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The Theory of Crystallization as Viewed from Experiences with Electrolytic Systems[a,b]

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By reviewing older results, especially those of v. Weimarn and Odén, on the examples of differences between sparingly soluble sulfates and halides, new approaches to the diagramatical presentation of the characteristic features of precipitation and crystalization processes and structures were used. Namely, in order to enable comparison, various systems were observed under fixed temperature and pressure in developmental stages according to their position in the so-called "cube of dilution", and were represented as specific time-dependent "precipitation bodies".

It is pointed out that the emergence of the solid phase from solution is a complex phenomenon where a large number of non-equilibrium states may interfere with each other in such a way that already the concentrational parameters of various species in preembryonation stages, as well as in the methorical layer of embryos, nuclei, primary particles, and secondary aggregates in formation, reflect both the direct growth of smaller units, and their aggregation controlled mainly by stability/instability relationships.

In order to explain the critical steps (the role of "new parts" and "surfaces of discontinuity" of Gibbs) in the transformation of the homogeneous solution to the heterogeneous system, schemes of various parts of chemical potential in ionic interactions, the "surfaces of discontinuity" in the methorical layer, the boundary of the growing crystal, and the stability/instability conditions of the emerging embryos, nuclei, or primary particles in solution, are given.

1. *Introduction*

The early period of attempts to elucidate the mechanism of crystallization was closely connected with processes of precipitation from solution of electrolytes. Among the first generalizations those of P. P. v. Weimarn[1], which were developed during the first quarter of this century, should be mentioned. Nowadays, it seems necessary to review the essential findings and concepts which are relevant, or — moreover — pertinent to an adequate presentation of the situations encontered in crystallization or in the formation of ionic precipitates from aqueous solutions in general.

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[a] Found in the inheritance of the late Professor B. Težak

[b] Contribution No. 199 from the Laboratory of Physical Chemistry

Starting with v. Weimarn's numerical and graphical data we have to reconcile his approaches with contemporary concepts of mechanisms, processes and structures of precipitating and crystallizing systems. In order to be both brief and illustrative it seems advantageous to follow v. Weimarn's mode of presentation and to pointing out the necessary corrections and developments.

First of all the reproduction of v. Weimarn's main scheme and some of the experimental results cited by him as fundamental either in *International Critical Tables*[2] or earlier is given in Figure 1. For the sake of consistency the scheme contains the approximate positions of the experimental Ag_2SO_4 and $BaSO_4$ systems, and — in addition, — the origin of the diagram has been reversed in such a way that it is possible to start from defined concentrated solutions and to proceed towards extremely dilute ones, following the logarithmic scale of concentrations in mol or gramequivalents* dm^{-3} per dm^3.

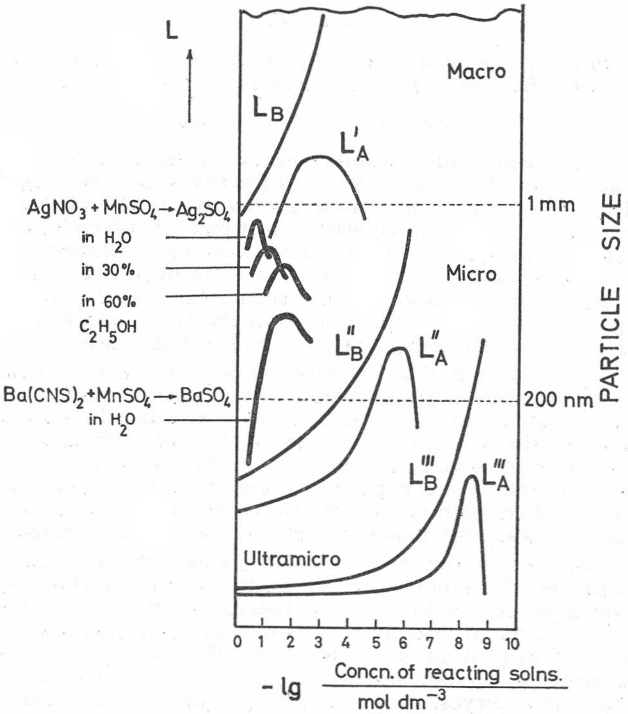

Figure 1. P. P. von Weimarn's schemes of precipitation curves presented as the final solubility L_A for the precipitation component A or L_B for B (— general pattern; — experimental data for Ag_2SO_4 and $BaSO_4$) versus concentration of reacting solutions.
The particle sizes in macro, micro and ultramicro regions are denoted on the right-hand ordinate.

