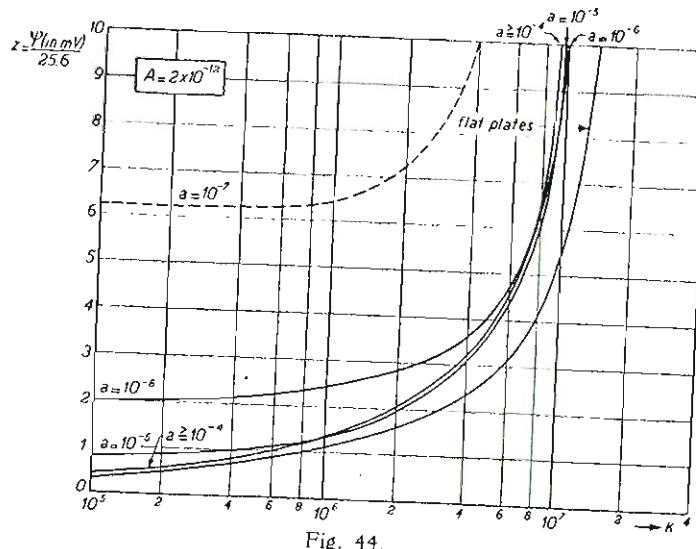


Fig. 43 and 44. Curves separating regions of stability from regions of instability, the curves uniting points where the stability ratio  $W = 10^5$ . Monovalent electrolyte.

A casual inspection of these curves reveals the following acts. Small particles ( $a < 10^{-7} \text{ cm}$ ) need an exceedingly high

value of the potential  $\psi_0$  for their stability, and it is uncertain whether these high values are ever attained. This low stability of small particles is brought about by the low absolute value of the repulsive potential energy. According to the expressions (56) and (80) the repulsive potential energy is proportional to the radius of the particle, and, as explained above, sufficient stability is not possible while the total potential energy remains under a value of about  $15 kT$ .

Even if we neglect the London—Van Der Waals attraction completely, and take for the repulsive potential energy the value it has when  $s = 2$ , the stability-ratio  $W$  cannot exceed

$$W \sim 2 e^{\frac{V_R}{kT}} \int_2^\infty \frac{ds}{s^2} = e^{\frac{V_R}{kT}} \quad (93)$$

So for  $W$  to be  $10^5$ ,  $V_R$  has to be equal to  $\approx 13.5 kT \approx 5.55 \times 10^{-13} \text{ ergs}$ . Now for very small  $\propto a$ ,  $V_R = 0.307 r a \psi_0^2$  (c.f. Table XXII, linear approximation) or

$$5.55 \times 10^{-13} \approx 1.76 \times 10^{-7} a z^2, \quad (94)$$

which means that, for  $a = 10^{-7}$ , the necessary  $z$  is certainly larger than 5.6, for  $a = 10^{-6}$ ,  $z > 1.77$  and for  $a = 10^{-5}$ ,  $z > 0.56$ , etc.

The low stability of small particles found here is well in accord with the practice of colloid chemistry, as hydrophobic sols of such small particle dimensions do not seem to exist, and the preparation of amicronic sols ( $a < 10^{-6} \text{ cm}$ ) is known to be extremely intricate.

On the other hand, the curves for  $a = 10^{-4}$  practically coincide with those for  $a = \infty$ \*, and the curves for  $a = 10^{-5}$  lie very close to this limit. This is explained by the fact that, for a particle radius larger than  $10^{-5} \text{ cm}$ , all energies involved are much larger than  $kT$ , so that it does not make much difference whether the height of the maximum has to be  $\approx 25 kT$ ,  $\approx 15 kT$  or  $0 kT$ .

At first sight it may seem strange that the curves for flat plates and for very large spherical particles do not coincide. One should bear in mind, however, that if two spherical particles are brought to the same distance where for flat plates  $V = \frac{dV}{dd} = 0$ , only two points of the surfaces are at this favourable

\* The curves for  $a = \infty$  were obtained by determining the values of  $x$  and  $\psi_0$  for which the function (cf. Table XIV and eq. (86))

$$\frac{V}{za} = \frac{G}{x} - \frac{A}{12r(s-2)}$$

has the maximum value, which is equal to zero.

distance, all other point being at greater distances from each other, where the total potential energy is negative. Consequently the potential energy for these spherical particles is on the average still distinctly negative. Either the potential has to be increased or the concentration diminished in order to reach stability.

The curves for  $a = 10^{-6}$ , which may be considered as representative for the particle dimensions usually found in colloid chemistry, show a very satisfactory course. For low concentrations of electrolyte ( $z \approx 10^5 - 10^6$ ), the potential must have at least a minimum value of about 50 millivolts\* in order to ensure reasonable stability, whereas for higher concentrations of electrolyte ( $z > 10^6$ )  $\psi_0$  must be larger. This increase of  $\psi_0$  occurs the sooner, the higher the value of  $A$ , just as in the case of flat plates. The very steep upward turn of the curves indicates that in this region the stability is very sensitive to small changes in the concentration of electrolyte. This explains why it was possible to determine flocculation values with fairly great accuracy, and why this quantity played such a preponderant part in the experiments on stability.

Further inspection of the curves reveals that, although stability generally increases with increasing dimensions of the particles, there are some exceptions to this rule. These will be explained on pages 177 and 178, in reference to Figure 49.

All the curves clearly have a positive slope, meaning that at a constant potential stability always decreases with increasing concentrations of electrolyte.

The experimental fact that several colloids lose their stability on extremely prolonged dialysis should evidently not be ascribed to the extreme expansion of the double layer by loss of electrolyte, but to a decrease in the surface potential as a result of the removal of potential determining ions. The lack of stability of suspensions in weakly dissociating liquids may also be explained by a lack of sufficient potential determining ions to give the particles the necessary value of  $\psi_0$ .

The influence of the valency of the electrolyte is shown in Fig. 45. The lines for 2-2 and 3-3 valent electrolyte do not extend beyond potentials of  $5 \times 25.6$  and  $3.33 \times 25.6$  millivolts respectively, because the highest available value of  $z$  is 10,

\* In experiments with the AgI-sol this critical potential was found to be of the order of 100 millivolts: that is to say that, to ensure stability, the concentration of the potential determining ions has to be about  $10^2$  times larger than the concentration in the zero-point of charge. Cf. § 6, Chapter II. As regards the order of magnitude, both values are in good accord, although the experimental value is somewhat higher than expected from the theory. This again forms an argument for the application of the Stern correction, which combines a high value of the total potential drop with a lower value in the diffuse double layer.

$\psi$  being  $25.6 z/v$ . Nevertheless it is clear from this figure that a further increase of the potential  $\psi$  would have practically no influence on the concentration limit of stability (stability meant here in the sense that  $W = 10^5$ ).

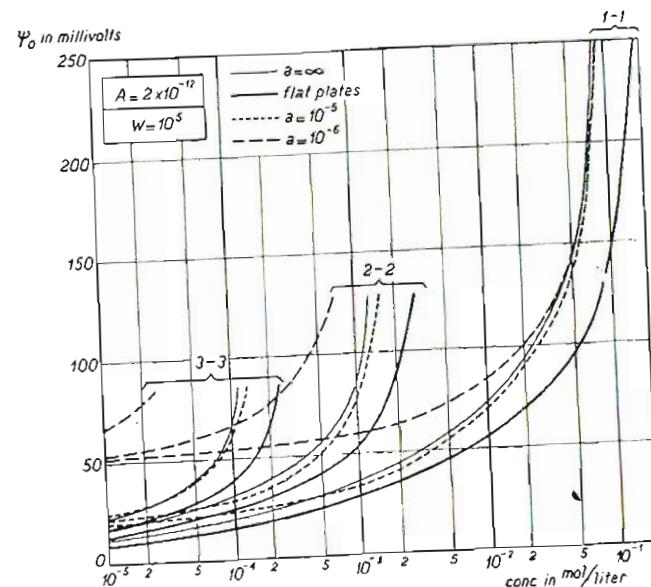


Fig. 45. Showing the influence of the valency of the electrolyte on the stability, when the stability is fairly large ( $W = 10^5$ ).

