THE FORMATION OF PRECIPITATES FROM ELECTROLYTIC SOLUTIONS AS A MODEL SYSTEM FOR SOME GENERAL CHEMISTRY AND SURFACE SCIENCE PHENOMENA

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Abstract—In order to find out where and when the distinction between the operating forces at elemental and group levels can be applied, the systematic variations of substantial and concentration composition of the precipitating solutions are undertaken.

Especially, the relationships between the concentration of electrolytic components and critical time that characterize the discontinuities in precipitation, as the criteria for the role of complexation, ion-pairing, embryonation, nucleation, crystal growth, and aggregation (coagulation, flocculation, formation of crystalline aggregates), on one hand, and the role of short and long range forces, on the other hand, are considered.

The results are treated under the headings of (i) thermodynamics (systems approaching to the equilibrium state), (ii) kinetics (changes of the systems far from equilibrium), and (iii) mechanisms of elementary processes (pointing to the distinction between effects of short range and long range interactions.)

In the stage of the formation of new, solid phase, the role of the processes and structures of the transitional region between the solution and the emerging phase (the methoric layer) are emphasized. For the stability or instability condition of the dispersions the concentration relationships of kinetically active species in methoric layer and in bulk solution are used: $c_{meth} > c_{bulk}$ for stability, and $c_{meth} < c_{bulk}$ for instability.

In addition, the temporal characteristics of the composite assemblies with half lives from about 10^{-6}–10^6 sec are taken into account.

By constructing the "precipitation bodies", PB, from experimental data as spatial-temporal diagrams, the rational basis is given for the presentation of specific systems. In general, in the morphological organization of matter, the significance of the whole spectrum of spatial and temporal dimensions for the interactions of various entities are underlined.

It was 100 yr ago that J. W. Gibbs published his paper[1] "The Equilibrium of Heterogeneous Substances". While it is true that in his theory Gibbs treated the heterogeneous masses in contact as separated by mathematical surfaces, he was nevertheless aware that the "surfaces of discontinuity" between phases might be exposed to "conditions allowing the possible formation of situations unlike any previously existing...", that is, states which would be "entirely different in state and composition...", representing "new parts" which naturally would be characterized by their own specific energy, entropy, volume and quantity of components. Now, complementary to Gibbs thermodynamics and statistical mechanics of equilibrium states, we have to study the systems which are not in equilibrium, and moreover, are very far from equilibrium. Of such a kind were the experiments that led to P.P. von Weimarns' generalisations[2] about "Die Allgemeinheit des Kolloidzustandes", which emphasized the close relationship between spatial and temporal aspects that is demonstrated in precipitating systems.

Our approach is to use the relationships between concentration and critical time which characterize the discontinuities in a precipitation process as the criteria for the role of embryonation, nucleation, crystal growth, and aggregation, and to use the substantial composition, including the role of short and long range forces, to provide an overall mechanism of precipitation.

The results have to be treated in the context of (I) thermodynamics (equilibrium systems), (II) kinetics (nonequilibrium systems), and (III) the mechanisms of elementary processes (short range and long range interactions.)

GENERAL INTRODUCTION TO PRECIPITATION FROM ELECTROLYTE SOLUTIONS

Our aim is to find out where and when the distinction between operating forces at elementary and group levels occurs. In other words, if one carries out a systematic variation of substantial composition and thermodynamic parameters there is the possibility of determining the time constants and their trends, which may enable us to differentiate the specific and general characteristics of the investigated systems.

For both short range and long range interactions in homogeneous liquid systems we already have a very representative collection of time constants[3] relating to spectroscopy, reaction rates, exchange processes, relaxation times, and diffusion characteristics; the range is very wide, with variation from 10^{-15} to ~1 sec. In precipitation processes, again, we may have, simultaneously or consecutively, not only the effects of short range and long range interactions at both the molecular and ionic level, but also their combination with interactions involving very complex aggregates, mainly those of amicronic, ultramicro and macro dimensions. Consequently, in addition to very rapid interactions it is possible that some mixed processes may appear which could have much longer but nevertheless characteristic periods of time. Experience has shown that in precipitation processes the characteristic or critical times are usually in the range between 10^{-6}–10^6 sec. When determining critical times, graphical analysis of precipitation development with respect to the concentration of the effective component is used as follows. Taking the initial stage of precipitation as a criterion, a family of precipitation curves corresponding to different concentrations of the critical component are

systematically obtained, and these reveal underlying processes by means of characteristic continuities or discontinuities. In this way, if we are studying an open system in flux, there will be assemblies and ensembles of fluctuating sizes, steady states, and stability/instability mechanisms, and their composite life is usually determined by complex transformation of intermediates, each of which has its own half-life.

Figure 1 is a scheme depicting some characteristic features of the transition stages involved in passing from homogeneous to heterogeneous states. Starting from an aqueous solution of electrolytes, by changing the concentration, different interactions cause dynamic changes of solvent structure, solvated ions, inner and outer sphere complexes, ion pairs, ionic and molecular clusters, fluctuating holes, and of other formations which are affected by numerous "specific" and "general" forces. In our scheme there is a time scale for interactions in both the homogeneous and heterogeneous systems.

