75 Years of Study in the Precipitation, Crystallization, Coagulation, and Flocculation in Ionic Solution — A Partisan Review

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To the memory of
Johanes Volkmar KOHLSCHÜTTER (1874—1938)
Peter Petrovič von WEIMARN (1879—1935)
Niels BJERRUM (1879—1958)
Wolfgang OSTWALD (1883—1943)
Sven Ludvig Alexander ODÉN (1887—1934)
Victor K. LAMER (1895—1966)
Lars Gunnar SILLÉN (1916—1970)

Assuming that the precipitation of slightly soluble substances from aqueous solution represents the possibility to establish the general and special characteristics of precipitation, crystallization, coagulation, and flocculation processes, the researches of G. A. Hulett, P. P. von Weimarn, S. Odén, A. Smekal, V. Kohlschütter, Wo. Ostwald, V. K. LaMer and others are reviewed by pointing to the accord and differences in the experimental results and their interpretations.

Essentially the same mechanism of the stability/instability states is applied for all component subsystems (embryonation, nucleation, coagulation or flocculation of primary particles) of precipitation processes.

Special attention was paid to the role of concentrational and spatial-temporal factors in the appearence of intermediates and various entities controlling the formation of the usually non--equilibrated structures. The findings are examined from a more unified point of view by taking into account the short-range and long-range forces in discontinuities of spatial-temporal functions.

An attempt was made to use kinetic and thermodynamic data to give a statistical picture of the systems in which the mechanism of interactions representing molecular and ionic forces in the bulk solution and in the methorical layer of the solid is expressed.

In trying to find a rational basis for the interpretation of a large spectrum of critical interactions involved in the transition from homogeneous to heterogeneous systems, the so-called »precipitation bodies«, PB, and their relationships to other diagrammatical presentations of distribution functions are presented.

INTRODUCTION

In these 75 years we have witnessed a very profound change in the understanding of the nature of physical, chemical, geological, and biological systems, i. e. of states and processes where besides quantum mechanics, nuclear, electronic, atomic, intra- and inter-molecular, as well as amicronic, ultra-micronic, microscopic, macroscopic, and cosmic structures are involved. The continuity and discontinuity notions are now more easily definable, and the

distinction between words, units, constants, and relationships in various fields of mechanics, have, by the introduction of certainty and uncertainty limits and principles, put the emphasis on definitions and meanings representing our knowledge in a much higher degree of precision and accuracy than they were in nineteen century.

Although we are aware of the fact that according to semantics »words are not things, and maps are not territories« we are obliged to use words, maps, diagrams, and relationships both in the numerical and nonnumerical expressions of dimensions and units which are frequently beyond our comprehension in the threedimensional space including the forth dimension of time. However, it is surprising how few attempts have been made to follow the more comprehensive definition of the systems which are certainly ones of the most essential for our orientation towards the events in nature, and in our technological interventions, namely, the formation and the dissolution of the solid phase in the liquid, and especially in the aqueous medium. The continuities and discontinuities in more or less static structures, and in much more dynamic interactions in liquids, and the order and disorder functions are manifested here in such a way that we can follow transitions not only from macro to micro, but also from micro to ultramicro and further to smaller dimensions where the accuracy and precision of our observation goes to the limits of our measurements.

Taking into account that the determinations of our fundamental SI units: meter-kilogram-second, are now approaching to the limits of 1 in 10^9 reproducibility, we also have to look at the phenomena of precipitation in relationships which could be expressed in the characteristic range of 10^{-9} to 10^9 units of space and time. In this respect just space-mass-time relationships, or concentration — substantial composition — critical time system interdependencies, and their interpretations including chemical, *i. e.* atomic (ionic) — molecular interactions in approximate and most direct volume and time expresions appear to be able to clarify many confusing concepts, and elliminate from the scientific literature, and even from textbooks, the elements of scientific folklore which were introduced at the time when many of the experimental and theoretical tools now in use were nonexistent.

The need for a comprehensive interpretation at various levels, on the one hand, and for ascertaining the most simple relationships, on the other hand, will justify an approach where the observable and experimentally easily definable facts have to be correlated with the experiences and insights gained in these 75 years about the states and processes which have some common features in such areas as those of the phenomena in the vast oceanic and fresh water systems, in the formation of bones and teeth or — generally — of various electrolytic and macromolecular interactions in living beings, in numeroues technologies, and in many analytical and scientific practices and theories. We will first analyze some case histories including experimental and theoretical elements appropriate to the time of their development. Afterwords we will try to consolidate the presentation of experimental results in some diagrams bearing the comprehensive but most obvious features of mutual relationships. Finally, we will look at the field in a broad conceptual framework, in which spatial-temporal elements are considered within a wide spectrum of interactions between atoms (ions), molecules, clusters, primary, secondary and higher aggregates, playing part in precipitation phenomena.

SOME CASE HISTORIES

Historically, we can follow the development of some notions and cognitions which play quite an exceptional role in the elucidation of the mechanism of ionic precipitation processes. One of such notions is to prepare at will positive or negative sols of silver halides which was clearly demonstrated by Lottermoser who summarized the experience gained in the nineteenth century. The origin of charges on colloid particles had been subject to a bitter discussion and the controversies divided colloid chemists into many groups during the first quarter of this century. Now, it is high time to give the entity bearing the charge at the interface between the solid matrix and solution at least a definite name. The name given by v. Weimarn was the homoatomic complex compound. We used the term complexoid. The chemical and physical interactions of such entities with the environment, their discrete character, the two-dimensional or limited three-dimensional concentration according to special equilibrium, and the general texture of charge distribution are special questions, which in addition to others have to be answered by using advanced methods and instrumentation. In the past such questions were discussed mainly on the ground of experimental evidence of adsorption, inclusion-occlusion, coprecipitation, and mixed crystal formation or solubility.

Richards[1], Hulett[2] and Kohlschütter[3] introduced the problem of obtaining pure solid substances, and the problem of inclusion or occlusion and solubility into an experimental frame which has through the experiments of Johnston[4], Weiser[5], Paneth[6], Fajans[7], O. Hahn[8], Kolthoff[9], Balarew[10], Karaoglanov[11], Pinkus[12], Težak[13], and others, mainly on barium sulfate or silver halide systems, explained or nearly clarified the phenomena of »inner« adsorption. However, the relationships between the solubility and size of ionic crystals have remained obscure even after the investigations of Hulett[14], Dundon[15], and many others[16,17] working on the fundamental theory of precipitation. The fact that the role of various precursors and various chemical equilibria have to be taken into account when the tranformation of smaller particles into larger ones are observed must be interpreted in the light of new data about the formation, persistence and solution of chemically different species or defficient structures, and not as a result of instability of smaller particles against larger ones.

With regard to adsorption laws, the formulations of Paneth[6], Fajans[7] and O. Hahn[8], with some modifications, seem to be correct. Hahn's formulation of Paneth-Fajans rule is as follows: An ion from any dilution will be adsorbed by a precipitate (adsorbent) when the precipitate has a surface charge opposite to that of the adsorbed ion and the adsorbed compound is sparingly soluble in the solvent taken. To this statement it was added[18] that the degree of similarity of the adsorbed ion to the one of the constituent ions of the crystalline adsorbent is a very influential factor.

Quite in line with such results were the discussions about mixed crystal formation, and the differences between real and ideal crystals[19], emphasizing the genotypical and phenotypical factors[20] in the structure of precipitates, as manifested by the phenomena of aging. Willstätter[25], V. Kohlschütter[3], Kolthoff[9], Balarew[10], and Karaoglanov[11], deserve the most credit for the clarification of the relationships between the chemical composition and physico--chemical properties of the precipitate.

However, the general approaches to concentrational-temporal factors, including the adsorption effects, were developed by v. Weimarn[22], Odén[23],

Haber[24] and Kohlschütter[3]. It is interesting to note that after v. Weimarn's publications, mainly during the first quarter of this century, and following two of v. Weimarn's summarizing reports[25,26], not a single comprehensive and coherent paper has been published on the guiding principles for the interpretation of precipitation phenomena in electrolytic solutions. Balarew's[27] approach was limited to a hypothetical statement that the thermodynamic equilibria are closely connected with particles of colloid dimensions; and that of Volmer[28], based on Gibbs' fundamental concepts, dealt with general principles without pointing to the essential differences between the phenomena of precipitation occurring in different media. Some more detailed reports, such as the report on precipitation phenomena by Walton[29], or on crystallisation by Mullin[30], do not present sufficiently clearly the common, most essential relationships, even in the precipitation stages of sparingly soluble substances.

Probably by experimenting with one system only, usually with $BaSO_4$, and applying very consequently the principle of supersaturation, v. Weimarn succeded in drawing generalizations of the great coherence of induction and deduction elements which he could immediately use as universal approaches. Mention should be made of the universality of the colloidal state, including the significance of spatial-temporal relationships, and the notion of vectoriality in the processes of condensation of the matter.

The somewhat modified (starting from the highest concentrations) main scheme and the experimental results illustrating v. Weimarn's precipitation maxima are given in Figure 1. V. Weimarn's precipitation laws are as follows[25]: »With increasing concentration of the reacting solutions, the average size of the precipitated crystalline individuals (not their aggregates) (1) passes through a maximum during, and (2) decreases continually after the completition of the process of direct crystallization; (3) for the same absolute concentration of the reacting solutions (other conditions being equal), with decreasing solubility of a substance, the average size of the precipitated crystals also decreases«.

In many of his papers and books[31] v. Weimarn has formulated the expressions for the function relating to the size of grains:

$$G (Q - L)^n = \text{const.}$$

where G is size, Q the total concentration, and L the final solubility; n is the number characteristic for a system. At the extremes of supersaturation there are few single crystals at very small supersaturation, and jellies or gelatinous precipitates are formed in highest concentrations. The only difference between the jelly and a gelatinous precipitate appears to be that in the latter case contraction has taken place with the excretion of liquid between the minute aggregates of the hydrated solid.

In v. Weimarn's

$$W = K \frac{\text{condensation pressure}}{\text{condensation resistance}} = K \frac{Q - L}{L} = K \frac{P}{L} = K. U.$$

W is the initial rate of precipitation, and Q—L=P amount of supersaturation. The ratio P/L = U is the percentage supersaturation at the moment when precipitation begins. The velocity of the second stage is given by the Noyes-Nernst equation: $V = D/S \cdot O \ (c - 1)$, where D is the diffusion coefficient,
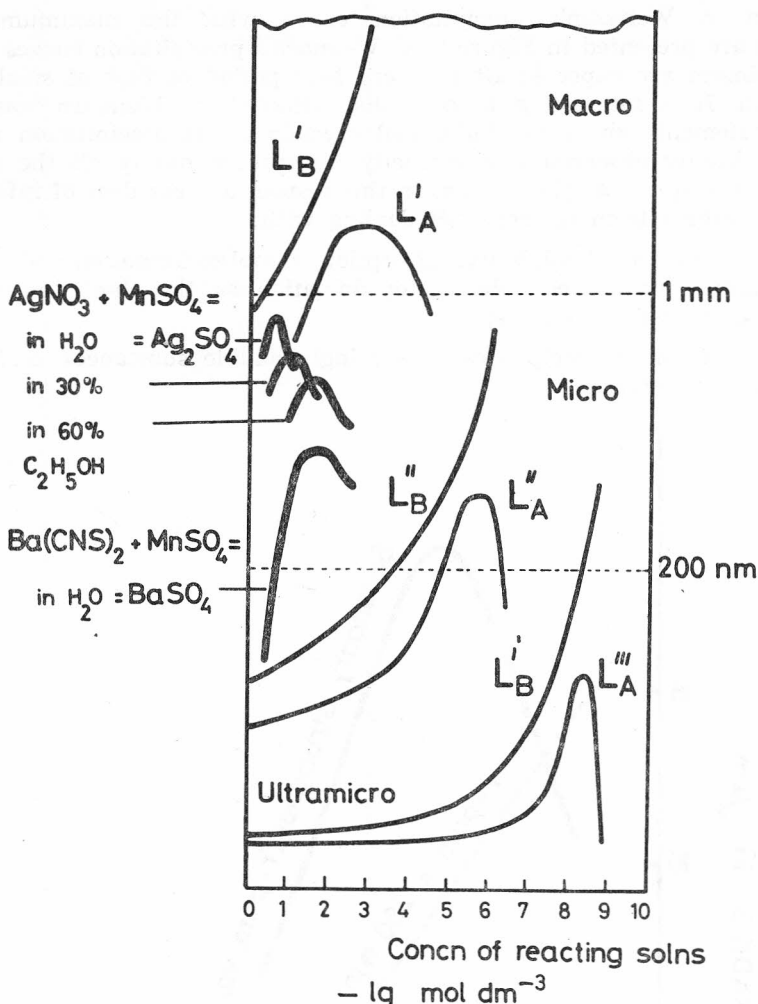
Figure 1. — P. P. v. Weimarn's schemes of precipitation curves (general, and some systems of silver sulfate and barium sulfate).