Taking as an example a potential of 75 millivolts, we see that the electrolyte concentrations permissible as upper limits to ensure a reasonable stability are,

for  $a = 10^{-6}$ , 6.5, 0.2 and 0.02 millimols/liter  
and for  $a = 10^{-5}$ , 13, 1 and 0.12 "

For a potential of 100 millivolts these concentrations are

for  $a = 10^{-6}$ , 20, 0.45 and 0.05 millimols/liter  
and for  $a = 10^{-5}$ , 26, 1.3 and 0.15 "

Although these concentrations are rather low, we already find a considerable spreading in the direction of the rule of Schulze and Hardy. In the approximative theory, working with the equations for small values of  $\psi_0$ , in which the influence of the valency is expressed only through  $z$ , the concentrations of 1-1, 2-2 and 3-3 valent electrolytes should be in the proportion  $1:1/4:1/9$ , deviating considerably from the proportions demanded by the rule of Schulze and Hardy.

As the approximation of small potentials is the best for small particles (as was expounded in Part I) it may be expected that, for sols with very small particles ( $\sim 10^{-7}$  cm), the Schulze-Hardy spreading is smaller than normal. It should be interesting to look for experimental evidence in this direction. The effect might be enlarged by choosing a sol with a small surface potential. However, these two requirements (small particles and small surface potential) are more or less mutually contradictory, so it is not strange that the effect alluded to here should not yet have been found.

Nevertheless, the concentrations mentioned above are the limits for a fairly great stability, whereas the Schulze-Hardy rule is usually determined by flocculation experiments. For this reason we constructed another set of curves, in which  $W = 10$ , i.e., for rather rapid flocculation (Figure 46). Comparing with Figure 45, all stability limits have shifted to higher concentrations and lower potentials. But the general aspect of both figures is the same.

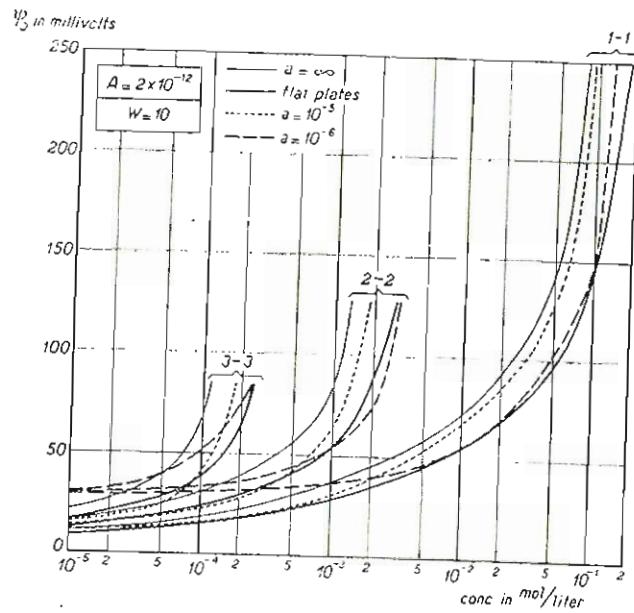


Fig. 46. The same as Fig. 45 for small stability ( $W = 10$ ).

Again, taking a potential of 100 millivolts and a radius of  $10^{-6}$  we find the flocculation values at 47, 2.6, and 0.3 millimols/liter. These flocculation values do not differ very much from those found in Part II and based on the model of flat plates. For larger particles the flocculation values are shifted to somewhat smaller concentrations. We return to the influence of the particle radius further on in this section.

For the construction of Figure 46 the value  $W = 10$  was chosen, because for still smaller values of the stability ratio

$W$  it is difficult to find the exact values of  $z$  and  $\psi_0$  as the maximum of the energy curve becomes flatter and shifts to larger values of  $s$ , where calculations are less certain.

This is illustrated in Figure 47, where we have plotted the stability ratio  $W$  for an arbitrary case against the concentration of the electrolyte. Whereas in the middle part these curves are very steep<sup>1</sup> (stability increases with a factor 2 for a change in concentration of 15 or 20%), the lower part of the curves is much less steep,  $W$  being in that part not very sensitive to the concentration. An analogous effect is shown in figure 48, in which  $W$  is plotted against  $\psi_0$ . From these figures it will be clear that the choice of  $W = 10$  is a reasonable one.<sup>2</sup>

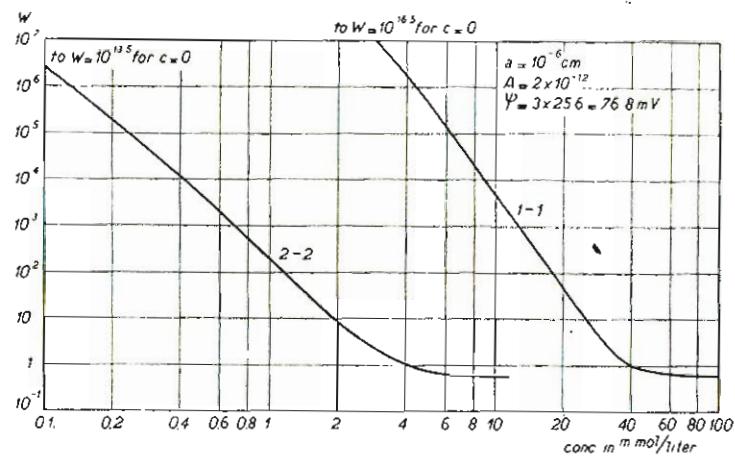


Fig. 47. Stability ratio  $W$  as a function of the concentration of electrolyte for 1-1 and 2-2 valent electrolytes.

These curves, especially those of Figure 47, are another remarkable confirmation of the facts of colloid chemistry. It is well known that flocculation values can be determined with fairly great accuracy, once the stability criterion has been chosen. Usually this criterion is chosen in such a way that a practically complete flocculation has to result in times varying from a few minutes to 24 hours. This would correspond to

<sup>1</sup> If we had chosen a larger value of  $a$  the curves would have been still steeper, because the energy  $V$  is proportional to the radius of the particle, and enters into  $W$  exponentially.

<sup>2</sup> It may seem strange at first sight that  $W$  can be smaller than 1, as is shown in the figures. This means, however, that the flocculation is more rapid than when no forces act between the particles.  $W < 1$  means that the stability is diminished by attractive forces, viz. the London-Van der Waals forces, which act practically unhampered by the repulsion for large concentrations of electrolyte or for small surface potentials (Fig. 47 resp. Fig. 48).

a value of  $W$  somewhere between 5 and 1000, where  $W$  changes very rapidly with the concentration. To cite only one example we mention the coagulation of silveriodide sol, investigated by Kruyt and Troelstra<sup>1</sup>, where  $W$  is found to change from about 60 to about 7 when the concentration of  $\text{Ba}(\text{NO}_3)_2$  is increased from 2.0 to 2.5 millimols/liter. This is about twice as steep as the curve in Fig. 47, but the radius of the silveriodide particles was also 2 or 3 times as large as the case for which Fig. 47 is constructed. The concordance may be called good.

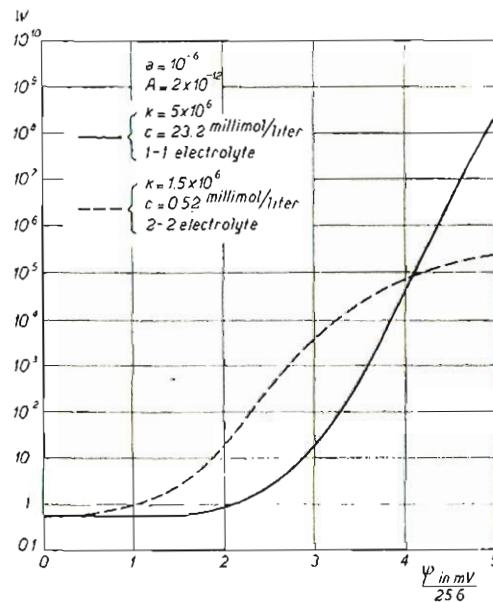


Fig. 48. Stability ratio  $W$  as a function of the surface potential.

On the other hand it is very difficult to establish the limit of really rapid coagulation ( $W = 1$  or even  $< 1$ ), and this may now be explained by the flatness of the  $W - \alpha$  curves for small values of  $W$ .