At higher concentrations (i.e. approaching or exceeding the solubility limit) the products may be the ionic and molecular aggregates, or longer living clusters, which give the solution some quasi heterogeneous character. The formation times of such structures are certainly longer than those seen with elemental interactions, and the resulting configurations and ensembles represent a composite "spectrum" of times. This is much more the case with heterogeneous systems, where it seems advisable to distinguish states according to the old amicronic, ultramicro, micro, and macro divisions. Also, it is true that in these regions, for control of both the spatial and temporal dimensions, it is necessary to take into account intermittent steady state and stability/instability relationships which reflect the life of higher aggregates, and the intermediates of which their boundary layers are composed. These aggregates may be embryos, nuclei, micelles, and other primary particles, either in a state of growth or of interaction with other similar particles. A sudden process of agglomeration of larger units, such as, e.g. a rapid precipitation, coagulation, or flocculation, also may interfere with continuously running processes.

At the stage of the formation of a new, solid phase, the role of both the processes and the structures in the

transitional region between the solution and emerging phase are of utmost importance. Such a region of discontinuity, in Gibbs terminology, the "new parts", has to be treated as a third phase in reality, or at the very least as an interphasial layer with its own characteristic spatial and temporal dimensions, constituents, and structure. The peculiar properties of such a layer are a function of the regular or distorted crystalline matrix of the solid on one side, and the substantial and structural properties of the solution in bulk on the other side.[4] Small volume chemistry and physics with special respect to the dynamics of boundary states has to be applied to such cases, and the most appropriate name for a region between two definable bulk phases, as proposed by Wo. Ostwald, is the term *methoric* or *methorical* layer.

It is quite normal that any interactions, especially those between a pattern of discrete charges on the wall of a solid or semi-solid particle, and those of the oppositely charged species in the methoric layer, will have an effect on the stability/instability mechanism for the dispersed particles of the new phase. In the case of adsorption processes similar effects may be also expected. All these processes are reflected on the time-scale as the more or less distinguishable concentration—critical time relationships. The simple formulations are expressed in Fig. 1 as concentration relationships for kinetically active species in methoric layer, and in bulk solution $C_{meth} > C_{bulk}$ for the stability condition, and $C_{meth} < C_{bulk}$ for the instability. Such a mechanism is applicable not only to the processes of precipitation, aggregation of crystallites, coagulation, and flocculation, but also to other systems where the dispersed units are not of the same kind (e.g. in flotation). Moreover, by following the effect on critical times of systematically changing concentration and composition of a system, there is the possibility of finding out which mechanism at the elementary level controls the process. Only experiments can show us how far we can pursue this reasoning.

APPROACHING AND DEFINING THE EQUILIBRIUM STATES BY PRECIPITATION

By mixing two precipitating components in more and more diluted solutions a limit will be reached when the
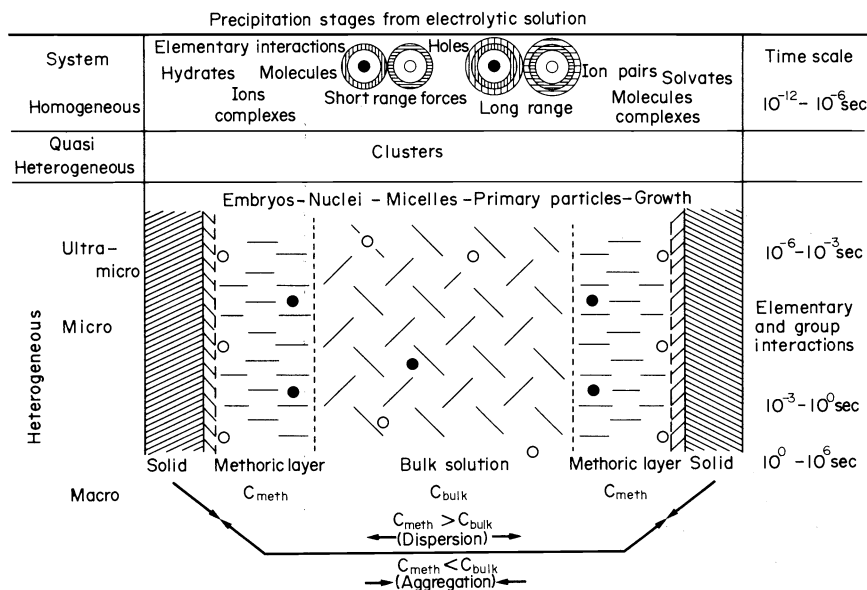

Fig. 1. Schematic presentation of the transition stages from homogeneous to heterogeneous systems.

