COAGULATION AND FLOCCULATION

GENERAL INTRODUCTION

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If colloids are defined as dispersed systems with particle sizes ranging between atomic dimensions and microscopic visibility, the fundamental problem of colloid science is: What determines the degree of dispersion? This problem has obviously two aspects. One aspect is concerned with the size and shape of the individual particles, the other aspect with the question whether the particles are free and independent or whether they are united in large aggregates. Using the terminology of the phase rule somewhat loosely, the question is: What determines whether a colloidal system is a one-phase liquid, *a sol*, a one-phase solid, *a gel*, or whether by *coagulation, flocculation* or *coacervation* it separates into two macroscopically distinct phases?

This problem cannot be treated without considering the existence of two types of colloids, the irreversible, hydrophobic type, for which the gold sol is the classical example and the reversible, hydrophilic type exemplified by proteins, soaps and the like.

With hydrophobic systems the dispersed state is never a state of true equilibrium. It is only the presence of energy barriers that prevents the dispersed particles from coagulating and forming a stable precipitate. For these systems stability of the dispersions and loss of stability by coagulation therefore have a very pronounced kinetic aspect. With hydrophilic systems, however, both the dispersed and the flocculated or coacervated states may be true equilibria and these equilibria are often more important than the kinetics leading to them.

A common point in the study of both types of systems is that our ultimate interest is not in the directly observable kinetics or equilibrium states, but in the mutual interactions of the particles and those between particles and dispersion medium, allowing us to explain the observable properties.

Interactions occurring very generally are electrical forces connected with the charge of the particles and leading as a rule to a repulsion between them. Indeed, the connections between colloid stability and electrical phenomena are so close, that in the General Discussion on the Electrical Double Layer [1] that the Faraday Society had intended to hold in September 1939 most of the subjects that will be discussed in the present meeting have been treated already and in a number of cases even by the same authors. Personally I feel that notwithstanding the dissimilarity in the titles the present Discussion is a natural continuation of that on the Electrical Double Layer of 1939. The period of 15 years between the two events has served to elaborate many of the ideas already present around 1940 and to improve the quantitative aspects of the theories and to design special experiments to test the theories. In fact, the last 20 years might be considered as the period in which the study of colloids has evolved from an art into an exact and quantitative science.

Unfortunately work has been hampered by the war and its aftermath and especially the lack of contact between different groups of investigators has been a serious drawback. We should therefore feel all the more grateful to the

Organizing Committee of the present General Discussion on Coagulation and Flocculation, not only for having it organized at this moment but especially for having given it a very international character. I hope that nobody will feel his own work passed by, if I make special mention of the importance of the Russian contributions to this Discussion.

I just mentioned *forces of electrical origin* as very important. Their existence seems to be well established. The principles on which they have to be treated are clear. However, the quantitative side of the treatment in cases with high charge densities still leaves much to be desired and adequate experimental data are still lacking in all but the most simple cases.

Other generally occurring forces are of the *dispersion or London-van der Waals* type. They will in most cases cause attraction and promote coagulation. Although they have been incorporated into present theories of colloid stability, together with electrical forces, their actual role is still open to discussion. Quantitative data are scarce and even conflicting. It is hoped that this Discussion, if it does not solve the conflict, will at least stimulate further research in this field.

In several papers presented at this meeting a third type of force is mentioned, viz. the *repulsive action of adsorbed layers or solvation layers* not connected with electric charges. It would be of value if these ideas could be cast into a more quantitative form.

Finally it is evident that flocculations between antigens and antibodies, as mentioned in part III of this Discussion are based upon very *specific*, presumably *short range interactions*. It will be one of our tasks to consider how far the more general, non-specific interactions mentioned above are also important in biological systems.

In part II on Coacervation, we shall meet cases where consideration of forces alone, though important, is insufficient. Cases of true phase equilibria can only be understood by combining forces or energy with entropy.

I have been asked to give an introduction to the first part of this Discussion, which will be devoted to *classical coagulation*, that is to the stability of hydrophobic suspensions and emulsions and to closely related subjects. From the remarks made above it will be clear what I consider the main lines of investigation in this field. They are: kinetics of coagulation and especially the modification of the kinetics by interactions between particles. Still more fundamental are investigations on the forces of interaction themselves. Keeping these principles in mind, the contributions to part I can be grouped in a very natural way.

Two papers, one by Derjaguin and one by Sparnaay and myself aim at a direct determination of the force between suitable objects. Although the ideal, the determination of a complete curve of interaction between two " particles " separated by an electrolyte solution is still far away, experiments such as those of Derjaguin and Malkina hold considerable promise and show the feasibility of this type of approach.

Norrish in his study on the swelling of clays also obtains rather direct information on forces between clay particles.

One of the advantages of direct determination of forces with macroscopic objects over derivation of particulars of interaction from flocculation kinetics is that the larger surfaces used in these investigations are more homogeneous and better defined in their electrical and other properties. How bad the inhomogeneity of the surfaces of small particles can be is well illustrated by Schofield and Samson's contribution on the flocculation of kaolinite, which is caused by the mutual attraction of negative and positive regions that coexist on the same particle. Rehbinder also points to the heterogeneity along the surface of the particles as a prerequisite of thixotropy and gel formation.

Kinetics of coagulation will also receive due attention. All the contributions in this field are still based upon Smoluchowski's admirable analysis[2] of 1916.

It is probably fitting to introduce in this Discussion the distinction between *initial rate of coagulation* and *complete coagulation kinetics.* The initial rate is only concerned with the formation of binary particles from single ones, whereas the complete kinetics have to include multiple particles as well. Lawrence and Mills point out the advantage of using emulsions, because primary as well as multiple particles are truly spherical. The present author believes, however, that spherical multiple particles are only obtained if coagulation is followed by coalescence and thus in point of fact one studies a succession of two essentially different kinetics.[3]

The other papers on kinetics are all concerned with the initial rate of coagulation. Booth extends Smoluchowski's method to non-spherical particles. Derjaguin calculates the rate of flocculation for pairs of dissimilar particles. Reerink and myself have determined initial rates of coagulation in different electrolyte solutions and used these data to obtain information on forces between particles in the form of surface potentials and van der Waals' constants.

Quite often the colloid chemist, in studying coagulation, takes the size of the primary particles as given. In this Discussion, however, we shall hear many contributions on sols *in statu nascendi.* The subject would seem difficult combining as it does the processes of crystal nucleation and crystal growth with actual coagulation. But being the first step in any preparation of a sol and starting with well-defined pure solutions, it has attracted many investigators. Težak's contributions belong to this field, so do those of French and Cobbett, of Packter and Matalon, and of Jonker and Kruyt.

Težak's work should also be mentioned in another respect. His ideas on the theoretical background of stability and flocculation deviate markedly from those of most of the other contributors. He considers present theories of colloid stability as " somewhat too speculative and unable to embrace many important experimental findings ". As an alternative he proposes an empirical relation between Bjerrum's distance and the flocculation value. Now it is immediately conceded that the quantitative agreement between the present rather coarse and schematized theories and experiments is never very good and that notably one of the weak points in the theory of electrical interaction is the inadequate treatment of short-range interactions between particles and counterions (Stern[4] theory). In my opinion the question should be put in the following way: Is the partial agreement that exists good enough to make further refinement of the theory and related experiments promising, or should we deduce from the lack of agreement that present theories are on the wrong track ? And if so, what is the right track and how do we know it is?

The first part of our programme is typical *hydro*phobic, in that it is concerned nearly exclusively with aqueous solutions as dispersion media. It may be good that in a paper by Koelmans and myself non-aqueous solvents are considered and that even in completely non-polar solvents repulsion by Coulomb forces is often found to be the stabilizing mechanism.

I hope that these remarks, none of which are very new or original, may be of some use as a framework to guide our discussions.

[1] *Trans. Faraday Soc.*, 1940, **36**, 1-322, 711-732.

[2] Smoluchowski, *Physik. Z.*, 1916, **17**, 557, 585; *Z. physik. Chem.*, 1917, **92**, 129.

[3] see van den Tempel, *Thesis* (Delft, 1953); *Rec. trav. chim.*, 1953, **72**, 419 433 442.

[4] Stern, *Z. Elektrochem.*, 1924, **30**, 508.

GENERAL DISCUSSION

Dr. E. J. W. Verwey and Prof. J. Th. G. Overbeek (*van't Hoff Laboratory, Utrecht*) (*communicated*): In footnotes to his Discussion papers Prof. Derjaguin has reproached us with failing to quote several of his papers [1, 2] in our monograph [3] on the same subject and with asserting our priority for the explanation of the stability of strongly charged sols.

We admit these facts and we want to express our great regret that we have overlooked these papers [1, 2] in writing our monograph. Especially the 1941 paper by Derjaguin and Landau contains already the essential elements of the theory of the stability of hydrophobic colloids as treated in our monograph,[4] notably a combination of van der Waals' forces with double layer theory for high potentials and it is certainly prior to our own publications on the subject.

We feel that we may be partly excused for overlooking these papers because all the work for our monograph was performed during the war when the German

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[1] Derjaguin, *Trans. Faraday Soc.*, 1940, **36**, 730.

[2] Derjaguin and Landau, *Acta physicochim.*, 1941, **14**, 633; *J. Expt. Theor. Physics* (*Russ.*), 1941, **11**, 802; *J. Expt. Theor. Physics* (*Russ.*), 1945, **15**, 662. This is a second printing of the paper in Russian of 1941.

[3] Verwey and Overbeek, *Theory of the Stability of Lyophobic Colloids* (Elsevier, Amsterdam, 1948).

[4] Verwey, *Chem. Weekblad.*, 1942, **39**, 563 (in Dutch).

occupation of our country cut us off from all Allied information and the papers [1, 2] were published during this occupation. We are grateful to Prof. Derjaguin for now having pointed out our omission and for having provided us with photostat copies of the relevant papers.

It can be shown that our work was independent of Prof. Derjaguin's later publications by pointing to the existence of a number of publications [4-9] prior to our monograph [3] where especially the 1944 one (of which the 1945 one is a nearly literal translation) contains already all the essentials of our work.

Summarizing we may say that:

(i) We want to express our regret for overlooking some of Prof. Derjaguin's papers;[1, 2]

(ii) we recognize Derjaguin and Landau's priority in formulating a theory of colloidal stability based on a quantitative combination of van der Waals' attraction with repulsion of Gouy-Chapman double layers;

(iii) our own work on the stability of colloids has been independent of Prof. Derjaguin's papers published between May 1940 and 1945.

Prof. B. Derjaguin (*Academy of Sciences of U.S.S.R., Moscow*) (*communicated*): I should like to express my full satisfaction at the reply of Prof. E. J. W. Verwey and Prof. J. Th. G. Overbeek to my remarks concerning the historical aspects of the development of the theory of the stability of lyophobic colloids.

In concluding I must stress that, on my part, I also very highly appreciate Verwey and Overbeek's work in this field, summed up in their book in an exceptionally clear and systematic form. This book contains much material not discussed by me, e.g. the interpretation of peptization phenomena and the considerations based on the application of the Stern theory, just as my and Prof. Landau's papers contain points not touched by Verwey and Overbeek, e.g. some results concerning the coagulating effect of asymmetric electrolytes (treated also in Prof. Levine's remark).

Dr. R. S. Bradley (*University of Leeds*) (*communicated*): Some years ago I studied the force of attraction between spheres of silica which had been fused.[10] The attraction was measured *in vacuo* in the presence of a radioactive deposit. I showed theoretically that a law of force λ'/r^n between molecules gives an attractive force between spheres of radii r_1 and r_2 equal to

$$\frac{4\pi^2 q^2 \lambda'}{(n-1)(n-3)(n-4)(n-5)}\left(\frac{r_1 r_2}{r_1 + r_2}\right)\frac{1}{d^{n-5}},$$

where q is the number of attractive molecular centres per cm^3 and d is the nearest distance apart of the spheres (i.e. the smallest distance between the centres of the surface molecules of one sphere and those of the other). The dependence of the

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[1] Derjaguin, *Trans. Faraday Soc.*, 1940, **36**, 730.

[2] Derjaguin and Landau, *Acta physicochim.*, 1941, **14**, 633; *J. Expt. Theor. Physics* (*Russ.*), 1941, **11**, 802; *J. Expt. Theor. Physics* (*Russ.*), 1945, **15**, 662. This is a second printing of the paper in Russian of 1941.

[3] Verwey and Overbeek, *Theory of the Stability of Lyophobic Colloids* (Elsevier, Amsterdam, 1948).

[4] Verwey, *Chem. Weekblad.*, 1942, **39**, 563 (in Dutch).

[5] Verwey, *Tweede Symposium over sterke electrolyten en over de electrische Dubbellaag* (Utrecht, 3 and 4 July, 1944), pp. 111-132 (in Dutch).

[6] Verwey, *Philips Res. Rep.*, 1945, **1**, 33 (in English).

[7] Overbeek, *Grenslaagverschijnselen* (Symposium 5 and 6 July, 1946), *Verhand. Kon. Vlaamse Acad. Wetenschappen, Letteren en Schone Kunsten van Belgie*, 1947, pp. 130-156 (in Dutch).

[8] Verwey and Overbeek, *Trans. Faraday Soc.*, 1946, **42*B***, 117.

[9] Verwey, *J. Physic. Chem.*, 1947, **51**, 631.

[10] Bradley, *Phil. Mag.*, 1932, **43**, 853.

force on $r_1r_2/(r_1 + r_2)$ was verified experimentally and from the slope of the graph of force against $r_1r_2/(r_1 + r_2)$ and a plausible value for d we may find λ' and hence λ. It is interesting to observe that if we assume that the surface consists of oxygen atoms and assign to d the value of twice the van der Waals radius of oxygen (van der Waals radius $\sim 1{\cdot}4$ Å) we obtain from these experimental results a value of $\pi^2q^2\lambda = 2 \times 10^{-12}$ ergs, which is near to that predicted. It should be noted that for $n = 7$, $\lambda'/(6r^6) = \lambda/(r^6)$, where λ, as used by Overbeek and Sparnaay, is such that the energy between two molecules is given by λ/r^6.

The assumption of a molecular surface of oxygen is likely in view of the way in which the spheres were prepared in air, although the nature of the valencies of the underlying silicon atoms are uncertain, and there may be some vacancies in the surface where SiO molecules have vaporized.[1]

Prof. B. Derjaguin and **Prof. I. Abricossova** (*Academy of Sciences of U.S.S.R., Moscow*) said: Prof. Overbeek and Dr. Sparnaay's paper on London-van der Waals' attraction between macroscopic objects deals with the same problem as the second paragraph of our paper on surface forces written in collaboration with I. Abricossova. But the results of Prof. Overbeek and Dr. Sparnaay's studies, in contrast with ours, are at variance with the modern theory of molecular long-distance forces. As has been repeatedly noted by Verwey and Overbeek in their earlier studies,[2] Casimir and Polder's theory leads to the conclusion that at distances exceeding 1000 Å interaction should decay with distance one power of distance greater than given by London's law. In Prof. Lifshitz's theory of the interaction of macroscopic bodies [2] containing no special assumptions, and especially no groundless or rough approximations, the conclusion is drawn in the most general way that the interaction force at the long distances to which Prof. Overbeek and Dr. Sparnaay's experiments are undoubtedly related should decrease as the inverse fourth power of the gap width between plane bodies and also should be much smaller but not greater than according to London-Bradley-de-Boer-Hamaker's extrapolated formula.

This conclusion is in accord wih the results of our measurements, which moreover show a much better reproducibility than the results achieved by Prof. Overbeek and Dr. Sparnaay. Our personal experience in studying molecular attraction between macroscopic bodies has led us to the suggestion that the reason why there is a difference between Overbeek and Sparnaay's results and conclusions on the one hand and ours and Casimir-Polder and Lifshitz's theory on the other may consist in the fact that Prof. Overbeek and Dr. Sparnaay did not take sufficient precautions to remove electrostatic charges from the glass surfaces.

While working over this problem we found that the removal of charges by ionizing agents, even with the more favourable shape of the gap between the plane and the sphere as used in our experiments, is only possible under the necessary condition that the surfaces are preliminarily separated for several mm and the period of ionizing action is not less than 30 min or 1 h. Otherwise the interaction forces became invariably of the same order of magnitude and character as in Prof. Overbeek and Dr. Sparnaay's experiments and the reproducibility was poor. This circumstance can be easily and naturally explained by the fact that in the narrow air gap the number of ion pairs which might arise as a result of ionization is not sufficient to compensate or neutralize the charges responsible for the electrostatic interaction forces which, according to our observations as well as those of Overbeek and Sparnaay, decrease quickly in such cases as the gap is increased. Prof. Overbeek and Dr. Sparnaay assert that such a rapid decrease indicates the non-electrostatic nature of the effect. This assertion is correct for homogeneous or almost homogeneous surface charge densities. For

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[1] cf. Brewer and Edwards, *J. Physic. Chem.*, 1954, **58**, 351.

[2] Verwey and Overbeek, *Theory of the Stability of Lyophobic Colloids*, 1948, pp 105, 185; *Colloid Sci.*, ed. Kruyt, 1952, pp. 266, 269.

a heterogeneous charge density this assertion is obviously incorrect. As a matter of fact any unhomogeneous distribution of charges of like signs can be obtained by means of the superposition on the homogeneous electrification of a mosaic distribution of charges of both signs over the surface with the algebraic sum of charges equal to zero.

The interaction of these charges, separated by the gap and displaying some mobility or even displacement along the surface, will lead to the state in which the areas carrying opposite charges will be located more often in front of one another on both sides of the gap, which in its turn will lead to the resultant attraction. This attraction will decrease rapidly with the distance if these micro-areas are sufficiently small compared with the width of the gap. Therefore, the steep decrease with distance does not prove the molecular origin of the corresponding forces. Prof. Overbeek and Dr. Sparnaay's experiment with thin semi-transparent metal layers on a glass surface also does not seem convincing. It is well known that such thin metal layers may not possess the conductivity of the metal in bulk and therefore cannot guarantee the removal of charges or their homogeneous distribution over the surfaces.

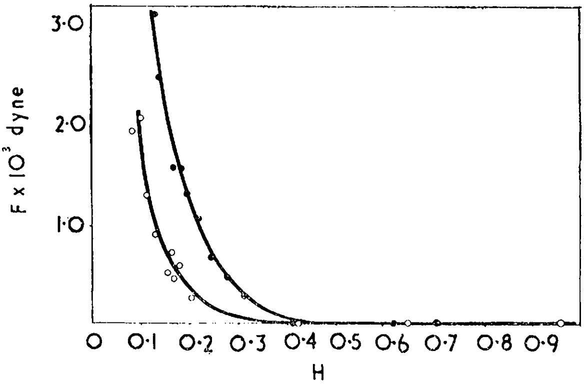

FIG. 1.—The force of attraction of a quartz plate and a quartz sphere of radius 10 cm (○○○) and 26 cm (●●●) *in vacuo* plotted against the gapwidth in microns.

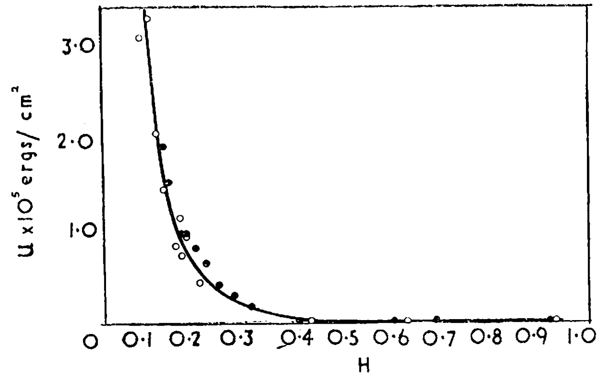

FIG. 2.—The energy of attraction per cm^2 of quartz plane surfaces calculated from experiments with spheres of radius $R = 10$ cm (○○○) and $R = 26$ cm (●●●) plotted against the gapwidth (*in vacuo*) inmicrons.

The only necessary and sufficient criterion of the molecular nature of interaction forces observed can be a reproducibility of the force values and impossibility to reduce them further by any treatment, especially by any ionizing agents with a sufficient width of the air gap. In our opinion, our experiments, but not those of Overbeek and Sparnaay, agree with this criterion.

It therefore seems to us that there are no grounds for doubt as to the applicability of Lifshitz's theory, which has in essence a semi-phenomenological character and which covers as special limiting cases both London's theory and that of Casimir and Polder (for metals in particular).

In conclusion, we should like to note the following advantages of our method as compared with Prof. Overbeek and Dr. Sparnaay's method.

(i) The application of the negative feed-back coupling enables one to measure considerably smaller forces with a greater precision and ease than in using Prof. Overbeek and Dr. Sparnaay's method. At the same time, our method readily permits altering the period and sensitivity of the set-up over a wide range.

(ii) The use of a plane surface and a spherical one, instead of two plane surfaces, enables the removal of charges and dust particles to be effected from a considerably smaller area, simplifies the adjustment of surfaces, facilitates the measurement of the gap width by means of Newton's rings and makes it possible, through varying the radius of the sphere, to verify the reliability of the results obtained and to avoid errors due to the surfaces not being parallel and flat enough. The precision, reproducibility and reliability of our measurements are illustrated by fig. 1 and 2. In fig. 1 the attraction force F measured *in vacuo* is plotted against the gap width H for the sphere of radius $R = 10$ cm (circles) and $R = 26$ cm (points). In fig. 2, the results of fig. 1 are used to plot the energy of interaction per cm^2 of quartz plane surfaces against the gap width H. The full line represents formula (9) of Lifshitz's theory [1] wherein the value of dielectric constant of quartz is substituted. The practical coincidence of both sets of points with the theoretical curve in fig. 2 demonstrates the precision and strict reliability of our measurements and the molecular nature of forces measured.