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* In this paper the "gramequivalent" is defined in the following way: (a) for an anionic species, B^{+z}, as $M/|z|$; (b) for salts of composition $B_z^+ A^{-z}$ or $B^{+z} A_z^-$ as $M/|z|$; M denotes the molar mass in grammes and z the charge number (Editor's remark).

2. *Systems Along the Solubility Limit*

When the systems are not represented by precipitating components in equivalent amounts, there is the possibility of finding quite specific limits of precipitating-nonprecipitating regions, and an illustration of such cases is given in the upper part of Figure 2.

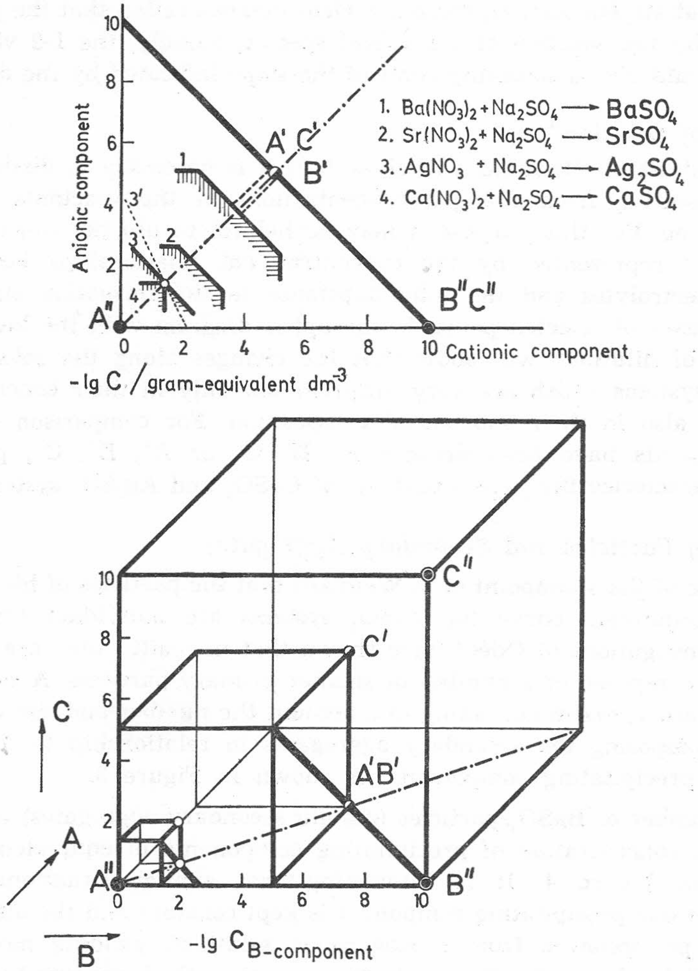


Figure 2. Solubility boundaries of barium, strontium, silver and calcium sulphate systems, plotted as the logarithm of the cationic against the anionic component concentration (upper part), and comparative positions of some points of solubility boundaries in the "cube of dilution" (lower part).

In the discussion of the upper and lower parts of Figure 2 it is necessary to point out clearly the misinterpretation in the presentation of the solubilities which is found in nearly all elementary textbooks. It is especially necessary to distinguish between solubilities determined by dissolving the mass of solid substances in the solution, and those derived from experiments of precipitation. Although Figure 2 gives a limited presentation of a few similar systems, there are great differences in their precipitating-nonprecipitating limits. Noting that determination of such limits was carried out 1 hour (24 hours for $CaSO_4$) after mixing the reacting components, the results show that the changes of the limits towards lower concentrations after longer periods of time will give the same overall picture. It is significant that the constancy of the solubility product is limited at both ends of $BaSO_4$ and $SrSO_4$[3] while for $CaSO_4$ it cannot be applied at all. For Ag_2SO_4 there is a clear demonstration that the precipitate is formed by the reaction of 1-1 valent species; namely, the 1-2 valent ions' reaction would give a solubility limit of the slope indicated by the dotted line.