precipitate will not appear, even after a very long time. Such a systematically determined limit may represent an equilibrium state which sometimes corresponds to the solubility of the solid in the solution. However, appreciable differences between the observed values of the saturation solubilities may arise in a large number of cases when the precipitating components are in equivalent ratio, and much more so if it is to be expected that the solubility product constant could be applied by changing the relationship between cationic and anionic concentrations. In fact many complex factors may intervene in such a way that the determination of solubilities must be left to direct experiments. For the presentation of such results it seems appropriate to use two-dimensional and three-dimensional diagrams such as those shown in Fig. 2. In the upper part
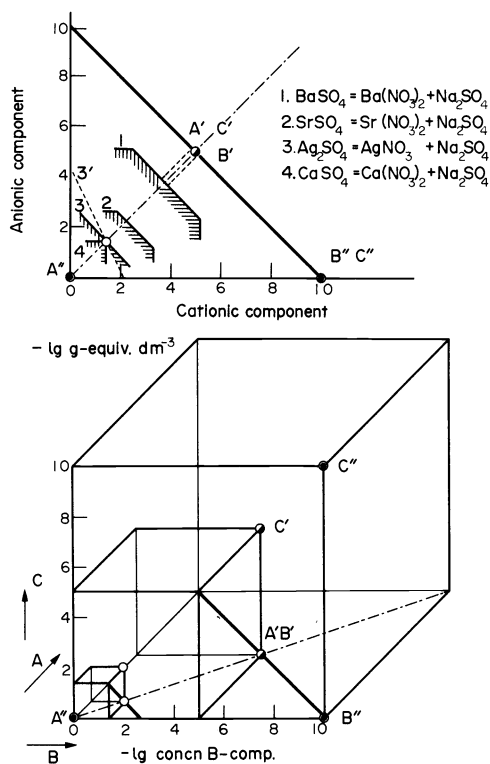

Fig. 2. Solubility boundaries of barium, strontium, silver, and calcium sulphate system as a plot of the logarithms of cationic against anionic component concentration (upper part), and comparative positions for some points of solubility boundaries in the "cube of dilution" (lower part).

of Fig. 2 are seen the precipitation boundaries for barium, strontium, silver, and calcium sulphates depicted as a logarithmic plot of cationic against anionic concentrations. Corresponding to such a plot is a spatial model with three mutually perpendicular axes on which the logarithms of concentration of cationic and anionic precipitating components are again plotted, together with the resulting real amount of precipitate.

Taking the highest concentrations of our reacting substances as being situated at the origin of our spatial model, by gradually diluting the system with solvent ("expanding the cube"), there is a proportional increase in average interionic distances, which should have some influence on the interaction time. Also, it should be noted that moving along the line of solubility product constant a great difference in the amount of precipitated mass

appears. This is seen by comparing the A'B'–C' situation with that of A''–B''–C'' in the three dimensional model in Fig. 2. This, together with the fact that isoelectric particles appear in the equivalence region which militate against the formation of complex species (which would be formed when one of the precipitating ions is in excess), is responsible for the fact that the critical concentration in the equivalence region represents the most favorable condition for precipitation.[5] The precipitation boundaries are a function of the species[6] controlling the transition from solution to solid phase, and their slopes may be used for determining the composition of such species and defining the equilibrium conditions. Inside the boundaries, on the precipitating side, are processes and structures which kinetically represent various features of the so-called "precipitation bodies", PB, while their outer contours indicate, after a reasonable time, true or very near equilibrium states. In fact, it is possible to differentiate[7] at least four types of "precipitation bodies", which are illustrated in Fig. 3. These PB-types are distinguished according to which of the following is dominant: (A) neutralization; (B) ionic solubility; (C) formation of ion pairs and associates; and (D) unsymmetrical ionic activity (involving of the chemical interactions with solvent). For each of the PB-types in Fig. 3, some actual examples are given.

In many cases the experimental PB is a combination of two or three types. For example, in Fig. 4, the precipitating system of silver bromide represents a combination of three types, if, in addition to the outer boundaries, the very distinct internal contours are considered.[8] Not only silver bromide, but all the silver halides have nearly symmetrical, neutralization zones delineating both sides, and experimentally well-defined negative and positive colloid systems of the so-called sols in statu nascendi. Owing to the wealth of information found is such features it seems worthwhile to study the kinetics of appropriate systems inside the precipitation boundaries of our PB, and to complete the data on the equilibrium states.

KINETICS OF PRECIPITATION PROCESSES

While the outer contours representing the solubility boundaries of the general precipitation diagrams (or as we called them, the "precipitating bodies") PB, are determined after a reasonable time in order to ensure attainment of equilibrium, the mechanisms of the underlying processes controlling the systems inside the PB can be found only by following the kinetics of precipitation as closely as possible.

The relationships between concentrations and critical times for an initially detected change of the system were usually determined along one section through PB. The values of scattered light or of particle size were plotted as a function of time (time-tyndallograms and time-dispersoidograms respectively). The tangents to the steepest parts of the precipitation curves were extrapolated back to intersect with the abscissae, where times were in logarithmic scale, in order to give the critical times, t_{crit}. If the logarithms of concentrations were in linear relationship with critical times, it was highly probable that the same underlying mechanism affected both parameters.