Fig 2 shows also that out results are in exact quantitative accord with the theory of Lifshitz. This is a striking proof of the theoretical formula containing no empirical constants.

Prof. Dr. J. Th. G. Overbeek (*van't Hoff Laboratory, Utrecht*) said : It is difficult to explain the large difference in the value of the van der Waals' constant as found in Derjaguin and Abricossova's experiment on one hand and in Sparnaay's and my own experiment on the other. Prof. Derjaguin's suggestion that our results are disfigured by a large electrostatic component is not in agreement with the fact that we took exactly the same precautions (and some additional ones) as used in their experiments. A radioactive source was always present, distances between the plates were often increased up to 4 cm. Some experiments were continued several days without change in interaction.

Looking for a type of error that might lead to too low a result in Derjaguin and Abricossova's experiments, two suggestions can be made. The presence of dust particles or gel particles between the lens and the plate would counteract the attraction. Is it certain that they were avoided? In our own experiments Dr. Sparnaay has observed several times that prolonged increasing of the air gap resulted in a smaller attraction but this was always coupled with a loss of the free vibration of the upper plate, a clear indication of the presence of obstacles between the plates.

Friction in the agate bearings of the balance might be another source of error. It would lead to a bending of the balance beam rather than allow an actual turning in the bearings. Thus the displacement of the mirror S (see fig. 5, 6) would be much smaller than the corresponding displacement of P.

Prof. B. Derjaguin and **Prof. I. Abricossova** (*Academy of Sciences of U.S.S.R., Moscow*) said; Overbeek in his reply to my discussion remarks concerning his

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[1] Lifshitz, *C.R. Acad. Sci. U.S.S.R.*, 1954, **97**, 643.

and Dr. Sparnaay's report makes an attempt to account for the divergence of the order of 10^3-fold between the results of his and our experiments by questioning the correctness of our measurements He points to two sources of error: the interference of dust particles and the friction in the " agate bearings ".

To Overbeek's question as to whether the effect of dust particles was eliminated we may answer without ambiguity: yes, it was. A method of their removal had been carefully elaborated and, which is the main point, the accidental presence of dust particles capable of affecting the results was in all cases readily revealed by the development of repulsive forces on narrowing the gap. In such cases the experiment was stopped. In our apparatus the repulsive forces could be registered with the same degree of accuracy as the attractive ones. The measurements were not carried out unless the narrowing of the gap down to 0·05-0·1 μ revealed no forces but those of attraction.

As regards the friction on the " agate bearing " the question seems to be due to a misunderstanding. The term " bearing " was used in my report to denote an agate plate supporting an agate prism and not in the sense of a sliding or rolling friction bearing of any kind.

The English engineering term "*fulcrum* bearing" was expressly used in my report to avoid such misunderstanding. Moreover, fig. 5 clearly shows that the geometric axis of rotation was the line of contact between the sharp edge of an agate prism and a plane of an agate plate as in an ordinary analytical balance.

In a good analytical balance with the total weight of the beam and pans not exceeding a few tens of grams, the friction does not prevent weighing with a sensitivity to 10^{-5}-10^{-6} g. As is well known, friction is approximately proportional to the load. This accounts for the fact that our balance, with a balance beam weighing *ca.* 0·2 g, yielded an effective sensitivity of from 10^{-7} to 3×10^{-8} g. That such sensitivity was actually attained and that the value (in g) of the scale division of the microammeter in the feed-back coupling circuit was determined correctly (and not underestimated by a factor of 10^3-fold as Overbeek seems to presume) follows from the fact that the value of the scale division was determined by calibration of the balance, as described in the report, in the presence of the same friction on the fulcrum bearing which existed during the actual measurements. It follows that all the factors which could affect the value of the scale division and the sensitivity of the apparatus in the course of measurements had also been present in the process of calibration and were therefore automatically allowed for.

That Overbeek's attention, instead of noting the above circumstance, has been called to the " possible " bending of the balance beam arm carrying the mirror * seems to be due to the fact that he has not fully grasped the idea underlying the application of feed-back coupling to the process of weighing.[1]

Negative feed-back coupling has rendered our balance an apparatus in which the moment of the measured force is " automatically " balanced by the moment of the electromagnetic forces acting on the coil. The balance sensitivity therefore depends exclusively on the number and shape of the coil turns and on the magnetic field intensity, but neither on the extent of bending of the beam nor on the sensitivity of the photoelectric relay. The balance sensitivity (value of scale division) could therefore be determined by Ampère's law, the results being in agreement with those of direct calibration. It follows that the balance sensitivity was determined correctly and was unquestionably sufficient to measure forces 10^3-fold smaller than those which would correspond to Overbeek and Sparnaay's experiments and conclusions.

Moreover, had the frictional forces appreciably exceeded the sensitivity of our balance (10^{-7} g), rending it spurious, or had any other sources of error been

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* It is hard to understand how the molecular forces acting on the *left*-hand arm of the beam can bend the *right*-hand arm carrying the mirror.

[1] Derjaguin, *C.R. Acad. Sci. U.S.S.R.*, 1948, **61**, 275.

present, the reproducibility of our measurements would certainly have disappeared. Hence, Overbeek's doubts as to the correctness of our measurements are based on a misunderstanding and are inconsistent with the character of the results obtained.

It may accordingly be stated that if Overbeek and Sparnaay's measurements of the forces are also correct at least in the order of magnitude (which we have no reason to doubt), then the divergence of the order of 10^3-fold between his and our results remains a real fact. Inasmuch as no treatment of the surface and no effect of ionizing agents can reduce the molecular forces to one-thousandth or even to one-half, it should be concluded that only one-thousandth part of the forces measured by Overbeek is of the van der Waals nature, the rest having some other, evidently electrostatic origin.

From Overbeek's reply we learn that prior to the action of the ionizing agents he and Sparnaay moved the surfaces to a considerable distance apart in the same way as was done in our experiments. In some cases we also sometimes failed to reduce the forces to stable reproducible and ultimate values by prolonged ionization alone, even with wide gaps. In most cases, however, this could be achieved after preliminary more thorough cleaning of the surfaces (e.g. in glow discharge). In some cases we suspected the effects of contamination of the surfaces by organic substances, e.g. by traces of shellac (which were subsequently carefully avoided). All this leads us to the suggestion that this effect is due to the presence of foreign films on the surfaces. An essential feature of the attractive forces observed in such cases is their hysteresis which accompanies the variation of the gap width as has been noted in our first publication [1] on this investigation. The hysteresis effects exhibited by the interaction forces in these cases, as well as their high values which exceed the maximum values corresponding to metals according to Lifshitz, suggest their electrical nature (perhaps associated with spontaneous bulk electrification) rather than molecular one.

Mr. H. B. Klevens (*Pittsburgh, Pa.*) said : It would appear that the roughness factor of the glass and quartz samples would be of extreme importance in the measurements of London-van der Waals' forces. With extremely fine rouge, as well as by carefully controlled chemical polishing, we have not been able to rid our samples of grooves and scratches which may be as large as 10^4 Å, although better results were obtained with chemical polishing. Metal spattered on a number of these samples appeared to exaggerate this effect in that the apparent difference between the top and bottom of the grooves increased.

These results might tend to explain the scatter observed in fig. 3. With flat surfaces, as well as with one flat surface and one curved surface as used by Prof. Derjaguin, this roughness factor may be of some import, and it may explain the differences reported by Prof. Overbeek and by Prof. Derjaguin.

Prof. B. Derjaguin and Mrs. I. Abricossova (*Academy of Sciences of U.S.S.R., Moscow*) (*communicated*): The accidental grooves and scratches, as well as general roughness, could not have much effect on our measurements of molecular attraction, as the force measured represents an effect integrated over the surface.

Accordingly, the scatter of the results (depending on all sources of errors) obtained for different parts of surfaces and different quartz pieces, even of different curvature, amounted to no more than some scores of percents. Therefore the 10^3-fold divergence between Prof. Overbeek's and our own results has no relation to surface irregularities.

Prof. Dr. J. Th. G. Overbeek (*van't Hoff Laboratory, Utrecht*) said : In our experiments on the van der Waals forces, the distance between the plates varied between 6000 and 18000 Å. Irregularities in the surface of 1000 or even 2000 Å would not have affected the order of magnitude of the results. They might explain the rather large spreading of the results. The suggestion of Dr. Klevens to use chemical polishing is gratefully accepted.

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[1] Derjaguin and Abricossova, *J. Expt. Theor. Physic.*, 1951, **21**, 495.

Dr. D. G. Dervichian (*Inst. Pasteur, Paris*) said: Prof. Overbeek and Dr. Sparnaay should be congratulated for accomplishing the construction of their ingenious apparatus and for the delicate measurements they have undertaken. I think these experiments deserve to be quoted in text books of physics and physical chemistry as a demonstration of the van der Waals' forces.

It is to be feared, however, that the fact that these experiments are reported in this Discussion on Coagulation and Flocculation may give the illusion that the theories on the stability of colloidal systems are thus at least partly confirmed, simply because these theories make use of van der Waals' forces.

I hope that the authors will admit that their experiments demonstrate simply the existence of van der Waals' forces between macroscopic objects and the law of variation of these forces as a function of the distance. The validity or non-validity of the theory of the stability of colloidal systems cannot be deduced from the results of these experiments.

Prof. J. Th. G. Overbeek (*University of Utrecht*) said: The relation between our experiments and those of Prof. Derjaguin on van der Waals' forces and the use of these forces in the theories of the stability of colloids is of the same kind as the relation between macroscopic electrostatics and electrodynamics and their application to electrons and protons. It is a lengthy extrapolation that has to justify itself by the consequences to be drawn from it.

Prof. B. Derjaguin (*Academy of Sciences of U.S.S.R., Moscow*) (*communicated*): Prof. Dervichian expressed the opinion that the direct measurements by Prof. Overbeek and Dr. Sparnaay of the attraction between two glass plates demonstrates the existence of long-distance van der Waals' forces, but bear no relation to the foundation of the theory of stability of colloids.

I have already stated that Mrs. Abrikossova's and my own measurements (but not those of Overbeek and Sparnaay) are in strict quantitative accord with Prof. Lifschitz's modern theory of long-distance van der Waals' forces and this justifies their use as a basis for the theory of colloid stability, particularly the use of the H^{-2} law of the attraction force variation with the gap width between two spheres for *sufficiently small* values of H.

It is this law that leads to the form of Hardy-Schulze's rule, in which the coagulating effect is proportional to the sixth power of the charge of counter-ions.[1] Accordingly, such experiments as ours or those of Prof. Overbeek on macro-objects have a direct relation to the foundation of the theory of colloid stability.

I cannot agree with Prof. Overbeek's comparison of the situation with that existing in the scope of electrodynamics. The application of electrodynamics to an electron—an elementary particle—requires a fundamental change of approach rather than simple extrapolation. On the contrary, there are no evident reasons why any change should be required when applying the H^{-2} law to two colloid particles of radius $r \gg H$.

Dr. S. Levine (*Manchester University*) said: I wish to comment on eqn. (1), the fundamental formula in Derjaguin's theory of the force between two colloidal particles. Recently N. E. Hoskin, in a paper (part 1) submitted for publication, has solved the Poisson-Boltzmann (P.-B.) equation for the potential distribution in the double layers of two identical spherical particles, which have a uniform surface potential and are immersed in a binary symmetrical electrolyte. The P.-B. equation was expressed in dipolar co-ordinates and then replaced by a difference equation which was solved by an iterative process on the Manchester University electronic computer. The potential was determined at a total of 144 mesh points in one quadrant of a plane containing the line of centres of the two particles. The use of dipolar co-ordinates ensured that the majority of the mesh

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[1] Derjaguin and Landau, *Acta physicochim.*, 1941, **14**, 633 ; *J. Expt. Theor. Physics* (*Russ.*), **11**, 802 ; 1945, **15**, 662.

points lay in the region between the spheres where the effect of the interaction was greatest. The following sixty different cases were chosen:

κr	1	5	15	—	—
κh	0·5	1	1·5	2	3
$ve\psi_0/kT$	2	4	6	8	—

Here κ is the characteristic parameter in the Debye-Hückel theory of electrolytes, r the radius of a particle, h the distance of nearest approach of the two particles, v the valency of the (positive) ion, e the electronic charge, ψ_0 the surface potential, k Boltzmann's constant and T the absolute temperature. Each solution of the P.-B. equation required about 40 min on the electronic computer.

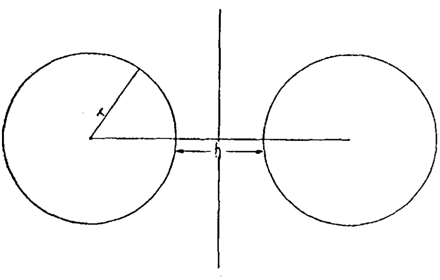

FIG. 1.

In a second paper (part 2) by Hoskin and Levine, these results have been applied to determine the interaction energy of the electric double layers of the two particles and the accuracy of Derjaguin's eqn. (1) has been tested. The most accurate method of determining this energy numerically is to integrate with respect to the separation a formula for the force which is expressed in terms of the potential distribution on the median plane. This formula reads

$$\int_{S_m}\left[\frac{\epsilon E^2}{8\pi}+\Delta\Pi\right]\mathrm{d}S,$$

where ϵ is the dielectric constant of the electrolyte dispersion medium, S_m the surface of the median plane, E the electric intensity at any point on S_m and $\Delta\Pi$ the difference in " ideal " osmotic pressure between the point on S_m and the bulk of the electrolyte. It is possible to obtain this expression for the force by differentiating with respect to the particle separation a general formula for the free energy of the electric double layers which was derived by Levine,[1] namely,

$$-W-\int_V \Delta\Pi \mathrm{d}v,$$

where W is the ordinary electrostatic energy, and V the volume of the diffuse layers (which is assumed to extend to infinity) ; here the difference in osmotic pressure $\Delta\Pi$ refers to a point in V.

TABLE 1.—RATIO OF VALUE FOR FORCE ACCORDING TO DERJAGUIN FORMULA TO VALUE OBTAINED ON ELECTRONIC COMPUTER

	$ve\psi_0/kT=2$					$ve\psi_0/kT=6$				
κh	0·5	1	1·5	2	3	0·5	1	1·5	2	3
$\kappa r=1$	0·89	0·99	1·15	1·37	1·75	0·87	0·86	0·91	0·97	1·17
$\kappa r=5$	0·97	0·99	1·01	1·05	1·12	0·95	0·94	0·93	0·92	0·94
$\kappa r=15$	1·01	1·01	0·99	0·99	1·02	0·98	0·95	0·94	0·92	0·92

The ratio of the value for the force between two spherical particles as given by Derjaguin's formula (1) to that calculated on the electronic computer are shown for $\kappa r=1$, 5 and 15 and $ve\psi_0/kT=2$ and 6. Usually the condition under which formula (1) is considered to apply is $\kappa r \gg 1$; we see that the agreement is still reasonable at $\kappa r=5$. However, the error in (1) increases not only

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[1] Levine, *Proc. Physic. Soc. A*, 1951, **64**, 781.

when κr decreases but also when the separation becomes larger. This is to be expected for when the diffuse layers of the two particles overlap very slightly and κr is not very large, a good approximation cannot be obtained by replacing the two spheres by a set of parallel rings, each pair of rings being treated as sections of infinite parallel plates. Fortunately the Derjaguin formula can be applied in the range of separations which are relevant to stability properties.

Mr. J. E. Adamson (*Hendon, N.W.*4) (*communicated*): The following explanation is advanced for the existence of a sharp boundary to the electrical double layer, suggested by Derjaguin, Titijevskaia *et al.* It also provides an alternative explanation for the electrophoretic anomaly mentioned by Koelmans and Overbeek.

It can be shown that there exists a zone of polarization at an interface, which is given by

$$P = (R_a - R_b)/8\pi, \tag{1}$$

where P is the polarization and R_a and R_b are the reaction fields of the dielectrics in contact. One can write down an expression for the dielectric phase boundary potential ρ (not necessarily identical with the electrokinetic potential ζ) which for uniform fields, is given by

$$\rho = 4\pi P\tau = 4\pi Q, \tag{2}$$

where τ is the thickness of the polarized zone and Q the integrated displacement current which flows when the phase boundary is created or destroyed.

It is easy to show qualitatively that when an electrolyte is added to a polar liquid such as water, the ions will tend to adsorb as an ion-pair lamina at the sub-interface between the polarized zone and the liquid phase, with the cations preferentially oriented towards the polarized zone. Two immediate consequences are:

(i) Since the lamina is a conductor, the electrical potential on the solution side of the lamina must be zero. Since it is also an equipotential surface, the interphasial field must be normal to it, as well as to the interface; the field is therefore uniform and at least at the saturation value. The double layer must therefore have a sharp boundary as indicated by Derjaguin.

(ii) If a d.c. potential is applied parallel to the interface, laminar ion migration will occur. Because of the different solvent structures on either side of the lamina, solvent migration will occur preferentially in the liquid phase and electroendosmosis will be observed if the second phase is fixed. Since this effect is not possible in the absence of ions, effects such as streaming potentials and electroendosmosis are not likely to be complementary unless the ion lamina is complete. It is suggested that the electrophoretic anomaly of van der Minne and Hermanie [1] and the electroendosmotic anomaly of Rutgers [2] are due to the presence of an incomplete lamina. The arguments outlined above are most useful in explaining electrokinetic phenomena in particular and have the advantage of suggesting new types of experiment similar to ballo-electricity,

The results of Derjaguin and Malkina on surface adhesion can be interpreted using the same model, for if two polarization zones, with their attendant laminae, are sufficiently close to interact, then the unfavourable charge distribution $+ - - +$, normal to the plane of contact, will produce a high energy barrier. Subsequent ionic rearrangement to the form $+ - + -$ and later migration of ions from the interface will create a time barrier. The converse process is to be expected on separating the phases. No time lag would be expected if the fibres were to make contact in the presence of water which was subsequently replaced by electrolyte.

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[1] van der Minne and Hermanie, *J. Colloid Sci.*, 1952, **7**, 600; 1953, **8**, 38.

[2] Rutgers and De Smet, *Trans. Faraday Soc.*, 1952, **48**, 635.

An important result is the existence of limiting adhesional energies of approximately 20 and 35 ergs/cm² shown in fig. 10 of their paper. The behaviour of the surface of a liquid can be studied by means of the following equations:

$$1/A = (-1/kT)\mathrm{d}\sigma/\mathrm{d}\ln p, \tag{3}$$

$$F = \sigma_0 - \sigma, \tag{4}$$

$$FA = kT/n_0. \tag{5}$$

The symbols are conventional, but σ_0 is the estimated surface tension at 0° K, n_0 is the number of polarized molecular layers below the surface, while p is the vapour pressure at T° K. Values of n_0 and FA for water are given in the accompanying graph.

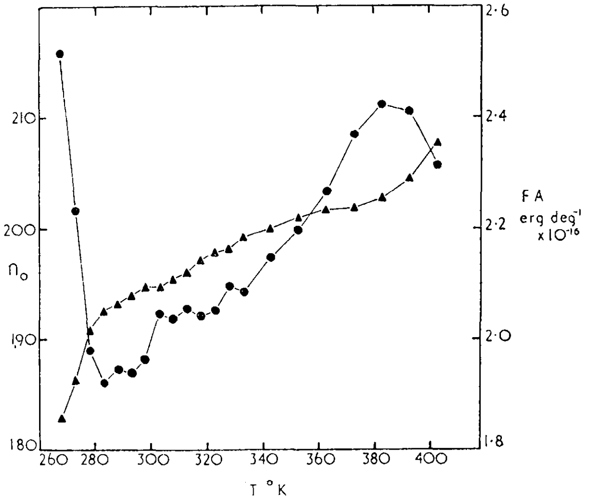

FIG. 1.—Number of polarized molecular layers and the interphasial energy for water as a function of temperature.

It will be seen that the FA curve shows arrest points at approximately 30, 50 and 95° C. The corresponding values of the polarization energy per 2 cm² of interface have been calculated and are shown below, compared with the reported limiting adhesional energies.

discontinuity temp.	30° C	50° C	95° C
polarization energy (ergs/2 cm²)	29	36	52
limiting adhesional energy (ergs/cm²)	20·5	34·8	—

The numerical agreement may be fortuitous but it seems reasonable to predict a further limiting adhesional energy at least, corresponding to the arrest point at 95°. This should have a value approaching 50 ergs/cm² at observational temperatures between 60 and 90° C. Other discontinuities of function are known to the writer in colloid and biological systems but detailed interpretation by the methods just described must await fuller investigation.

Dr. A. K. Holliday (*Liverpool University*) said: The theory advanced by Koelmans and Overbeek, that flocculation by electrolyte is the final cause of electro-deposition in non-aqueous media, is supported by the results of some experiments in aqueous medium, using a red (nuclear) gold sol. Passage of a current through the sol, using a rotating platinum gauze anode (very low current density) maintained at a potential to avoid gas evolution, did not produce any deposition of gold or any apparent change in the sol; there was no evidence of any limiting current density in the current-voltage plot. If, however, electrolyte (sodium chloride) was added to produce a slow coagulation from red to blue, then subsequent passage of current gave an adherent deposit of blue gold on the anode, and the current-voltage curve showed a rather ill-defined step, corresponding presumably to the limiting current density for the deposition process. The amount of gold deposited per coulomb, when plotted against added sodium chloride concentration, passed through a maximum; the decrease in deposition at higher electrolyte concentration was attributed to removal of sol particles by sedimentation of the rapidly coagulating sol. Using the optimum electrolyte concentration for deposition, the amount of gold deposited per coulomb was measured at various times after addition of electrolyte, and was found to pass through a maximum. Hence although addition of electrolyte must *immediately* alter the charge and ξ-potential of the particles, optimum conditions for deposition are not attained until some coagulation has occurred—it is the *coagula* which deposit, and when these grow to a size at which sedimentation is rapid, deposition necessarily diminishes. With the optimum conditions for deposition as determined above, measurements of the amount of deposition by varying currents were made. A plot of amount deposited against current gave a straight line making an intercept with the current axis, suggesting that a critical current (and therefore probably a critical potential) must be reached before deposition can begin.