The influence of the particle radius on stability is a rather complex one. Incidentally this problem has already been dealt with above, for instance where we discussed the instability of sols with small particles. It is interesting to consider it here in some other respects. The conclusions arrived at will be partially the same as those found more qualitatively on the

<sup>1</sup> H. R. Kruyt and S. A. Troelstra. *Kolloidchem. Beihefte*, 54 (1943) 225.

basis of the model of the flat plates, but they follow more rigorously from the present theory for spherical particles.

Although as a rule we find increasing stability with increasing dimensions, there are exceptions to this rule, as we already mentioned in connexion with Fig. 44. When the particles are small as compared to the dimensions of the double layer, stability always increases with increasing particle dimensions. As mentioned before, the repulsion in these cases reaches much farther (range of the order  $1/\alpha$ ) than the London-Van der Waals force (range  $\sim a$ ), and the stability is practically determined by the height of the repulsion curve only. Now the

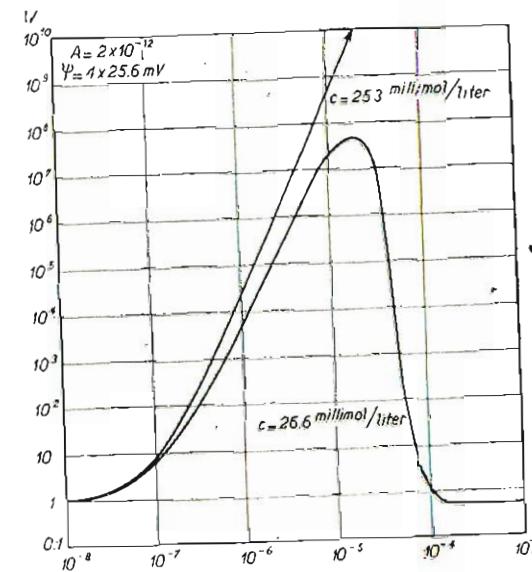


Fig. 49. Stability ratio  $W$  as a function of the particle radius.  
Monovalent electrolyte.

repulsion is proportional to the radius of the particles (c.f. equations 56 and 80), and stability increases with the radius. When the concentration of electrolyte is small, this increase continues up to the largest particles. But in the neighbourhood of the flocculation limit we may find decreasing stability with increasing radius, because then the London-Van der Waals attraction plays a much more important part, and may even become greater than the repulsion. This is illustrated by Fig. 49, in which, for a concentration of 25.3 millimols/liter, we find continuously increasing stability, but for a concentration of 26.6 millimols/liter stability decreases when the particle radius is more than  $2 \cdot 10^{-5}$  cm, so that particles of  $10^{-4}$  cm are not

stable under the same conditions under which smaller particles are perfectly stable<sup>1</sup>.

Now this dependence of the stability on particle dimensions may be very important for the course of the flocculation process. Suppose we start with particles somewhat smaller than  $10^{-6}$ , potential and concentration being those mentioned in Figure 49, then we have a slowly coagulating sol. But when the particle dimensions are doubled by coagulation, stability is increased by a factor 15, thereby considerably slowing down the coagulation process, which may eventually be completely stopped. This slowing down is often found during coagulation experiments<sup>2,3</sup> and may accordingly be explained by the increase in the average particle dimensions. It should be pointed out, of course, that this does not give a quantitative picture of the retarded coagulation, because even when we start with a monodispersed sol the coagulation process makes it polydispersed, and, moreover, the complexes formed differ from massive spherical particles of the same weight. Nevertheless it will be felt that the explanation given here of the retarded flocculation is essentially right.

Another application of the curves of energy of interaction may be found in the theory of the electrodeposition of fine suspensions mentioned in the introduction on page 16. In the theory of electrodeposition given by Hamaker and Verwey<sup>4</sup> it is assumed that the electric field, transporting the particles by electrophoresis to the object to be coated, is of sufficient strength to pull the particles together against the repulsion caused by the potential barrier between them.

To give a provisional quantitative test of this theory, we consider the case of two spherical particles with a radius of  $1 \mu$ , a surface potential of  $102.5 \text{ mV}$  ( $z = 4$ ), a dielectric constant of 26 (acetone), an amount of monovalent electrolyte resulting in a value of  $\kappa$  of  $10^5$ , and a London-Van Der Waals constant of  $2 \cdot 10^{-12}$ . The relevant part of the interaction curve<sup>5</sup> is given in Fig. 50.

<sup>1</sup> It seems surprising that this effect, which is to be expected on general grounds, is so very critical to the concentration, as a change from 26.6 to 25.3 millimols/liter causes the effect to disappear. In all probability, therefore, an experimental confirmation will be very difficult to obtain.

<sup>2</sup> H. R. Kruyt and A. E. Van Arkel, *Rec. trav. chim.*, 39 (1920) 656; 40 (1921) 169.

<sup>3</sup> G. H. Jonker, (On the AgBr-sol). *Thesis, Utrecht* (1943).

<sup>4</sup> H. C. Hamaker and E. J. W. Verwey, *Trans. Faraday Soc.*, 36 (1940) 180.

<sup>5</sup> As the repulsive energy is proportional to  $r$  (cf. note 1 on page 140), and Table XIV being calculated for a value of  $G$  78.55, we have to divide the values of  $G$  by 78.55/26.

The force exerted on the particles by the electric field may be estimated by the electrophoresis equation

$$v = \frac{\epsilon \psi_0 E}{4\pi \eta} \quad (95)$$

where  $\psi_0$  is the surface potential,  $E$  the field strength and  $\eta$  the viscosity of the liquid.

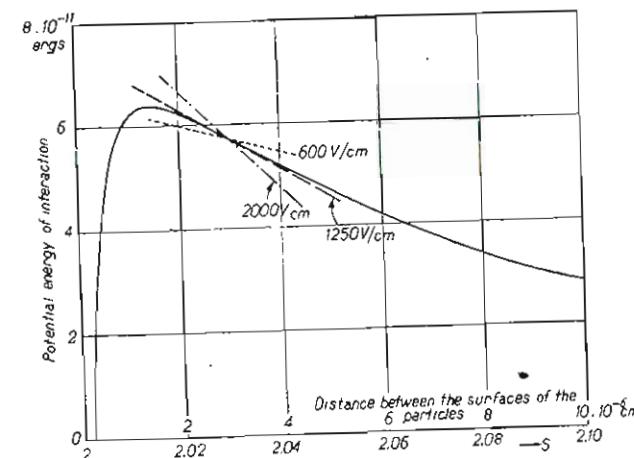


Fig. 50. A potential curve typical for a suspension used for electrodeposition, ( $a = 10^{-4}$ ,  $\psi_0 = 100 \text{ mV}$ ,  $\kappa = 10^5$ ,  $\epsilon = 26$ ,  $A = 2 \cdot 10^{-12}$ ) with three straight lines illustrating the force exerted on the particles for three different field strengths. A field strength of 1250 V/cm would be just sufficient to pull the particles past the energy barrier.

In this equation, account is taken of the force exerted on the particle by the motion of the double layer in the electric field, and we can calculate the resultant force on a particle (force exerted directly on the charge of the particle, minus force exerted by the motion of the double layer) by calculating the force necessary to give the particle the velocity  $v$ , that is by Stokes's law  $6\pi\eta av$ . This force is found to be equal to

$$\frac{1}{2} \epsilon \psi_0 E a,$$

or, in the case considered above,  $4.4 \cdot 10^{-9}$  dynes for a field strength of 1 V/cm. If this force is either equal to, or larger than, the repulsive force corresponding to the steepest part of the repulsion curve, it is possible for two particles to be forced together. The straight lines in Fig. 50 are drawn for three different field strengths; one too small, the second just great enough (1250 V/cm), and the third greater than is neces-

sary to allow passing of the barrier and formation of a strongly coherent precipitate.

In Hamaker's experiments the field strengths applied are of the order of 100 V/cm.