The complexities of the processes are best disclosed by observing the concentration–critical time relationships along characteristic sections of PB in comparison with the stages of development of precipitation of fixed time.
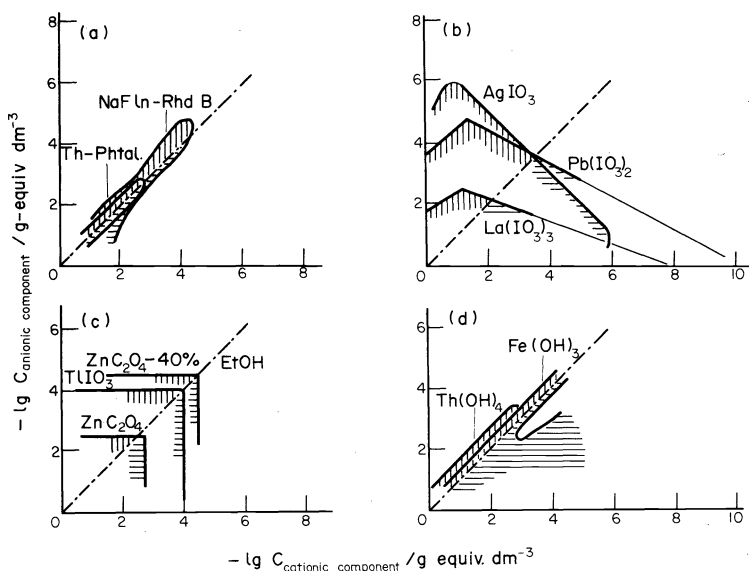
Fig. 3. Types of "precipitation bodies", PB, for: rhodamin B–sodium fluorescein, and thorium nitrate–potassium phthalate, A-type; silver, lead, and lanthanum iodate, B-type; thalium iodate, and zinc oxalate in water and 40% ethanol, C-type; ferric and thorium hydroxide, D-type; all depicted as plots of the logarithms of cationic against anionic component concentration.
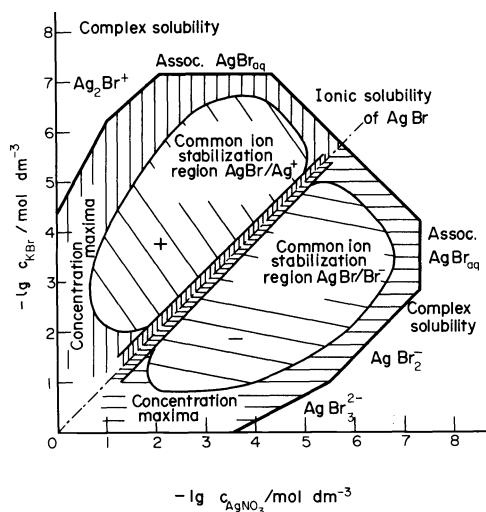

Fig. 4. Precipitation body, PB, of silver bromide showing the contours of precipitation development inside the body of solubility boundaries.

We have chosen two cross-sections through the PB of silver bromide (represented in Fig. 4) to illustrate this. In Fig. 5, experimental cases with two concentrations of silver nitrate are shown: 5×10^{-6} mol dm^{-3} (II), and 1×10^{-4} mol dm^{-3} (I). For comparison, in Fig. 5 the ordinate represents relative percentage of micro heterogeneity of the systems after 7.2×10^3 s, while in Fig. 6 the ordinate represents the critical time in logarithmic scale; both figures have as abscissae the logarithm of potassium bromide concentration.

If we follow the precipitation curve of the systems with 5×10^{-6} mol dm^{-3} silver nitrate it is obvious that silver bromide precipitating under such circumstances exhibits two large maxima, in the regions of highest and lowest concentrations, the so-called concentration[9] and crystallization[10] maxima respectively. Between them

there may appear also the so-called isoelectric and transition maxima.

More than 30 yr ago, when these effects were found with systems of silver chloride, attempts to explain them usually supposed that on dilution there was a relationship between periodical changes in the structure of the transition layer on the growing crystal, and greater or smaller probabilities for direct crystal growth or aggregation of primary particles. Nowadays, we are aware that each of the slopes of the concentration–critical time relationships may represent a different mechanism, or a combination of various mechanisms. Some of these mechanisms may be demonstrated by using carefully prepared systems, where the elements of composite mechanism are clearly distinguishable. The choice of such a model system will depend mainly on finding a system characterized by some very rapid processes followed by the very slow ones. In the interesting "empty" periods it is easy to observe the effect of introducing some additional factor. Also, the introduced factor may be especially active in the initial moments of a precipitation process, and by systematic changes of its characteristics the mechanism of its action on the precipitation may be revealed. Therefore, in the series of silver halide precipitates we were able to ascertain the key phenomena affecting coagulation and flocculation of primary particles, while with sparingly soluble sulphates it was possible to demonstrate the delaying action on formation of embryos or nuclei[11] (reverse Schulze–Hardy rule).