Dr. C. G. Sumner (*Orpington, Kent*) (*communicated*) : In part 1 of their paper, Koelmans and Overbeek remark that Span 80 and Span 40, though ostensibly non-ionic compounds, behave as ionic stabilizers. It may not be generally realized that many commercial emulsifying agents of the partial-ester type contain small percentages of sodium soaps, e.g., in a sample of Span 40 examined in my laboratory the soap content was 0·5 %. This may account for the behaviour reported.

The flocculation theory of electrophoretic deposition, advanced in part 2, is in agreement with mechanisms suggested by other authors for aqueous systems. In a paper [1] on the anodic deposition of oleo-resinous lacquers from emulsions, submitted in 1939 for the proposed Discussion on the Electrical Double Layer, I put forward a similar indirect mechanism to explain:

(1) the existence of an initial period during which no appreciable quantity of deposit was formed, followed by a sharp drop in current as the electrode became coated;

(2) the reduction in the amount of electricity required to initiate deposition, as the applied voltage was increased, and

(3) the dependence of the weight of deposit per coulomb on variations in emulsion composition, etc.

In my own experiments, support for the coagulation theory was found in the behaviour of electrolytes, such as sodium aluminate and sodium silicate, with anions capable of yielding precipitates on hydrolysis. With aqueous sodium aluminate, for example, the passage of current resulted in a deposit of hydrated alumina on the anode on account of the local reduction in pH value. I do not know whether similar experiments are possible with methanol as solvent, but the authors may be interested in this line of approach.

Dr. R. H. Cousens (*I.C.I. Paints Division, Slough*) (*communicated*) : Using suspensions of organic and inorganic pigments in organic liquids of low dielectric constant, we have obtained results which agree quite well with those of Koelmans and Overbeek. We have used a moving boundary method because the experimental technique is simple, but the results are less precise than can be obtained

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[1] Sumner, *Trans. Faraday Soc.*, 1940, 36, 272.

from the microscopic method because boundary anomalies may occur.[1] The apparatus can be either a Burton type U-tube with two pre-formed boundaries, or a straight, vertical tube with an autogenic boundary.

Migration velocities and stability relationships have been obtained which are similar to those described in the above paper. For example, a phthalocyanine pigment dispersed in a 50 mM solution of Aerosol OT in 100°-120° C petroleum ether was negatively charged. Its velocity of migration was 0·23 μ/sec per volt/cm corresponding to a ζ-potential of about 87 mV.

Van der Minne and Hermanie[2] have shown that dispersing agents which give the suspended particles opposite signs of charge, cannot be mixed without reducing the charge and stability of the suspension. In this sense the agents may be described as antagonistic to one another. We have examined the parallel case of mixtures of two pigments which, separately, bear charges of opposite sign in the same medium. As would be expected, such mixtures are less stable and carry less charge than the component suspensions. In the mixture ranges where only partial neutralization of charge occurs, fairly stable systems are formed in which the electrophoretic migration is homogeneous, i.e. there appears to be no separation of particle species in the electric field. In contrast to this, mixtures of two pigments bearing charges of the same sign, exhibit independent migration, i.e. the particle species move with their individual velocities, so that two boundaries are formed.

Preliminary examination indicates that the ζ-potential as calculated from Hückel's equation is independent of the viscosity of the medium. This was tested using petroleum ether ($\eta = 0{\cdot}5$ centipoise) and highly refined liquid paraffin ($\eta = 1{\cdot}0$ poise) as solvents for Aerosol OT.

Complex polyesters and resins with mean molecular weights of a few thousands will disperse some substances to give stable suspensions, although the particles appear to be uncharged. In these cases the steric hindrance mechanism must be operating successfully. However, other pigments are charged in the presence of these resins and if two such pigments with opposite charges are mixed, flocculation can occur. Under these conditions it would appear that the combination of van der Waals' forces and electrical attraction overwhelms the steric hindrance. The source of the ions in these cases is uncertain, so that detailed interpretation of the results is not yet possible.

In general, the electrokinetic phenomena in liquids such as xylene or petroleum ether are qualitatively similar to those in aqueous solution except that excess of the dispersing agent does not usually lead to a decline in stability. This is presumably because the ionic strength can never increase sufficiently to cause much diminution in the Debye " thickness " of the double layer.

Prof. Dr. J. Th. G. Overbeek (*van't Hoff Laboratory, Utrecht*) said : In answer to a question on the stability of water-in-oil emulsions I see no reason why the electrical stabilization of suspensions in oil would not work in the case of emulsions. We have just embarked upon an investigation of emulsions of water in oil to try to prove this point.

Dr. G. H. Elton and Mr. R. G. Picknett (*Battersea Polytechnic, S.W.* 11) (*communicated*): With reference to Prof. Overbeek's remark, we have been studying the stability of emulsions of water in toluene, prepared by a standardized mechanical disintegration technique, without the use of surface-active stabilizers. Preliminary turbidimetric studies indicate that the emulsion stability is affected appreciably by the concentration and valency of cations added to the water.

It has yet to be determined how far such effects in W/O emulsions are due to (i) interaction of the very diffuse " external " electrical double layers in the hydrocarbon phase surrounding the water droplets; (ii) interaction between

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[1] Henry and Brittain, *Trans. Faraday Soc.*, 1933, **29**, 798.

[2] Van der Minne and Hermanie, *J. Colloid Sci.*, 1953, **8**, 38 ; 1952, **7**, 600.

" internal " double layers in individual water droplets; or (iii) other effects, such as the operation of an energy barrier to coalescence after collision. This should prove a fruitful field for theoretical investigation.

Mr. C. G. A. Hill (*Levy West Laboratories, Wembley*) said : In the course of the work on cataphoretic deposition from organic media [1] referred to by Prof. Overbeek in which the existence of a critical time was found, some experiments were carried out on the sediment volumes of the suspensions used for the coatings. Certain observations made during these experiments are relevant to the present paper.

Suspensions in methyl alcohol of barium strontium carbonate, prepared by precipitation at 85° C from aqueous solution of the mixed nitrates with either ammonium or sodium carbonate, and dried at 120° C *in vacuo*, were milled in porcelain mills with steatite balls for at least 12 h. On removal from the mill, the suspensions were transferred to glass cylinders of about 3 cm diam. and allowed to sediment. The appearance of the suspension for the first 24 h was quite normal, but thereafter narrow bands 2-5 mm in thickness separated by layers of clear medium began to develop in the upper part of the suspension, where only the finest particles remained ($< 0{\cdot}1\ \mu$). It was established that neither radiation nor temperature variation was responsible for the banding by carrying out experiments in the dark and at constant temperature. No account of such a periodic banding phenomenon in suspensions has been found in any of the standard works on colloids, although no exhaustive search of the literature has been made.

The tentative explanation put forward by my colleague Dr. Rees at the time was as follows. As the banding only appears after a certain time, the phenomenon must involve flocculation of the particles of colloid dimensions, which are sedimenting only slowly from the upper layers of the suspensions. The particles sedimenting on the bottom of the vessel must dissipate some part of their ionic double layers when they come into contact with each other, with the result that disperse medium having an increased concentration of ions will be diffusing upwards in the vessel. The increased ion concentration may well be sufficient to cause flocculation of the smaller particles remaining suspended. As this flocculation proceeds the flocculated particles will settle more rapidly than before, leaving a region free from particles across which the ion-enriched medium must diffuse before it encounters further particles. Here again flocculation takes place and the process is repeated. Evidence in support of this mechanism is the increase in conductivity observed when particles are sedimented from these suspensions. One such suspension of concentration 50 g/l., as taken from the ball mill, showed a conductivity of $3{\cdot}45 \times 10^{-5}$ ohm^{-1} cm^{-1}, and after centrifuging the remaining medium had a conductivity of $4{\cdot}0 \times 10^{-5}$ ohm^{-1} cm^{-1}, some 15 % greater. As the removal of less than 15 cm^3 of an insulating solid per litre of suspension cannot possibly account for more than a 2 % increase in conductivity, it must be assumed that the increase in conductivity is due to ions expelled from the particle double layers.

The main deposit formed by sedimentation from these suspensions is compact and firm, and closely resembles that formed by cataphoresis. Since in this case there is no " electrode reaction " it appears that the accumulation of particles must here play some part in the formation of a coherent deposit, although Prof. Overbeek's mechanism is undoubtedly active in normal cataphoretic deposition.

Dr. J. N. Phillips (*University of London, King's College*) said : Dr. Mirnik has raised the question as to the nature and magnitude of the potential to be used in the calculation of the electrical repulsion between charged colloidal particles and I wish to report some experiments carried out by Mr. Haydon and myself at King's College relevant to this problem. We have been interested in the relationship between the surface charge density and the potential and for this

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[1] Hill, Lovering and Rees, *Trans. Faraday Soc.*, 1947, **43**, 407.

purpose we have measured the ξ potential of oil droplets (the oil being petroleum ether, b.p. > 120° C) stabilized by a number of cationic and anionic detergents. The number of detergent ions per sq. cm. may be determined independently by a number of techniques and the usefulness of such a system is illustrated by the fact that both the electro-kinetic potential ξ and the surface potential ΔV may be studied as a function of the charge density and the electrolyte concentration.

Perhaps it is not surprising that the ξ potential does not equal the calculated Gouy potential at the surface (ψ_0)—in fact the ratio ξ/ψ_0 was found to vary between 0·2 and 0·8. What is more disturbing, however, is

(i) that ξ (at constant charge density) does not vary with the electrolyte concentration in the theoretical Gouy manner—whilst under the same conditions ΔV does, and

(ii) that under certain conditions ξ and ψ_0 vary in the opposite direction, i.e. ξ increases whilst the charge density decreases over a limited region.

It appears that one must come to the conclusion that at least with charged oil drops there is no direct relationship between ξ and ψ_0. In general, though not always, a variation in ξ reflects a variation in ψ_0 and accordingly ξ may be used as a relative measure of ψ_0 and hence of colloid stability. However, the substitution of ξ for ψ_0 as in Koelman's and Overbeek's paper, in quantitative calculations of electrical repulsion could be misleading.

Prof. B. Težak (*University of Zagreb*) said: There are some points in my view on the interpretation of the mechanism of coagulation which are essentially different from the theory of Verwey and Overbeek and Derjaguin.

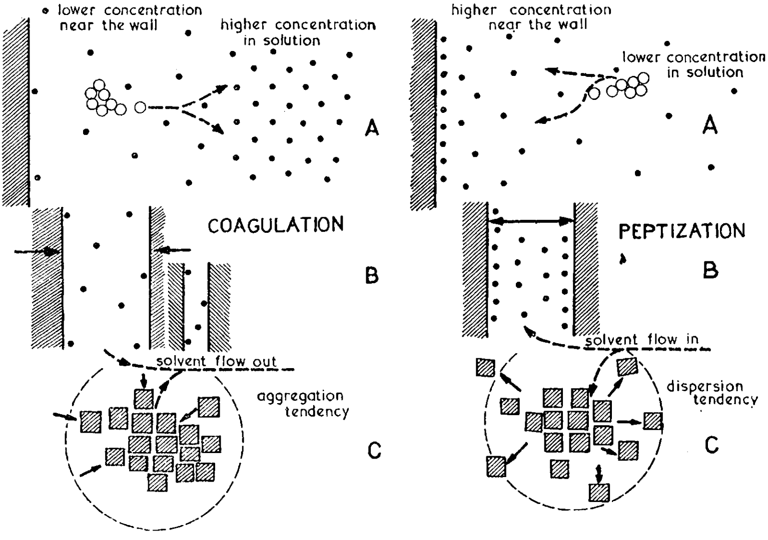

FIG. 1.—Schematic representation of the situation near the surface of the colloid particle (macrocomponent) when the concentration of the microcomponent near the surface is (i) lower than in the bulk solution; as a result of the differences in osmotic pressures there is the tendency to coagulation (left); (ii) larger than in the solution in bulk; as a result of the differences in osmotic pressures there is the tendency to peptization (right).

GENERAL CONCEPTS.—(i) It seems necessary to differentiate at least three units in every colloidal system which are responsible for its behaviour: (*a*) the macrocomponents, (*b*) the microcomponents in the bulk solution, and (*c*) the microcomponents in methorical layer.

(ii) The concentration differences of microcomponents (especially ionic) in the methorical layer and the solution in bulk are supposed to be the main factors controlling the stability-instability relations: the greater concentration of the osmotically and electrically active microcomponents in the methorical layer is taken as responsible for the greater stability of the sol.

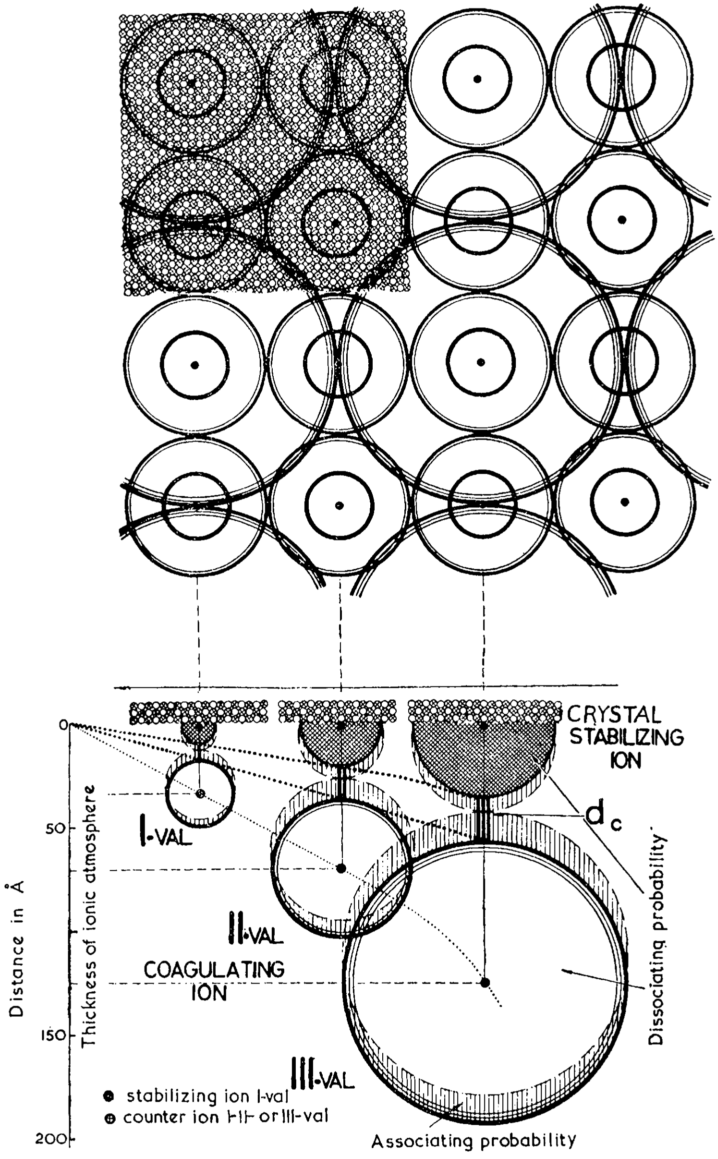

FIG. 2.—First and second projection of the schematic presentation of the configuration of the boundary state of uni-, di-, and trivalent coagulating ions against univalent stabilizing ions (adsorption surface parallel to the second projection plane).

(iii) The differences in concentration of microcomponents are caused by the surface density of the potential-determining complexes. Using the same principle it is possible to explain the coagulation and the peptization processes without the long-range London-van der Waals attractive forces. The somewhat naïve but probably basically sound presentation of the state of things is given by the rough schemes of fig. 1.

UNITS FOR DESCRIPTION.—(i) The critical concentration of neutral electrolyte inducing coagulation (coagulation value) should mean that corresponding states for the concentration and electrical factors in the methorical layer and in the bulk solution have been reached.

(ii) It is supposed that the distribution of the potential-determining complexes (the surface density of which is usually so low that their distribution may be taken as consisting of isolated univalent ions, ten or more ängström units apart) enables us to consider their coulombic interaction with counter ions as elementary processes representing the association-dissociation equilibria of ion pair formations. In order to visualize the statistical set-up near the wall the schemes of something like the first and second orthogonal projection of the ionic distribution is given in fig. 2.

(iii) Generally, the stabilizing ion and counter ion interaction can be represented by ionic distribution spheres with shells indicating the association probabilities; the thickness of the shells may be taken as corresponding to the simple Bjerrum's distance, d_c:

$$d_c = z^- z^+ e^2 / 2DkT,$$

where $z^- z^+$ are the valencies of the ions, e the electronic charge, D the macroscopic dielectric constant, k the Boltzmann constant, and T the absolute temperature.

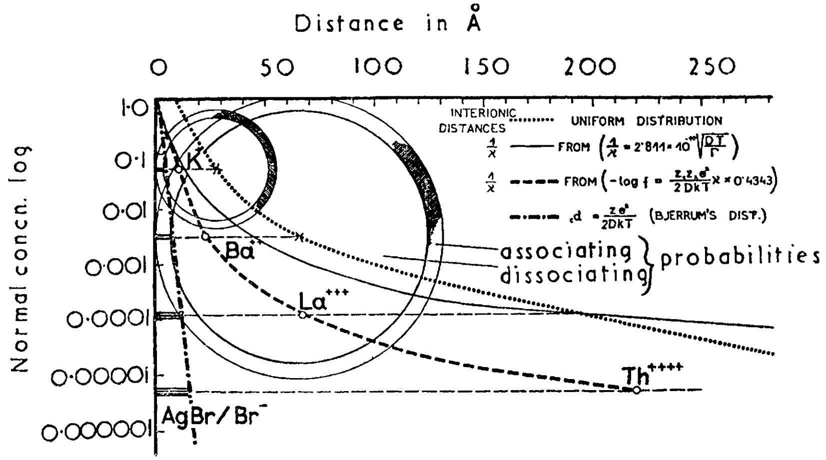

FIG. 3.—Schematic representation of the relationship between Bjerrum's critical distances (— · — · — · line), thicknesses of ionic atmosphere (———— curve), and distances between ions when uniformly distributed in solution (. . . . . . curve) against the logarithm of coagulation values for ions of various valencies. The circles represent the ionic distribution spheres, while the partially shaded shells give the probabilities of association of the stabilizing-coagulation ion pairs.

THE LINEAR RELATIONSHIP.—(i) Fig. 3 shows a schematic representation of the Schulze-Hardy rule (the characteristic relationship for the interaction between univalent stabilizing ion * and the univalent, divalent, trivalent and tetravalent counter ions), as well as the plot of the logarithm of the coagulation values and the corresponding interionic distances in solution (assuming their uniform distribution); the circles give the distribution spheres for interactions between uni-

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* It seems that stabilizing complexes on the wall may be generally treated as univalent in their actions towards counter ions.

valent stabilizing ion and univalent and divalent coagulating ions (K^+ and Ba^{2+}), and the short, thick, either single, double, triple or quadruple lines, show the thicknesses of the corresponding association shells for counter ions of various valencies (K^+, Ba^{2+}, La^{3+}, and Th^{4+}), all for the negative silver bromide sol in aqueous solution.

(ii) The schematic representation of fig. 3 is drawn on the assumption that at the critical concentration for coagulation the simple picture of elementary associating-dissociating processes between stabilizing charges and counter ions in the methorical layer should be taken as statistically representative for the similar ion pair formation in the bulk solution. Fig. 4 shows that these relationships are experimentally justified for silver iodide sols also; the results of Dr. Schulz from our laboratory are given here showing clearly the effect of radius of counter ions and the influence of the accompanying (NO_3^- and SO_4^{2-}) ions. The same conclusion may be reached from the results of experiments with various media where the dielectric constant was varied from 30 (87 wt. % ethanol; 80 wt. % acetone) to 126 (2 M glycine) as shown in fig. 9 and 10 of our paper.

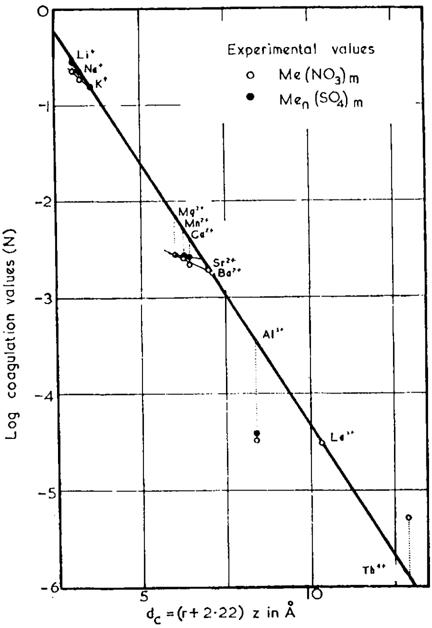

FIG. 4.—The relationship between critical distances and logarithm of coagulation values of various metal nitrates and sulphates for the precipitation system: 0·0005 M $AgNO_3$ + 0·004 M KI + 0·004 M HNO_3. Abscissa unit is 5·8 times greater than the ordinate unit.