S the thickness of the adherent film, Q the surface, c the concentration of the surrounding solution, and 1 the solubility of the dispersed phase for a given degree of dispersity; $(c - 1)$ may be termed the absolute supersaturation. From these general formulations, v. Weimarn arrived at the conclusion that amorphous precipitates and jellies are obtained when ratio P/L, that is the percentage of supersaturation U, can be enormous.

Odén[32] has shown that the definition of crystalline individuals in the experiments of v. Weimarn do not hold true in reality. In fact, the majority of grains obtained in practice are aggregates of crystallites, and by using Odén's results on the determination of the sizes of primary particles, and taking into account their number in secondary structures, it is possible to

construct v. Weimarn's precipitation curve with the maximum. These relations are presented in Figure 2. V. Weimarn's precipitation curves without the maximum are expected after a very long period of time at small super-saturation. It is interesting to note that although v. Weimarn was wrong in his statements about the individual crystals in his precipitation maxima, he very keenly observed and correctly interpreted nearly all the essential stages of precipitation phenomena. In this respect a great deal of information can be obtained from his reports[33] dealing with:

»The influence of solubility, adsorption, complex-formation and solvation upon stability of the colloidal state; Solvation as the chief factor of the stability of colloidal solutions;

Dispergation of precipitates of sparingly-soluble substances, and disper-gation in *statu nascendi;*
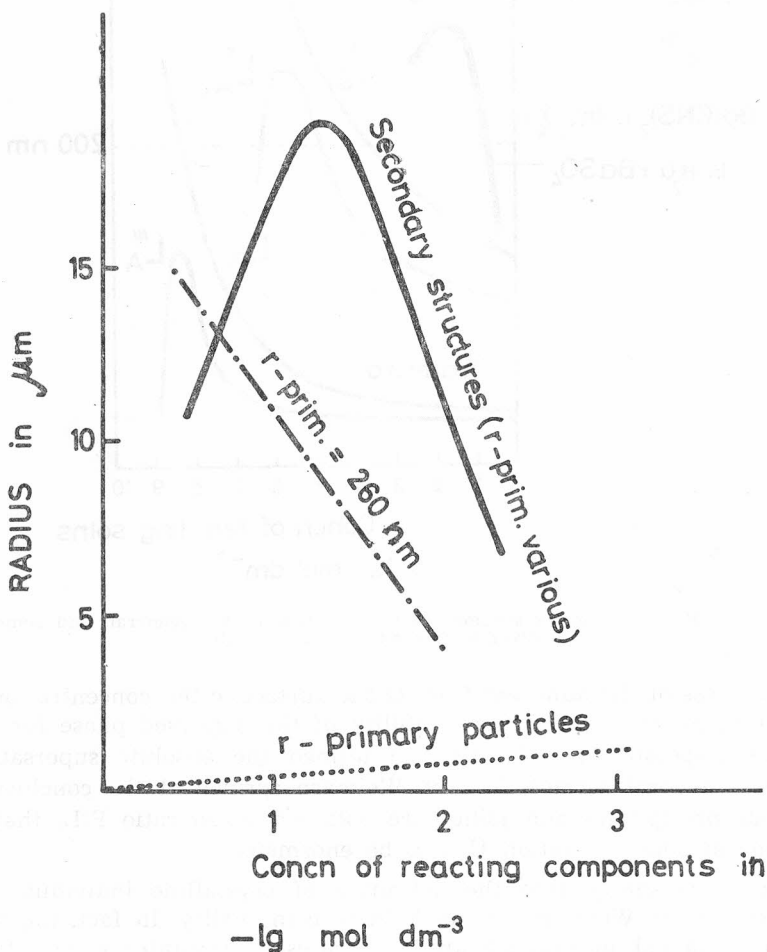

Figure 2. — Construction of the v. Weimarn's precipitation curve of barium sulfate taking into account the Odén's analysis (formation of secondary structures by aggregation of primary particles).

Surface-adsorption and dispergation of $BaSO_4$ in alcoholicaqueous solutions of $BaCl_2$, $BaBr_2$ and BaJ_2;

Surface-adsorption, inclusion-adsorption and capillar-adsorption;

Aplicability of Wo. Ostwald's dispergation law to the case of $BaSO_4$".

As mentaioned above, Odén's studies were complementary to v. Weimarn's investigations. Odén[34] introduced into the field of precipitation processes not only a very powerful instrumentation, namely the registrational sedimentation balance, but also the full significance of relationships between primary and secondary particles.

The special role of primary particles was emphasized by Mecklenburg[35] in very complex case of SnO_2-acids. The physical or colloidal against chemical aspects have then divided the scientific community, but now we have to give full support to the reconciliatory statements of Zsigmondy[36].

In Odén's view the formation of precipitates may be summarized as representing the following stages:

(I) The formation of nuclei consisting of a condensation of ions and molecules until the more stable unit cell is completed. The relation between the total number, n, of primarly formed nuclei and the concentration of the reacting ions c_1 and c_2 is

$$n = \text{const. } (c_1 \cdot c_2)^\alpha,$$

where α seems to be dependent on the number of ions which constitute the unit cell. This relation leads to v. Weimarn's qualitative law on the increasing size of particles with the decreasing concentration of reacting solutions.

(II) The growth of these nuclei has been found to follow the law

$$-\frac{dc}{dt} = \frac{D}{\delta} \cdot O_t \ (c_t - c_\infty), \quad \text{where} \quad -\frac{dc}{dt}$$

is the velocity of growth, D the coefficient of diffusion, δ the thickness of the layer of adhesion, O_t the total surface of the primary particles, c_t the concentration at time t, and c_∞ the concentration of solubility. When this growth is completed, $c_1 = c_\infty$, and the primary particles are formed.

(III) The aggregation of primary particles to secondary aggregates is analogous to the coagulation of colloids and may be summarized as follows:

(a) With decreasing charge of the particles because of the ions of the system a critical point is reached when the primary particles aggregate.

(b) Passing below this charge, there will be a greater number of particles in the aggregate the smaller the charge of the individual particles, thus tending to form aggregates of an unlimited size with a zero--charge of the particles.

(c) In the reversible aggregate there is no amalgamation of the individual particles and probably no equalization of the charge on the particles,

or else we could not account for the fact that addition of certain
ions will again increase the charge and cause disaggregation and
freeing of the crystal individuals. The aggregates have been found
to retain a certain charge and thus a difference towards the fluid.

(d) A longer period of time is needed for the complete formation of these
aggregates than for the formation of nuclei and their growth is inver-
sely proportional to the number of primary particles per cc if the
electrolytes are present in the same amount, but it decreases rapidly
with the increase in the concentration of the electrolytes and in most
cases it is less than one minute.

(IV) The fourth stage consists of the formation of irreversible aggregates of
the primary particles either

(a) of a definite structure in crystal forms;

(b) spherolites;

(c) or an irregular shape under the pressure of external influences.

In the formation of the irreversible aggregates the water envelopes
covering the surface are burst open and crystal surfaces come into
contact.

(V) The fifth and last stage is the growing of bigger crystals at the expense
of smaller ones. The conditions are not only a difference in solubility
with size but also a variation in size. The more prominent the latter,
the more rapidly the recrystallization or »ripening« takes place.

In the final version Odén's stages of precipitation are:

(i) Formation of nuclei   v. Weimarn, about 1905

(ii) Growth of nuclei into   Noyes and Whitney; Nernst;
    primary particles   Werner:

$$- \frac{dc_t}{dt} = \frac{D}{\delta} \cdot O_t (c_t - c_\infty)$$

(iii) Formation of aggregates   Odén, 1920; N. τ = const.

(iv) Changes of reversible
    aggregates into:
    (a) larger crystalline individuals;
    (b) secondary particles without
        any orientation;
    (c) irreversible aggregates
        (amorphous precipitates)

(v) Ripening   Wi. Ostwald, 1894.

The coagulation phenomena with primary particles of barium sulfate
under the influence of various concentrations of ammonium nitrate were also
studied, and by using Odén's results our Figure 2. was constructed.

Thus, the reversibility and irreversibility of the aggregation of primary
particles into secondary structures, and the distances between micelles, as

evidenced by the peptization phenomena, were familiar to the older resear-chers in the field.

A similar development may be traced in the formation of real crystals. While certain crystal properties have the dimensions expected from the lattice theory, other appear to give results, quantitatively expressed, which are of a different order of magnitude from those anticipated from theory. Smekal[37] has given names to these two sorts of properties the latter he calls »structure sensitive«, and the former, »structure insensitive«. Thus, the latter include density, lattice dimensions, chemical properties and the energy content. The »structure sensitive« properties are: thermal and electrical con-ductivity, diffusion phenomena, photo-electricity, phosphoresence, resistence to acids, etc. Generally speaking, when different samples yield different results, the properties usually belong to the »structure sensitive« phenomena. Smekal believes that the »structure sensitive« properties are due to the mosaic stru-cture of real crystals. Smekal's blocks are very small, being of the order of 10 nm maximum width. But the evidence of the existence of such blocks, or larger units of submicrons, provided by Traube[38], has not been sufficiently appreciated. Figure 3 may be taken as a proof of the fact that monodisperse particles obtained under conditions of homogeneous precipitation[38a] are in fact aggregates of primary particles which are smaller than 10 nm.

In the interpretation of precipitation phenomena the role of the medium, that is the influence of the »internal environment« of the growing crystal, has been too frequently overshadowed by the discussion of the first step in the numerous »repeatable« steps of the continuous or discontinuous pro-cess of cristal growth. It seems that to great an emphasis was laid on the presence of various Kossel-Stranski-Volmer-Frenkel[39] »kinks«, »dislocations«, and »roughnesses« of the crystal surface compared with the actual role of the constituents in the methoric space, that is in the region between the solid and liquid phases. The arrangement of the constituents of the methoric layer may be either of fixed or kinetic character, and in such a dynamic system of considerable thickness we have to look for the mechanisms of ordering and exchanging the ions and molecules with special preference to those constituents and clusters which may give to the whole system the transition structure of greatest probability. Besides, the possibility that the molecules of the solvent may be built, at least temporarily, into the crystal lattice, or, in general, the effect of the stereochemical and stoichiometrical relationships of the adjacent region in respect to the specific structure of the crystal lattice, must also be recognized.