It is quite apparent that systems of silver halides are very convenient for the study of colloidal behaviour when we consider the very large differences in critical times between the slowly precipitating systems in the central concentration region of our diagram in Fig. 6, and the usually encountered rate of rapid, and relatively fast coagulation processes; these differences may be many powers of ten.

In Fig. 7 the results of experiments with 4×10^{-4} AgNO$_3$ and 1.2×10^{-3} KBr systems are shown. The "empty" period of time was at least 3 orders of magnitude. With
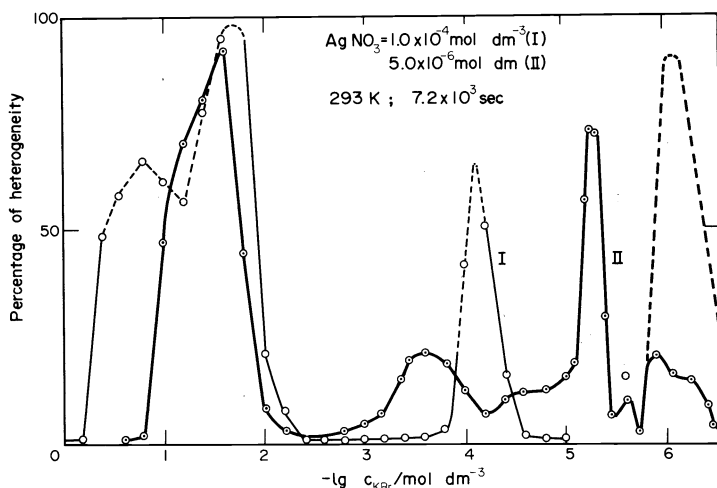
Fig. 5. Formation of silver bromide precipitate in a plot of logarithm of potassium bromide concentration against relative microheterogeneity of the system after 7200 s for different concentrations of silver nitrate: 1.0×10^{-4}, and 5.0×10^{-6} M at 20°C.
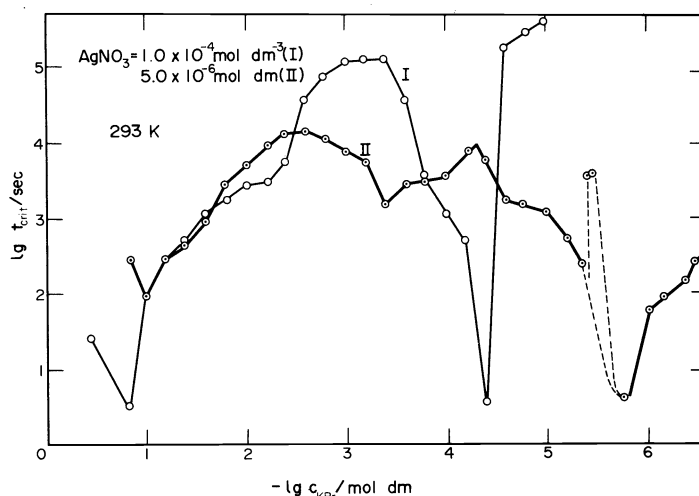

Fig. 6. Formation of silver bromide precipitate in a plot of logarithm of potassium bromide concentration against logarithm of critical time, t_{crit}, in seconds, for different concentrations of silver nitrate: 1.0×10^{-4}, and 5.0×10^{-6} M, at 20°C.

such systems the experiments of coagulation and flocculation were performed[12] as usual with the sols *in statu nascendi*. The coagulants were the salts KNO_3, $Ba(NO_3)_2$, and $La(NO_3)_3$, and the flocculant was nonionic Triton T-X-305.

In the diagram of Fig. 7 the abscissa represents the logarithm of equivalents of inorganic salt, or of moles of surface active substance; the ordinate correspond to critical time, again on the logarithmic scale.

In all these cases negatively charged primary particles were immediately formed after the mixing of precipitating components, which either rapidly interacted with counter ions as coagulating agents, or in more concentrated systems, through adsorption of molecules, were sensitised, reached the flocculation maximum, and then became stabilized. Coagulating actions of counter ions were in accord with the Schulze–Hardy rule, and the course of flocculation was normal.

Both groups of phenomena, i.e. coagulations and flocculations, are easy to explain applying the basic concepts of our scheme[13] in Fig. 1. In coagulation, the deficit in concentration of kinetic species in the methoric

layer is caused by formation of ion pairs between stabilizing ions and counter ions. In flocculation, at the sensitisation stage, the deficit in the methoric layer is
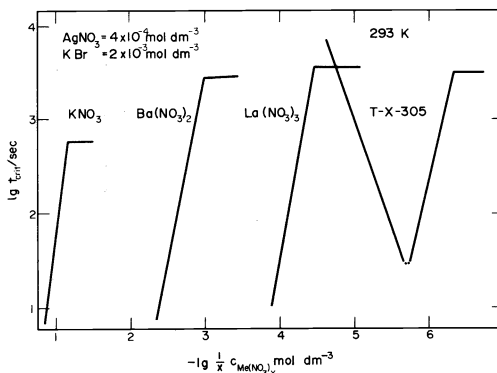

Fig. 7. Critical times, t_{crit}, in logarithmic scale, of coagulating action of potassium, barium, and lanthanum ions, and flocculating action of nonionic Triton T-X-305, for silver bromide sols *in statu nascendi*.

caused by adsorption; the coverage of the surface reaches one half at the flocculation maximum, and at higher concentrations, after complete surface coverage, more and more molecules are left in the methoric layer until the stabilization concentration is reached.