(iii) By using the concept of corresponding elementary processes in methorical layer and solution in bulk it is possible to interpret, qualitatively at least, the trends of coagulation values for univalent and trivalent counter ions which vary with stabilizing ion concentration. One possible way of applying this principle would be to consider the variation of the association probability; one of the factors of this probability could be obtained by comparing the size of the distribution spheres of counter ions with the number of the stabilizing charges situated at the corresponding area of the wall. In this way it might be possible to explain many other phenomena not only of lyophobic but of lyophilic systems as well.

As it is pointed out in our paper, with our interpretation it is possible to make a distinction between the specific (substantial and crystalline) characteristics of the macrocomponent interactions with the environment giving the density of distribution of the potential-determining complexes on the wall, the semi-specific coulombic stabilizing ion-counter ion interactions giving some manifestations of the ionic individuality (valency, radius, hydration, etc.), and finally, the colligative, osmotically-active concentration factors.

If one chooses a functional approach, the experimental steps should include the answers to complex questions regarding the relationship between various electrokinetic and electrochemical potentials in the critical region of the so-called isoelectric maxima, and from this point of view it seems that some results of Dr. Mirnik from our laboratory may be quite promising.

Prof. B. Derjaguin (*Academy of Sciences of the U.S.S.R., Moscow*) said: I am in complete accord with the statements by Prof. Težak and his colleagues that in developing a general theory of coagulation and stability of colloids and in studying a number of other surface phenomena it is necessary to take into account the peculiarities of the liquid layers lying near the surface boundary (named the methorical region by Prof. Težak). A similar point of view served as the basis for a series of studies carried out by myself and by my colleagues, and also by Dumansky [1] and his school, in the field of investigation of thin polymolecular boundary films and of the surface forces acting there. In particular, the investigation of boundary viscosity using the " blowing-off " method,[2] and of polymolecular adsorption using the optical micro-polarization method,[3] led to the conclusion that when the lyophilic solid surface is approached the structure and properties of layers of the liquid at a distance of the order of 10^{-7}-10^{-6} cm from the surface may change abruptly similarly to a phase change.

This shows that the theory of colloid stability, developed by Landau and myself and later elaborated in more detail by Verwey and Overbeek, which fits the case of lyophobic colloids well, on being applied to sols and suspensions whose particles are solvated requires the introduction of corresponding improvements and corrections. The investigation of the disjoining action of free films reported in my paper also points towards the necessity for such corrections and indicates their character. Further development and improvement of this theory represents, however, something directly opposite to abandoning it.

It seems to me that especially unfounded is the call to pursue Ostwald's idea of the part played by the medium in determining colloid stability. There can be no doubt that the conception according to which the threshold of coagulation depends only on the dispersion medium and is not connected with the van der Waals' forces of interaction of colloid particles is erroneous.

After the rule, suggested purely empirically by Ostwald, was derived by Landau and myself [4] in a changed (but close to the original) form and after it thus obtained physical meaning based just on taking into account the van der Waals' forces, it would be an entirely unjustified backward step in the development of a theory of colloid stability to return to the ideas of Ostwald which are devoid of real physical meaning.

Dr. A. Packter (*F. W. Berk & Co.*) said: I agree with Tezak and co-workers that the simplified theory of Verwey and Overbeek has neglected many important factors. Our work has been carried out mainly with the sols of the insoluble silver, copper and lead salts of solubility products in the range 10^{-5} to 10^{-2} g equiv./l., i.e. higher than those of the silver halides; and we have also used two-dimensional precipitation diagrams for systematic representation of the peptization and flocculation phenomena accompanying the precipitation of a particular material.

In general our work has shown that equivalent sols of most silver and simple copper salts, lead chromate, etc., are readily peptized by excess anion, and generally coagulated by excess cation. The sols of copper chromate, on the other hand, are peptized by excess copper ion.[5] The silver halides sols are unique, in that they are peptized by even slight excess of either of the reacting ions.

Furthermore, whereas the latter show only two distinct regions (i) complete peptization or (ii) rapid coagulation to give a gelatinous precipitate, the salts

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[1] Dumansky, *Lyophilic Properties of Disperse Systems* (Voronej, 1940).

[2] see, e.g., Karassev and Derjaguin. *Colloid J.* (*Russ.*), 1953, **15**, 365.

[3] Derjaguin, *Trans. Confer. Colloid Chem.* (ed. by Acad. Sci. Ukrain, S.S.R., Kiev, 1952, p. 26. Derjaguin and Zorin, *C.R. Acad. Sci. U.S.S.R.*, 1954, **98**, 93.

[4] Derjaguin and Landau, *Acta physicochim.*, 1941, **16**, 633; *J. Expt. Theor. Physics* (*Russ.*), 1941, **11**, 802; reprint, *J. Expt. Theor. Physics* (*Russ.*), 1945, **15**, 662.

[5] Ovcharenko, *Coll. J. U.S.S.R.*, 1940, p. 200.

we have examined generally show an intermediate range of slow coagulation of partially peptized sols to give crystalline precipitates.

This region is of great importance for the study of the Liesegang phenomena; for only systems showing a wide range of slow coagulation will lead to a rhythmic precipitation when a solution of one of the reacting ions is diffused into a set gel containing the second ion. Indeed, examination of rhythmic precipitation has been found to be an excellent technique for studying peptization and coagulation phenomena.[1]

Prof. B. Težak (*University of Zagreb*) said: I would like to ask three questions which are connected with interpretation of some experimental results which I find difficult to reconcile with the Verwey-Overbeek theory.

It seems to me that it would be useful to know something about the possibilities of incorporating in the theory:

(i) the phenomena of peptization;

(ii) the antagonistic effects of the mixture of electrolytes on coagulation values, and

(iii) the trends of the coagulation values for univalent and trivalent ions with decreasing concentrations of stabilizing ions.

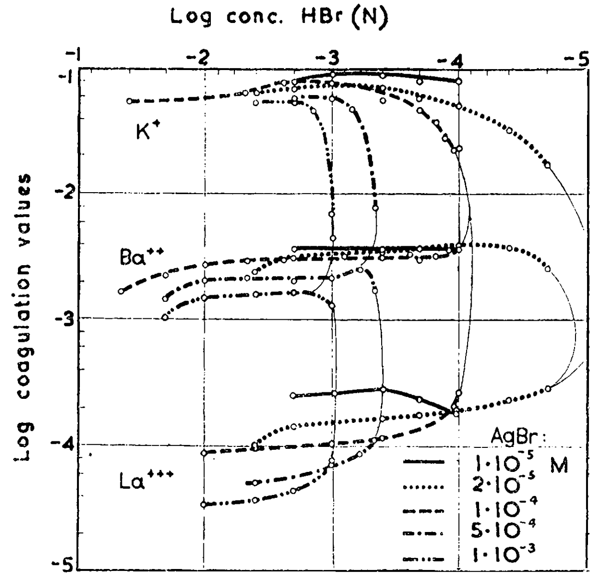

FIG. 1.—Effect of the concentration of sols (AgBr) and stabilizing ions (Br^-) on the coagulation values of potassium, barium and lanthanum nitrates.

Fig. 1 gives the coagulation values determined experimentally; a similar effect is obtained for silver iodide, silver bromide, and silver chloride, as shown in fig. 2. According to the theory of Verwey and Overbeek the trends should be irrespective of the valency, while in fact the effects with trivalent ions are opposite to those of univalent ones. Moreover, in experiments in mixed solvents (water + ethanol, water + acetone, fig. 6 of our paper) the effects of counter ions of all three valencies are not consistent with the Verwey-Overbeek theory.

One other point may be mentioned here, namely, that in the theory of Verwey-Overbeek there is no clear differentiation between the thickness of the diffuse

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[1] Packter, *Thesis*, University of London, 1953.

double layer of the colloidal particles, and the Debye-Hückel thickness $1/\kappa$. Although the value of $1/\kappa$ of the electrolyte in the bulk solution (intermicellar liquid) and the critical thickness of the stabilizing ion-counter ion interactions in the methorical layer may correspond in some critical circumstances, in the majority of cases they certainly differ. It seems highly probable that the stability-instability conditions are mainly dependent on this difference, while only at the critical concentration of coagulation (at coagulation values) is it experimentally justifiable to assume some definite correspondence between the state for the interactions of the stabilizing ion-coagulating ion pairs on the one hand, and the formation of ion pairs in bulk solution on the other.

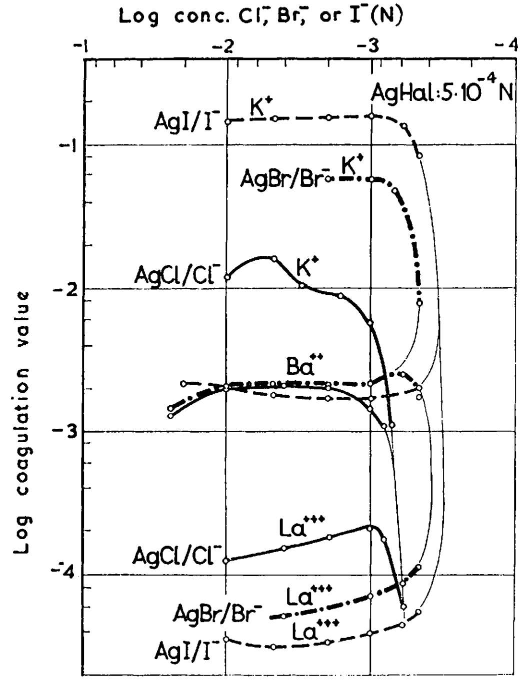

FIG. 2.—Effect of the concentration of the stabilizing ions on the coagulation values of potassium, barium and lanthanum nitrates for sols of silver chloride, silver bromide, and silver iodide *in statu nascendi.*

Prof. J. Th. G. Overbeek (*van't Hoff Laboratory, Utrecht*) said : In reply to Prof. Težak : in the present form of the theory of stability in which flocculation takes place in an infinitely deep minimum of energy, peptization is inconceivable. The obvious extension of the theory that would allow us to understand peptization is the inclusion of a Born repulsion between the surface atoms of the particles. Moreover, there are several indications that in cases of very easy peptization the particles are kept separated by one or a few layers of strongly adsorbed molecules (water in the case of clays, acetone in the case of AgI). A simple way to include these in the theory would be to describe them as equivalent to an infinitely high energy barrier, preventing particles from coming closer than, say, 10 Å to each other.

The explanation of antagonism as a general phenomenon will probably demand the inclusion in the theory of Debye-Hückel interactions in the bulk of the solution [1] as considered by Loeb [2] and by Levine and Williams.[3]

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[1] Kruyt, *Colloid Sci.*, (Elsevier, Amsterdam, 1952), vol. 1, p. 313.

[2] Loeb, *J. Colloid Sci.*, 1951, **6**, 75.

[3] Levine, *Proc. Camb. Phil. Soc.*, 1951, **47**, 230; *Proc. Physic. Soc. A*, 1953, **66**, 365. Williams, *Proc. Physic. Soc. A*, 1953, **66**, 372.

It is known that if flocculation values are expressed as activities rather than as concentrations, antagonism is greatly diminished and it often disappears completely.[1]

The fact that in the presence of a high concentration of peptizing ions flocculation by polyvalent ions takes place at a relatively low concentration might be explained by interactions between individual peptizing ions and counterions giving rise to an attractive component in the force between particles. In order to incorporate this effect in the double-layer theory it would be necessary to apply corrections for the fact that both surface charge and space charge are not really smeared out but have reference to individual ions.

Finally, Prof. Težak asks for a clear differentiation between the thickness of the diffuse double layer of colloidal particles and the Debye-Hückel length, $1/\kappa$. The thickness of a diffuse double layer can be defined in various ways (e.g. distance between the wall and the centre of gravity of the counter charges or the distance at which the energy of interaction of two double layers equals kT) leading to different values, all of the same order of magnitude as $1/\kappa$. In the theory of the stability the thickness of the double layer does not occur explicitly. The Debye-Hückel length of the bulk of the solution, $1/\kappa$, however, occurs in it as a fundamental parameter, more fundamental than concentration of ions, valency, dielectric constant and temperature out of which it is composed.

Dr. A. Packter (*F. W. Berk & Co.*) said: Težak and his co-workers have emphasized the importance of adsorption effects on the stability of silver salt sols. The earlier work of Lange is very important, as also that of Dhar, who indicated the effect of adsorption phenomena on the Burton-Bishop and Schultz-Hardy laws.

We have in fact found that the latter law is not obeyed for positively charged silver chromate sols. The univalent chloride bromide and iodide ions have a marked flocculating effect, the divalent sulphate is less active, while trivalent citrate will repeptize the dilute sols. The results for Cl ion were as follows:

[sol]	[Cl$^-$]/[sol] ratio for max. flocculation
M/2000	0·1
M/1000	0·02
M/400	0·004
M/200	0·0009

It is seen that silver chromate sols prepared from equivalent solutions of the reacting ions, are positively charged, and owe their stability to the adsorbed Ag^+ ion. The stability falls rapidly with increase in the sol concentration, due to decrease in the charge density of the double layer.

Dr. G. H. Jonker (*Philips' Res. Lab., Eindhoven*) said : An objection against the use of the critical distance of Bjerrum used by Prof. Tezak is that in d_c the valencies of the positive and the negative ions have the same importance, whereas it is known experimentally that the flocculation value depends in the first place upon the valency of the oppositely charged ions.

If Prof. Težak would plot his log C values against log D and against log Z^+ he would find that his experiments are roughly in accordance with the theoretical formula given by Derjaguin and by Verwey and Overbeek.

In his theory the flocculating force is the difference in osmotic pressure between the solution and the double layer. But on the addition of flocculating electrolytes the concentration in the double layer is increased so that this osmotic force acts in the wrong direction.

Prof. J. Th. G. Overbeek (*van't Hoff Laboratory, Utrecht*) said: The basis of Prof. Težak's theory of stability is the difference in concentration of osmotically active components between the interface and the bulk of the solution. Both

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[1] Kruyt, *Proc. Kon. Ned. Akad. Weten.*, 1935, **38**, 464. Vester, *Thesis* (Utrecht, 1935).

the theory of the electrical double layer and a series of experimental data on adsorption show that in all cases the concentration of ions near a charged particle is higher than in the bulk of the solution ($e^{+x} + e^{-x} > 2$). The situation pictured at the coagulation side of Prof. Težak's fig. 1 consequently does not occur in real systems. By adding electrolytes to a system, the excess concentration near the surface is even increased, both by increase of the surface charge and by decrease of the double layer thickness, as is proved by adsorption experiments, e.g. on mercury (electrocapillary curve) and on AgI (Mackor). Prof. Težak's explanation of peptization and coagulation therefore can not be correct.

Dr. S. Levine (*Manchester University*) said: There are four types of approximations in the formula (1.1) used by Reerink and Overbeek for the free energy of interaction between the electric double layers of two spherical particles. Firstly, it is based on Derjaguin's method which starts from the model of two parallel plates and is a good approximation at large τ. Secondly, it makes use of a formula for the free energy of parallel plates which applies to large separations ($\kappa H_0 = \tau u > 2$, say). Thirdly, the electrolyte is assumed to be a binary symmetrical type, and finally, the (Stern) potential ψ_δ is taken to be uniform over the surface of each particle and independent of the particle separation. (All undefined symbols have the same meaning as in the paper by Reerink and Overbeek.)

In table 1 the ratio of the interaction energy of two spherical particles in a symmetrical electrolyte, obtained on the Manchester University electronic computer by Hoskin, to that given by formula (1.1) is shown for various values of z, τ and κH_0. No analytical method of correcting for the Derjaguin approximation has been devised yet, but it is possible to improve upon the second type of approximation described above. If $V_p(H)$ is the free energy of interaction per unit area of two parallel plates at separation H, then the Derjaguin formula for the interaction energy of two spheres of radius a is

TABLE 1

	$z = 2$	(50 mV for 1:1 electrolyte)		$z = 4$	(100 mV for 1:1 electrolyte)	
κH_0 \ τ	1	5	15	1	5	15
1	0·67	0·83	0·86	0·80	0·90	0·91
2	0·56	0·84	0·93	0·68	0·87	0·93

$$V_s(H_0) = \pi a \int_{H_0}^{\infty} V_p(H) \mathrm{d}H.$$

Now Levine and Suddaby[1] have calculated the first three terms in a series expansion for $V_p(H)$ for a symmetrical binary electrolyte, which is particularly convenient at large H. This series is readily integrated term by term with respect to H and so we derive for the interaction of the electric double layers in a symmetrical electrolyte,

$$V_s^{(\mathrm{sym})}(H_0) = 8a\epsilon\left(\frac{kT}{ve}\right)^2 \gamma^2 \exp(-\kappa H_0)\left[1 - \gamma^2 \exp(-\kappa H_0) \, . \, (\kappa H_0 - 1 + 2\delta)\right.$$
$$\left. + \frac{8}{3}\gamma^4 \exp(-2\kappa H_0)\left\{(\kappa H_0)^2 + \kappa H_0\left(4\delta - \frac{11}{6}\right) + \frac{7}{18} - \frac{11}{3}\delta + 4\delta^2 - 2\mu\right\} + \ldots\right],$$

where $\delta = \cosh\left(\frac{z}{2}\right) \Big/ \sinh^2\left(\frac{z}{2}\right)$ and $\mu = \delta/\sinh^2\left(\frac{z}{2}\right)$. The first term in this

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[1] Levine and Suddaby, *Proc. Physic. Soc. A*, 1951, **64**, 431.

series is identical with formula (1.1) of Reerink and Overbeek. Typical values for the correction term in the square brackets above are:

κH_0 \ z	2	4
1	0·88	0·87
2	0·93	0·92

It seems that this series compares favourably with the results obtained on the electronic computer at $\tau = 15$, particularly at $\kappa H_0 = 2$. At $\kappa H_0 = 1$ the higher terms in this series presumably still contribute a few percent. This series has the advantage over the so-called exact formula of Verwey and Overbeek (which actually is based on the Derjaguin approximation) in that it avoids a tedious numerical integration. However, it does not seem reliable when κH_0 is appreciably less than unity.

In regard to the third type of approximation in formula (1.1) mentioned above, it can be shown that the corresponding series expansion for a 2 : 1 electrolyte reads

$$V_s^{(2,1)}(H_0) = 18a\epsilon(\boldsymbol{k}T/\boldsymbol{e})^2\Gamma^2 \exp(-\kappa H_0)\Big[1 - \Gamma^2 \exp(-\kappa H_0) . (3\kappa H_0 - 9 + \Delta)$$
$$+ 4\Gamma^4 \exp(-2\kappa H_0)\Big\{6(\kappa H_0)^2 + \kappa H_0(8\Delta + 29) + 133 + \frac{58}{3}\Delta + \frac{8}{3}\Delta^2 - 3M\Big\} + \ldots\Big].$$

where, if $y = \exp(-\boldsymbol{e}\psi_0/\boldsymbol{k}T)$,

$$\Gamma = \frac{1 - \{\frac{2}{3}(y + \frac{1}{2})\}^{\frac{1}{2}}}{1 + \{\frac{2}{3}(y + \frac{1}{2})\}^{\frac{1}{2}}}, \quad \Delta = \frac{9\sqrt{\frac{2}{3}}(y - \frac{1}{2})(y + 2)}{(1 - y)^2(y + \frac{1}{2})^{\frac{1}{2}}}.$$

and $$M = \frac{\sqrt{6}[2(1 - y)(4 - 18y^2 - y^3) + 27y^3]}{(1 - y)^4(y + \frac{1}{2})^{3/2}}.$$

It should be noted that κ is now the characteristic Debye-Hückel parameter for a 2 : 1 electrolyte. In table 2, we have evaluated the quantity in the square brackets in the formula for $V_s^{(2,1)}(H_0)$. Now Levine and Suddaby[1] have obtained an expression for the free energy of the double layers of two parallel plates in a 2 : 1 electrolyte in terms of elliptic integrals and have shown that provided κH_0 is not too large, the interaction energy for 2 : 1 and 2 : 2 electrolytes differ only by a few percent for equal concentrations of the divalent coagulating ion. This suggests that it is quite permissible to replace the 2 : 1 valency type by a 2 : 2 type, as Reerink and Overbeek have done for spherical particles. For large κH_0 ($\geqslant 3$, say), however, the ratio of the interaction energy for a 2 : 1 type (with a divalent coagulating ion) to that for a 2 : 2 type is very nearly

TABLE 2

$\boldsymbol{e}\psi_0/\boldsymbol{k}T$ \ κH_0	1	2	3
1	0·982	1·004	1·005
2	0·865	0·968	0·996
3	0·831	0·948	0·991

$$9(\Gamma/y)^2 \exp[\{\kappa(2,2) - \kappa(2,1)\}H_0] = A(z) \exp\left[\frac{(2 - \sqrt{3})}{\sqrt{3}}\kappa(2,1)H_0\right], \text{ say,}$$

where $\kappa(2, 1)$ and $\kappa(2, 2)$ denote the Debye-Hückel parameters for these two electrolyte types and $z = 2\boldsymbol{e}\psi_0/\boldsymbol{k}T$. The values of the factor $A(z)$ at $z = 2$, 4 and 6 (i.e. $\psi_\delta = 25$, 50 and 75 mV) are 0·78, 0·69 and 0·66 respectively. It is

[1] Levine and Suddaby, *Proc. Physic. Soc. A*, 1952, **65**, 405.

seen therefore that at large enough separations, we can no longer ignore the valency of the non-coagulating ion. The method devised for obtaining the above series for the interaction energy in a 2 : 1 electrolyte can be extended to the case of a 3 : 1 electrolyte, but this has not been done yet.

Finally, on the basis of the Stern theory of the double layer, the assumption that ψ_δ is uniform and independent of particle separation can be made at large separations but not at small separations. The Stern theory has been applied to the case of parallel plates and small surface potentials [1] and in some work which extends this analysis to larger potentials and which is still in progress, it is found that the interaction energy is always greater than that calculated on the original model of Verwey and Overbeek, in which the surface potential is kept constant. However, in general the difference only becomes appreciable at small separations ($\kappa H_0 < 1$, say).