The interesting phenomena reported by Bunn and Emmet[40], may find a ready interpretation from such a point of view. They have found that the spreading of crystallization is accomplished in a series of waves starting at some point near the centre of the crystal surface. The average thickness of the layers was found to be 200 to 400 nm. The substance on which layers were seen have moderate or high solubilities, and are either ionic or contain strongly polar groups. The adjacent solution region where the number of ions necessary for the building of successive layers is found should be put under the influence of each of the lattice layers in the formation state. Thus the layer of solution, the thickness of which is about, say 200 nm, must reflect the supersaturation change with the discontinuous formation of the »two--dimensional« nuclei and the continuous spreading of each of the lattice layers.

The lower the dielectric constant in the solvent the greater the attractivity between ions with a resulting thicker shell of association and a changed »packing« of the ions in the methoric space. This may permit explanation that the layers observed by Bunn and Emmet became thinner with an increasing proportion of alcohol.

In general, the crystallization of heteropolar systems is much more sensitive to the character and the conditions of concentration of all of the ions present in the precipitating medium than is the case in systems of nonpolar substances, and it cannot be directly compared with the condensation from the vapour phase. The difference from the crystallization of melts may also be manifested by comparing the phenomena of Tammann's nucleation and crystallization maxima with Težak's concentration, isoelectric, transition, crystallization and secondary maxima[4]. The answers to the questions open in this field could probably be found only in an apropriate recognition of the mutual interdependence between the role of the crystal, of the methoric layer, and of the solution.

In this sense the experiments of Davies and Jones (for AgCl)[42], and Turnbull (for BaSO$_4$)[43] show that the number of nuclei, their aggregation velocities, and the velocities of direct growth, are all dependent upon a small and sometimes only transient and local variation of the concentration during the mixture of the reacting components.

Cobbet and French[44] have shown conductometrically that the maximum rate of the dissappearance of ions from a solution is dependent on such factors as the total Ba^{2+} and SO$_4^{2-}$ concentrations, the ratio of Ba^{2+} and SO$_4^{2-}$ ions, and the presence of excess electrolyte. A considerable degree of supersaturation of the solution appears to be necessary before the reaction and visible precipitation can be detected. For some time the reaction appears to be of the 1st order, and in certain number of cases, it subsequently becomes apparently of the 3rd order. When the concentration product was below 1.59×10^{-8} no visible precipitation occurred, and no change in resistance with time could be detected in the solution. The normal solubility product must be exceeded about 160 times before the development of nuclei will occur spontaneously. Probably such results as well as the calculations of Kolthoff[45] showing that the solubility of minute BaSO$_4$-crystals of 0.04 μm in diameter is about 930 times the normal solubility, have to be attributed to special equilibria where many chemical species are involved. Collins and Leineweber[46] studied the kinetics of the homogeneous precipitation of BaSO$_4$ where the sulfate ion was generated by the LaMer and Dinegar method[47] of the persulfate-thiosulfate reaction. On the basis of the Becker-Döring[48] nucleation theory, it is assumed that the precipitation involves nucleation which occurs in a single burst and which is followed by the diffusion-controlled growth of the crystallites in the supersaturated solution. It has been found that the supersaturation ratio at the time of nucleation is strongly dependent on the purity of reagents.

The crystallization of BaSO$_4$ upon addition of seed crystals to stable supersaturated solutions has been studied conductometrically by Nancollas and Purdie[49]. After an initial surge the rate: $-dm/dt = k(m-m_o)^n$, where $n = 20$, follows the growth where $n = 2$.

The order of the reactions of nucleation and growth were discussed by LaMer[50], O'Rourke and Johnson[51], and especially by Christiansen and Niel-
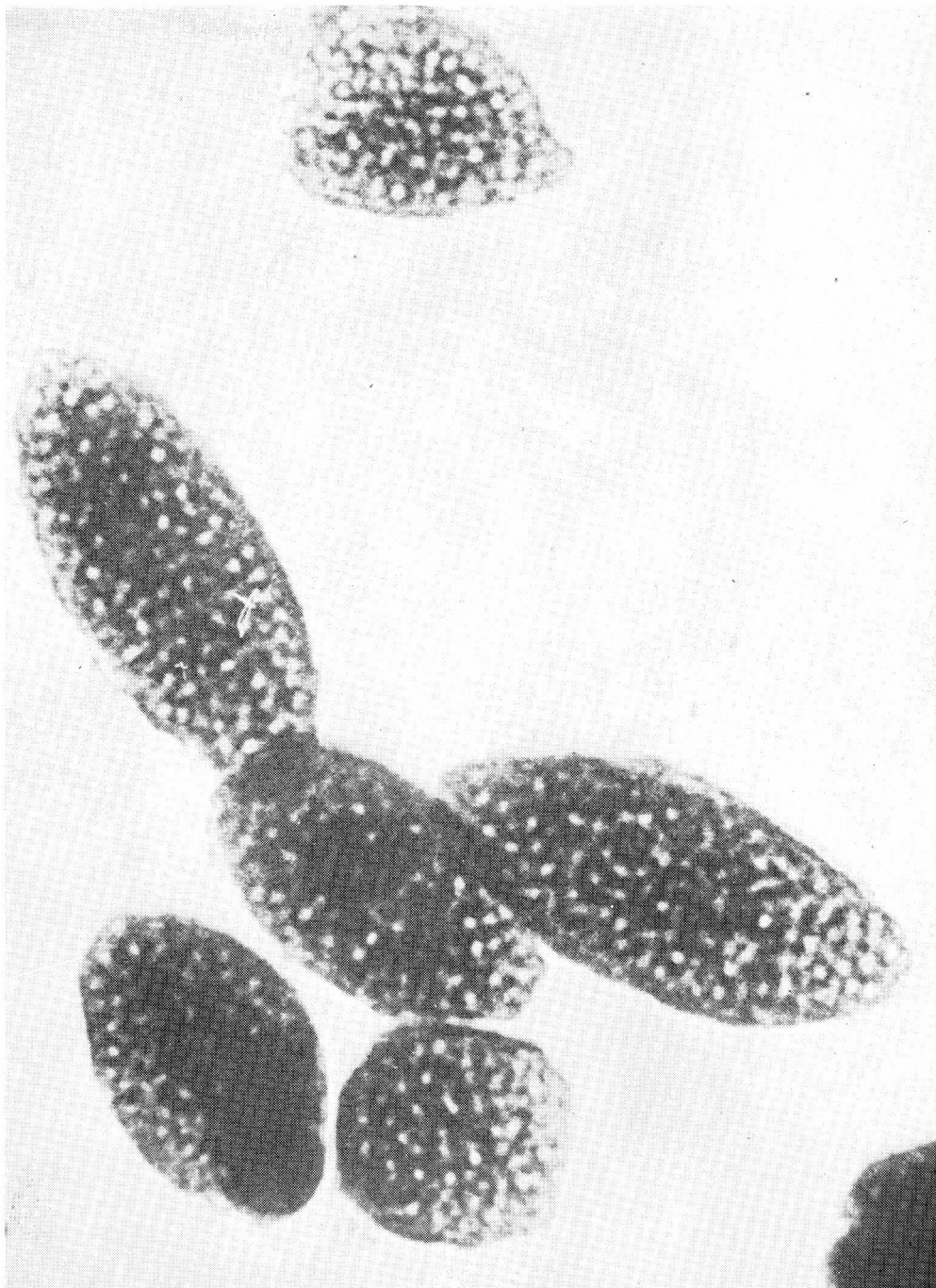
Figure 3. — Electron micrograph of typical ultrathin cestions of sponge-like barium sulfate particles prepared by the Takiyama method of homogeneous precipitation (magnification ~ 400.000 x; J. J. P e t r e s, Gj. D e ž e l i ć and B. T e ž a k Croat. Chem. Acta **41** (1969) 183).

sen[52], who tried to find a similar expression to Odén's $N \cdot \tau = \text{const.}$ LaMer's relationship was $c^p t = \text{const.}$, and $-p (\log c) = \log t - \log. \text{const.}$; taking $(p + 1)$ as the order of reactions. In most cases the induction time was observed. Nielsen[53] has observed nucleation and growth in highly supersaturated solutions of $BaSO_4$, $BaCrO_4$, $BaMoO_4$, $BaWO_4$, $BaCO_3$, $PbSO_4$, $PbCrO_4$, $PbCO_3$, $SrSO_4$, and $CaWO_4$. In the concentration range where the number of homogeneously nucleated particles is larger than that of heteronuclei the induction period decreases from 1 to 10^{-4} s, and the number of particles found per cm^3 increases from 10^7 to 10^{12} with increasing concentration.

The induction period may range from 1 ms to several days, depending on the initial supersaturation.

The rate of nucleation:

$J = kc^n$, and the slope of the curve $\log J$ versus $\log c$ equals n (which some authors consider to be the number of molecules in the critical nucleus), is the same expression as the one used by Paine[54] very early for the velocity of coagulation:

$R = \text{konst.} c^p$, where R is the velocity of coagulation, c the concentration of the salt causing coagulation, and p an experimentally determined number. Therefore, it is justified to think about the application of the v. Smoluchowski[55] theory of rapid and slow coagulation in the analysis of precipitation processes. The time T in v. Smoluchowski's expression (time from $t = 0$ till the time when the number of all particles is halved; or the number of primary particles reduced to 1/4) is:

$$T = \frac{1}{4\pi DR\nu_0},$$ where D is the diffusion coefficient, R the radius of the sphere of interacting particles, and ν_0 is the number of primary particles in unit volume at zero time. Thus the concentration-time relationships are very far-reaching, and may be applied also to such systems describing the peptization of equivalent sols of slightly soluble metal salts by solutions of organic acids and by suspensions of gelatin and agar, as reported by Packter and Matalon[56].

On the other hand the precipitation effects in gels may be used in the determination of isoelectric or equivalency relationships in ionic systems sensible to the acidity of aqueous media (Težak[57]), as well as in studies of the stoichiometry of precipitation under conditions of diffusion. Pučar, Pokrić, Graovac and Živković[58], have used the double diffusion method for determining the critical concentrations of precipitation. It has been shown that precipitation under the conditions of double diffusion obey the »equivalency rule« $c_A = c_B = c_{crit}$ rather than the ionic solubility law $c_A \cdot c_B = K_S$.

Besides »classical« systems of $BaSO_4$ and Ag-halides almost all kinds of inorganic substances have been investigated, including those where the solvent, especially water, is a very chemically active component in the precipitation process. Such a field of metal hydroxides was attacked by Sillén's school[59], while the complex systems of metal-oxide and hydroxide sols have played a very prominent role in the clarification of questions of the colloidal and general chemistry throughout these 75 years. A very interesting recent contribution is the preparation of monodisperse hydrous oxide sols by Matijević and coworkers[60].