Many other experiments were performed to provide data on the influence of ionic size, different electrolyte mixtures, solvents, temperature, and other factors. Directly gathered experience on precipitation kinetics has been complemented by determinations of adsorption rates, exchange rates, electrophoretic velocities, optical and electron-microscopical observations, X-ray determinations, chemical analyses, and other procedures; and in the light of all these experiments the mechanisms at the level of the elementary process can be considered.

ROLE OF SHORT-RANGE AND LONG-RANGE FORCES

The solubility, the crystal structure, and the existence of a variety of species and entities representing intermediates at elemental ionic-molecular, and sub-colloid levels, can be responsible not only for the composition and structure of the core of the primary particles, but also for the pattern of the discrete charges on the boundary of the solid or semi-solid phase. All these effects may be understood as the result of more or less completed equilibria where short range and long range forces between various constituents are involved. The products of short range interactions are usually characterized either by dynamic changes of environment (in solution) or by nearly static behavior (in solid), but for all of them their formation time will be, immediately after mixing of the precipitation components, probably less than 10^{-6} sec i.e. in the range of rapid reactions. The long range forces manifest themselves through the coulombic term involving the macroscopic dielectric constant, and they are relevant to the solution in bulk and the volumes of methoric layers of all emerging particles. Therefore a formation of a precipitate is a cooperative effect involving a variety of forces which influence the half-lives of various intermediates. Some of these intermediates are substantially different species, while others are either the result of "general", long range forces, or of aggregates (embryos, nuclei, primary particles, micelles) of varying

stability. Regarding the appearance of micro-heterogeneity as the critical phenomenon for precipitation, critical stages may be either very rapid growth of ultramicro particles under steady-state conditions, or their aggregation, or both. Probably, for each of these two stages it is possible to find a part of our precipitation diagram in Fig. 5 where one specific process is dominant However, in continuation of our discussion of coagulation and flocculation phenomena, we will try to find out the role of long range and adsorption forces in aggregation of primary particles.

The size and valency[12] of the counter ions has a very characteristic effect on coagulation. In numerous cases the relationship between the logarithm of critical coagulation concentration and valency of counter ion can be expressed in terms of Bjerrum's critical distance: $d_{crit} = (z_1 z_2 e^2 / 2kTD)$, where z_1 is the univalent potential-determining ion fixed to the wall of the particle and z_2 the valency of the counter ion. Similar considerations may include the influence of the ionic radii, and of the dielectric constant.[14] In Fig. 8 the experimental results with mixed solvents are shown. The linearity was proved very frequently and in a diversity of systems, that both the regular features and exceptions enable us to analyse many essential parts of composite mechanism. In this sense, one of the first interpretations[15] already may be of some use.

In Fig. 9, there is shown a system involving interacting univalent counter ions with chloride ions fixed on silver chloride; the assumptions are more here, in that the critical energy is 1 kT and its linear equivalent in critical distance (for univalent electron charges, $T = 293$ K, and $D = 80$) is 7.2 Å. It is quite clear that the relationship between concentration and distance can only be treated as an expression of statistical events. In the space therefore between the interacting ions is a statistically determined composition of molecules, which determines the value of the macroscopic dielectric constant. It follows that the average distances in accompanying distribution volumes have to be compared with the distribution volumes in bulk solution under corresponding conditions of coagulation. Such distribution volumes or "cages" of polyvalent counter ions may include more than one of the potential
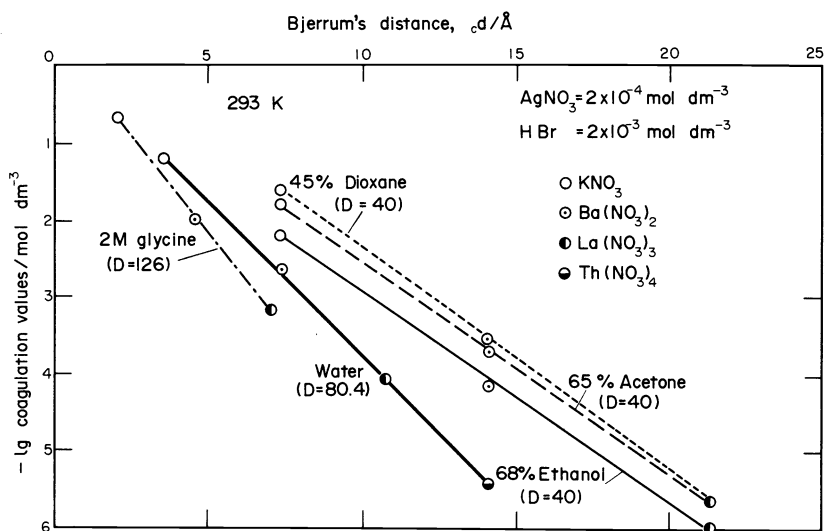