On page 17 we described how, as an intermediate stage before the final deposition of the particles, a concentrated suspension is supposed to be formed in the immediate neighbourhood of the electrode. This point of view accords very well with the results of our theory. The applied field strength (e.g., 100 V/cm) is generally too low to pull the particles past the potential barrier, but great enough to bring about the high concentration around the electrode. Now in this concentrated suspension the electric resistance will be much greater than in the bulk of the liquid, as is proved by Hamaker's<sup>1</sup> experiments. Consequently, in this layer the potential gradient will become greater. As soon as, through this mechanism, the critical field strength (in the example of Fig. 50 1250 V/cm) is surpassed, the final deposition will take place. The layer formed by electrodeposition may be expected to be very closely packed, because (1) the deposit is formed out of the concentrated suspension around the electrode and (2) contacts between the particles are only possible in the direction of the lines of force, whereas, in a direction parallel to the surface of the electrode, the double layers retain their activity, thereby allowing the particles to reach the most favourable packing. Hence, even in quantitative respects the accord between theory and experiments is satisfactory.

We should not forget, however, that we made a rather daring approximation in considering only the interaction of two particles in those concentrated suspensions. Eq. 95, too, will lose its quantitative validity when the concentration of particles becomes very high.

We did not intend to go very deeply into this subject, but we wished to show how, here too, theory is confirmed by experiment, and that here, again, there is scope for a further quantitative test of the theory.

### § 3. Introduction of the Stern correction

We have hitherto reasoned as if the potential  $\psi$  were constant during all changes in the electrolyte concentration. This would be right if we could describe the double layer completely by the theory of Gouy-Chapman. But as we have seen (§ 5 of Chapter VII), especially for larger concentrations some correction has to be made in respect of the dimensions and the specific adsorption of the ions, and a possible form of this cor-

<sup>1</sup> H. C. Hamaker, *Trans. Faraday Soc.*, 36 (1940) 279.

rection (for a flat double layer) has been proposed by Stern. It has been expounded there that the application of the Stern correction results in a decrease of the "effective" surface potential with increasing concentration of electrolyte. It seems to follow from electrophoresis measurements that the effective potential decreases faster by the addition of polyvalent electrolytes than with monovalent electrolytes. This would result in a still greater spreading of the flocculation values for different valued electrolytes.

That the Stern-correction is necessary for the understanding of the differences between electrolytes of one valency type (lyotropic influence) was already explained in Part II.

### § 4. Repeptization phenomena

It is well known that many flocculated colloidal systems (e.g., different sulphides) may be made to form stable sols again simply by washing out the flocculating electrolyte. In this, it is not sufficient to decrease the concentration of electrolyte just below the flocculation value, but it must be decreased to a very low value by carefully washing out the precipitate before repeptization occurs.

The repeptization cannot be explained by the theory as it is presented here, for in a flocculated system the particles are considered to be in direct contact with an infinitely large negative value of the potential energy, since for direct contact ( $s = 2$ ) the London-Van der Waals energy goes to  $-\infty$ . It is clear, therefore, that for a complete picture of colloidal behaviour yet another sort of forces has to be considered, *viz.* the repulsive force appearing when the electronic shells of two atoms interpenetrate each other (Born-repulsion)<sup>1</sup>. By introducing this sort of forces, the infinitely deep minimum of energy is replaced by a minimum with a finite value, thereby creating the possibility that, by removing the flocculating electrolyte, the repulsion by the double layer system may become great enough to cause this minimum completely to disappear, so that spontaneous repeptization may follow.

It will be clear from the theory developed in the foregoing chapters why there is such a great difference between the flocculating and the repeptization concentrations. Consider Figure 51, in which the potential curves for the limit of flocculation and the limit of repeptization are sketched. The flocculation value is determined mainly by the height of the maximum A above the axis, whereas for repeptization the vertical dis-

<sup>1</sup> H. C. Hamaker, *Rec. trav. chim.*, 56 (1937) 3, introduced this repulsion explicitly.

tance between the minimum  $B$  and the maximum  $A$  has to be smaller than a few times  $kT$ . The state  $R$  is only reached for a very much higher repulsion than the state  $F$ . So the electrolyte must be washed out to a very large extent.

The fact that the degree of repeptization often depends very much on the previous history of the system, especially on the time the system has been in the flocculated state, is easily explained by secondary changes such as recrystallization of the precipitate.

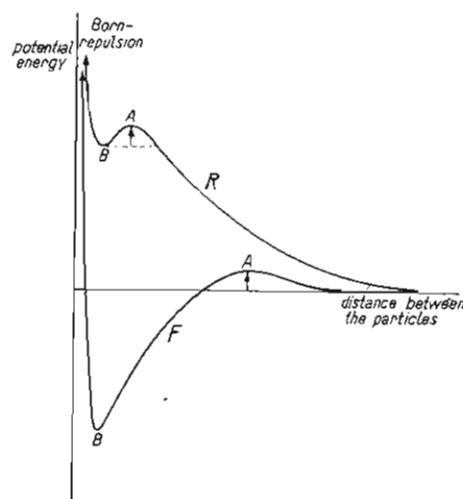


Fig. 51. Illustrating the large difference in concentration of electrolyte for flocculation (curve  $F$ ) and repeptization (curve  $R$ ).

Another factor, probably important for the understanding of repeptization, is the roughness of the surface of the particles. Real colloidal particles never have absolutely flat surfaces; neither are they ever exactly spherical. So, when the particles are in contact, they touch only in a few protruding points and only at these points does the potential energy reach the large negative values mentioned above. For repeptization it is necessary only to overcome the attraction at these points, which will evidently be less difficult than tearing loose perfectly regular particles.

#### § 5. The minimum in the potential curves for great distances

As in Part II, we have hitherto neglected the influence of the secondary minimum in the potential curves situated at comparatively large values of  $s$ , where the London-Van der Waals force again surpasses the repulsion. As already pointed

out in Part II, this secondary minimum, if deep enough, may lead to a coagulation, distinguished from the coagulation in the deep primary minimum by being more reversible. This reversible flocculation may simply be described by the application of Boltzmann's theorem, because the secondary minimum, contrary to the deep minimum at  $s = 2$ , can be reached without surmounting a potential barrier.

The number of particles found in the immediate neighbourhood of a certain specified particle is given by

$$\int n_0 4\pi R^2 dR e^{-V/kT} = \int n_0 a^3 \cdot 4\pi s^2 e^{-V/kT} ds \quad (96)$$

$n_0$  being the number of particles per unit volume of the suspension. The exact limits of integration are not important, since on account of the exponential in the integrand the major contribution to the integral is found for values of  $s$ , very near the minimum of  $V$ .

As a condition of stability we may demand that the integral (96) be smaller than 1/10. The integral can be evaluated graphically.

It is then found that for small particles ( $a \leq 10^{-6}$  cm) this new condition of stability (96) does not interfere with the stability conditions found earlier. If the maximum in the potential curve is high enough to prevent flocculation, the secondary minimum is so shallow that the integral (96) only has a small value and consequently it does not diminish the stability of the sol.

For larger particles, however, flocculation in the secondary minimum may appear at a low concentration of electrolytes, when the maximum is still high enough to prevent flocculation in the deep, primary minimum.

In figure 52, for example, we give the potential curves for  $a = 10^{-4}$ ,  $A = 5 \times 10^{-13}$  from which it can be computed that, on account of the secondary minimum, the stability limit should lie at about  $\kappa = 10^6$  i.e. at an electrolyte concentration of about 1 millimol/liter. In that case the depth of the minimum is about  $6 kT$ .

Now as far as experimental evidence goes, the limit of stability of coarse suspensions is not very different from that of fine sols i.e. about 20–100 millimol of a monovalent electrolyte and not a much lower value as would be suggested by the above considerations. It is true that the retardation effects on the London force (c.f. p. 104) make the secondary minimum less pronounced, but it will not disappear completely and the effect of retardation will be only to shift the limit of the radius of the particles for which the secondary minimum determines the stability to higher values.