Data showing that the charges on pure crystals which are in equilibrium with their saturated solution have also to be taken into consideration may be found both in older (e. g., Michaelis and Dokan[61]; Kruyt and van der Willingen[62]) and recent reports. Weiss, Ericson and Herz[63] have shown that AgBr-crystals for all the 10^{-3} M sols have a zero point of charge (zpc) at pAg 5.3 ± 0.2 independently (a) of the crystal habit, (b) crystal size from 0.4 to 1.6 μm edge-length, (c) crystal size distribution, and (d) incorporation of 4 mol $^0/_0$ iodide into the crystal. However, mere dilution of this sol to 10^{-5} M AgBr lowered the zpc to pAg 2—4. On the same 10^{-3} M AgBr dispersion at pBr 3 independent electrophoresis and adsorption measurements were carried out when varying amount of a cationic cyanine dye were added. A simple linear relation was established between the electrophoretic mobility and the adsorbed dye ions; the adsorption of 10^{14} dye ions/cm^2 was just sufficient to reduce the initial negative mobility of AgBr to zero. This amount of cyanine dye coincides with the concentration of Br$^-$-ions adsorbed to cubic AgBr-crystals at pBr 3, suggesting simple charge neutralization at the surface. Therefore, interesting relationships have to be expected with systems where the ratio between the precipitating ions is radically changed either in or without the presence of foreign ions or molecules.

As can be seen from the examples reported we have limited our presentation to slightly soluble substances. The behavior of such systems cannot be considered to be the same as the crystallization of soluble salts, where high concentrations must be reached to provoke a precipitation. At high concentrations the ions are already under the direct influence of their long-range coulombic interactions, and one of the first steps in the precipitation may proceed in a way very similar to the squeezing of the solvent under the internal pressure of the condensing ions. The ability of solvent molecules to fit into the crystal lattice or to enhance the probability of various crystal forms, especially of a transient character, must not to be overlooked under such circumstances, and such situations are considered in this review only in wider aspect.

However, V. Kohlschütter's[64] data about the formation of »somatoids« may be considered representative for all precipitates.

The term »somatoid« denotes small independent particles — mostly of crystalline structure — which have a characteristic shape, but are nevertheless essentially different from the true, perfect or only partially developed crystals.

In this respect Wesselowski and Wassiliev[65] describe single species on the basis of several orders of structural elements. The parameters and mutual relations of these elements determine the nature of a given disperse body.

They distinguish the following orders:

(1) Crystallites (as defined by Tammann) of all forms and sizes down to ultra-microns;

(2) Characteristic aggregations of crystallites which play the role of bricks in the building-up of larger bodies (analogous to V. Kohlschütter's »somatoids« or to the »micelles« of colloidal chemistry);

(3) Textures, i. e. still larger elements, forming the greater part of macroscopic bodies.

Crystallites have always been considered »elements of the first order«.

One step further has been made by H. W. Kohlschütter[66] who, in addition to Wesselowski-Wassiliev's »systematics of disperse bodies«, which calls all particles of dimensions larger than molecules »disperse structures«, different-iates »discrete disperse« and »compact disperse« systems.

When speaking about systematics mention should be made of Wo. Ostwald's[67] very far-reaching frame embracing the whole of colloid science, from which we have taken a term which is especially relevant and pertinent to disperse systems in solution: it is methoric and methorical, clearly pointing to the significance of the t w o or more boundaries and the region between them.

PRESENTATION OF EXPERIMENTAL RESULTS BY DIAGRAMS

In order to demonstrate the mutual relationships between various results on precipitate formation and dissolution, we have plotted observable systems in XYZ-diagrams where the perpendicular axes show both the spatial (con-centrational) and temporal states of the two main precipitation components, and of the precipitate itself. That such an approach may clarify some funda-mental questions will be shown by discussing cases of dissolution of solid ionic substances in comparison to the processes and states encountered in the formation of the solid phase, all in aqueous solutions. To rationalize the use of parameters in the changing fourdimensional space we have to start with the point of origin where the distances between interacting units, ions, atoms, molecules, as well as between them and their aggregates, are given in their closest approach, while on the three perpendicular axes are in logarithmic scale the initial or resulting concentrations of the main precipitating compo-nents, and of the corresponding solid, or any of the intermediate products after a definite period of time.

By Figure 4 presenting the »expanding cube« of solutions and the »dis-persion spaces« we will try to define the positions of various spatial-temporal configurations belonging to pointed mutual relationships.

In case of dissolution, by adding to a original solid a kind of solvent, e. g., water, the resulting equilibrated solid/solution system will be represented by the position of the solid in the equivalency section, while the dimension of the cube will correspond to solubility.

For orientational purposes it may be useful to present in brief some structural aspects which accompany the transformation of a simple ionic sub-stance in the process of systematic dilution. The first extensive study of such kind was given by Narten, Vaslow and Levy[68] not long ago.

Aqueous LiCl solutions of near saturation concentration expressed in units ratio H_2O or $D_2O : LiCl = 3$, till $LiCl \cdot 136 H_2O$ or $LiCl \cdot 66.9 D_2O$, were studied by X-ray and neutron diffraction, respectively. All data are shown to be consistent with a simple model involving only the nearest neighbor interactions. The co-ordination of water oxygen atoms around Cl^- appears to be mostly octahedral, while around Li^+ it appears to be tetrahedral. The $LiCl \cdot 3H_2O$ is similar in composition to the crystalline dihydrate precipitated from sa-turated LiCl solutions. There is only a very small total number of water molecules, and many of them are shared between the hydration layers of the ions. The liquid character is displayed by the high fluctuations of the OCl and
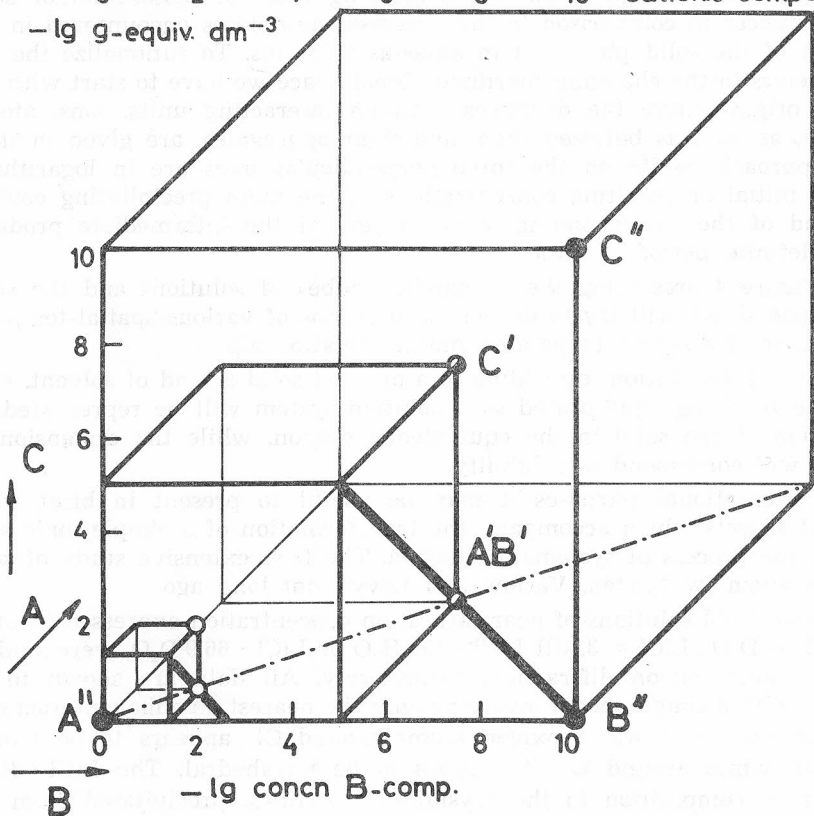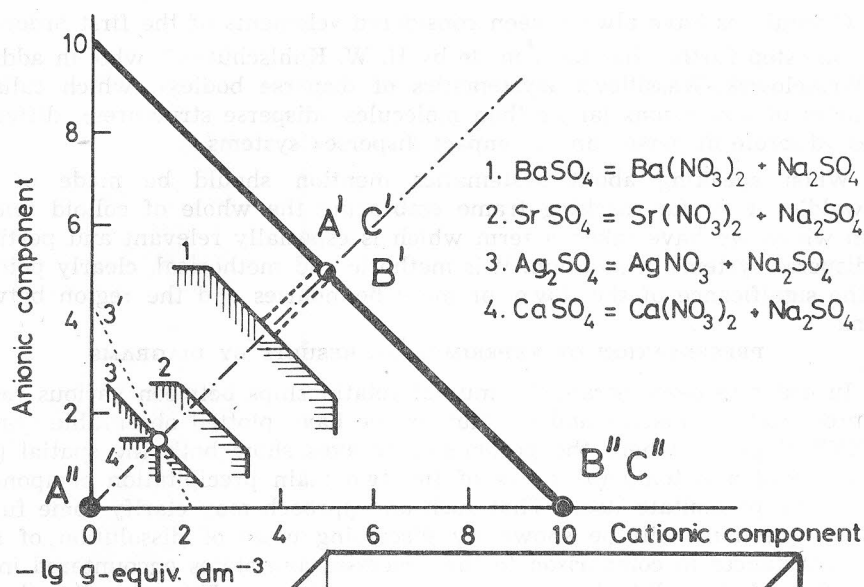
Figure 4. — Precipitating-nonprecipitating boundaries of barium sulfate, strontium sulfate, silver sulfate, and calcium sulfate systems in a plot of logarithm of cationic vs. anionic component concentration (upper part), and comparative positions of some points of solubility boundaries in the »cube of dilution« (lower part).

OLi distances. When the molar composition of the solution becomes about 10 the diffraction pattern begins to be shifted towards that of pure water. For all but very concentrated LiCl solutions, dynamic effects cause the coordination numbers to fluctuate as 6 ± 1 and 4 ± 1, respectively. In our diagram the LiCl solid/solution equilibrated system will be presented by a very small cube near the origin; and on the basic plot along the X and Y axes there will be only cationic and anionic aquo complexes, respectively. Obviously, similar systematic data on less soluble substances in diluted solutions obtained by relaxation spectrometry may reveal the effect of long-range forces resulting in the formation of various complexes, ion-pairs and clusters, and thus filling the gap between the concentrated systems and those where the Debye-Hückel treatment of the dilute electrolyte solutions could be applied. How great the influence of the amount of solid (by application of Wo. Ostwald's[69] »Boden-körperregel«) will be, may be a special question.

If we have to prepare the precipitate from a solution, the situations are fundamentally different from the corresponding system of dissolution, and we have to take into account all the elements mentioned in various case histories which were presented in the previous chapter. And there are even more complicated factors when the precipitating components are not in equivalent relationship of the precipitating components or there are foreign accompanying ions in the initial salt solution. In fact, a whole range of processes and states are encountered here before and after the equilibrated state is reached. Much more so in the case of systems very far from equilibrium, especially when one of the precipitating components is in great excess, or when there are foreign ions and molecules in the medium. The experimental data may be indicative of situations in the bulk solution, in the methoric layer between phases, and in the emerging solid phase, but most frequently of their common and complex interactions. Depending on the state of the system interpretations may be given in terms of thermodynamics, kinetics or elementary processes, taking into account the very different temporal characteristics of various intermediate component processes and structures. For illustration we will give some examples.