Fig. 8. Plot of Bjerrum's distance against logarithm of critical coagulation concentrations for univalent, divalent, trivalent, and tetravalent counterions: negative silver bromide sol *in statu nascendi* in water, water + glycine, water + ethanol, water + acetone, and water + dioxane.
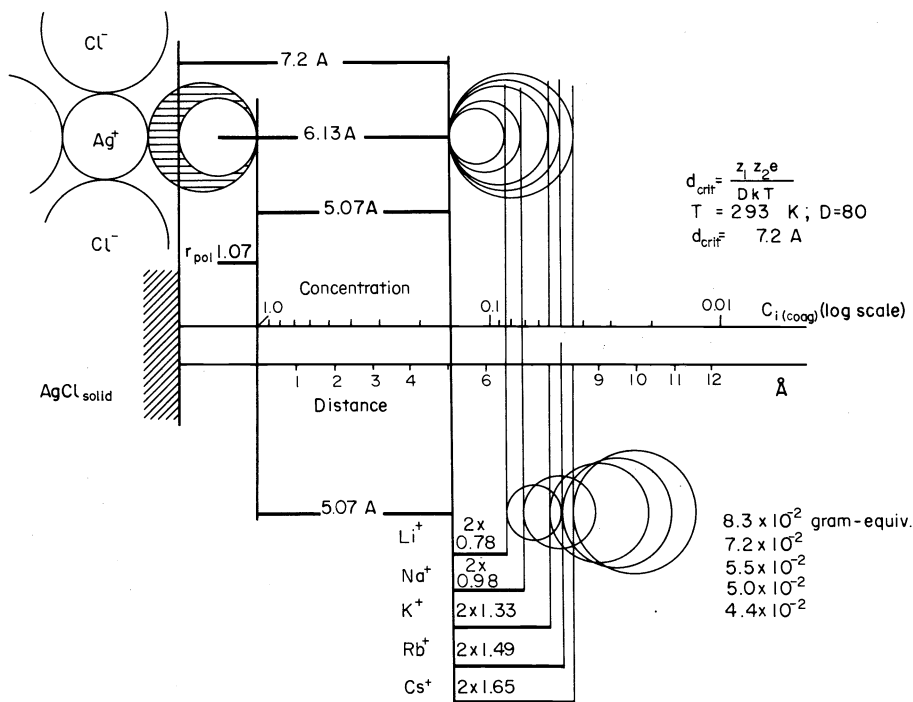
Fig. 9. Schematic presentation of the relationship between the critical distance, d_{crit}, and the logarithm of critical coagulation concentration of univalent alkaline ions; the scheme shows critical distances and concentrations just inside or outside, respectively, the range of formation of ion pairs between the stabilizing chlorine ion and counter ion (adapted Figs. 9 and 10 from Z. physikal. Chem. **A191**, 270 (1942).

determining ion, but adsorption determinations have shown that equivalent amounts of counterions are found with coagulated particles. This fact reminds us of the existence of spatial-temporal stoichiometric relations.

A scheme depicting the mechanism whereby ion-counter ion pairing is stabilized[16] is shown in Fig. 10. The diagram includes distribution spheres for univalent and divalent counter ions, and some distances of interest for configurations in the methoric layer (interionic distances of uniform distribution, $1/\chi$ distances, and critical distances for coagulation); the shell thicknesses of the corresponding ionic distribution spheres may be corre-

lated with the probability of association of the oppositely charged ions.

In the mechanism of flocculation, instead of coulombic interactions, it is adsorption, and the resulting distribution of the adsorbed species between the methorical layer and bulk solution, that are the preponderant factors determining instability and stability in the systems. If physical and chemical (and perhaps stereochemical) forces of some molecular or ionic species that interacts with colloid particles attain a sufficient magnitude for appreciable differences in the distribution of osmotically active units between bulk solution and methoric layer to occur, then
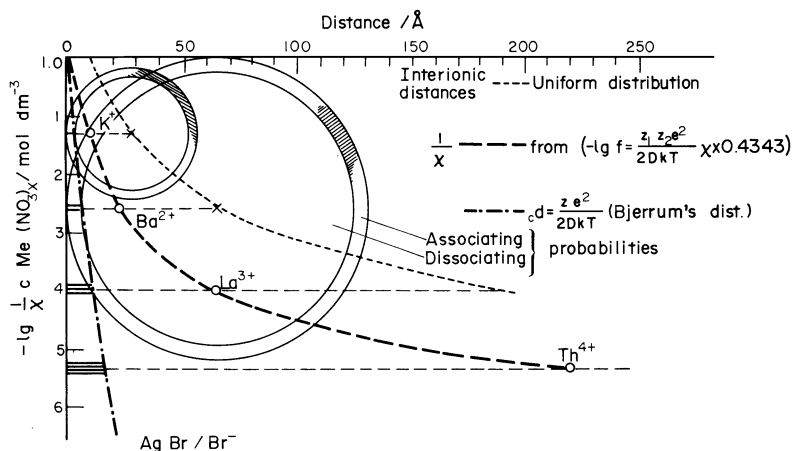