The application of the various results described above would certainly be relevant to a more accurate theory of the interaction of the electric double layer of two spherical particles.

Dr. H. Reerink (*Koninklijke/Shell-Laboratorium, Amsterdam*) said: Unfortunately we were obliged to make use of the approximate methods for the calculation of the electrical repulsion between spherical particles. The necessity for these approximations has now largely been removed by the important work of Levine and Hoskin. From the tables given by Levine it follows that our values are in error by about 20 %. I would like to point out, however, that these errors cannot be responsible for the striking variation in ψ_δ and the van der Waals constant A as shown in table 4 of our paper.

It is seen that ψ_δ decreases with increasing particle size. According to Levine's table 1 the reverse should be true since the relative correction is highest for low values of $\tau = \kappa_a$. It seems probable, as already stated in our paper, that deviations from spherical shape play a role here. The value of A is calculated with the help of the value of ψ_δ; therefore it is to be expected that A will show the same trend with particle size as ψ_δ. This is fully confirmed in our table 4.

Table 4 shows that for each sol the value of A increases with increasing valency v of the counter ions, while ψ_δ is nearly constant. Dr. Mackor [2] has drawn my attention to the fact that H_{om}, the particle distance at the maximum in the interaction energy curve, also increases with v. Now the attraction has been found from the difference between the total interaction energy (derived from the experimental stability factor W) and the calculated electrical repulsion, both at this particular distance H_{om}. This means that, using the theory of Hamaker, an increasing value of A is obtained when the particle distance increases. A constant A can be obtained if the assumption is made that the attraction decays more slowly with distance than according to Hamaker. There is, however, no theoretical justification for this assumption if no other than dispersion forces are taken into account. The same conclusion has been reached by Mackor [3] from his experiments on the coagulation of AgI sols in water + acetone mixtures, and by Norrish [4] from the swelling of montmorillonite in electrolyte solutions.

Dr. M. Mirnik (*University of Zagreb*) said: I think it necessary to point out in connection with the paper by Reerink and Overbeek that $W = 1$ for rapid coagulation * is in general an assumption and not an experimental fact, as could be concluded from their sentence: "The proportionality constant is evaluated from rapid flocculations, where $W = 1$." In the rapid coagulation region the coagulation rates are probably not constant in general, as could be concluded from

[1] Levine, *J. Colloid Sci.*, 1951, **6**, 1.

[2] Mackor, private communication.

[3] Mackor, *Rec. trav. chim.*, 1951, **70**, 841.

[4] Norrish, this Discussion.

* i.e. for coagulation in systems with the concentration of the coagulating ions above the point of the intersection of the inclined line with the $\log_{10} W = 0$ axis in fig. 6 and 7. Apparently this value is equal to the coagulation value of Prof. Težak and co-workers.

the horizontal parts of the $\log_{10} W$ against $\log_{10} c_e$ plots in fig. 6 and 7. The number of systems investigated in the rapid coagulation region is too small (for trivalent ions not a single point was given) to enable us to evaluate the change of the $\log_{10} W$ against $\log_{10} c_e$ plot with increasing concentration of the coagulating ions. The important fact, however, is in our opinion a discontinuity in the $\log_{10} W$ against $\log_{10} c_e$ plot at the coagulation value.

In our laboratory, many measurements in the rapid coagulation region have been obtained but only a small part of these are published as yet. Usually the points obtained inside this region were not plotted because they do not influence the coagulation values. The initial rate of the change of the tyndallometric value with time is generally not constant, usually increasing and then decreasing again with increase concentration of the coagulating ion. The consequence is a maximum in the concentration tyndallogram,[1] e.g. (I) fig. 5 and 8; (II) fig. 1. The initial slope in the fast coagulation region is also dependent on the manner of mixing or addition of the coagulating ions to the sols or precipitation components. The same applies to rapid coagulations in the "equivalency coagulation region".

The total energy of interaction V as well as the stability factor W are obtained in the theory of Verwey and Overbeek from values of a, v, κ, A, H_{om} and ψ_δ, of which only a is accessible to direct measurements. The possibility of an overestimation of the effect of the particle size was in fact questioned by the authors themselves; in addition the independence of the "negative stability limit"[2] of the particle size is discussed in my remarks on the paper of Jonker and Kruyt. The coagulation values obtained with coarse aged sols and with sols in the nascent state, in which the smallest possible particles are present, are also practically the same.[3]

The agreement or disagreement with the empirical Schulze-Hardy rule represents a check of the theory with respect to the valency v of the coagulating ions and has been discussed by Prof. Težak. An experimental check of the theory with respect to the use of the Debye-Hückel thickness $1/\kappa$ as the thickness of the diffuse double layer is given by the change of the coagulation value with the change of the activity of the stabilizing ions. This influence was also discussed by Prof. Težak.

Discussion on the van der Waals constant A is incomplete and it will take probably some time to obtain reliable values at the solid/liquid interface between the particle and the surrounding solution. A check on the justification for the introduction of long-range van der Waals attraction forces in the theory of stability will be impossible as long as there are no reliable A values.

The constant H_{om} is a theoretically deduced entity which is calculated entirely on the basis of values for a, v, κ, A and ψ_δ The correctness of the theoretical requirement

$$H_{om} = 1/\kappa$$

cannot be checked directly by any experimental method.

Why should be it permissible to omit in the calculations of the potential functions of the double layer the values of other known potentials, such as the surface potential, the dipole part of the Galvani potential difference g_D,[4] surface potential in the restricted sense [5] (p. 124) as well as the value of the Volta potential difference $\Delta\psi$[4] or cavity (contact) potential,[6] dielectric phase-boundary potential, especially in the region of low activities of potential determining ions. As long as no evidence is given that these potentials have real significance and as long as their

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[1] Težak *et al.*, *J. Physic. Chem.*, 1951, **55,** 1557, 1567.
[2] Mirnik and Težak, *Trans. Faraday Soc.*, 1954, **50,** 65.
[3] Schulz and Težak, *Arhiv. kem.*, 1954, **26,** 187.
[4] Lange and Schuecker, *Z. Elektrochem.*, 1953, **57,** 89.
[5] Kruyt, *Colloid Science* (Amsterdam, 1952), vol. 1.
[6] Grahame, *Chem. Rev.*, 1947, **41,** 441.

values and influence on the potential distribution function are unknown, it is probably incorrect to ascribe any physical meaning to values of potentials upon which the stability calculations are based. Therefore, any plane at any distance from the surface, which is up to now supposed to exist (e.g. the surface of the solid, the inner or outer Helmholz plane, slipping plane of electrokinetics or another plane) could be made responsible for stability.

In 1948 it was supposed by Verwey and Overbeek [1] that the surface is the critical plane and that the ψ_0 value, which corresponds to the ionic part of the Galvani potential difference, should give the necessary value. Jonker and Kruyt in the present paper still use this value, calculated from the zero point of charge from the activity of the potential determining ions. Later in 1952 in " Colloid Science " [2] and in the present paper, the value ψ_δ, which represents the difference between the potential in the bulk of the solution and in the plane of rigidly adsorbed counter ions (outer Helmholz plane [3]) is supposed to be the right value. In the present paper of Koelmans and Overbeek the ξ-potential is used in the calculations. Of course, significant for the calculations are the absolute values and not their physical meanings. As long as used or calculated values in a theory can vary between 10 to 100 mV, without any means to prove whether these values really cause stability or coagulation in the predicted way, I think it better not to ascribe to them a precise physical meaning.

One of the main results of Reerink and Overbeek's paper is a sequence of ψ_δ values given in tables 4 and 5; these were calculated on the basis of five other values, of which only two or three are known with any degree of certainty. The calculated values cannot be checked because their physical meaning is unknown, and as a consequence their measurement is impossible. Can a sequence of unchecked values under such conditions be taken as a quantitative or even qualitative check of the theory upon which the calculations are based?

Prof. Dr. J. Th. G. Overbeek (*van't Hoff Laboratory*, *Utrecht*) said : With regard to the value of the collision efficiency at high electrolyte content, the fact that $W = 1$ (all collisions effective) for rapid flocculation is derived from the following data :

(i) counting of particles for sol E with 300 mmole/l. KNO_3 gave good agreement with Smoluchowski's equation for rapid flocculation. Collision radius $\approx 2 \times$ radius of particles;
(ii) further addition of electrolytes did not speed up the flocculations in the region of rapid flocculation;
(iii) for hydrophobic sols for which absolute kinetics of flocculation have been determined (gold, selenium) collision efficiency was always found to be close to 100 % for rapid flocculation.

In the older versions of the stability theory the double layer was assumed to be completely of the Gouy-Chapman type with the surface potential ψ_0 as the determining potential for the interaction. In more refined considerations, account has to be taken of the insufficiency of the Gouy-Chapman theory for the layers close to the surface. Corrections of the type introduced by Stern, and treated in more detail by Grahame and by Levine have to be applied. A good approximation is obtained by treating the interaction as one between two Gouy-Chapman double layers with a surface potential equal to the Stern potential ψ_δ. In Koelmans' experiments on the stability in non-polar oil, the double layers are so diffuse that the gradient of potential is quite small and the differences between ψ_0, ψ_δ and the ζ-potential are negligible. The χ-potential being located very close to the

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[1] Verwey and Overbeek, *Theory of the Stability of Lyophobic Colloids* (New York, 1948).

[2] Kruyt, *Colloid Science* (Amsterdam, 1952), vol. 1.

[3] Grahame, *Chem. Rev.*, 1947, **41**, 441.

interface is not expected to influence the interaction between two particles directly. Whether changes in ψ_δ occur as a consequence of the dependence of the χ-potential on the composition of the medium is another matter, but bears no direct relation to interaction theory.

The adsorption of a non-ionized capillary active substance would certainly change χ, and carry with it a change of ψ_δ. The interaction between two double layers on such modified particle surfaces would, however, be practically determined by the modified ψ_δ.[1]

Dr. Mirnik has further criticized the application of the stability theory in its present form to our data on the kinetics of flocculation of AgI and he has especially objected to our conclusion that the values of ψ_δ and A as obtained in tables 4 and 5 are an indication of the essential correctness of this theory. Here I would like to point out that a very close agreement between theory and experiments should hardly be expected in view of the shortcomings in both. Dr. Levine has pointed out in this discussion that calculations on the double layer can still be improved by applying computer techniques. The particles in our AgI sols are certainly not spherical but the theory is for spheres. The size of the particles is not known with precision, as the sols are far from isodispersed. But all this does not alter the fact that the data and the theory as used are the best available. The fact that solely from coagulation kinetics, values of the van der Waals constant and the Stern potential can be derived which are of a very reasonable order of magnitude, proves that the theory in its present form is already good enough to describe a comparatively small detail such as the change of the energy barrier with electrolyte concentration.

The lack of complete quantitative agreement should encourage us to improve theory and experiments, the theory by including more complicated forms than just spheres or flat plates, the experiments by adding independent information on ψ_δ (see Grahame, Mackor) and on the van der Waals constant (Abricossova, Sparnaay).

Dr. M. Mirnik (*University of Zagreb*) said: At least one of the constants or variables (ψ_δ) upon which the theory of Verwey and Overbeek, and probably some other similar theories, are based, is not unambiguously defined nor can it be measured by a direct experimental method. A theory cannot claim acceptance as long as only one of the fundamental variables or constants upon which it is based can be defined unambiguously or measured at least in principle.

On the other hand there are experimentally accessible parameters, the role of which in the stability-instability relations has not in our opinion yet been elucidated sufficiently experimentally (e.g. ref. (5), p. 231, fig. 33) and not considered in these theories. In the case of the double-layer potentials such measurable values are the electrode potentials of the Ag/AgI electrode, electro-osmotic and electrophoretic potentials, and the adsorption of potential-determining ions.[2] For the characterization of the stability-instability relations we proposed the "positive" and "negative" stability limits of activity[2] for the isoelectric or equivalency coagulation, and for the coagulation with neutral electrolytes the "coagulation values".[3]

The concept of the electrical origin of stability had its origin mainly from the electrophoretic observations that sols with potential-determining cations contain positively charged particles and those with anions negatively charged ones. This is an observation which could easily be confirmed by an electro-osmotic study of analogous coagulated, and thus unstable, systems. Apart from such qualitative observations, little quantitative experimental evidence is given which would help to elucidate the role of those measurable potentials in stability relations.

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[1] Mackor, *Rec. trav. chim.*, 1951, **70**, 747, 841.

[2] Mirnik and Težak, *Trans. Faraday Soc.*, 1954, **50**, 65.

[3] Težak, *et al.*, *J. Physic. Chem.*, 1951, **55**, 1557, 1567.

Investigations are now proceeding in our laboratory,[1] to consider the electrokinetic and electrode potentials as a consequence of the state of the solid rather than its cause. The work is not sufficiently advanced as to report it in detail, but a schematic representation of some of the results already obtained is given in fig. 1 and 2.

The electrokinetic potential curves may be later changed somewhat due to some minor uncertainties as well as secondary effects such as concentration of the sol, concentration of the neutral electrolyte, the method of preparation of the precipitating systems, age of precipitates, duration of the measurements, applied potential, etc., which cannot be discussed here. In particular, the absolute value of the electrokinetic potential is uncertain because of the uncertainty of the Smoluchowsky's equation factor (4π or 6π; 6π used here). Despite this the general form of the curves is sufficiently precise to draw some interesting conclusions.

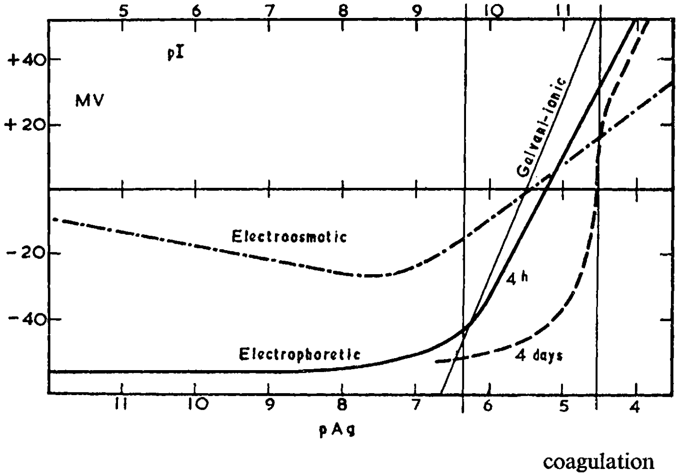

FIG. 1.—Plot of electrophoretic and electro-osmotic potentials against the pI (pAg).

The electrophoretic curves were obtained with sols of concentration 10^{-4} M AgI and 10^{-3} N $NaNO_3$. An apparatus was used with two capillaries to eliminate the electro-osmotic effect.[3] The 4-h curve was obtained with particles which were still in the nascent state in the stable regions (positive and negative). In the region of coagulation the particles grow to 170 mμ. After some hours these particles sediment and after shaking form visible flocks. After 3-4 days, there are still some unsedimented small particles in the clear solution above the sedimented flocks. On the right of the coagulation region the systems are, after some days, coarsening. But even after some weeks the particles will not sediment completely. The sedimented part can be redispersed by shaking. The unsedimented particles do not change their electrophoretic mobility after 3 to 4 days.

For a comparison of experiments with aged sols of other authors with ours it is necessary to keep in mind that sols, aged at pI < 5-6 a few hours after fresh $AgNO_3$ was added to them to obtain the desired pAg, cannot be considered as aged any more. In the first place, the adsorbed I^- will be neutralized and on the surface fresh AgI will be formed. As aged sols or suspensions with aged surfaces, only systems which were aged during the period after they were prepared in their final composition can be considered.

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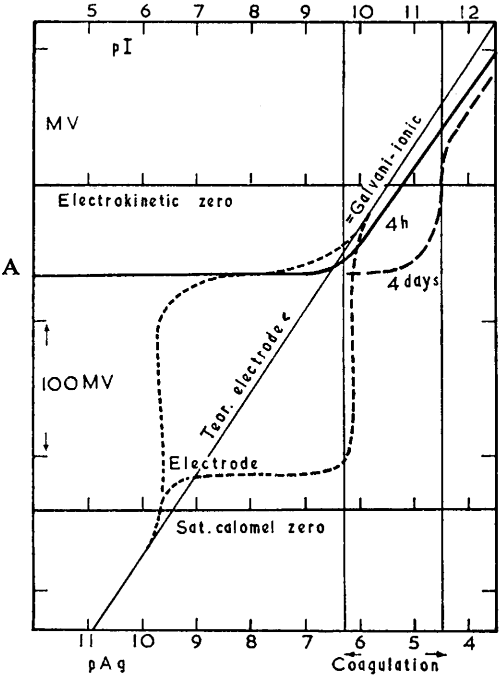
[1] Mirnik and Težak, to be published. Mirnik, Flajšman and Težak, to be published.
[2] Mirnik, Flajšman and Težak, *Arhiv kem.*, to be published.
[3] Težak and Wolf, *Arhiv kem.*, 1953, **25**, 39.

The electro-osmotic curve was obtained with suspensions precipitated (flocculated) in a concentration of AgI 10^{-3} M at pAg $\simeq$ 5. After some minutes various quantities of NaI and $AgNO_3$ solutions were added in order to obtain systems covering the range of necessary activities. These systems were left to stand for 7 days and the electro-osmotic measurements were made with a micro-electro-osmotic cell.[1]

To compare electrokinetic and electrode potential measurements a knowledge of the relative difference between the zero points of potential is necessary. One criterion is to ascribe a value of zero to the ionic part of the Galvani potential at the zero point (activity) of charge, which is supposed to be between pAg 5·5 to 6.[2]

Fig. 2 shows the relative position of the electrophoretic and electrode potential plot against the logarithm of the activity of the potential-determining ions. The zero point of charge is taken as 5·5. With a value of 6 and a factor 4π the conclusions are qualitatively the same.



A, electrophonetic

FIG. 2.—A comparison of the plots of electrophoretic and electrode potentials against the pI or pAg.

The main conclusion is that the potential-determining process (probably there are two) at the electrode covered with fresh colloidal AgI is not the same as the process at a reversible electrode in the region pI $\sim$ 6 to pAg $\sim$ 6. Only the first part of our work with the Ag-AgI electrode has been published as yet [3, 4] and investigations are still proceeding. The most striking fact is that the potential of a (rotating!) electrode with fresh AgI increases in the region pI 5 to 6 faster than the theoretical value to become in the region pI 6 to pAg 6 practically constant. Also the plots of e.m.f. against pI(pAg) are independent of the direction of the activity change. The upper or the lower type of plots (fig. 2) may be obtained in both directions. Among others, these facts indicate that not a simple time lag or non-reversibility could explain these characteristics of the electrodes.

The electrodes were usually investigated in solutions of 10^{-3} N $NaNO_3$ and with not more than 10^{-5} M AgI formed. Checked with 10^{-3} N NaOH the most important behaviour of the electrodes remained unchanged. Similarly, the process determining electrophoretic mobilities of fresh and aged stable particles does not depend upon the activity of the potential-determining ions in the region from pI $\sim$ 4 to pAg $\sim$ 6 and under some circumstances up to pAg $\sim$ 4·5.

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[1] Mirnik and Težak, to be published. Mirnik, Flajšman and Težak, to be published.

[2] Kruyt, *Colloid Science* (Amsterdam, 1952), vol. 1.

[3] Težak *et al.*, *J. Physic. Chem.*, 1951, **55,** 1557, 1567.

[4] Schultz and Težak, *Arhiv. kem.*, 1954, **26,** 187.

A further important conclusion is that the potential difference between the theoretical electrode potential and the ζ-potential (4 days electrophoresis) of small stable particles could be responsible for stability. A theoretical electrode potential which is greater than the 4-day ζ-potential of stable particles of the same sign gives stability. A negative ζ-potential of small stable particles and a more positive potential of the theoretical electrode causes coagulation.

The electrokinetic behaviour of sols and suspensions, the behaviour of electrodes prepared in different ways, and the stability relations, can hardly be explained by the simple Gouy-Stern picture of the double layer;[1] probably the introduction of the dipole part of the Galvani potential g_D, dielectric phase-boundary potential, or surface potential χ and/or the Volta potential difference would be helpful.

Prof. J. Th. G. Overbeek (*van 't Hoff Laboratory, Utrecht*) said: As Dr. Mirnik's electrical data are announced as provisional a lengthy discussion is not warranted. However, a few short remarks might be made.

In the interpretation of electrophoretic and electro-osmotic data the relaxation effect, the surface conductance and possibly the conductivity of the solid AgI should be taken into account. The two ζ-potentials may then become more nearly identical.

Non-reversible behaviour of the AgI electrode between pAg 6 and 10 in unbuffered solutions is well known and could in our experience always be ascribed to lack of equilibrium.

If the difference in the zero points of electro-osmosis (pAg 5·5) and electrophoresis (pAg 4·5) of aged AgI (fig. 1) should be substantiated by later measurements, this would force us to a fundamental change in the comparatively simple picture that we use to have of the double layer around AgI. Our own data,[2] however, indicate a zero of electrophoresis of aged AgI between pAg 5 and 6, that is in agreement with Dr. Mirnik's data on electro-osmosis.

Dr. K. Durham (*Unilever Limited, Port Sunlight*) (*communicated*): In the theory of Verwey and Overbeek the interaction of two double layers is calculated using the simple diffuse double layer picture due to Gouy. This is based on the well-known Boltzmann formula

$$n_r/n^{\pm} = \exp \mp (Ze\psi(r)/kT),$$

in which the assumption is made that the ions are mathematical points. Such assumption is clearly only applicable to low concentrations of electrolyte. This limitation has been partially avoided by the introduction of the Stern correction into the theory and at the moment a good approximation can be obtained by considering the interaction of two Gouy-Chapman layers where the surface potential is the Stern potential (ψ_δ). A difficulty in the application of the Stern correction is that the specific chemical adsorption potentials (ϕ) of the adsorbed ions are unknown quantities.