APPROACHING AND DEFINING THE EQUILIBRIUM STATES BY PRECIPITATION

By mixing two precipitating components in more and more diluted solutions the limit will be reached when no precipitate will appear, even after a very long period of time. Such boundaries between precipitating and non--precipitating systems determined in a systematic way may represent equilibrium states which sometimes may correspond to the solubilities obtained by dissolving the solids in adequate solutions. For the presentation of such results our three-dimensional diagram in Figure 4 or a presentation in two-dimensional reduction on the basic XY plane may be used. The precipitation boundaries reflect the existence of species controlling the transition from solution to solid phase ,and the slopes may be used for the determination of the composition of such species and definition of the equilibrium conditions. Inside the boundaries, on the precipitation side, there are processes and structures which kinetically represent various features of the so-called »precipitation bodies«, PB, while their outer contours indicate, after a reasonable period of time, the true or very near equilibrium states. In fact, we could differentiate[70] at
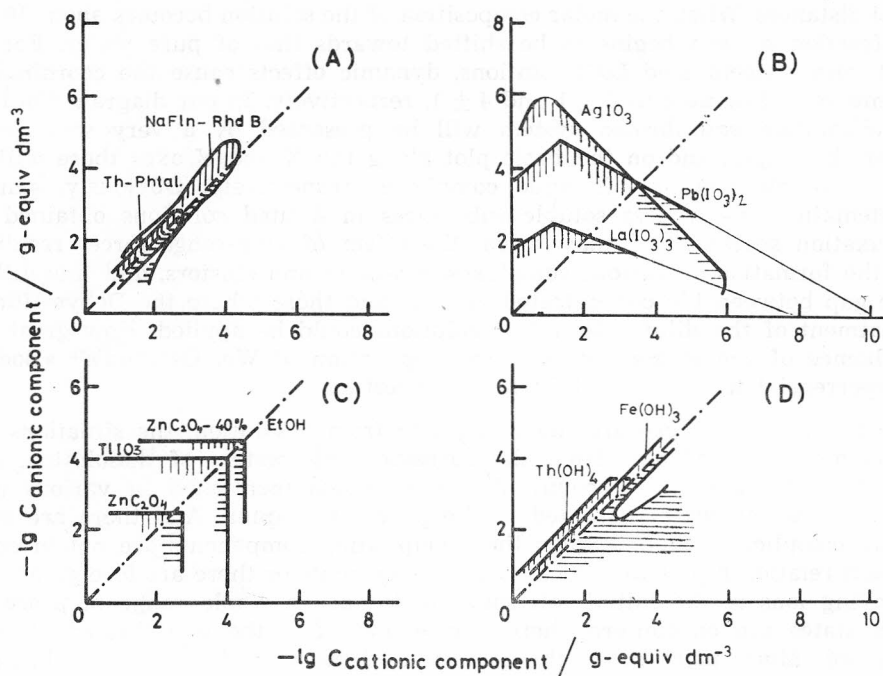
Figure 5. — Types of »precipitation bodies«, BP, for: rhodamin B — sodium fluorescein, and thorim nitrate — potassium phtalate (A-type); silver, lead and lanthanum iodate (B-type); thalium iodate, and zinc oxalate in water and 40% ethanol (C-type); ferric and thorium hydroxide (D-type); all represented in a plot of logarithm of cationic *vs.* anionic component concentration.

least four types of »precipitation bodies« which are illustrated in Figure 5 by examples. These PB-types are distinguished by the dominant processes of: (A) neutralization; (B) ionic solubility; (C) formation of ion-pairs and associates; and (D) unsymetrical ionic activity (involving the chemical interactions with solvent).

In many cases the experimental PB are combinations of two or three types. *E. g.*, the precipitating system of silver bromide represents a combination of three types, if besides the outer boundaries, the very distinct internal contours are also considered. Not only silver bromide, but all the silver halides have a neutralization zone along the equivalency ratio of the precipitating components delineating on both sides almost symetrical and experimentally well defined negative and positive colloid systems of the so-called sols in *statu nascendi*. Since these features are very revealing it seems worthwhile to study the kinetics of appropriate systems inside the precipitation boundaries of our PB, and to complete the data representing 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, have to be determined after a reasonable time in order to reach

the equilibrium states, the mechanisms of the underlying processes controlling the systems inside the PB can be detected only by following the kinetics of precipitation as closely as possible.

The relationships between concentrations and the critical times for the initially detected change of the system were usually determined along one section through PB. The values of scattered light or of particle sizes may be plotted as a function of time (time-tyndallograms resp. time-dispersoidograms), and the intersections of the tangents to the steepest parts of the precipitation curves with the abscissae, where times are in logarithmic scale, give the critical times, t_{crit}. If the logarithms of concentrations are in linear relationship with critical times, then it is highly probable that the underlying mechanism is the same. Otherwise discontinuities indicate a change in the character of the controlling mechanism.

We have chosen two cross-sections through the PB of silver bromide. In Figure 6, experimental cases with two concentrations of silver nitrate are shown: 1×10^{-4} mol dm^{-3} (I), and 5×10^{-6} mol dm^{-3} (II). The ordinates represent the critical times in logarithmic scale, while as abscissae are logarithms of potassium bromide concentrations.

If we follow the precipitation curve of the systems with 5×10^{-6} mol dm^{-3} silver nitrate we can see that silver bromide precipitating under such circumstances shows two very expressive maxima, in the region of the highest and lowest concentrations. These are the concentration[71] and crystallization[72] maxima, respectively. Between them the so-called isoelectric and transition maxima may appear, while the »empty« periods between the maxima may be
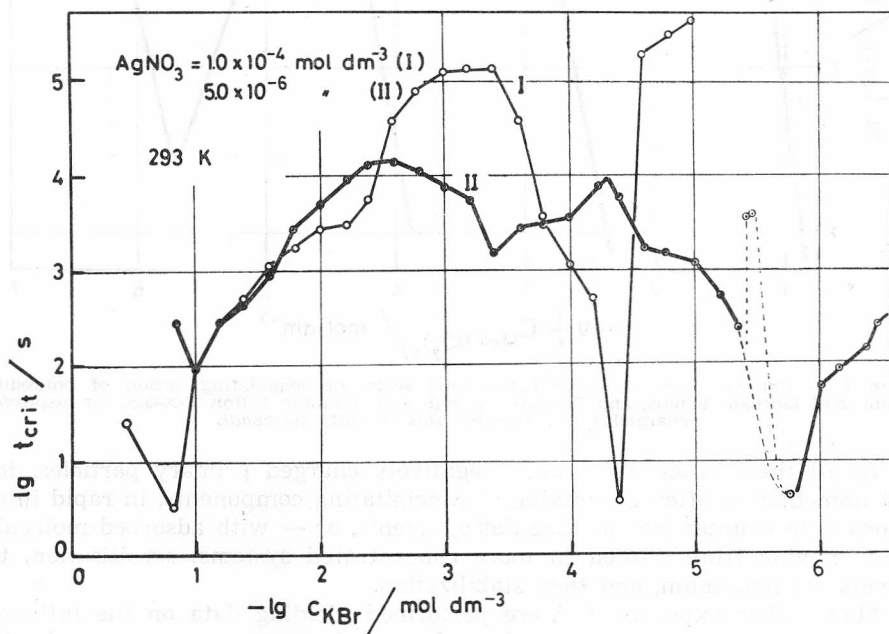

Figure 6. — Formation of the silver bromide precipitate in a plot of logarithm of potassium bromide concentration *vs.* logarithm of critical time, $t_{crit.}$, in seconds; for concentrations of silver nitrate: 1.0×10^{-4} and 5.0×10^{-6} molar, at 20 °C.

used to study the influence of various additional factors. Accordingly, in a series of silver halide precipitates we were able to observe the key phenomena of the coagulation and flocculation of primary particles, while in cases of sparingly soluble sulfates, following opposite effects, it was possible to demonstrate the delaying action on embryos or nuclei formation[73] (reverse Schulze-Hardy rule). Figure 7 shows the results of experiments with 4×10^{-4} M $AgNO_3$ and 1.2×10^{-3} KBr systems .The »empty« period of time is at least of 3 orders of magnitude. Using such systems the experiments of coagulation and flocculation were performed in a way commonly used for sols in *statu nascendi*. The coagulants were 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 Figure 7 the abscissae values are logarithms of equivalents of inorganic salts, or of moles of the surface active substance; the ordinates are corresponding critical times on the logarithmic scale.
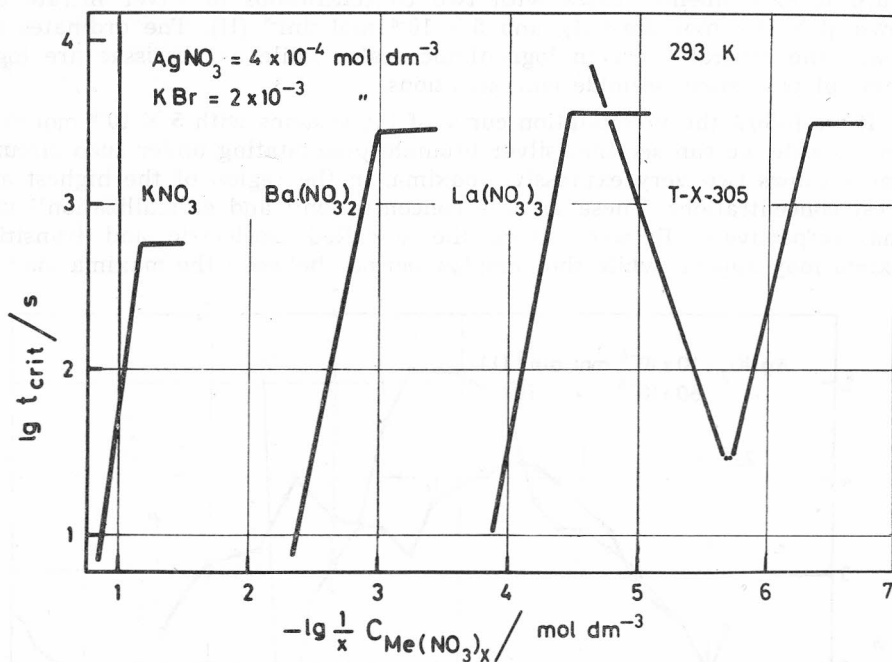

Figure 7. — Critical times, $t_{crit.}$, in logarithmic scale, of coagulating action of potassium, barium, and lanthanum ions, and flocculating action of nonionic Triton T-X-305, for negatively charged silver bromide sols in *statu nascendi*.

In all these cases there were negatively charged primary particles, formed immediately after the mixing of precipitating components, in rapid interactions with counter ions as coagulating agents, or — with adsorbed molecules — by moving from diluted to more concentrated systems: sensitisation, the flocculation maximum, and then stabilization.

Many other experiments were performed yielding data on the influence of the ionic size, the mixture of electrolytes, solvents, temperature, and other factors[74]. The directly obtained data on precipitation kinetics have been completed with determinations of adsorption[75], exchange rates[76], and electro-

phoretic valocities[77], then by optical and electron-microscopical observations[78], X-ray determinations[79], chemical analyses[80], and other procedures; and in the light of all these data the mechanisms at the level of elementary processes have been analyzed.

TO THE SET-UP OF ELEMENTARY MECHANISM

There are very characteristic effects of the size and valency of the counter ions or accompanying ions of the main precipitating components in the precipitation phenomena, especially with sols in statu nascendi. In numerous cases the relationship between the logarithm of the critical coagulation concentration (c. c. c.) and the valency of the counter ion could be expressed by Bjerrum's critical distance[81]:

$d_{crit} = \dfrac{z_1 z_2 e^2}{2kT\,D}$, assuming that z_1 represents the univalent potential deter-

mining ion fixed to the wall, and z_2 the valency of the counter ion. Similar considerations may include the influence of the ionic radii and of the dielectric constant[82]. In Figure 8 the experimental results obtained with mixed solvents are shown. The linearity was proved so frequently and in such diversity of systems[83], that the regular features and exceptions will enable us to analyse many essential parts of the composite mechanism. In this sense, already one of the first interpretations[84] represented by Figure 9 may be of some use.