Fig. 10. Schematic presentation of the relationship between Bjerrum's critical distance (—·—·— line), thicknesses of ionic atmosphere (—————curve), and distances between ions uniformly distributed in solution (····· curve), vs logarithm of critical coagulation concentration for ions of various valencies. The circles represent ionic distribution spheres, while the partially shaded shells give the probabilities of association of the stabilizing–coagulating ion pairs.

the phenomenon of flocculation will be encountered. This phenomenon is not limited to macromolecules, very large polyelectrolytes, or various surface active agents, but also to ions and molecules below molecular weight of 1000 which can exert a behaviour characteristic of flocculation. We have observed a typical flocculation maximum with strychnine nitrate, quinine sulphate, various compounds of the fluorescein series, organic dyes, as well as with large ionic and nonionic substances. The flocculation effects were observed in many cases in spite of the fact that the flocculants possessed the same charge as the colloid particles. With flocculation phenomena we have systems in which it is necessary to differentiate between the time-spectra for adsorption–desorption dynamics in the methoric layer, and the critical times for aggregation. On the stabilization side such aggregation times may be very long.

Both coagulation and flocculation involve mechanisms in which the statistical mechanical events at the ionic-molecular level affect the statistical mechanics of the interacting units of ultramicro and micro dimensions. It is probable that in order to obtain a complete picture of all the intervening mechanisms, it is also necessary to include quantum mechanical events. However, the central problem is of assignment of various parts of the wide time-spectrum (from 10^{-15} s to geological times of about 10^{15} s) to identifiable and spatially definable groups. We are trying to make an approach in this direction (just in the middle of this cited spatial-temporal spectrum) by using precipitation phenomena as model systems.

CONCLUDING REMARKS

Recognizing that all equilibrium states are dynamic in nature, the objective of colloid and surface science is to examine an essential sector of the spatial-temporal spectrum as a contribution towards an overall picture of processes and states. In this respect the transformations from homogeneous to heterogeneous systems offer an excellent opportunity to study the characteristics of quasi statistical as well as of the dynamic elements of equilibrium states. Furthermore it is important to find the relationships between concentrations and critical times for precipitation processes in electrolytic solution.

In putting into a coherent frame the results of Faraday and Tyndall (scattering of light), Graham (diffusion), Arrhenius (ionic dissociation), van't Hoff (osmotic pressure), Wo. Ostwald (metastable state), Tammann (nucleation and crystal growth), Lottermoser (surface charges), Schulze and Hardy (coagulation rule), Zsigmondy and Svedberg (heterogeneity of dispersed systems), v. Weimarn (precipitation laws), Hulett and Richards (occlusion), Odén (aggregation of primary particles), Paine and Smoluchowski (kinetics of aggregation), Haber (aggregation and orientation velocities), Donnan (membrane equilibria), Bjerrum (ion pairs), Perrin (sedimentation), Langmuir, O. Hahn, Paneth and Fajans (adsorption), Kohlschütter (time factor), Tiselius (electrophoresis), Sillén (polynuclears), La Mer (flocculation), and of many others, it is now possible to formulate a scheme for the stability/instability mechanism of colloid particles.

In quasi-heterogeneous and heterogeneous systems the significance of the structure and the role of the region lying between the bulk phases and its interactions with the liquid phase, cannot be over-emphasized; the condition $C_{meth} > C_{bulk}$, with respect to $C_{meth} < C_{bulk}$, may be taken as the controlling factor for stability or instability of the dispersed solid phase.

For a rational presentation of precipitation equilibria and kinetics, the characterization of the various substances by means of the so-called "precipitation bodies", PB, in a "cube of dilution", may not only be a very simple, but also a very useful tool for clearing up many erroneous assumptions commonly implicit in the presentation and use of solubility product constant data *apropos* of real solubility results.

Information on critical times for various processes characterized by discontinuities enables distinctions to be made between steady-state mechanisms and those controlled by stability/instability relationships.

The precipitation structures arise from embryos, nuclei, micelles, and various other directly growing particles, representing in shorter or longer periods of time the so-called sols *in statu nascendi*. All of them may aggregate, coagulate or flocculate as classically prepared sols.

In general, the critical times in the sector $10^{-6}–10^6$ s in the total "spectrum" of $10^{-15}–10^{15}$ s are much too important in so many aspects of human life to be neglected, and therefore it seems advisable for colloid and surface scientists to make efforts in order to systematize the time factor. This should be done in a similar way as Wo. Ostwald[17] did 60 yr ago in his "Die Welt der vernachlässigten Dimensionen", when he called for attention to be given to the problems of the spatial dimensions of those systems belonging neither to our ordinary homogeneous nor the heterogeneous world.

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