3. *"Cube of Dilution"*

An analysis of situations will show that it is necessary to distinguish the systems resulting from changed concentrations of the reactants along the solubility line. For this purpose it may be helpful to use the so-called "cube of dilution" represented by the concentrational relationships between the reacting electrolytes and the solid substance in the formation stages[3]. The correspondence of selected points in the upper diagram with the lower one in the "cube of dilution" will show that the changes along the solubility line represent systems which are very different not only in their concentrational aspect but also in their substantial composition. For comparison the corresponding points have been denoted A′, B′, C′, or A″, B″, C″; points A‴, B‴, C‴ characterize the joint situations of $CaSO_4$ and Ag_2SO_4 systems.

4. *Primary Particles and Secondary Aggregates*

In spite of the standpoint of v. Weimarn that the particles of his maximum of the precipitation curve for $BaSO_4$ systems are individual crystals, the careful investigations of Odén[4] have shown that in reality they are secondary aggregates composed of a number of smaller primary particles. A construction of v. Weimarn's maximum, taking into account the number and size of primary particles composing the secondary aggregates in relationship to the concentration of precipitating components[5] is shown in Figure 3.

The number of $BaSO_4$-particles (mainly secondary aggregates) in relationship to the concentration of precipitating components in equivalent amounts is given in Figure 4. It is interesting that similar situations may be found when one precipitating component is kept constant and the other varied. Moreover, precipitation from homogeneous solution[6], yielding monodisperse $BaSO_4$-particles, by application of the Takiyama[7] method, produced sponge-like aggregates of primary particles of an approximate size of 4—5 nm, while the spindle shaped grains were about 200 and 100 μm, in the long and short axes respectively[8]. By showing also the "effect of salts dissolved in the dispersion medium on the duration of life of dispersoidal solutions" for 0.0125 gramequivalent dm^{-3} $MnSO_4 + BaCl_2$ system in 63% ethanol in the diagram of Figure 4, we are narrowing the gap between $BaSO_4$ and the similarly soluble system of AgCl where relatively stable sols *in statu nascendi* could be found in pure aqueous solutions.

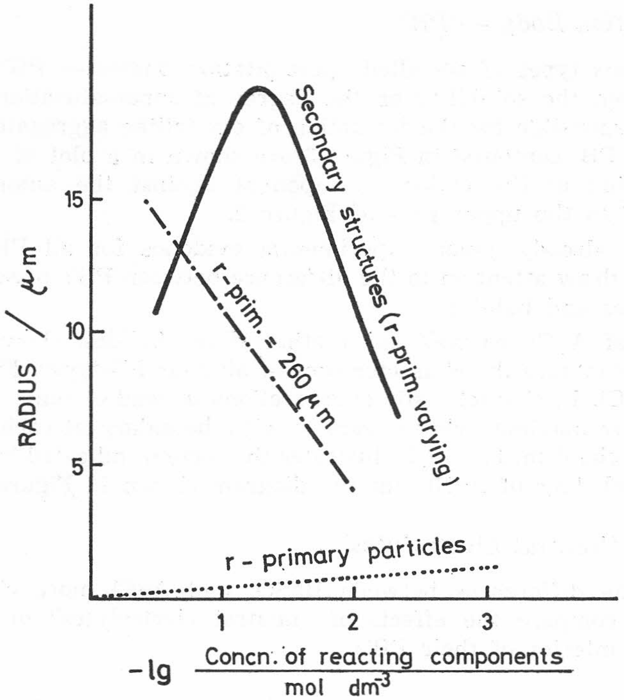


Figure 3. Construction of v. Weimarn's precipitation curve of barium sulphate taking into account Odén's analysis (formation of secondary structures by aggregation of primary particles).