In Figure 9 there is a set-up of interacting univalent counter ions with chlorine ions fixed on silver chloride; all under the assumption that the critical energy is 1 kT (owing to the reduced degree of freedom), and its linear equivalent in the critical distance (for univalent electron charges, T = 293 K, and D = 80) is 7.2 Å. It is quite clear that the relationship between concentrations and distances could be treated only as an expression of statistical events, and thus leaving room in the space between interacting ions for the statistically determined composition of the molecules expressing the macro dielectric constant.

Therefore, the average distances in the accompanying distribution volumes have to be compared with the distribution volumes of ions in bulk solution under corresponding conditions of coagulation. Such distribution volumes or 'cages' of the polyvalent counter ions may cover more than one of the potential determining ions, but the determinations of adsorption[75] have shown that equivalent amounts of counterions are kept with coagulated particles. This fact may remind us of the presence of spatial-temporal stoichiometrical relations. Figure 10 shows a corresponding scheme.

In the mechanism of flocculation, instead o coulombic interactions, the role of adsorption, and the resulting distribution of the adsorbed species between the methorical layer and bulk solution, are the preponderant factors of the instability and stability states of the systems. If the stereochemical, or more generally, the physical and chemical forces of some molecular or ionic species for the interaction with colloid particles are of such a magnitude, that appreciable differences in the distribution of the osmotically active units in the bulk solution and methoric layer can occur, the phenomena of flocculation or stabilization are be encountered. Such flocculation phenomena have been
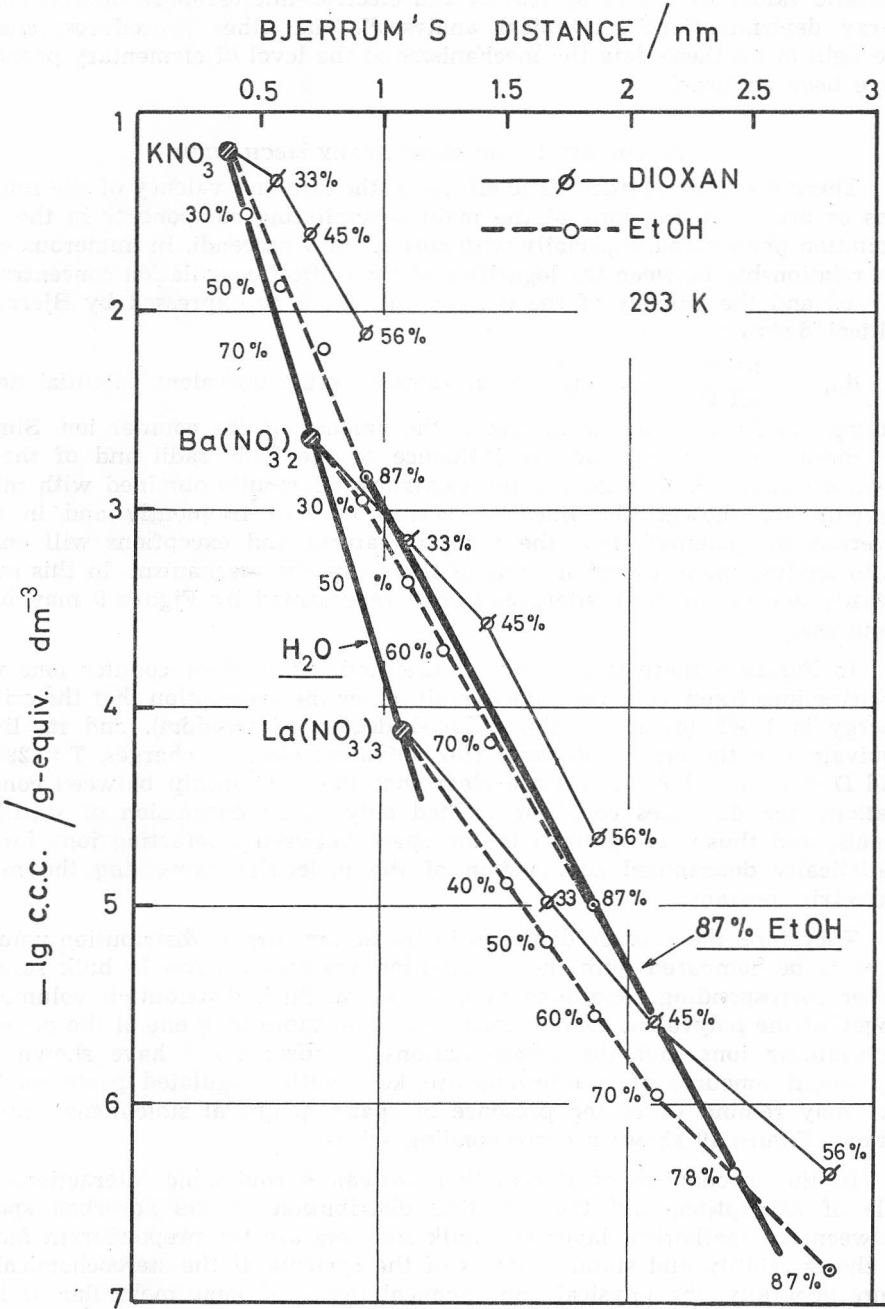
Figure 8. — The dominating linear relationships between critical coagulation concentration *vs.* Bjerrum's distance, $d_{crit} = \dfrac{z_1 z_2 e^2}{2DkT}$, as they change with the valency of counter ions for several dielectric constants of the ethanol-water and dioxan-water mixtures.
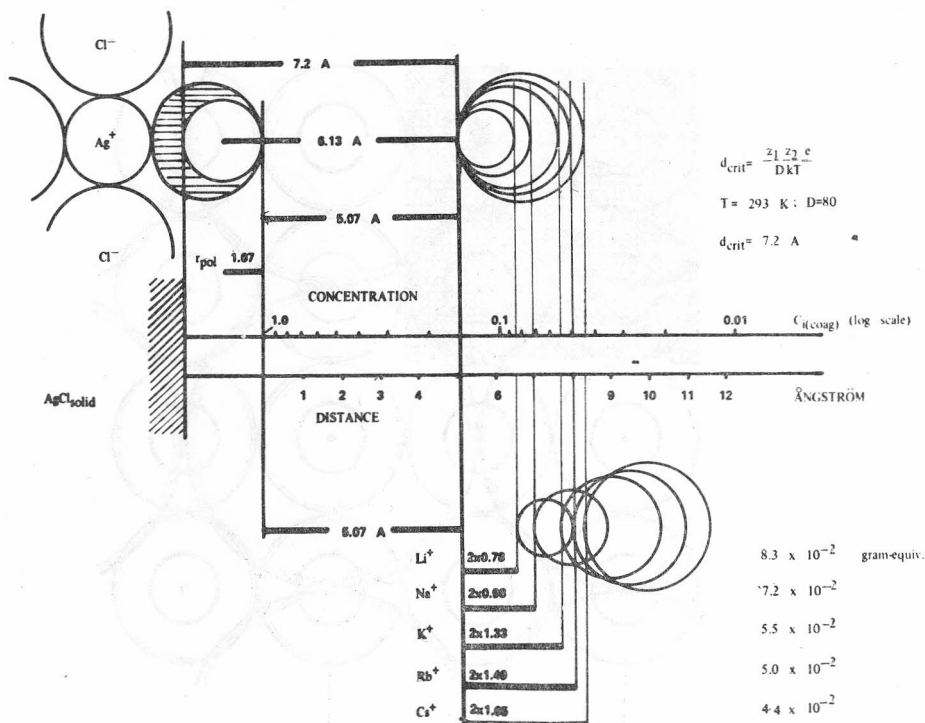
Figure 9. — Schematic presentation of the relationship between the critical distance, d_{crit}, and the logarithm of critical coagulation concentration of univalent alkaline ions *vs.* negatively charged surfaces of silver chloride particles; the scheme shows critical distances and concentrations just inside or outside the range of formation of ion-pairs between the stabilizing chlorine ion and corresponding counter ion (adopted Figures 9 and 10 from Z. physikal. Chem. A **191** (1942) 270).

studied by LaMer[86] using large macromolecules, although the effects are not limited only to macromolecules, very large polyelectrolytes, or various surface active agents; ions and molecules below the molecular weight of 1000 also display characteristics of flocculation[85].

It should be stressed that the basic common mechanism in coagulation by electrolytes, and in flocculation by adsorption, may be presented by the differences in the concentration of kinetically active units in the methorical layer and the solution in bulk; $c_{meth} > c_{bulk}$ for stabilization, and $c_{meth} < c_{bulk}$ for aggregation.

CONCEPTUAL FRAMEWORK

Naturally, the complex interactions between a large number of units characterized by a wide spectrum of reaction rates should be outlined in general terms, *i. e.* in a form which may be called a primitive model of ionic precipitation systems, including also some concepts of a primitive interpretation of situations generally encountered in electrolytic solutions. In this respect the first approach is to look at the processes along a spectrum embracing the events on the three- or two-dimensional space levels in close connection with the time scale.
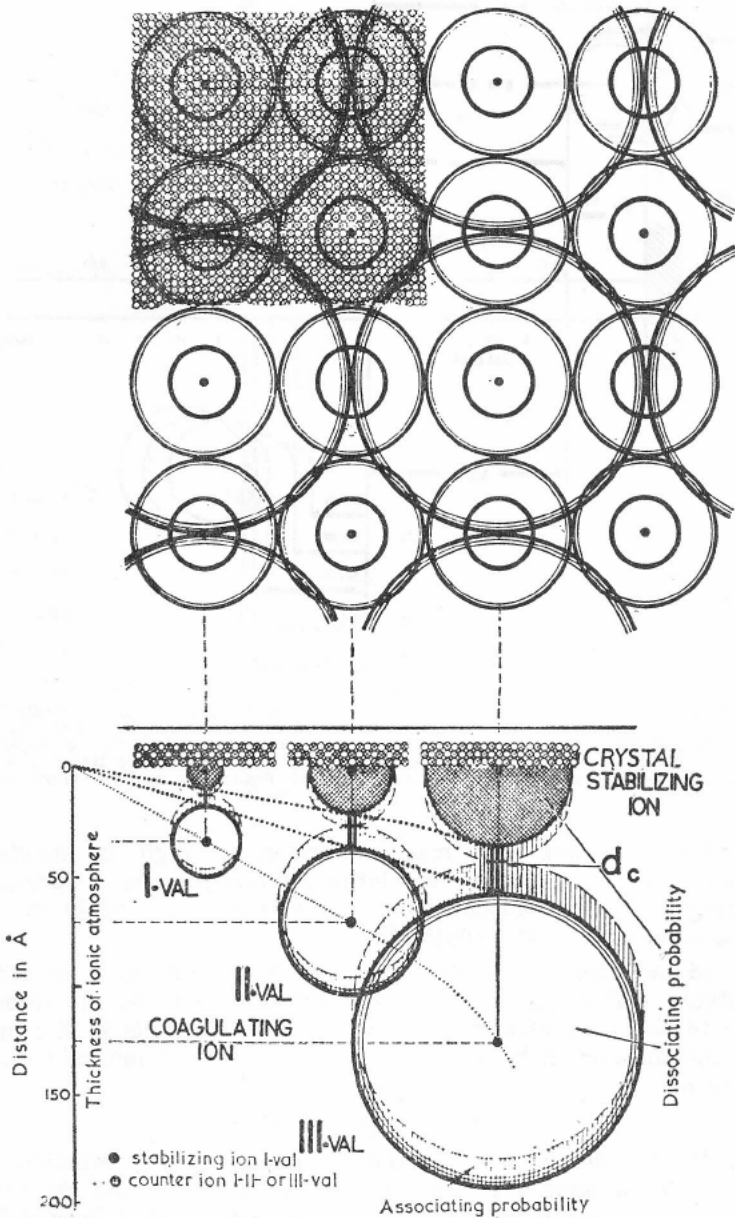
Figure 10. — First and second projection of the schematic presentation of the boundary state of uni-, di-, and tri-valent coagulating ions *vs.* univalent stabilizing ions (surface with fixed distribution of discrete charges parallel to the second projection plane). At the concentrations higher than critical coagulation concentration the dynamical configuration of counter ions corresponds to stoichiometrical relationship in spite of the fixed spatial distribution of the charges (complexoides) on the wall of particles. (*Discuss. Faraday Soc.* 18 (1954) 195)