A paper by Eigen and Wicke[3] published since the discussion may obviate the difficulty of ascribing a value of ϕ. These authors have derived a distribution formula in which hydration and ion volume effects are taken into account more rigorously. On the assumption that the "hydration shells" of Euken[4] are penetrable only for oppositely charged ions, Eigen and Wicke derive a distribution formula:

$$\frac{n_r}{n^{\pm}}\left(\frac{N^{\pm} - n^{\pm}}{N^{\pm} - n_r}\right) = \exp \mp (Ze\psi(r)/kT),$$

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[1] Rutgers and Nagels, *Nature*, 1953, **171**, 568.

[2] Kruyt and Van der Willigen, *Z. physik. Chem. A*, 1929, 139, 53; Troelstra and Kruyt, *Kolloid-Z.* 1942, **101**, 182; *Kolloid-Beih.*, 1943, **54**, 279.

[3] Eigen and Wicke, *J. Physic. Chem.*, 1954, **58**, 702.

[4] Euken, *Z. Elektrochem.*, 1948, **51**, 6.

where $N^{\pm}$ is the number of possible ion places per cm^3, corresponding to the reciprocal volume of the hydrated ion ($N^+ = 1/v^+$). The application of such ideas to the theory of colloid stability might be useful as they appear to be based on effects which are related to real physical phenomena.

Prof. B. Derjaguin (*Academy of Sciences of U.S.S.R., Moscow*) said: Dr. Booth's communication deals in particular with the question of the forces of interaction between a sphere and spheroid separated by a narrow gap. In order to take into account the shape factor Dr. Booth in mentioning, with reference to my paper in the *Transactions*,[1] the formula which refers to the case when there is a plane surface instead of a spheroid, suggests also making a correction for curvature of the spheroid by simply adding the mean curvature of the spheroid to the curvature of the sphere. This gives me an opportunity to note that my original paper,[2] published in 1934, dealt with the general case of the interaction of surfaces of any shape.

Applying the general formula, deduced rigorously in my paper, to the case under consideration, we came to the conclusion that the force of interaction must be proportional to

$$F \sim \frac{1}{\sqrt{\left(\frac{1}{r_0} + \frac{1}{r_1}\right)\left(\frac{1}{r_0} + \frac{1}{r_2}\right)}},$$

where r_0 is the radius of the sphere, r_1 and r_2 the radii of curvature of the main normal cross-sections of the spheroid in the vicinity of the minimum gap width. It can be easily shown on the basis of this exact formula that Dr. Booth's formula is an approximation, which may be used in the case when r_1/r_0 and r_2/r_0 are large.

Mr. F. Booth (*University of London, King's College, W.C.2*) said: It is interesting to note that according to current ideas antibody-antigen combination requires close approach of surface patterns of atoms which are complementary and also with the correct mutual orientation. It is easy to see how the concept of incomplete adhesion, which is incorporated in the theory in eqn. (2.18) and (2.19) of my paper, can be applied to this mechanism. If patterns are not complementary it is reasonable to suppose that α is zero, in which case no coagulation occurs. For complementary patterns α will not be zero, but in general will be less than 1 since adhesion will also require correct orientation. But unless α is very small compared with ρ/a, the rate of coagulation will not be very different from that for complete adhesion.

Since an approximate solution of eqn. (3.11) would be adequate, the following method is probably more useful than the one described in the paper. Suppose we first transform the θ variable to $x = \cos\theta$. Next the interval $0 \leqslant x \leqslant 1$ is divided into n equal parts and derivatives with respect to x replaced by differences. Eqn. (3.11) now reduces to a set of equations of the form:

$$D_m\left[\frac{1}{r^2}\frac{\mathrm{d}}{\mathrm{d}r}r^2\frac{\mathrm{d}c_m}{\mathrm{d}r} + \frac{c_m}{kTr^2}\frac{\mathrm{d}}{\mathrm{d}r}r^2\frac{\mathrm{d}V_m}{\mathrm{d}r} + \frac{1}{kT}\frac{\mathrm{d}V_m}{\mathrm{d}r}\frac{\mathrm{d}c_m}{\mathrm{d}r}\right]$$
$$+ \frac{1}{C_b}[kT\{(n^2 - m^2 + m)c_{m-1} + (n^2 - m^2 - m)c_{m+1} - 2(n^2 - m^2)c_m\}$$
$$+ \tfrac{1}{2}\{(n^2 - (m+1)^2)^{\frac{1}{2}}L_{m+1}c_{m+1} - (n^2 - (m-1)^2)^{\frac{1}{2}}L_{m-1}c_{m-1}\}] = 0,$$

where f_m denotes the value of f at the end of the mth interval. This set of equations can be solved by suitable methods of successive approximations. For example, as a first approximation the second part involving C_b could be dropped and the first part solved for the c_m. For a second approximation, the second term could be retained but with the first order solutions substituted for the c_{m-1}, c_m and c_{m+1}

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[1] Derjaguin, *Trans. Faraday Soc.*, 1940, **36**, 203.

[2] Derjaguin, *Kolloid-Z.*, 1934, **69**, 155.

in it. The whole set of equations can now be solved by the method of variation of the constants.

In the expression for the diffusion coefficient D in the paper by Lawrence and Mills, the expression for *solid* spheres is used. The general theory for Brownian motion gives $D = kT/f$, where f is the force required to drag the sphere through the medium with unit velocity. Hadamard[1] and Riabouchinsky[2] showed that for a *liquid* sphere the Stokes formula for f should be replaced by

$$f = 2\pi R\eta(2\eta + 3\eta')/(\eta + \eta'), \tag{1}$$

where η' is the viscosity of the liquid within the sphere. Hence, if η' is small compared with η, an appreciable correction to D is obtained.

For liquid droplets, Smoluchowski's theory may require some correction in another respect. It is assumed in this theory that the friction constant, and consequently the diffusion constant, remains independent of the degree of separation of two coagulating drops. In fact, of course, the diffusion constant must alter as one droplet approaches another since the flow distribution round one affects the frictional resistance of the other. If the functional dependence of the diffusion constant on the separation is known, it is easy to correct Smoluchowski's analysis. For, suppose we consider diffusion to a spherical sink of radius a, in an infinite medium, r being distance measured from the centre of the sink, and D being a function of r. Fick's law now gives

$$\frac{\partial}{\partial r} r^2 D \frac{\partial c}{\partial r} = 0, \tag{2}$$

c being the concentration. It is easily verified that the solution of this equation with the conditions $c = 0$ at $r = a$, and $c = c_0$, $r \rightarrow \infty$ is

$$c = c_0\left[1 - \int_r^\infty \frac{\mathrm{d}r}{Dr^2} \Big/ \int_a^\infty \frac{\mathrm{d}r}{Dr^2}\right]. \tag{3}$$

From eqn. (3) it follows that the diffusion constant in Smoluchowski's analysis should be replaced by the quantity $\left[a\int_a^\infty \frac{\mathrm{d}r}{Dr^2}\right]^{-1}$.

To make further progress it is necessary to know how the droplets behave when they coalesce. I should therefore like to ask the authors if they made any observations on this; for example, one would like to know whether they remain spherical until contact or whether there is considerable shape distortion on approach and, if so, its nature.

As the authors have pointed out in the introduction to their paper, observations on the coagulations of emulsions should provide a better check of Smoluchowski's theory than measurements on solid suspensions since, unlike solid particles, two liquid spheres must give another sphere after coagulation. Thus the fundamental equations for the rate of growth of N_k, the number of k-mer drops of radius r_k, namely,

$$\mathrm{d}N_k/\mathrm{d}t = 2\pi \sum_{i+j=k} D_{ij}(r_i + r_j)N_iN_j - 4\pi N_k \sum_{n=1}^{\infty} D_{kn}(r_k + r_n)N_n,$$

where

$$D_{ij} = \frac{kT}{6\pi\eta}\left(\frac{1}{r_i} + \frac{1}{r_j}\right), \tag{4}$$

will apply strictly, apart from the correction already discussed.

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[1] Hadamard, *Compt. rend.*, 1911, **152,** 1735.

[2] Riabouchinsky, *Bull. Acad. Sci. Cracow*, 1911, 40.

To get the formula used by Dr. Lawrence and Dr. Mills for N_r however, it is necessary to introduce the simplifying assumption that

$$\left(\frac{1}{r_i} + \frac{1}{r_j}\right)(r_i + r_j) = 4. \tag{5}$$

This approximation is satisfactory provided that i and j do not differ much, but for an exact test of the theory it seems worthwhile to see if it can be avoided. For emulsions this is not difficult since, from volume conservation of the coagulating droplets it follows that

$$r_i = ri_1^{\frac{1}{3}} \tag{6}$$

Hence we can put

$$\left(\frac{1}{r_i} + \frac{1}{r_j}\right)(r_i + r_j) = 4(1 + \lambda_{i,j}), \tag{7}$$

where

$$\lambda_{i,j} = \frac{1}{4}\left[\left(\frac{i}{j}\right)^{\frac{1}{6}} - \left(\frac{j}{i}\right)^{\frac{1}{6}}\right]^2. \tag{8}$$

If eqn. (7) is substituted in eqn. (4) no simple exact solution can be written down immediately. But from eqn. (8) we see that $\lambda_{i,j}$ will be very small unless the ratio i/j of its inverse is large. In the early stages of coagulation the concentration of spheres of large index will be small and so it is easy to conjecture that the Smoluchowski theory might be satisfactory for the early stages, but deviations will develop as the time t increases. This also suggests that eqn. (4) can be solved exactly by successive approximation methods, using as a basis the Smoluchowski solutions. Preliminary calculations indicate that the mean drop volume is no longer linearly dependent on the time, and we can write, in the notation of Lawrence and Mills,

$$\bar{v}_t = v_0(1 + \beta N_0 t - \lambda_{1,2}(\beta N_0 t)^2 + \text{terms of order } t^3). \tag{9}$$

From eqn. (8) we have $\lambda_{1,2} = 0{\cdot}0114$. Full details will be published in due course.

A further modification of the Smoluchowski theory which may be of importance is indicated by the following apparent paradox. In the Lawrence and Mills formula for the mean volume, v_t increases indefinitely with the time. This must clearly be incorrect for t sufficiently large, since the ultimate stage is one in which all the droplets have coagulated into a single drop or at any rate into a separate phase. It is easy to see that this result arises because the Smoluchowski theory ignores boundary effects. The model postulates a sink in an *infinite* medium and near the boundaries this model will overestimate the coagulation rate. The effect of the boundaries will increase in importance as the size of the droplets increases, and it will depend on the size and shape of the containing vessel. A theoretical analysis would be difficult, but it should be possible to see whether it is of importance in any set of experiments simply by making observations using containers of different dimensions.

Dr. A. S. C. Lawrence and Mr. O. S. Mills (*Sheffield University*) (*communicated*): With respect to the first point raised by Dr. Booth it can be shown that the viscosity correction to the Stokes formula for f is negligible in the present case. Roughly, the ratio η'/η for ditolyl + water is 6 so that $2\eta + 3\eta'/\eta + \eta'$ becomes 2·9 instead of 3 for solid spheres. As far as distortion of droplets on approach is concerned, no detectable changes occurred with droplets not actually touching; on contact, slight flattening was occasionally noticed for large drops, but this may have been due to the effect of the cover slip.

The simplifying assumption (5) is contained in Smoluchowski's paper which also indicates that the subsequent treatment might only be applicable over a limited time. It is interesting to note that the extension suggested should cause $\bar{v}_t$ to increase less rapidly after longer times. In the particular apparatus used, observations beyond those quoted in the paper showed that $\bar{v}_t$ appeared to go through a maximum. This cannot, of course, be a consequence of coalescence and was attributed to dispersed phase clinging to the glass walls of the rotating tube, such adherence being plainly visible. It may be that the first falling-off with time from linearity is to be partly, at least, attributed to the effect suggested. The equation for $\bar{v}_t$ can only be correct over limited ranges of physical conditions such as that of time in a finite apparatus. A similar restriction applies to phase volume.

Dr. M. van den Tempel (*Rubber-Stichting, Delft*) said : Measurements of the average volume of oil droplets, as a function of time, are more rapid and more accurate by counting the number of particles. It is easy to show that a decrease in particle concentration of, say, 10 % is accompanied by a volume increase of only 3 %, which cannot be measured with sufficient accuracy. Results of determinations of the particle *concentration* as a function of time have been published in the literature; in all cases the inverse of the particle concentration was found to vary linearly with time.

Some confusion is found regarding the definition of the terms coagulation and coalescence. The theory of Smoluchowiki is concerned with the process of *flocculation* and has nothing to do with the *coalescence* of two adhering oil globules into one larger droplet. From the data presented I have the impression that it is assumed that coalescence follows immediately upon flocculation. This is certainly not the case. We have been able to separate flocculation and coalescence experimentally, and to measure the rates of both processes. The results show that coalescence, in the kind of emulsions studied by Dr. Lawrence, occurs at a rate of about 10^{-3} sec^{-1}. This is exactly the value which he found for the "probability of collision", and I might suggest that, actually, he has been measuring the rate of coalescence in these experiments.

Dr. A. S. C. Lawrence and Mr. O. S. Mills (*Sheffield University*) said: Dr. van den Tempel is, of course, correct in stating that we have measured the kinetics of coalescence; one of the major objects of the work was to investigate the relation between the rate of collision and rate of coalescence. The results show that only one in 10^3 collisions result in coalescence in non-stabilized emulsions.

The matter of clustering, which several speakers raised, requires some consideration. We found, in non-stabilized emulsions, very little clustering: in soap-stabilized ones, however, there was more but very much less in our "rotated" specimens than in similar mixtures standing at rest. We cannot regard clustering as coagulation comparable with that in sols in which the dispersed phase is a solid: such coagula are *not* re-dispersed or prevented from forming by slight shearing forces whereas the emulsion clusters are. The latter appear to be more comparable with tactoids in aged sols in which the particle size has become large.

Dr. L. Cohen (*Simon-Carves Ltd., Stockport*) said : It occurs to me that the rate of coagulation of a sol could be followed by observing the Tyndall spectrum caused by the scattering of white light by the sol. I am not sure, at the moment how changes in this spectrum are correlated with the change in particle size distribution but this could, no doubt, be worked out. It is well known that highly monodisperse hydrosols can be produced by controlled precipitation (e.g. of sulphur) and are characterized by the visibility of the high orders of the Tyndall spectrum. As the aeresol ages the higher orders become diffuse and finally disappear and thus indicate the increase in polydispersity.

Highly monodisperse liquid aerosols can also be produced fairly easily, as shown by La Mer and his co-workers, and the Tyndall spectra observed. It would be of interest to observe the ageing process in such an aerosol and to compare it with the process in a similar hydrosol.

Prof. B. Težak (*University of Zagreb*) said: There are many indications that the light-scattering technique may be useful when carefully applied to observation of precipitation systems. I have used tyndallometrical measurements for more than 20 years,[1] and by observing the scattered light of white sols in many spectral regions (e.g. in the blue and red) it is possible to determine roughly the particle sizes between 30 to 300 mμ by so-called tyndallometrical dispersion quotients.[2]

The main condition for obtaining relatively simple relationship between the concentration of the sol and the intensity of the scattered light is to perform measurements with an experimental set-up which ensures the application of the Lambert-Beer law (small thickness of the cell and concentration of sol). Under such conditions there is a linear relationship between absorption coefficients and scattering coefficients as may be seen in fig. 2-7 of an earlier publication.[3]

Mr. R. J. Cole (*Long Ditton, Surrey*) said : In the course of the Discussion, Mr. Hill referred to bands which he had observed in certain sedimenting systems and mentioned that he had not come across any analogous phenomena in the literature. I should like to point out that stratification has been observed in other systems and that the literature on the subject is reviewed in Søren Berg's book.[4] Mendenhall and Mason,[5] using pulverized stone, found that even with otherwise good temperature control, strata formed when a suspension was kept in an ordinary lighted room but none formed if the suspension was transferred to the dark. The conclusion they came to was that strata arise only when there is a horizontal temperature gradient in suspension which gives rise to local systems of convection currents characterizing each stratum. Berg, on the other hand, obtained results which deviated somewhat from those of M. and M.; these latter results suggested that step-wise variation in particle size distribution also has to be taken into account.

Mr. C. G. A. Hill (*Levy West Laboratories, Wembley*) (*communicated*): I am grateful to Dr. Cole for the references to banding during sedimentation. In our case neither temperature variation nor illumination were necessary for the development of the bands. A stepwise particle size distribution was not present either since the bands all moved down the tube at a constant speed.

Dr. H. Koelmans (*Phillips Res. Lab., Eindhoven*) (*communicated*): The formation of bands in sedimenting suspensions reported by Dr. Hill was frequently found in our experiments too. As we also observed this phenomenon in stabilized suspensions in xylene, where a flocculation by electrolyte seems to be excluded, I wonder whether the explanation offered is correct.

Prof. B. Derjaguin (*Academy of Sciences of U.S.S.R., Moscow*) said: In my opinion the most important result of the communication of Dr. Norrish seems to be the conclusion concerning the law of decrease of attraction forces between silicate sheets as a function of their distance. It is found that these forces must decrease as the inverse 1·8 power of sheet separation. It seems to me that such a slow decay of these forces, if assumed, points to their electrostatic rather than molecular origin, which may be explained on the basis of the results of Prof. Obreimoff, Dr. Krotova and Mr. Karassef on the electrical effects accompanying the splitting of mica and other solid bodies.

It was proved that after the splitting of mica and many other crystals the new surfaces reveal a mosaic of alternate charges. The interaction of these charges with the opposite charges via the gap formed is the cause of high and non-equilibrium values of the work of splitting.[6] The most striking proof for the existence of high local potential differences (about 10^4 and 10^5 V) involved in the process of splitting is the autoelectronic emission found by Mr. Karassef and Dr. Krotova.[7]

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[1] Težak, *Glas. Hem. Društva Kr. Jugosl.*, 1933, **4**, 137; *Kolloid-Z.*, 1934, **68**, 60.

[2] Težak, *Z. physik. Chem. A*, 1935, **175**, 219; 1936, **175**, 284; *Kolloid-Z.*, 1936, **74**, 16.

[3] Težak, *Kolloid-Z.*, 1936, **74**, 16.

[4] Berg, *Studies on Particle Size Distribution* (Copenhagen, 1940), pp. 186-216.

[5] Mendenhall and Mason, *Proc. Nat. Acad. Sci.*, 1923, **9**, 199, 202.

[6] Derjaguin and Krotova, *Adhesion* (Moscow, 1949) (ed. Acad. Sci. of U.S.S.R.), *C.R. Acad. Sci. U.S.S.R.*, 1948, **61**, 849.

[7] Karassef, Krotova and Derjaguin, *C.R. Acad. Sci. U.S.S.R.*, 1953, **88**, 777.

This permitted us to measure the corresponding velocities and energies of electrons and eventually the potential differences (*ca.* 10^4-10^5 V) set up. It is possible that an analogous although much smaller effect arises when the silicate sheets are split and moved apart by the disjoining action of aqueous solutions in the process of swelling.

When even a slightly heterogeneous distribution of charges is retained in the presence of electrolyte solution, an electric attraction must be present which may vary very slowly with the separation; it varies the slower the smaller the gap width divided by the mean linear dimension of individual areas of the corresponding mosaic of alternating charges.

An alternative, perhaps more probable, possibility of accounting for Norrish's results lies in the assumption that for small gaps between the crystal sheets the theory of interaction of ionic layers is inapplicable owing to the preponderance of the effects due to the formation of polymolecular solvate layers and to their disjoining pressure. This is analogous to the case observed in the investigation of the disjoining pressure isotherms of the free films of aqueous soap solutions, described in our paper.

Dr. G. A. H. Elton (*Battersea Polytechnic, S.W.*11) (*communicated*) : I should like to compliment Prof. Prokhorov on his exceptionally neat method of following the coagulation of water droplets in an aerosol under continuous-flow conditions. This technique should prove valuable in studying several outstanding problems in aerosol physics, such as the effects of electrification, hydrodynamic interaction and double layer interaction on the stability of aerosols.

I think that it may be wrong to assume that the limiting collision efficiency reached in Prof. Prokhorov's experiments is necessarily 100 %. Langmuir [1] showed theoretically that the collision efficiency for drops in fogs and clouds is probably very much less than unity owing to hydrodynamic interaction between the moving droplets. The calculated collision efficiency for two droplets of radius about 5 microns is less than 5 %. Sartor,[2] in an experimental study, found collision efficiencies rather larger than those predicted by Langmuir, but showed that only a small proportion of collisions produced coalescence, except in the presence of an applied electric field. It thus appears likely that, with droplets of the size studied by Prof. Prokhorov, the collision and coalescence efficiencies are still quite low, even in the presence of saturated vapour.

Mr. D. R. Griffiths and I have used an aerosol generator very similar to that described by Prof. Prokhorov, but have studied the collision of the droplets by a less direct method (by measurement of light transmission). Preliminary results indicate that factors other than humidity deficit affect coalescence efficiency. For example, small amounts of anionic surface-active agents present in the droplets tend to lower the coalescence efficiency for water droplets, while small amounts of cationic or non-ionic surface active agents tend to raise it.