It is, therefore, necessary to consider other aspects of the stability. A flocculation value is generally determined as the concentration of electrolyte in which conglomerations of particles are formed which cannot be divided into single particles by simple shaking of the sediment. Now by shaking much larger forces are exerted on large particles than on small ones. Moreover the influence of gravity on larger particles becomes comparable to and finally surpasses the forces of interaction. As the secondary minimum is in any case rather shallow

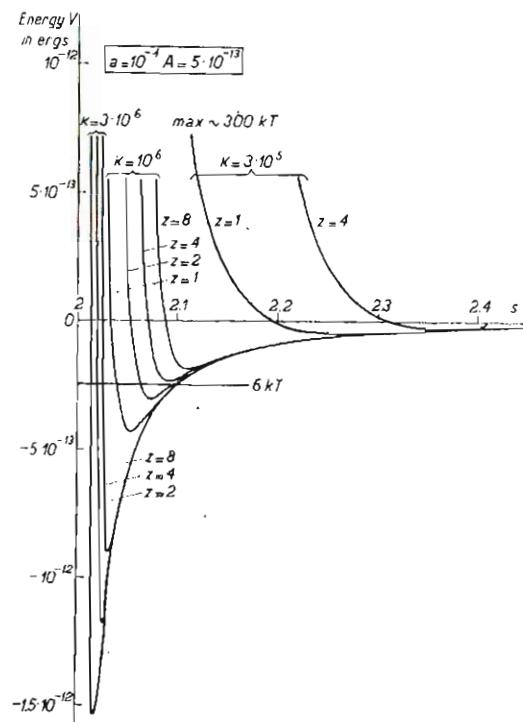


Fig. 52. Secondary minima in the energy curves for coarse particles ( $a = 10^{-4}$ ,  $A = 5 \cdot 10^{-13}$ ).

the bond between two particles will be easily broken and it is not so strange that this influence of the secondary minimum has never been observed. Or rather it has not been observed in the stability of suspensions with more or less spherical particles. As soon as the particles are elongated whereby the influence of the potential minimum is enhanced against the influence of gravity and streaming of the liquid (shaking) the secondary minimum manifests itself (see page 124, 125).

Another experiment where the secondary minimum plays

probably a rôle is the determination of adherence of quartz particles to a plane quartz or glass wall<sup>1</sup>.

Von Buzagh let a dilute suspension settle on a glass plate. After reversing the glass plate under the liquid he observed that a smaller or larger part of the particles fell from the glass plate but another part adhered to it. The percentage of adhering particles was strongly increased by increasing the concentration of electrolyte.

That this adherence may be accounted for by the secondary minimum may be concluded from the fact that the particles while adhering to the glass wall still show a lateral Brownian motion and that the adherence is most pronounced for particles with a diameter of about  $3 \mu$ , the smaller ones falling down because the potential minimum is not deep enough compared to  $kT$ , the larger ones because they are too heavy.

More quantitative conclusions as to the importance of this secondary minimum can only be obtained on the basis of a more detailed knowledge of the attractive potential function for larger particle distances. The calculation of this potential function is now made possible by the Casimir-Polder theory (cf. p. 105) for large distance Van Der Waals-London attractive forces including retardation. The considerations in Chapter VII, § 4, and the remarks given above, may suffice to show that the rôle of the secondary minimum is an essential feature in our theory of the interaction of colloid particles and deserves a more detailed examination. Further theoretical and experimental work on this subject is in progress.

<sup>1</sup> A. von Buzagh, *Kolloid-Z.*, 47 (1929) 370; 51 (1930) 105.

## APPENDIX

## XIII. THEORETICAL WORK ON THE STABILITY OF LYOPHOBIC COLLOIDS BY PREVIOUS AUTHORS

## § 1. Introduction

The first attempts at a theoretical treatment of the problem of lyophobic colloid stability were those by Gyemant<sup>1</sup>, O. K. Rice<sup>2</sup> and W. C. M. Lewis<sup>3</sup>. It is remarkable that this work, carried out almost twenty years ago by three authors, obviously independently of each other, shows a common fundamental mistake. The rather complicated and sometimes not quite consistent calculations of these authors are all based on the same principle. All of them thought that they were computing the stability of a lyophobic colloid with respect to coagulation. Actually they calculated the stability with respect to "coarsening" (increase of the particle size), i.e. they tried to determine the degree of dispersion as a function of the properties of the system. Proof that such calculations must fail is that the condition of equilibrium sought does not exist: colloid chemical experience has shown long before (see, for instance, the introduction of the well known book "Colloids", by H. R. Kruyt) that a lyophobic colloid is never stable in the thermodynamic sense, and that coarsening must always occur (though often extremely slowly). This means that there is no definite degree of dispersion which is more stable than others. The degree of dispersion depends solely on the method of preparation and the further treatment. The authors mentioned tried to show that under certain conditions the free energy of the double layer is sufficient to outweigh the free surface energy of the uncharged interface (interfacial tension). They failed to recognize that actually the latter is always predominant, so that the most stable state is that with the smallest total interfacial surface.

It is nevertheless interesting to observe that these authors were partially on the right track in that they considered the free energy of the electric double layer as the "stabilizing" factor (more than the electric repulsion of the particle charges).

The same applies to the paper by March<sup>4</sup>; this author con-

## § 2

sidered the free energy of the entire colloid system, and came to the correct conclusion that the free energy of the double layer and the entropy of the separate particles are together much too small to counteract the tendency to decrease the total interfacial surface caused by the surface tension. March inferred that there must be some unknown protecting layer surrounding the particles, preventing what he considered to be "coagulation".

A more satisfactory treatment only was possible after the discovery of the nature and the laws of the Van Der Waals-London forces and their introduction into colloid science. In Chapter I we already mentioned the general theory developed by Hamaker and the attempts of various authors to give a more quantitative treatment of the interaction of colloidal particles. With the exception of Langmuir's paper this work is based on the same general principles as we used in the foregoing pages, i.e. the authors mentioned in Chapter I (and cited occasionally in the other chapters) consider the potential energy, or the force between two particles or plates, as a function of the distance in order to derive criteria of stability. They assume that the Van Der Waals-London forces supply the coagulating factor and consider (or believe they consider), the free energy of the electrical double layer as the factor counteracting the agglomeration. We shall now analyse the work of these authors in more detail, in order to emphasize in what respects their work differs from our own, and to show a way out of the difficulties raised by the divergent results of some of these authors. The paper by Langmuir, approaching the problem from an altogether different point of view, will be discussed separately.

## § 2. Force methods

It will be convenient first to consider those authors (Bergmann, Löw Beer and Zocher<sup>1</sup>, Derjaguin<sup>2</sup> and also Langmuir<sup>3</sup> who examined the force acting between the particles. Their attempts to arrive at expressions for the repulsive force between two (flat) double layers are essentially correct and led to results differing only on minor points. For a discussion of the different methods to calculate this force we refer the reader to Chapter V. § 3, where this part of the work of Derjaguin and Langmuir is fairly extensively

<sup>1</sup> A. Gyemant, *Grundzüge der Kolloidphysik*, Braunschweig, Sammlung Vieweg (1925); *Z. Physik*, 36 (1926) 457.

<sup>2</sup> O. K. Rice, *J. Phys. Chem.*, 30 (1926) 189, 1660.

<sup>3</sup> W. C. M. Lewis, *Trans. Faraday Soc.*, 28 (1932) 597.

<sup>4</sup> A. March, *Kolloid-Z.*, 45 (1928) 97.

<sup>1</sup> P. Bergmann, P. Löw-Beer and H. Zocher, *Z. physik. Chem.*, A 181 (1938) 301.

<sup>2</sup> B. Derjaguin, *Trans. Faraday Soc.*, 36 (1940) 203.

<sup>3</sup> I. Langmuir, *J. chem. phys.*, 6 (1938) 893.

discussed. The method applied by Bergmann c.s. is quite comparable to that of Derjaguin.

As Langmuir's paper will be considered separately and the paper by Bergmann c.s. runs on somewhat different lines (explanation of the formation of "Schiller layers" in sols of blade-shaped particles), we shall here summarize only briefly the way in which the force equation is involved in Derjaguin's theory of stability. A drawback of this work is that the double layer repulsion is only considered in the linear approximation ( $v e \psi_0 \ll kT$ ), excluding all possibility of understanding some of the essential features of stability, such as the Schulze-Hardy rule in the coagulation by electrolytes. Moreover, instead of using the concept of the relatively far-reaching London forces, Derjaguin introduces the attraction by applying the substitute of extremely steeply decaying attractive forces which are active only when the particles are in immediate contact. It has been shown in our work that a farther reaching attraction is an equally important condition for quantitative agreement between theory and experiment. Hence Derjaguin's considerations, though essentially correct, cannot give a satisfactory explanation of the phenomena observed, such as the values of flocculating concentrations and of the essential electric surface potentials as found experimentally.