Such a spatial-temporal set-up may reveal the successive or simultaneous appearance of dominant 'spectral' lines according to the position of the smallest volume unit of the distribution function which is representative for the identification of the system as a whole. In Figure 11 there is a schematic presentation of such relationships. In homogeneous and quasi-homogeneous systems with amicronic units of such distribution volumes, the linear dimensions of interactions between atoms, ions, and molecules are very near to the state of smallest approach, but the spectrum of energy, entropy and time exchanges may be very wide, including photonic, electronic, vibrational, rotational, and other configurational effects. By the formation of larger aggregates the representative volume units have to embrace the mechanisms of at least three different groups: (1) the bulk of liquid phase, (2) the bulk of solid or semi-solid phase, and (3) the region between these two bulk phases (methoric layer), as well as the resulting mutual interactions.

SPATIAL—TEMPORAL SPECTRA OF REPRESENTATIVE
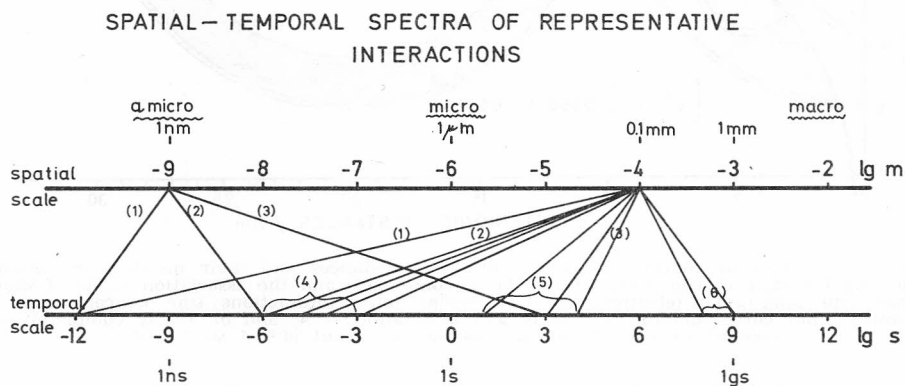INTERACTIONS

Figure 11. — The distribution function of units in transition from homogeneous system to heterogeneous one is accompanied by characteristic changes in interactions of ions, molecules, and particles, on both, spatial and temporal scales, including quantum-mechanical (non--classical), electrostatic, and other exchanges in bulk phases, in methorical layers, and in interactions between emerging colloidal particles; scheme represents probable situations corresponding to volumes of 10^{-9} and 10^{-4} M of linear dimensions.

Under vigorous stirring of a solution in which precipitation occurs the representative volume units and the interacting entities may reach macroscopic dimensions and the times of interactions are mainly divided between two phases and mechanical interventions. Generally speaking, the results of our observations are display of cumulative effects, while the identification of discrete spectra will be a formidable task. Naturally, some correlation between macroscopic phenomena and elementary structural dynamics could be revealed if the influence of the step-by-step variations of components or factors were followed and intepreted in the broader terms of the averaged space and time notions. In this sense the averaged time for interacting precipitating ions may be, in the first approximation, divided according to concentration into three main space regions. The dominant distribution sphere can be simply obtained if the actual volume of the system given by concentration is divided by the number of ions. The function of the thus obtained interacting distances against concentration may be used for construing relationships between corresponding averaged spatial-temporal volume areas indicating the probabilities that the
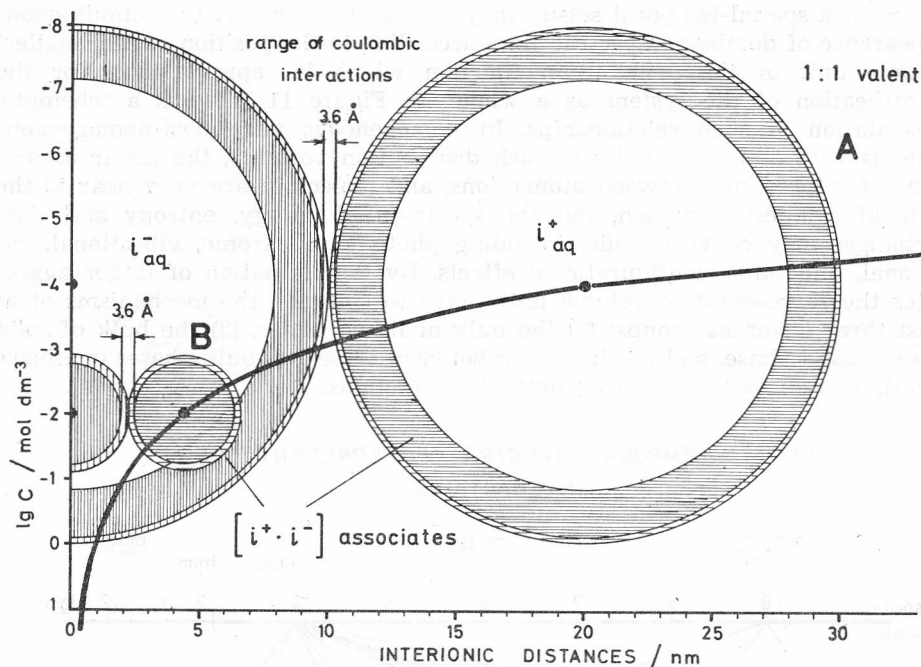
Figure 12. — Plot of concentrations *vs.* interionic distances and their distribution volumes reflecting the state of free solvated ions (aquo-complexes) and the association shells of short--range and long-range (electrostatic) 1 : 1 valent ionic interactions (the concentration of solubility limit corresponding to case of 50% association — A, and of nearly completely associated case — B), for a substance of about 10^{-4} M solubility.

ions is found either in the state of a hydrated complex (free ion), or that of a chemically associated entity of precipitating ions, or of the Bjerrum's coulombic ion-pairs, including the formation of various clusters. All these relationships are given schematically in Figure 12. For a solute of the symmetrical 1-1 charge type in a boarderline case of solubility equilibrium the averaged time of associations (chemical and coulombic) for precipitating ions may be taken as corresponding to the equal volumes of a spherical shell of the radius r and thickness dr, and an internal sphere of $(r-dr)$ radius representing hydrated ions in free state. Inside the association shell there may be, at the outer periphery, a shell of the thickness representing the critical Bjerrum's distance, while the full thickness of the shell corresponds to the chemical interactions of the oppositely charged ions preceding a precipitation. In our case, when the concentration of the precipitating ions is changed from 1×10^{-4} M (case A) to that of 1×10^{-2} M (case B), the corresponding averaged spatial-temporal configuration of free hydrated ions has practically disappeared leaving only about 1% of the precipitating substance in the solution, with the same configuration as in the case of the borderline solubility condition. In this way configuration B has to be accompanied by configuration A, but the main association volume will represent depending on the chosen time, some or almost all subsystems from clustering, embryonation, nucleation, formation of primary particles of some stability (sols in *statu nascendi*), to secondary and

higher structures, representing the results of direct growth or agglomeration of smaller units, or both.

If there is a case of 2 : 2 electrolyte with a much higher solubility, the corresponding configurations are shown in Figure 13, where besides analogous cases A' and B' to the scheme of Figure 12, the position of very soluble substance (case C) are represented. In cases of very soluble substances the interacting distances are within the sphere of long-range forces, and the critical precipitation concentrations represent something the like contraction of the distorted dynamical lattice under the influence of already acting short-range forces. In fact, the 1×10^{-4} M case is near to the circumstances of the AgCl system (or that of $BaSO_4$ if the range of coulombic interactions is changed from 3.6 to 14 Å), that of 3×10^{-2} M to the $CaSO_4$, and that of ~ 5 M to NaCl. The differences in ensembles, caused by short-range and long-range forces are certainly manifested also by various higher structures in the precipitate formation.
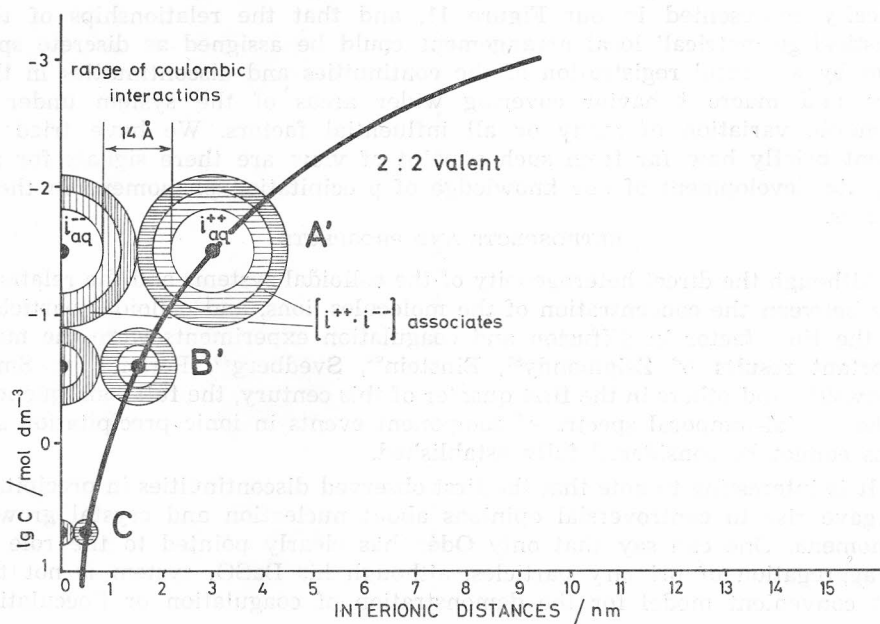

Figure 13. — Plot of concentrations vs. interionic distances and their distribution volumes reflecting the state of free solvated ions (aquo-complexes) and the association shells of short--range and long-range (electrostatic) 2 : 2 valent ionic interactions (at the concentration of solubility limit corresponding to 50% association — A', and of nearly completely associated case — B'), for a substance of about 3×10^{-2} M solubility; C represent a case of 1 : 1 valent system of high solubility (about 0.7 M).

The interplay of aggregation (coagulation and flocculation) and direct and indirect growth processes play an important role in the development of larger spatial-temporal units. In this very interplay one of the most significant roles is to be assigned to the formation of the configurational relationships of the methoric layer in comparison to the more static structure of the emerging solid phase, on the one hand, and the dynamic structure of the solution in bulk, on the other hand. Again, a conceptual scheme of such relationships

is given in Figure 14. The three areas in Figure 14 have to point the states and processes in homogeneous, transitional (amicronic, ultramicro and micro) heterogeneous, and macro heterogeneous subsystems, from which precipitation systems are usually composed.