Mr. K. Durham (*Unilever Ltd., Port Sunlight*) said : In the absence of high surface viscosity which might influence film drainage and thickness, the most important factors which determine the thickness of a free film are, as Derjaguin says, the nature and concentration of electrolyte in solution. Thinning of a film will proceed until a critical thickness is reached below which further thinning is opposed by the repulsive forces between the double layers associated with the surfaces. Since the double-layer thickness is inversely proportional to the (ionic strength)$^{\frac{1}{2}}$ the addition of electrolyte should promote greater thinning and instability of films.

A 0·1 % sodium laurate solution adjusted to pH 10 does not foam; on addition of electrolyte (NaCl, Na_2SO_4, $NaNO_3$), however, foaming ability returns and the foams may be very stable (half-life of several hours at a sodium ion concentration of 0·1 M). Such foams drain very quickly and the films thin very rapidly

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[1] Langmuir, *J. Meteorology*, 1948, **5**, 175.

[2] Sartor, *J. Meteorology*, 1954, **11**, 91.

to an apparently steady thickness which may be maintained for hours. The reduction in surface tension produced by addition of electrolyte is in itself insufficient to account for the foam stability and the surface viscosity was unchanged. If the forces responsible for foam stability are primarily repulsive electrostatic forces the addition of electrolyte up to 0·1 M should not result in increased foam stability.

It would appear, therefore, that the statement of Prof. Derjaguin that " the life of a film is determined by the kinetics of its thinning to the critical thickness at which there occurs a transition to an unstable state " requires some modification when applied to foams possibly subject to thermal and mechanical disturbance. In such cases probably the most important factor in stability is the rate of attainment of equilibrium surface tension which gives the surface film elastic properties. This idea was first introduced by Gibbs [1] and extended recently by Burcik.[2]

Dr. G. A. H. Elton (*Battersea Polytechnic, S.W.*11) said : Prof. Derjaguin claims in his paper that the results of my work [3] on the behaviour of thin liquid films between approaching surfaces have been disproved.[4] My work was carried out using water and aqueous salt solutions (no surface-active solutes were investigated), and the results obtained indicated that any thick disjoining films observed in such liquids [5] were not at equilibrium, but thinned slowly and, after many hours, became undetectable. I should like to point out that Evans and Ewers [6] obtained results in qualitative agreement with mine, while Evans,[7] using water which had been very carefully purified, duplicated my results. Evans [7] also found that in water containing a surface-active agent at concentration 3×10^{-6} M, equilibrium films of thickness about 1000 Å were obtained. These films responded to changes in bubble pressure, temperature and electrolyte concentration in the same way as those observed by Derjaguin and Kusakov [5] in supposedly pure water. It was found to be very difficult to prevent such effects from arising from contamination of the bubble surface, and Evans suggested that the results of Derjaguin and Kusakov were probably due to such contamination.

I would therefore submit that, although the existence of equilibrium disjoining films in solutions containing surface-active substances seems to be established beyond doubt, the bulk of the evidence available at present indicates that in pure water such films, if they exist at all, are very thin indeed.

Prof. B. Derjaguin (*Academy of Sciences of U.S.S.R., Moscow*), said: Space does not permit me to deal with Dr. Elton's remarks concerning the measurement of the disjoining pressure of thin films; moreover the essence of the matter was discussed in detail by Prof. Koussakov and myself elsewhere, and none of our arguments have been refuted.[8] It was shown there that Dr. Elton's approach to our investigations is an erroneous one. I shall therefore confine myself only to comments on the investigation by Evans mentioned here. In an earlier paper [9] Evans used the investigation of disjoining pressure in studying the mechanism of flotation. In a recent article [10] Evans, in pointing out the influence of surface-active substances on the equilibrium thickness of wetting films, makes the assumption that the film thickness found by Koussakov and myself may be explained mainly by the influence of such substances present in the solution. It follows

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[1] Gibbs, *Collected Works of J. W. Gibbs* (Longmans, Green & Co., 1933), pp. 300-314.

[2] Burcik, *J. Colloid Sci.*, 1950, **5**, 421.

[3] Elton, *Proc. Roy. Soc. A*, 1948, **194**, 275.

[4] Derjaguin and Kusakov, *J. Physic. Chem.* (*Russ.*), 1952, **26**, 1536.

[5] Derjaguin and Kusakov, *Acta physicochim.*, 1939, **10**, 25.

[6] Evans and Ewers, *Symposium on Recent Developments in Mineral Dressing* (Institution of Mining and Metallurgy, 1952), p. 457.

[7] Evans, *Nature*, 1953, **172**, 776.

[8] Derjaguin and Kussakov, *J. Physic. Chem.*(*Russ.*), 1952, **26**, 1536, 1540.

[9] Evans, *Recent Development in Mineral Dressing* (London, 1953).

[10] Evans, *Nature*, 1953, **172**, 776.

from theoretical considerations, especially from those contained in my paper on heterocoagulation presented at this Discussion, that adsorption of surface-active molecules on both surfaces bounding the wetting film, by changing the charge of those surfaces, can increase their equilibrium thickness. This is not in contradiction with out experiments, and, as a matter of fact, was observed and commented upon.[1] However, Evans' statement that in the absence of surface-active impurities the equilibrium thickness of the films becomes extremely small is in contradiction to our experiments, and the assumption made of an influence on them of surface-active impurities which were not removed is unfounded. We took great care in this respect, e.g. by the exclusion of paraffin and the careful purification and distillation of the water, etc.

I should like to point out that Evans' experiments in essence also confirm the existence of an equilibrium disjoining pressure and refute the assumption of a different, for instance an electroviscosity, nature.

Dr. W. H. Banks (*Printing, Packaging and Allied Trades Res. Assoc., Leatherhead*) (*communicated*): The observations of Prof. Derjaguin on the contrasting behaviour of quartz fibres in water and magnesium sulphate solution may well arise through the accumulation of basic magnesium compounds on the quartz. Unpublished observations which I have made on solutions of cations capable of giving insoluble products of hydrolysis show that the accumulation of such basic compounds at interfaces while small, is measurable and is both pH and time dependent. Such accumulation of a " cementing " gel would be consistent with Prof. Derjaguin's observation that at least protracted contact and the presence of magnesium sulphate were necessary conditions. It would be therefore desirable to extend these observations to divalent cations which do not give insoluble hydrolytic products and also to solutions of magnesium sulphate over a wide range of pH.

Prof. B. Derjaguin (*Academy of Sciences of U.S.S.R., Moscow*) (*communicated*): I must stress that the phenomenon of slowly rising adhesion between crossed quartz fibres immersed in water or in another liquid is of a quite general nature. Mrs. Malkina and myself particularly investigated[2] the influence on the adhesion kinetics of other salts, e.g. of KCl, $AlCl_3$ and found it analogous to that of $MgCl_2$. It follows that the phenomenon investigated cannot be understood on the basis of any particular mechanism, similar to that suggested by Dr. Banks, but must involve a general mechanism such as that discussed by Dr. Adamson.

Prof. B. Derjaguin (*Academy of Sciences of U.S.S.R., Moscow*) said: The interesting paper presented by Prof. Schofield and Dr. Samson is concerned with the peculiarities of the flocculation and deflocculation of clay minerals which depend upon the interaction forces between oppositely charged areas of the surfaces of two adjacent particles whose quantitative theory has been developed in my paper on heterocoagulation, presented at this Discussion. It is not difficult to see that the theory and experiment are in accord and indicate that heterocoagulation, in contrast to usual coagulation, can take place when the diffuse double later is not compressed but thickened, as for instance, in the case of a univalent electrolyte of low concentration (the inversion of Hardy-Schultz rule). In this case the radius of action of the attraction forces which arise as a result of the overlapping of oppositely charged ionic atmospheres increases and sometimes these forces predominate even when repulsion forces are present owing to the formation of polymolecular hydrate layers.

The data presented by Prof. Schofield and Dr. Samson are particularly interesting since they seem to show that similar repulsion forces can be greater when the clay particles are brought together face to edge than when they are drawn

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[1] Derjaguin, Kussakov and Lebedeva, *C.R. Acad. Sci. U.S.S.R.*, 1939, **23**, 668. Kussakov and Titijevskaya, *C.R. Acad. Sci., U.S.S.R.*, 1940, **28**, 333.

[2] Malkina and Derjaguin, *J. Coll. Sci.* (*Russ.*), 1940, **12**, 431.

together face to face. Otherwise it is difficult to understand why the preferential face-to-face coagulation ever occurs, since in this symmetrical case the electrostatic repulsion cannot be smaller than in the asymmetrical one.

In connection with the results presented by Prof. Schofield and Dr. Samson concerning the determination of the specific surface of clay minerals, I should like to point to the possibility of determining this value by the method based upon the filtration of a rarefied gas under Knudsen's regime with the application of the formula derived by me in 1946 which connects the resistance of filtration in this case with specific surface.[1]

The corresponding method has been developed by Prof. Zachavaeva, Fridland and others (see e.g. ref. (2)) in the Institute of Physical Chemistry of the Academy of Sciences of U.S.S.R. and in the Leningrad Agrophysical Institute. This method has some advantages over that based upon the adsorption of nitrogen; it affords much greater simplicity and quickness of measurement with a wider range of accessible specific surface values. The verification of this method by comparing the values of specific surfaces of the same powders measured by this method and by the method based on the low-temperature adsorption of nitrogen has been made by a number of authors.[3] The average difference of 2-4 % found by these authors lies within the range of experimental errors. This shows that the precision of this method is probably not less than that based upon the adsorption of nitrogen. At the same time the former method, in contrast to all methods of adsorption, is an absolute one since it does not require the determination of the area occupied by the molecules in the absorbed layer, and does not introduce any empirical constants.

Prof. Dr. J. Th. G. Overbeek (*van't Hoff Laboratory, Utrecht*) said : In fig. 3 of Schofield and Samson's paper where the deflocculation of kaolin by different salts is depicted, we see a clear case of a double Schulze-Hardy rule, viz., an influence of the valence of both positive and negative ions. This occurs often with lyophilic colloids and is always an indication of the simultaneous presence of positive and negative charges on colloidal particles (Bungenberg de Jong). Although not being as conclusive as Dr. Schofield's method using the positive and negative adsorption of Cl^- ion, the double Schulze-Hardy rule should be regarded as easily obtainable " circumstantial evidence ".

Dr. S. Lifson (*Weizman Institute of Science, Israel*), said : Thiessen [4] in 1942 proved that the edges of certain kaolinites were carrying positive charges, while their surfaces were charged negatively. He used the electron-microscope technique and found that negatively charged colloidal gold particles were adsorbed on the edges of the kaolinite flakes, but were repelled from the flat surfaces. A. Oplatka and myself, following Thiessen's results, have assumed that the flocculating effect of long chain polyacidic molecules (e.g. Krillium) which are used as soil conditioners, may have a similar origin: the very long, negatively charged molecules may interact simultaneously with the edges of two or more clay particles, thus causing flocculation and aggregation. Electron microscopic study of this assumption by A. Oplatka is now in progress. He also found that high-molecular weight polyphosphates cause flocculation like other polyacids, while low molecular weight polyphosphates, whose molecules probably adhere to single colloidal particles, have a peptizing effect.

Dr. H. Yaalon (*Hebrew University, Jerusalem*) said : In the paper by Schofield and Bunson the anions mentioned as being adsorbed by flocculated kaolinite

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[1] Derjaguin, *C.R. Acad. Sci. U.S.S.R.*, 1946, **53**, 623.

[2] Derjaguin, Fridland and Krylova, *C.R. Acad. Sci. U.S.S.R.*, 1948, **61**, 653; *J. Physic. Chem.* (*Russ.*), 1950, **24**, 1371.

[3] Zavaritzkaja and Grigorov, *C.R. Acad. Sci. U.S.S.R.*, 1952, **86**, 757. Kraus, Ross and Gerifalco, *J. Physic. Chem.*, 1952, **57**, 334.

[4] Thiessen, *Z. Elektrochem.*, 1942, **48**, 675.

are all of the di- or polyvalent type. However, the univalent fluoride also decreases the viscosity of the sol considerably and causes its deflocculation, while chloride, as shown by the author, does not.

I wonder whether Dr. Schofield has any clue as to the mechanism and reasons for this preferential adsorption by some anions. From experiments performed in Jerusalem we have reason to believe that the increase in inter-particle repulsive forces is due to the decomposition of the mineral by certain anions, since the removal of alumina from the lattice results in an increase of its negative charges.

Dr. M. van der Waarden (*Kon/Shell Lab., Amsterdam*) said : Is it possible that the phenomenon of positive charged edges found only on kaolinite, is due to the fact that the other minerals (illite and montmorillonite) consist of particles which are much thinner and smaller? This argument is used by the authors themselves in connection with a kaolinite sample. And is there any connection between the hypothesis on positive edges on kaolinite and the hypothesis of Van Olphen on montmorillonite, which was published in 1950 and 1951.

Dr. S. Lifson (*Weizmann Institute of Science, Israel*) said: A montmorillonite+water solution is an interesting example of a lyophilic system of plane parallel double layers. The following is an outline of a calculation of the electrostatic free energy of such systems. It is, at the same time, a generalization of Verwey and Overbeek's theory of the electrical double-layer interaction, containing (i) the surface charges and potential explicitly, therefore being adequate to apply to processes where either or both are variable, (ii) any number of ionic species and valencies, including the special case of the absence of any ions except counter ions (i.e. when the colloid is dissolved in pure water, without the additional electrolyte).

We follow almost the same model and notation as presented by Prof. Overbeek in Kruyt's *Colloid Science*,[1] starting with the differential equation,

$$\Delta\psi = -\left(\frac{4\pi}{\epsilon}\right)\sum_i z_i e n_{i0} \exp\left(-\frac{z_i e\psi}{kT}\right), \tag{1}$$

and its first integral,

$$\left(\frac{\partial\psi}{\partial x}\right)^2 = \frac{8\pi kT}{\epsilon}\sum_i n_{i0}\left[\exp\left(-\frac{z_i e\psi}{kT}\right) - 1\right]. \tag{2}$$

In performing the charging process [2] we impose, however, different conditions. These seem to be more suitable for lyophilic systems, although the results, like Verwey and Overbeek's results, will have general validity if properly used. The conditions maintained during the (hypothetical) charging process are:

(i) the number of charges on each of the two parallel plates is kept constant, so that no chemical adsorption is involved. Consequently the charging must be performed on the surfaces as well as in the bulk of the solutions, with the surface potential varying with the charging parameter (λ).

(ii) The parallel plates and the solution enclosed between them comprise a closed system; the distance between the plates as well as the number N_i of the diffuse ions of each type i (and their average concentrations $\bar{n}_i$) is kept constant.

We also use a different zero point for the electrostatic potential. This is, however, only a mathematical convenience and not an imposed condition, because only potential differences have physical significance. We put $\psi = 0$ in the median plane between two plates, i.e. where $\partial\psi/\partial x = 0$. It follows that n_{i0} are the

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[1] Overbeek in *Colloid Science*, ed. Kruyt (Elsevier, 1952), vol. 1, pp. 128, 142, 248.

[2] ref. (1), p. 142, eqn. (76).

concentrations of the ionic species at the median plane and so change during the charging process, approaching $\bar{n}_i$ when λ approaches zero. n_{i0} and $\bar{n}_i$ are related by

$$\bar{n}_i d = \int_0^d n_{i0} \exp\left(-\frac{z_i e\psi}{kT}\right) \mathrm{d}x, \tag{3}$$

where d is half the distance between the plates. The electrostatic free energy may be expressed in the form,

$$F_e = \frac{\epsilon}{8\pi}\int_{\lambda=0}^{1}\int_V (\mathrm{grad}\,\psi)^2\,\mathrm{d}V\frac{\mathrm{d}\lambda}{\lambda}. \tag{4}$$

This expression is integratable under the above-mentioned conditions and the result is

$$F_e = 2\nu z_1 e\psi_1 + kT\sum N_i \ln\frac{Vn_{i0}}{N_i} - kT\sum_i (N_i - Vn_{i0}), \tag{5}$$

where ν is the number of surface charges, z_1 their valency and ψ_1 the surface potential.

A set of auxiliary equations derived from eqn. (2) and (3) connects n_{i0} and ψ_1 with $\bar{n}_i = N_i/V$ and d.

$$d = \int_0^{\varphi_1} \frac{\mathrm{d}\psi}{\partial\psi/\partial x} \tag{6}$$

$$\bar{n}_i d = \int_0^{\varphi_1} \frac{n_{i0}\exp\left(-\frac{z_i e\psi}{kT}\right)\mathrm{d}\psi}{\partial\psi/\partial x}.$$

These integrals may be transformed into standard elliptic integrals in all cases where $|z_i| \leqslant 2$ and will take a simple trigonometric form when the only diffuse ions are counter ions, i.e. when the colloid is dissolved in pure water.

In comparing these results with Verwey and Overbeek's it must be borne in mind that because of the different conditions of the charging process, the two methods differ as to the free energy of the reference state (i.e. the state of the system when discharged). Details are too lengthy to be given here. The above results may be found suitable for calculating, for example, osmotic pressures or titration curves of bentonite + water solutions.

Prof. B. Težak (*University of Zagreb*) said: The observations of swelling of montmorillonite systems may be useful in answering some general questions about coagulation theory. First we have here examples where the coulombic interactions may give strong attractive potentials, much greater than those of the van der Waals' forces. Secondly, there is no agreement, for the observed inter-layer spacings from 30 Å to 130 Å, between the attractive and repulsive forces as calculated by the theory of Verwey and Overbeek. Thirdly, there is a pronounced effect of specificity of the ions on the one hand, and the surface density of charges on the other, as reflected in the swelling characteristics of the systems.

Using X-ray studies of similar systems it should be possible to examine many points of the detailed structure of the methorical layer. In this respect, work with various solvent extraction systems may also be very helpful.

Prof. P. Rehbinder (*Academy of Sciences of U.S.S.R., Moscow*) (*communicated*); Bockris and Parry Jones [1] have made measurements on zinc which confirm the results of our experiments [2] yielding a typical electrocapillary curve for the

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[1] Bockris and Parry Jones, *Nature*, 1953, **171**, 930.

[2] Rehbinder and Wenström, *Acta physicochim.*, 1944, **19**, 36; *C.R. Acad. Sci. U.S.S.R.*, 1949, **68**, 329.

pendulum hardness (by measuring the damping of oscillations) as a function of the potential of metals in electrolyte—a direct result of the reduction of metal strength by adsorption.

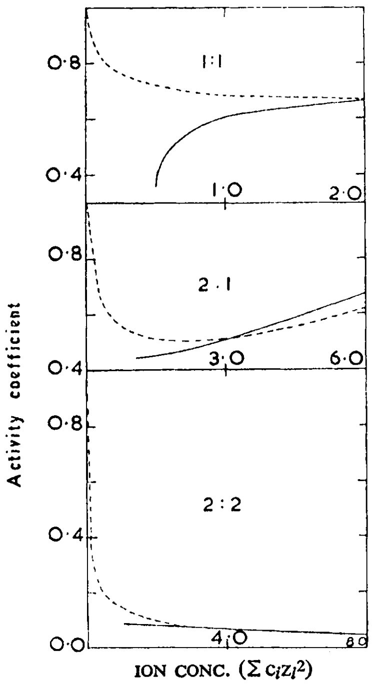
The authors, however, attribute these results to the reduction of the external friction due to the formation of an electric double layer.[1] As a matter of fact, this explanation not only fails to refute our interpretation but directly follows from it. The damping of the pendulum oscillations reveals both effects: when the loads on the pendulum are small, there occurs a reduction of the external friction, when the loads are large, a reduction of hardness manifests itself, i.e., as it were, an opposite effect.

Bockris and Parry Jones erroneously attempted to find a reduction of hardness due to adsorption by carrying out ordinary measurements of hardness using the Vickers pyramid-test: under these conditions the nature of straining at the surface (compression) does not favour the development of microcracks and therefore the adsorption effect.

It has been shown by our direct experiments that the electrocapillary strength reduction and the occurrence of the corresponding maximum are observed by measuring the rate of elongation (creep) of single-crystal and polycrystalline wires (Sn, Pb, Cd) where the external friction is eliminated. These experiments have been subsequently developed by G. Masing and his pupils.

Dr. P. Meares (*Aberdeen University*) said : During discussion of the paper by Joncker and Kruyt, Prof. Overbeek referred to the fact that the theory of Verwey and Overbeek takes no account of Debye-Hückel effects in the dispersion medium of a lyophobic colloid. Dr. Levine pointed out that the theory is restricted to symmetrical valence-type electrolytes. Experimental data concerning both these questions can conveniently be obtained from a study of electrolytes sorbed in highly swollen ion-exchanging resins. These materials have the advantage of stability and hence allow equilibrium measurements to be made and at the same time present a very large charged surface area to interact with a relatively small volume of electrolyte solution. The fraction of the total ions present which are involved in double-layer formation close to the charged surface is quite considerable and can be studied by measuring the thermodynamic properties of the system. It may be doubted whether the polymer chain segments forming the resin can be regarded as having equipotential surfaces, but for high capacity exchangers in which the ionizable groups are close together along the chain and fully dissociated this is probably a valid assumption.

Studies with 1 : 1 electrolytes and a granular cation exchanger have been reported by C. W. Davies and by H. P. Gregor both of whom found more electrolyte sorbed into the resin from a dilute aqueous solution than expected from a simple Donnan equilibrium between the phases which was obeyed at higher concentrations.