### § 3. Energy methods

The most detailed theoretical considerations (especially the work of Levine and Dube<sup>1</sup>) followed a different line of thought. They were based on the direct evaluation of the potential energy. Evidently this mode of treatment entailed serious difficulties.

Although treating of different cases, the paper by Corkill and Rosenhead<sup>2</sup> and the papers by Levine and Levine and Dube, on closer examination, appear to show a strong resemblance. Corkill and Rosenhead consider the double layer interaction for two flat plates, starting from the complete differential equation based on the Gouy-Chapman picture of the double layer. Levine and Dube chiefly consider the case of two spherical particles, using the linear approximation of Debye and Hückel. C. and R. find an attraction both for the case that the surface charge and the surface potential are kept constant in varying the plate distance; in order to obtain a

<sup>1</sup> S. Levine and G. P. Dube, *Trans. Faraday Soc.*, 36 (1940) 215, and elsewhere.

<sup>2</sup> A. J. Corkill and L. Rosenhead, *Proc. Roy. Soc., A* 172 (1939) 410.

repulsion they recur to a third case in which the electric potential difference between the plate surface and the solution midway between the plates is considered to be independent of the plate distance. L. and D. mainly consider the case of a constant charge of the particles where they find an attraction for small interaction and a repulsion for strong interaction; the potential curves thus obtained, showing a minimum for intermediate particle distance (which is considered to be an essential point by L. and D.), are combined with Van der Waals-London attractive potentials.

The common point in the work of C. and R. and in that of L. and D. is that they consider the total energy of the electric field of the double layer system, instead of its free energy,<sup>1</sup> as the energy quantity determining the work associated with a variation of the distance of the plates or particles.

In view of the strongly deviating results of these authors, Derjaguin, in his discussion with Levine, also considered the problem from the point of the free energy. This discussion, started during the first year of the war (1939-1940), was not brought to a satisfactory conclusion. Derjaguin there uses a method substantially equivalent to our "first method", described in § 2, Chapter III. He arrives at the same general conclusion as ourselves, namely, he finds a repulsion between the plates (or particles) for any distance between them; his expression for the repulsive potential between two flat plates is a special case of our own results for the linear approximation corresponding to  $v e \psi_0 < kT$ .

It is instructive, however, to consider the implications of the fundamental error involved in the work of C. and R. and of L. and D., and to show in what way this error is responsible for the very different results in the various cases dealt with by these authors.

On the basis of our considerations in Chapter III, we may describe this error (the use of field energy in stead of the free energy of the double layer) as consisting in the neglect of at least one of the two following effects: (1) entropy effects due

<sup>1</sup> In this section no account is taken of the new theory presented by Levine to the General Discussion on "Swelling and Shrinking", held by the Faraday Society in September 1946. His new method of approach, based on statistical mechanics leads to an expression for the free energy of a system of double layers, equivalent to our equation (26) of Chapter III, § 3. When in applying his new theory Levine still finds results differing from ours and more resembling his former results, we believe that this is due to the way in which boundary conditions are introduced and not to the principle of the method. In the discussion on Levine's paper (*Trans. Faraday Soc.*, 44 (1948) in press) we have subjected his way of introducing the boundary conditions to criticism.

\* S. Levine and G. P. Dube, *Trans. Faraday Soc.*, 36 (1940) 215, and elsewhere.

to the ions carrying the diffuse charge, and (2) chemical effects of the transport of ions to or from the wall.

The effect mentioned under (1) is important if we consider the case in which the charge of the particles is kept constant and the surface potential is a function of the distance of the particles (or plates). In that case no ionic transport from one phase to another occurs, and therefore no chemical effects are involved. Hence it appears that the fallacious results obtained in this case are entirely explained by the difference between field energy and free energy of the charges. Actually we find, for the two quantities, entirely different relations behaving very differently as a function of the distance of the particles.

The chemical effects mentioned under (2) are predominant in the case of a constant potential and largely explain the deviating results of the authors mentioned above.

We shall first consider the entropy effect (1).

The electric field energy considered by C. R. and L. D. is the energy obtained by subdividing the charge into small pieces, and bringing the latter to infinitely great distances from each other. Hence it is the total potential energy of all charges considered to be in fixed positions, and may be compared to the configurational energy in the Debye-Hückel electrolyte theory. It may be written

$$E = \frac{1}{2} \iiint \iiint \frac{\rho(r)\rho(r')}{\epsilon |r - r'|} d\tau \cdot d\tau' \quad (97)$$

which can be transformed into

$$E = \frac{1}{2} \iiint \rho(r) \cdot \psi(r) \cdot d\tau. \quad (97')$$

Hence it can be divided into two parts. The first is the energy of the surface charges, the second the field energy of the diffuse layer, or the energy of the charges in the solution layer of the double layer.

It will be seen that this field energy is certainly not identical with the free energy of the charges,  $F_e$ , as according to our model of the double layer the ions carrying the diffuse charge are subjected to thermal motion, and we must therefore consider, in addition, the entropy of the latter. In Chapter III, § 2, we have shown that the change in the entropy of these ions is able to counterbalance exactly the change of electric energy (i.e. of the second part of the total electric energy of the double layer), so that the free energy of the diffuse charge may actually be considered to be equal to zero. The energy in the case of two spherical particles are, therefore,

quite superfluous and the corresponding contribution should be omitted.

The difficulties of these authors were probably caused by the circumstance that, for a pure dielectricum, the field energy has the properties of a free energy: it includes the entropy terms associated with the thermal motion of the water molecules, vibrations of ions and watermolecules with respect to each other, etc., because we are working with the model of a continuum where all these effects are accounted for in the dielectric constant. With respect to the free mobile ionic charges, however, the field energy has the properties of an internal energy, as it gives us the work to be done for fixed positions of the ions. In the charging process considered in Chapter III we would have found  $E$  instead of  $F_e$  (as may be verified) if we had included the work of charging the diffuse space charge. We saw there, however, that this energy quantity is not available as a work quantity, but manifests itself as an amount of heat flowing out of the system.  $E$  and  $F_e$  are always positive (work must be supplied in building up the charges); we saw above that the former consists of two parts which must obviously have opposite signs (because of the opposite charges in both layers). Accordingly,  $E$  is always smaller than  $F_e$ , the difference corresponding to the amount of heat lost in the isothermal charging process considered in Chapter III.

Following the example of Derjaguin and L. and D. in their discussion referred to above, some of the principal points may be illustrated quantitatively with the aid of the simple formulae valid for the approximation for small potentials in the case of two parallel planes. For the free energy we have, in this case,

$$F_e = \int_0^a \psi_0' dx' = \frac{1}{2} \psi_0 a = \frac{2\pi\sigma^2}{\epsilon x} \cdot \coth \pi x d \quad (98)$$

and it will be seen that this quantity increases with decreasing value of  $xd$ , corresponding to a repulsion between the two plates (for the case that  $a$  is kept constant during variations of the plate distance).

The field energy is most easily found by converting eq. (97), according to well known methods in the theory of electricity (simplifying simultaneously for the case of two flat plates), into

$$E = \frac{c}{8\pi} \int_0^d \left( \frac{d\psi}{dx} \right)^2 dx \quad (99)$$

With

$$\frac{d\psi}{dx} = -\pi\psi_0 \frac{\sinh \pi(d-x)}{\cosh \pi d} = -\frac{4\pi\sigma}{2} \cdot \frac{\sinh \pi(d-x)}{\sinh \pi d}$$

this leads directly to the result:

$$E = \frac{\pi\sigma^2}{\epsilon x} \left( \coth \pi x d - \frac{\pi d}{\sinh^2 \pi d} \right) \quad (100)$$

This quantity has the property of decreasing with decreasing plate distance, which would correspond to an *attraction* between the plates!

The entirely different behaviour of the two quantities is also shown by the graphic representation (Fig. 53,  $(F_e)_\sigma$  and  $E_\sigma$ , in which the index  $\sigma$  denotes that both quantities refer to the case where the charge is kept constant).