The spatial-temporal configurations in upper area, show the role of short--range (s-r) and long-range (l-r) forces, as well as of various clusters; middle area represents: (a) the presence of embryonic solid, (b) the special texture of the so-called complexoid species (s-l) entities belonging simultaneously to one more static and dynamic (liquid) environment, (c) the configuration of the dynamic structure in the methoric layer, and (d) the distribution of elemental kinetic entities in the solution of the bulk; and lowest area shows the possible paths by which, separately or in a special kind of combination from ultra-micro- or micro-primary particles (sols in *statu nascendi*), the micro and macro heterogeneous systems are formed.

One should bear in mind that each of the experimentally observable steps may be composed of quite a wide spectrum of spatial-temporal events schematically represented in our Figure 11, and that the relationships of the 'statistical-geometrical' local arrangement could be assigned as discrete spectrum by a careful registration of the continuities and discontinuities in the micro and macro behavior covering wider areas of the system under a systematic variation of many or all influential factors. We have tried to present briefly how far from such a point of view are there signals for an adequate development of our knowledge of precipitation phenomena in these 75-years.

RETROSPECTS AND PROSPECTS

Although the direct heterogeneity of the colloidal systems and the relationships between the concentration of the molecules, ions, and colloidal particles, and the time factor in diffusion and coagulation experiments were the most important results of Zsigmondy[87], Einstein[88], Svedberg[89], Perrin[90], v. Smoluchowski[55] and others in the first quarter of this century, the full consequences of the spatial-temporal spectra of component events in ionic precipitation systems cannot be considered fully established.

It is interesting to note that the first observed discontinuities in precipitation gave rise to controversial opinions about nucleation and crystal growth phenomena. One can say that only Odén has clearly pointed to the role of the aggregation of primary particles, although his $BaSO_4$ system is not the most convenient model for the demonstration of coagulation or flocculation processes.

The other aspects of ionic precipitation were studied more extensively than coagulation and flocculation, but again without the full appreciation of the structural dynamics of all the essential parts which have to be reflected by the kinetics and morphology of the systems.

We have tried to detect various facets of the precipitation phenomena to learn more about the mechanisms which belong to the fundamental concepts of physics and chemistry: the notions of space and time.

Probably, because of the loss of interest in the study of systems in aqueous solution, and turning towards the crystal growth from melts and under special conditions of temperature and pressure, as shown by the reports presented in the Journal of Crystal Growth and by the material discussed at international
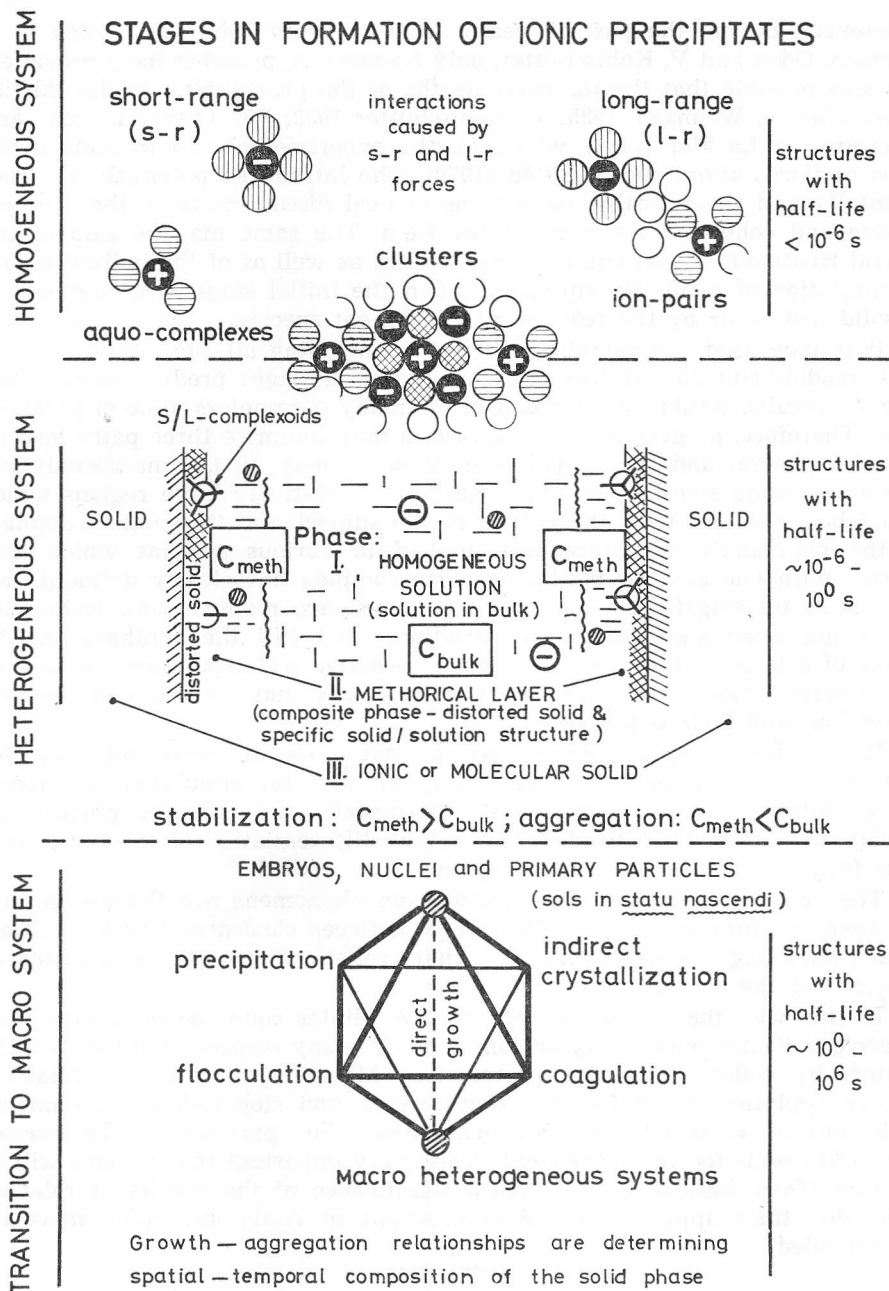
Figure 14. — Schemes illustrating the transition stages in formation of ionic precipitates pointing to the characteristic interactions and the dominating half-lives for structures at various levels of aggregation; the role of short-range and long-range forces in interactions between constituent ions and molecules in formation of clusters, embryos, nuclei, and primary particles, as well as in methorical layers between liquid and solid bulk phases is indicated. The transition of various kinds of primary particles into larger units proceeds either through direct growth or some of the abrupt aggregation processes (precipitation under condition of equivalency of precipitating ions; aggregation caused by exhaustion of kinetically effective species in the methorical layer caused by crystallization; coagulation or flocculation effects caused by presence of foreign substances in the medium of precipitation; in general, all processes controlled by $c_{meth} < c_{bulk}$ relationship). Besides genotypical structures such consecutive or simultaneous processes of various durations may be reflected in phenotypical characteristics of precipitates.

conferences, during the past 25 years, from the very coherent studies of v. Weimarn, Odén and V. Kohlschütter, only fragment approaches have prevailed. It is also possible that the too early deaths of the protagonists in the thirties (Odén, 1934; v. Weimarn, 1935; V. Kohlschütter 1938; Wo. Ostwald, 1943), and afterwards of La Mer (1966), who gave the experimental and theoretical denition of flocculation, and of Sillén (1970), who introduced polynuclears experimentally and theoretically, caused the critical discontinuity in the comprehensive and coherent treatment of the field. The same may be said of the general treatment of non-equilibrated systems, as well as of the indiscriminate interpretation of solubility equilibria when the initial stages are represented by solid bodies, or by the reaction of component species.

It is true, that a comprehensive theory including all the important concepts, models and partial theories, and giving the right predictions of experimental results, would be composed of too many parameters to be of practical value. Therefore, a »grand-design« approach may comprise three paths leading to useful general and special points of view, namely, (i) the macroanalytical procedures using step-by-step investigations of relatively large regions which should be consistent with the nature of the subject and the method applied; (ii) the microanalytical procedures applied to various systems which may interact with one another producing some complex but clearly definable results; such investigations covering various systems, methods and techniques should use some step-and-repeat variations; and (iii) the synthesis of the results of a large number of systematically-carried out experiments with current concepts, models and theories in such a way that the unity of thought, expressions and facts is preserved.

Now, when very advanced instrumentation is at hand not only for experimental determination of the facts, but also for simulation of models and moduls for a multidimensional interpretation of complex phenomena, priority should be given to clear conceptual differentiation of the component parts from which the investigated system is composed.

The best guides in complex precipitation phenomena are the continuities and discontinuities in various relationships between concentrations and critical times controlling the appearence of a characteristic form, size, composition or structure of the precipitate.

In this way the appearance of the precipitates could be used as a very sensitive indicator which may be compared, in many respects, with the results obtained by modern relaxation spectrometry. Moreover, there are potentialities that by applying to the full the step-by-step, and step-and-repeat immense posibilities of variations of components and other parameters, the spatial--temporal events for very complex but also very important real systems will be revealed. Thus, besides the analytical significance of the results of relevant researches, their applications and implications in vitaly important areas are also included.

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SAŽETAK

75 godina studija precipitacije, kristalizacije, koagulacije i flokulacije u ionskoj otopini — pristrani osvrt

Božo Težak

Uzevši da precipitacija slabo topljivih supstancija iz vodenih otopina predstavlja mogućnost za opću i posebnu karakterizaciju precipitacije, kristalizacije, koagulacije i flokulacije, prikazani su radovi G. A. Huletta, P. P. von Weimarna, S. Odéna, A. Smekala, V. Kohlshüttera, Wo. Ostwalda, V. K. LaMera i drugih, u ovih proteklih 75 godina, istaknuvši podudaranja i razlike u eksperimentalnim rezultatima i njihovoj interpretaciji.

Za stanja stabilnosti/nestabilnosti kod svih sastavnih subsistema (embrionacije, nukleacije, koagulacije i flokulacije primarnih čestica) precipitacijskih procesa, primijenjen je uglavnom isti mehanizam utjecaja razlike u koncentraciji mikrokomponenata između metoričkog sloja i unutrašnjosti otopine.

Posebno je naglašena uloga koncentracijskih i prostorno-vremenskih faktora u pojavljivanju intermedijara i raznih cjelina koje uvjetuju stvaranje neuravnoteženih struktura. Nalazi su promatrani s jedinstvenog gledišta uzevši u obzir sile kratkog i dugog dosega kod pojave diskontinuiteta u prostorno-vremenskim funkcijama.

Prikazani su na primjerima pristupi sa stanovišta termodinamike (uravnoteženih sistema), kinetike i elementarnih procesa. Relacije između koncentracije, prostorne raspodjele i trajanja raznih interakcija između molekula, iona i raznih agregata, predstavljaju podlogu za temeljne prostorno-vremenske spektre koji karakteriziraju pojedine jedinice precipitacionog procesa.

Tražeći racionalnu osnovicu za interpretaciju širokog spektra kritičnih interakcija kod prelaza homogenog sistema u heterogeni, izložena je primjena tzv. »precipitacijskih tijela« i drugih diagramskih prikaza distribucionih funkcija.

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