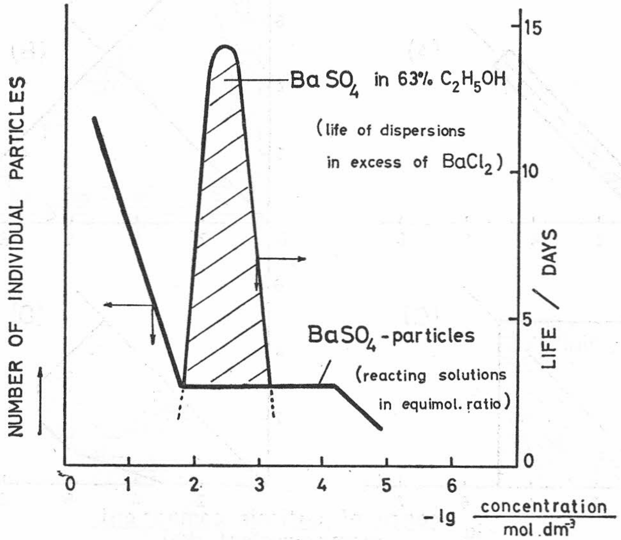


Figure 4. Number of particles as a result of changed concentration of precipitation components ($BaSO_4$ in water), and the life of $BaSO_4$ dispersions in excess of $BaCl_2$ ($MnSO_4 + BaCl_2$ in 63% ethanol).

5. *"Precipitation Body — PB"*

The various types of so-called "precipitation bodies — PB" demonstrate that apart from the solubility or the degree of supersaturation many other factors are responsible for the formation of crystalline aggregates. Four main types of such PB′ contours[9] in Figure 5 are shown in a plot of the logarithm of concentration of the cationic component against the anionic one, thus corresponding to the upper part of Figure 2.

We have, already, given experimental evidence for all PB-types[10], and here we shall draw attention to the difference between PB's of some sparingly soluble sulfates and halides.

The PB of AgCl, as well as of other silver halides, shows by internal and external contours the characteristics of all four PB-types. Figure 6 shows the PB of AgCl. In characteristic cross-sections instead of only one maximum there are many maxima, where every specific boundary of each is caused by a different mechanism; Figure 7 illustrates the section indicated by the ordinate at 1×10^{-4} mol dm^{-3} of $AgNO_3$ in the diagram shown in Figure 6.

6. *Effects of 'Neutral Electrolytes'*

To see the differences between $BaSO_4$ and AgCl more clearly it may be useful to compare the effects of "neutral electrolytes" on precipitation stages in the interior of their PB's.

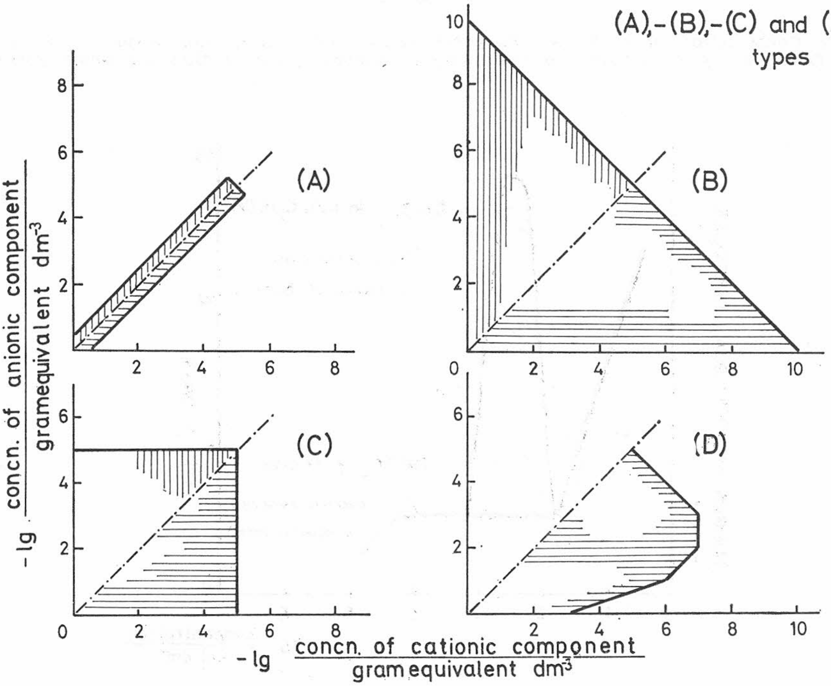


Figure 5. The types of "precipitation bodies" (PB) in a general precipitation diagram: (A) neutralization, (B) ionic solubility, (C) formation of ion-pairs and associates and (D) unsymmetrical ionic reactivity.