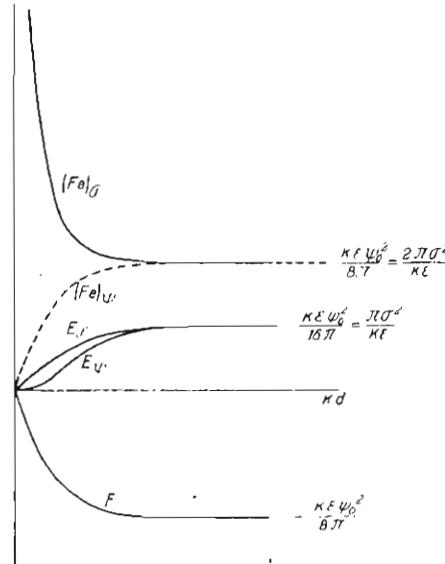


Fig. 53. Energies of interaction of two flat double layers as a function of the distance.

$E$  = total energy

$F$  = free energy

$F_e$  = electric part of the free energy.

The indices  $\sigma$  and  $\psi$  refer to the cases that the charge resp. the potential of the plates is kept constant.

That this difference between  $F_e$  and  $E$  is actually accounted for by the thermal motion of the ions may be shown by deriving  $E$  from  $F_e$  with the aid of the Gibbs-Helmholtz equation

$$E = F_e - T \frac{dF_e}{dT} \quad (101)$$

in which, consequently upon what we stated above, the dielectric constant  $\epsilon$  (although a function of  $T$ ) must be treated in the differentiation of  $F_e$  as a constant ( $E$  is already free energy with respect to the medium). Hence, in  $F_e$  only the quantity  $\chi$ , governing the diffuseness of the space charge due to the thermal motion of the ions, must be treated as a function of  $T$ , and that only insofar as it contains  $T$  explicitly. Accordingly we may write

$$\chi = \left( \frac{8\pi^2 e^2 v^2 n}{r k T} \right)^{1/2} = \frac{b}{T^{1/2}}$$

in which  $b$  is a constant. Inserting (98) into (101) we find:

$$\begin{aligned} E &= \frac{2\pi\sigma^2}{\epsilon} \left\{ \frac{\coth \chi d}{\chi} - T \cdot \frac{1}{b} \cdot \frac{\partial}{\partial T} \left( T^{1/2} \cdot \coth \frac{bd}{T^{1/2}} \right) \right\} \\ &= \frac{2\pi\sigma^2}{\epsilon} \left\{ \frac{\coth \chi d}{\chi} - T^{1/2} \cdot \left( \frac{\coth \chi d}{2T^{1/2}} + \frac{\chi d}{2T^{1/2} \cdot \sinh^2 \chi d} \right) \right\} \\ &= \frac{\pi\sigma^2}{\epsilon} \left\{ \coth \chi d - \frac{\chi d}{\sinh^2 \chi d} \right\}, \end{aligned}$$

i.e., we again find the result (100), showing that the divergent results may actually be linked together in this way.

We shall now consider briefly the case  $\psi_0 = \text{constant}$ , dealt with, e.g., by C.R. (and also by L.D. in the discussion with Derjaguin), in which both the entropy effects and the chemical effects were erroneously neglected. In this case the second neglection appears to have the most important consequences, as we saw in Chapter III that the total free energy of the double layer, including the chemical term, is always negative. (The double layer is formed autogeneously when particles and solution are brought into contact). If ionic equilibrium is maintained, a decrease of the particle distance effects a decrease in the double layer charge (for two plates finally even a complete suppression of the charge). This was seen to be the reason of the repulsion, as work must be supplied to force away this double layer charge, and it explains at the same time why C.R. find an attraction in this case, as they are working with a positive quantity reduced by the interaction. It is even more or less immaterial that they should have made the additional mistake of using  $E$  instead of the corresponding electric part of the free energy, as the difference is only a quantitative one, both quantities being positive.

These statements may also be illustrated quantitatively with the aid of the simple equations for flat plates in the linear approximation. We must now introduce  $\psi_0$  as a constant determining the properties of the system. Hence the equation for  $E$  is obtained from (100) by the substitution:

$$\sigma = \frac{\chi \epsilon \psi_0}{4\pi} \tanh \chi d$$

with the result:

$$E = -\frac{\chi \epsilon \psi_0^2}{16\pi} \left( \tanh \chi d - \frac{\chi d}{\cosh^2 \chi d} \right) \quad (102)$$

independently of whether we derived (100) directly from (99), or indirectly via the Gibbs-Helmholtz equation from the free energy (98). Expressed into the potential  $\psi_0$  we find, for the free electric energy,

$$F_e = \frac{\chi \epsilon \psi_0^2}{8\pi} \tanh \chi d \quad (103)$$

which differs, however, from the quantity  $(F_e)_\psi$  considered above in that it is only part of the total free energy, and cannot be considered separately, as it is impossible to change the free energy for constant surface potential  $\psi_0$  without changing the chemical free energy\*. The total free energy,  $F$ , includes the chemical free energy term  $-n\psi_0$  (see Chapter III) and therefore reads:

$$F = -n\psi_0 + (F_e)_\psi = -\frac{\pi\epsilon\psi_0^2}{8\pi} \cdot \tanh \pi d \quad (104)$$

The various quantities discussed here are found in Fig. 53, in which the index  $\psi$  indicates that we are now considering their properties for  $\psi_0$  independent of the plate distance. Curve  $E$ , eq. (102), would give the potential curve due to the interaction if we should follow the treatment of C.R. and L.D.; this curve corresponds to an attraction. The dotted curve,  $(F_e)_\psi$ , is the corresponding free electric energy according to eq. (103). The total potential energy curve found by adding the chemical free energy (eq. (104)) is represented by  $F$ , again showing a repulsion.

We have rather extensively discussed the principal points explaining the deviating results of C.R. and L.D., but the (at first sight) rather impressive work, of Levine especially, proves that a correct treatment of these double layer problems is not so obvious.

One might finally ask why the use of field energy instead of free energy should lead to an attraction instead of a repulsion between the plates. This may be understood by the following consideration, neglecting the re-arrangement of the charges in the interaction (this neglection gives no qualitative deviations). If we do not account for the entropy effects in the interpenetration of the diffuse charge layers, the predominating effect is that the diffuse charge of one plate enters into the potential field of the other one; the corresponding electric result would be an attraction, because the charge and the potential have opposite signs. In reality, however, also the entropy effects must be taken into consideration, with the result that the change in free energy in the interpenetration of the double layers is zero. In that case there remains to be considered the effect of the circumstance that the surface charge of one plate comes into the field of the other. We have seen that as a result of this interaction there will be either an increase in the surface potential or a decrease in the charge, dependent on the supposition of either constant charge or constant potential. In the first case there is an increase in electric energy; in the second mainly an increase in chemical energy, both leading to a repulsion.

\* For the same reason it is impossible to find  $E$  from eq. (103), because variation of  $F$  by varying  $T$  for constant  $\psi_0$  would always be accompanied by a transport of ions from one phase to another, so that it is impossible to consider purely electric effects in this way.

There is a difference between the problem of two flat plates and that of two spherical particles, in that the treatment of the latter according to the erroneous method of the above authors leads to a potential curve with a minimum, so that, for strong interaction, L.D. again find a repulsion. This is explained by the fact that the influence of the surface charges increases more rapidly with increasing interaction than the influence of the diffuse charges. For flat plates the former is never able to overcome the latter, as at any distance between the plates the diffuse charge is always at a higher potential (resulting from the second double layer) than the surface charge of the first plate, because the diffuse charge is nearer to the second plate than the surface charge is. For spherical particles, however, it may happen that the surface charge is at a higher potential than the corresponding diffuse charge. This may easily be seen by considering the case of a very expanded double layer. If two particles are then brought close together the first particle is practically at the potential of the second; but the first diffuse layer is practically at the potential of the second diffuse layer, which is certainly lower than the potential of the particle. Consequently the positive contribution by the surface charges to the energy outweighs the negative contribution of the diffuse charges, and the attraction will therefore change into a repulsion.