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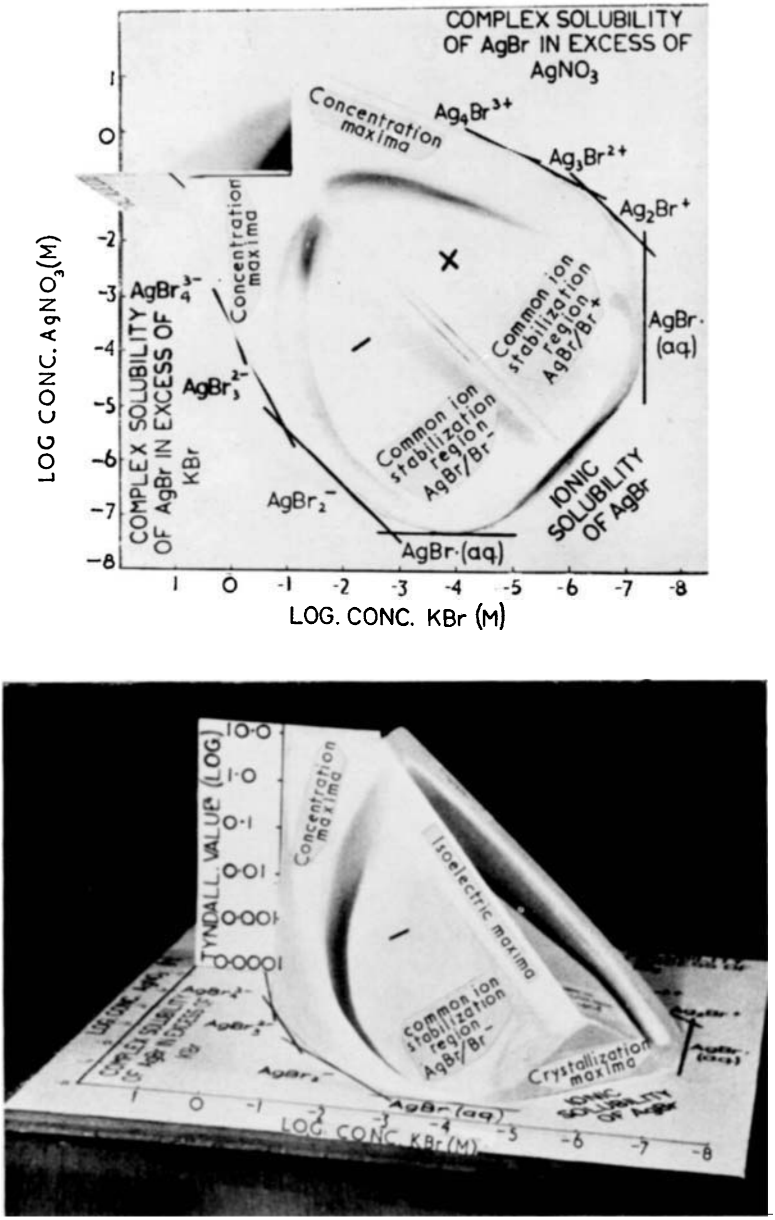
[1] Bowden and Tabor in *Properties of Metallic Surfaces* (Inst. of Metals, London, 1953).



Plates 1 and 2.—Three-dimensional model of the precipitation phenomena in the system, silver nitrate + potassium bromide in aqueous solutions at 20° C, 10 min after mixing components.

[*To face page* 223.

This work has been considerably extended by J. S. Mackie and myself using a thick membrane of a cation exchanger which imbibed about four times its own volume of solution in swelling to equilibrium. The sorption and diffusion of 1 : 1, 2 :1 and 2 : 2 electrolytes in this resin have been studied. The sorption results can be interpreted by calculating the activity coefficients of the electrolyte solution inside the resin phase relative to infinite dilution in water as the standard state. The figure shows activity coefficient against ion concentration plots for typical electrolytes of each valence type, the full lines refer to the resin phase and the broken lines to the same electrolytes in aqueous solution. For the 1 : 1 electrolytes the pronounced downsweep at low sorbed concentrations arises from the restriction of the cations into a layer around the negatively charged polymer chains. The curves unite at high concentration where the fraction of ions so restricted and the degree of restriction compared with the aqueous phase become unimportant. For 2 : 2 electrolytes the downsweep is absent and there is only a small divergence between resin and aqueous phases in the dilute region due to the very low values of the activity coefficients in the aqueous solutions of these electrolytes. For the 2 : 1 electrolytes the behaviour is different, the activity coefficient in the resin rising above the value in an aqueous solution of the same concentration. This is probably due in part to a penetration of some anions into the more firmly held regions of the cation layer and also to the release of anions from the atmospheres of the cations held in the double layer.

Experiments show that all the ions present in the resin are free to diffuse as if in aqueous solution. It seems therefore that the exchange of a free ion with one held firmly in the double layer takes place without surmounting an energy barrier and is therefore a reversible process in the thermodynamic sense.

Similar experiments using alcohol as solute reveal a different state of affairs. The apparent activity coefficient of alcohol in the resin is lower than in an aqueous solution of the same concentration. Diffusion experiments show that only about two-thirds of the alcohol in the resin is free to diffuse the remainder being held around the resin network. It is to be expected that alcohol would solvate the organic resin chains and the data show the existence of an energy barrier between solvating molecules and molecules in free solution within the resin phase. This emphasizes the difference between colloid stability derived from adsorption of ions and from solvation effects as referred to by Prof. Overbeek in his Introductory Paper. A full report of this investigation will be submitted shortly.

Prof. B. Težak (*University of Zagreb*) said: Although recrystallization processes may be important in the formation of coarse precipitates, the role of the crystallization should first be made clear.

We have found typical maxima of precipitation of silver halides in all limiting regions where the concentration of the precipitating components exceed either the ionic or complex solubility by a factor of 5 or more. Such maxima adjacent to the region of ionic solubility were first found with silver chloride and called crystallization maxima.[1]

In fig. 1 and 2 are given so-called 15-min concentration-tyndallograms and concentration-dispersoidograms for crystallization maxima of 1 μmole of silver bromide at 20° C, 30° C and 40° C. The appearance of the maxima shown in fig. 2 of the paper of Jonker and Kruyt may be attributed to the mixed processes of crystallization and recrystallization.

Generally, the effects of nucleation, the growth of primary particles by crystallization, oriented or irregular aggregation, coagulation, and other processes encountered in the formation of precipitates can be obtained only by accumulating and systematically examining all the important data. Such an attempt to present a large number of observations of the precipitation systems of silver bromide gives the three-dimensional model represented in plates 1 and 2.

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[1] Težak, *Z. physik. Chem.*, 1943, **192**, 101.

The primary maxima (maxima appearing after 10 min) are shown; the logarithm of concentration (in normalities) of silver nitrate against potassium bromide in aqueous media were used to construct the curves in the x, y plane.

For discussion of any of the precipitating systems it is necessary to know the region in which the processes occur, and therefore a clear-cut distinction between the various maxima (complex Gay-Lussac maxima, crystallization maxima, and isoelectric maxima, positive and negative concentration maxima as the primary maxima) is very useful. It is hoped that by constructing similar models for other precipitating systems the true nature of many essential relations between solubility, nucleation, crystallization, and coagulation will be elucidated.

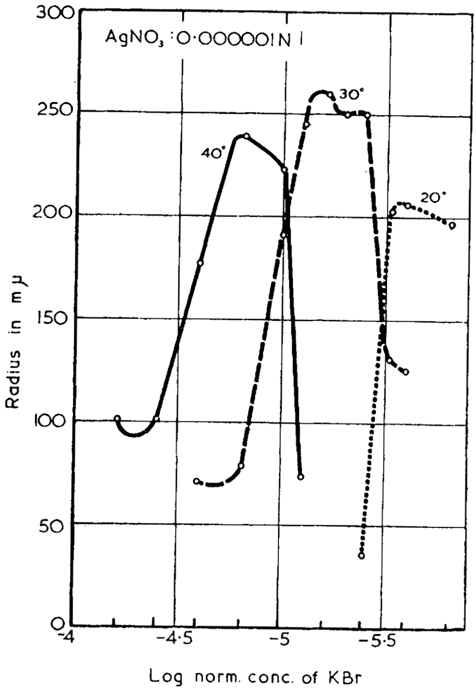

FIG. 1.—Concentration tyndallograms of the system, $AgNO_3$ (1 μmole) + KBr, at 20, 30 and 40° C, 15 min after mixing the components.

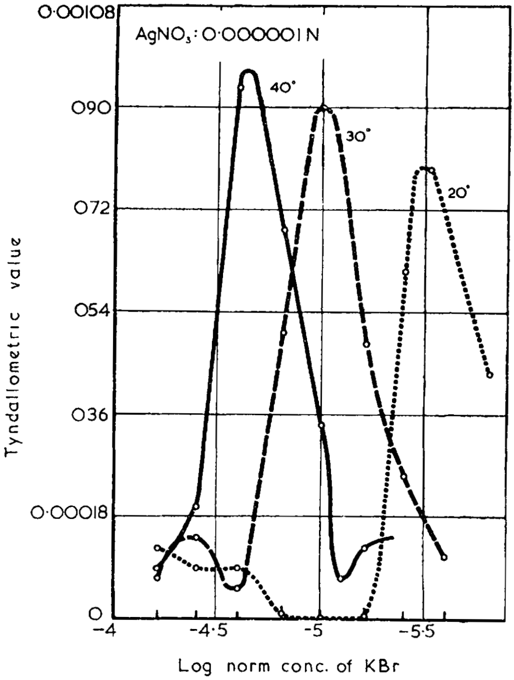

FIG. 2.—Concentration dispersoidograms of the same systems as given in fig. 1.

Dr. M. Mirnik (*University of Zagreb*) said: The maximum in fig. 1 of the paper of Jonker and Kruyt represents the so-called isoelectric maximum of coagulation. The point of intersection of the tangent at the steepest part of the tyndallometric curve with the axis of zero light scattering is called the " negative " or " positive activity limit of stability ".[1]

The negative stability limit was found to lie, in the AgI system, at a pAg of 6·2-6·3 and fig. 1 shows that this limit is practically independent of the concentration of the sol up to 10^{-3} M. We determined this value also for the AgBr and AgCl systems [2] and found that this limit was practically the same for all three systems. This fact implies that the negative limit of stability represents the

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[1] Mirnik and Težak, *Trans. Faraday Soc.*, 1954, **50**, 65.

[2] Mirnik, Flajšman, Schulz and Težak, to be published.

beginning of a process governed mainly by the Ag activities and the properties of water at the Ag halide/liquid interface which remain the same in all three systems.

A process analogous to the process of " abnormal coarsening " in the region pI = 5 to 8 in the AgI system was also described by us and called the " maximum at pI = 8 " [1] (fig. 7, 8, 9, 10; [2] fig. 3, 5). In the stability region ($\log_{10}$ [$NaNO_3$]<2, pI ~ 1 to pAg = 6·3) the light scattering increases for 7 days. After 7 days it remains practically constant if the stable sedimentations are repeptized by shaking. The resulting sol shows after some weeks of sedimentations three layers: (i) the uppermost layer is bluish having low scattering and the particles are very small (less than 50 mμ); (ii) the layer a few cm from the bottom is yellowish and the particles are about 170 mμ in diameter; (iii) on the bottom of the vessel is a thin layer of a yellow oily liquid with particles of about the same diameter which can be redispersed by shaking.

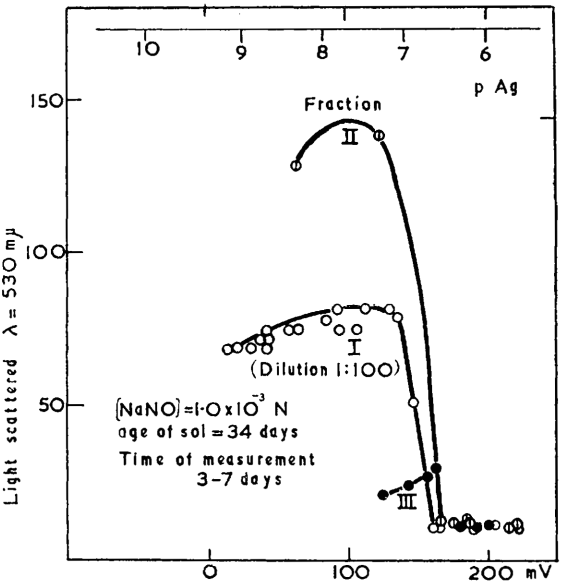

FIG. 1.—Effect of the sol concentration on the plot of the intensity of scattered light against the e.m.f. (or pAg).

Fig. 2 shows an activity tyndallogram of the negative stability limit for three such fractions of a 34-day-old sol and it can be seen that the activity limit is practically the same for all three fractions and equal to the limit of the sols *in statu nascendi*. The small difference is caused by the difference of the time of measurements of the activity, which effect is shown by curves I*a*, II*a* and I*b*, II*b* of fig. 1 of the paper.[3] The particle size is certainly not critical for the stability limit of aged sols nor for sols in the nascent state.

The quantity of coarse particles, formed on ageing and which sediment after some days, is greatest at pI = 8 and smallest at pI = 5. The point pI = 5 can be considered as that of maximum stability of the coarsening processes as has already been observed by Kruyt and Klompé [4] for repeptized, aged and dialyzed sols. A similar process is found in the region pI ~ 2-5 with a maximum near pI ≃ 2. The sedimented part may also be redispersed by shaking.

[1] Mirnik and Težak, *Arhiv kem.*, 1949, **21,** 109.
[2] Mirnik and Težak, *Arhiv kem.*, 1951, **23,** 44.
[3] Mirnik and Težak, *Trans. Faraday Soc.*, 1954, **50,** 65
[4] Kruyt and Klompé, *Kolloidchem. Beih.*, 1943, **54,** 484

The relative position between the different maxima may be observed on the 7-day tyndallogram ([1] fig. 1). In the region between pI $\sim$ 1, which represents the coagulation value for Na ions from NaI, and the pI $\simeq$ 2 value, the duration (i.e. the time after which the light scattering is practically constant) of the processes increases from some hours to weeks or even longer. These processes apparently correspond to those investigated by Reerink and Overbeek and are represented by the inclined lines in fig. 6. The sedimentations in such systems cannot be repeptized by shaking. After shaking, the particles form visible flocks. Težak [2] called these processes " transition " processes between typically stable and typically unstable (coagulations, fast coagulations) processes.

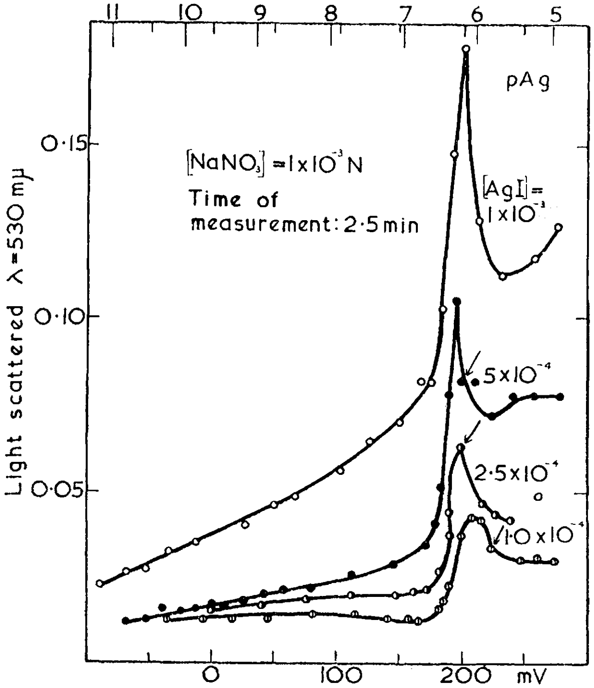

FIG. 2.—Effect of the sol sedimentation fractions on the plot of the intensity of scattered light against the e.m.f. (or pAg).

5 ml of (I) bottom fraction ([AgI] = 0·0055 M); (II) middle fraction; (III) uppermost sedimentation fraction of a 34 days old sol ([AgI] = 1·33 M, [$NaNO_3$] = 1·33 N, e.m.f. = + 15 mV) were diluted with 1·67 ml of various solutions of $AgNO_3$. After 3 to 6 days the light scattering, and after 7 days the e.m.f., were measured.

It was clearly pointed out by the authors themselves that there is a distinct difference between crystallization and recrystallization processes on the one hand (" abnormal flocculations ") and " normal " flocculations (experiments with protecting colloids) on the other. Is there, therefore, any justifications for the application of the same theory to such different processes? Up to now, has not the theory of Verwey and Overbeek been applied exclusively to " normal " fast and slow coagulations?

On the 7-day tyndallogram (fig. 1,[1] fig. 3,[3]) it can also be seen that between pAg = 6·3 to 8 is a minimum of tyndallometric values. The quantity of coarse,

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[1] Težak, *et al.*, *J. Physic. Chem.*, 1953, **57**, 301.
[2] Težak, *Arhiv. kem.*, 1947, **19**, 19.
[3] Mirnik and Težak, *Arhiv. kem.*, 1951, **23**, 44.

sedimented particles is very small. The unsedimented part as well as the sedimented particles remain unchanged for months or even longer. In this region a second maximum of stability occurs. The zero point of charge was repeatedly reported to lie at pAg 5·5 to 6. From the accuracy of the determination of the activity limit and the uncertainty of the zero point of charge it is possible that the pAg value of the last stable negative sol could be less than 0·1 pAg unit from the zero point of charge. The corresponding ψ_δ of the Gouy-Stern double layer would be in this case less than 6 mV, and the corresponding ψ_0 still smaller. Does the theory of Verwey and Overbeek postulate stability for such low values of double-layer potentials? What is the lowest potential for which particles of 20 to 170 mμ are stable for months.

Dr. G. H. Jonker (*Philips Res. Lab., Eindhoven*) (*communicated*): It can be seen from our experiments that the isoelectric points of the dilute sols shift to lower pAg values during the ageing process. This shift is much greater for the negative sols, which show after one day an isoelectric point at pAg = 4·4. This is a typical property of recrystallizing particles and is not present in concentrated sols. Therefore we do not find a constant " limit of stability ".

We have made plausible the theory that in negative dilute sols the particles recrystallize undisturbed to ideal crystals. The interaction between these crystals is intermediate between the interaction of flat plates and of spheres. A difficulty is that we know nothing about the charge distribution. Therefore our considerations are only qualitative.

The ψ_0 values have been calculated without a Stern correction from the difference in pAg with the isoelectric point. If this correction would be considerable, e.g. 50 %, the van der Waals constant which we need in our calculations can be decreased to a low value, e.g. 25 % of the high value we have used.

Dr. M. Mirnik (*University of Zagreb*) said: I would like to point out, with reference to the paper of Packter and Matalon, the meaning and value of the definition of an " equivalent " system. The activity of the precipitating component in excess can be a most important factor in the precipitating process.

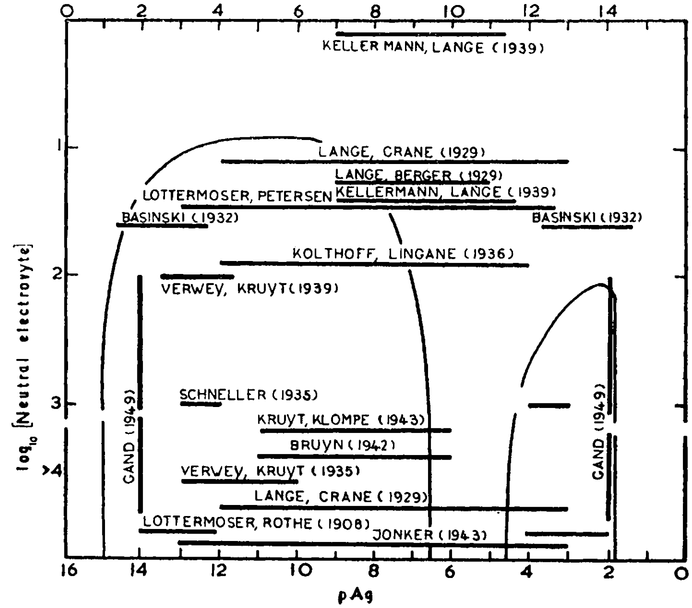

FIG. 1.—Regions of investigation of various investigators.

When mixing " equivalent " amounts of the precipitating components the activity of the component in excess depends on the accuracy of measurement of the amounts of the components and of the ionic product. If the ionic product of the insoluble salt is 10^{-2px} and the error of the quantity of the components is 0·1 %, the activity of the " equivalent " system for a concentration c of precipitate formed may take any value between $-\log_{10}(0{\cdot}001c)$ and pX for the component which is in excess. A really " equivalent " system may be obtained with certainty only when $\log_{10} c < 3$ (= pX). In any other case the range of activity values is in the " equivalent region " which is wider when the ionic product is smaller and the accuracy of measurement lower. This is one of the reasons why the preparation of systems with defined activities in the equivalence regions for salts with low ionic products is difficult.

This may also be the reason why the equivalence region of the most investigated precipitation, that of AgI, was seldom investigated systematically. The figure shows the region explored by various workers on the influence of excess concentration of the potential-determining electrolytes, without systematically investigating the influence of the concentration of the neutral electrolyte. Some investigations of Kruyt and van der Willigen (1928), Schneller (1935) and Gorochowsky (1935), all of which covered narrow ranges and none of which lay inside the region of pI $\sim$ 6 to pAg $\sim$ 6 are not included.

Težak and Schulz, and Težak and Herak, investigated coagulations with various neutral electrolytes of different valencies and different polarities in the regions of pI (or pAg) 6 to 2. My own investigations, in collaboration with Prof. Težak, were in this region and the interdependence of the precipitation processes (flocculations, coagulations, crystallizations and re-crystallizations at different rates) was examined by light-scattering, electrophoretic and electro-osmotic mobilities and adsorption of potential-determining ions, and correlated. In this way practically the whole region was investigated.

This figure explains why the results of various investigators apparently disagree, due to the fact that processes of a different nature lying in different activity regions of potential-determining ions and of neutral electrolyte were compared.