#### § 4. Langmuir's method

The work of Langmuir differs essentially from that of all other authors, including the considerations submitted in the present work. The main difference originates from the circumstance that, according to Langmuir, the London-Van Der Waals attractive forces are not able to act at a considerable distance, through the medium of the sol, as assumed by De Boer and Hamaker and all subsequent authors. Langmuir accordingly had to look for an alternative source of attractive forces, and he believes that they are found in the electric forces acting between ions and charged particles. In order to show this he considers, instead of two interacting particles, the colloid system as a whole. Only in the second part of his paper he passes over to the case of two particles in order to investigate the phenomena occurring when the particles approach each other more closely. As already stated in Ch. V, § 3 Langmuir derives there a general equation for the repulsive force which is completely correct. The present discussion, however, is entirely restricted to the theory developed in the first part of Langmuir's paper, treating the colloid as a system of many particles.

Langmuir starts from the statement that a sol possesses a tendency to contraction owing to the mutual attraction of sol particles and oppositely charged counter-ions, and makes a comparison with an expanded NaCl crystal, where the mutual attraction of  $\text{Na}^+$  and  $\text{Cl}^-$  exceeds the mutual repulsion of equally charged ions, contraction occurring until a further decrease of the lattice constant is prevented by the "dimensions" of the ions. He assumes that under certain conditions this inclination towards contraction will be stronger than the "pressure" or inclination towards expansion caused by thermal

motion. If this is the case free energy will be gained if the system separates into two layers, a concentrated sol (coacervate or coagel) and a liquid almost devoid of colloid matter. In order to prove this, L. makes use of the Debye-Hückel theory for the osmotic pressure of strong electrolytes, more especially of the equation:

$$\rho = kT \sum n_i - \frac{e^2 \kappa}{6\epsilon} \sum n_i v_i^2, \quad (105)$$

and applies this relation to the colloid solution as a whole, i.e. to all charge-bearing particles including the colloid-ions. In this equation, the first term represents the osmotic pressure of all dispersed particles if they were uncharged (ideal gas term), the second term gives the decrease in osmotic pressure due to the fact that each ion or sol particle is captured by its ionic atmosphere. Thus, L. tries to prove that, under certain conditions, the second term outweighs the first and changes the properties of the system.

If we consider a pure sol, i.e., a colloid containing only little electrolyte in the sol medium, the system is built up of colloid-ions and an equivalent amount of counter-ions only, and it is treated as a simple "electrolyte" in which one of the ionic species carries a very high charge ( $v_1 \gg v_2$ ). Introducing two constants  $C_1$  and  $C_2$  eq. (105) may be written in the form (after substitution of  $\kappa$ ):

$$\rho = C_1 n \left( \frac{1}{v_1} + \frac{1}{v_2} \right) - C_2 n^{3/2} (v_1 + v_2)^{3/2} \approx C_1 \frac{n}{v_2} - C_2 n^{3/2} v_1^{3/2}$$

(in which  $n = n_1 v_1 = n_2 v_2$  = the equivalent concentration). This relation shows that the osmotic pressure according to eq. (105), initially increasing with increasing sol concentration, will finally reach a maximum and decrease again beyond it. The maximum is reached for a concentration which is the smaller, the higher the charge of the particles. In the concentration region considered, therefore, L. still assumes that the charge on the particles is constant. For very large concentrations, however, the charge will have to diminish again in order to maintain the value of the surface potential on the particles. This problem is treated in more detail in the last section of L.'s paper for the model of two flat plates, and he there gives the expression for the repulsive force already mentioned in Chapter V of the present work. L. assumes that this effect becomes important for concentrations higher than that corresponding to the maximum, and the result will be that, in the second term,  $v_1$  is diminished; the influence of this term is decreased, and osmotic pressure will accordingly

increase once more. Consequently, osmotic pressure as a function of  $n$  will show qualitatively the form represented in Fig. 54. This very much resembles a Van Der Waals isotherm (equation of state), and the system will separate into two layers.

If other electrolytes are added to the system, eq. (105) is slightly more complicated; but similar considerations may hold, showing that the salt concentration influences the colloid concentration at which  $\rho$  reaches a maximum.

L. believes that, in this way, he can explain both the phenomena observed in pure sols and those obtained by the addition of electrolytes (coacervation of proteins, coagulation of lyophobic sols).

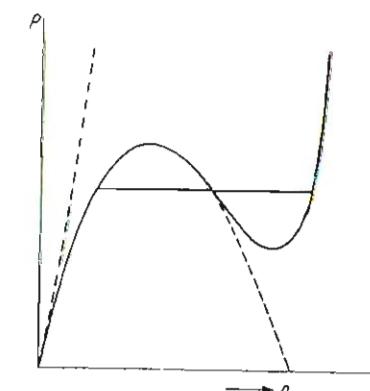


Fig. 54. Osmotic pressure ( $\rho$ ) as a function of the solconcentration ( $n$ ) according to Langmuir's theory.

Although it may be admitted that this theory is rather ingenious, very serious objections must be raised against it.

We observe that the important  $n^{3/2}$  term in Langmuir's theory originates from the fact that the amount of energy necessary to liberate all ions (or particles) from their ionic sphere, besides being proportional to  $n$  (the sol concentration) is moreover proportional to  $\kappa \sim n^{1/2}$ , because this amount of energy increases if the ionic sphere concentrates around each ion (particle).

It is important to stress here the danger involved in the use of the linear approximation characteristic of the Debye-Hückel theory. Indeed, when applied to the colloid-electrolyte, this theory would show that the thickness of the double layer is inversely proportional to the square root of the sol concentration. The double layer theory, however, shows that this thickness is determined by the electrolyte concentration

in the sol medium, far from any particle, and is, therefore, independent of the sol concentration (in dilute sols). This difference is caused by the different treatment. According to the picture presented by the D.H. theory, the double layer surrounding a sol particle would contain both other sol particles and counter-ions. Hence at a point where the potential is  $\psi$  it would contain a surplus fraction  $v_2 e\psi/kT$  of the latter, and of the former a deficiency of  $v_1 e\psi/kT$ . Both together would determine the thickness of the double layer (or rather, because  $v_1 \gg v_2$ , only the colloid ions: indeed  $z$  is proportional to  $\sqrt{n} (v_1 + v_2)$ ). According to the picture of the double layer theory, each colloid particle moves in the sol surrounded by its sphere of counter-ions. For dilute sols, the latter picture, definitely agrees better with reality. As pointed out before, the use of the D.H. approximation for the ions in the field of the double layer is already precarious. Hence we need not be surprised if we obtain erroneous conclusions when we apply this approximation to the colloid ions themselves, where the charge, and therefore  $ve\psi/kT$  is still much larger. (For the modest particle charge  $v_1 = 10$ , the use of the approximation is equivalent to the fact that, for a point in the neighbourhood of a particle, where for instance  $\psi = 25$  mV, one does not set the concentration of the colloid ions proportional to  $e^{-10}$ , i.e. practically zero, as in the double layer theory, but proportional to  $-9!$ )

The conclusion is that equation (11) is inadequate for calculating the osmotic pressure of a sol. It is more likely that this pressure will, for a diluted sol, approach the value  $p = kT.n$  (sol particle plus counter-ions one kinetic unit). Besides, there are other objections to the use of equation (11), for example the fact that the potential due to the ionic atmosphere at a considered (colloid) ion under consideration is really proportional to

$$\frac{x}{1+xa} \quad (a = \text{radius of particles}).$$

instead of to  $z$ , and therefore becomes independent of the sol concentration for  $xa \ll 1$  (soon reached for the colloid ion). The above considerations are, however, sufficient to prove that Langmuir's theory of the attraction force between the particles is untenable.

To conclude these considerations we will mention one more point raised by L. This author criticises Hamaker for using energy diagrams in the problem of the stability of colloids without taking account of thermal motion. As we have adopted the same method, this criticism would apply equally to our own work. It may be said in reply that, in our theory,

the thermal motion of the ions (by far the most important term) has certainly been taken into account by taking the diffuse double layer as a starting point. The question of whether the thermal motion of the particles can cause the stability of a sol was already investigated by March, who arrived at the conclusion that this factor is utterly insufficient. We may add that the thermal energy of the particles has been introduced into our theory by the application of Fuchs's theory of slow coagulation (Chapter XII).

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