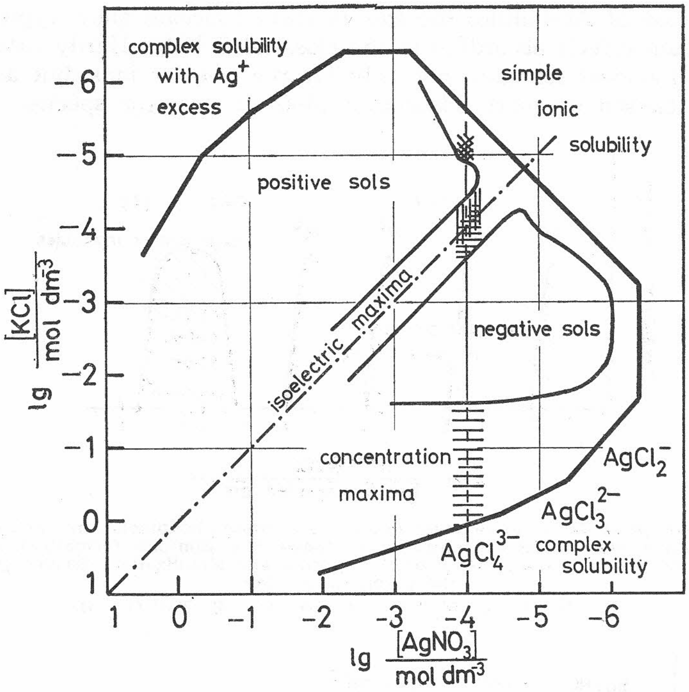


Figure 6. "Precipitation body" of AgCl appearing after mixing aqueous solutions of $AgNO_3$ and KCl at 293 K; the cros-section at 1.0×10^{-4} mol dm^{-3} $AgNO_3$ corresponds to the tyndallogram presented in Figure 7.

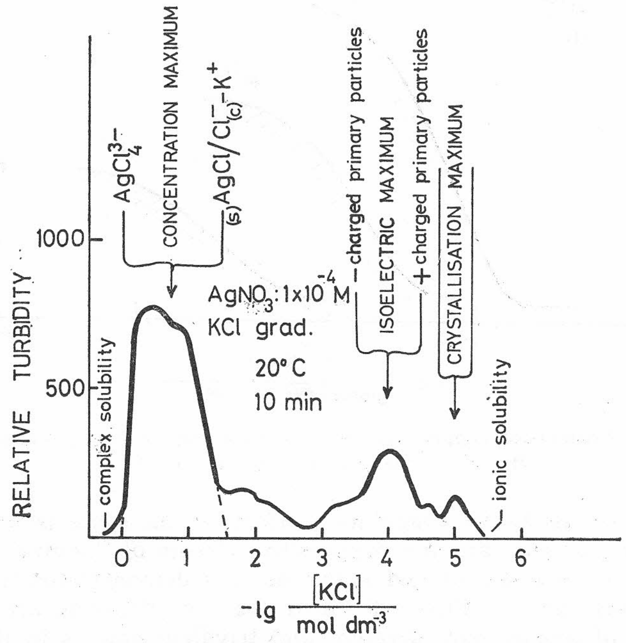


Figure 7. Cros-section of the "precipitation body" (see Figure 6) appearing 10 minutes after mixing 1.0×10^{-4} mol dm^{-3} $AgNO_3$ with varying concentrations of KCl at 293 K.

In the case of Ag-halides the sols *in statu nascendi* show typical counter ion coagulation effects according to the classical Schulze-Hardy rule; Figure 8 gives the behavioral schemes, not only for the counter ions, but also for the flocculation caused by more adsorbable ionic or nonionic species.

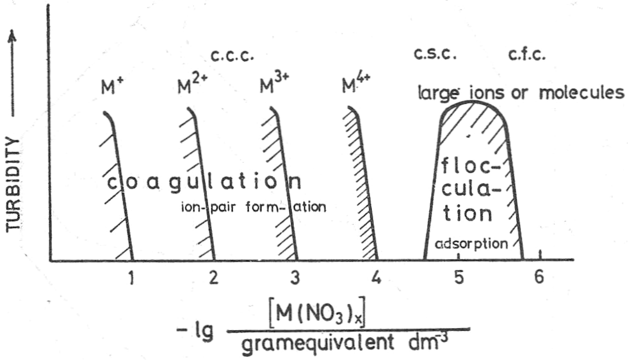


Figure 8. General presentation of coagulation and flocculation phenomena: interacting mechanism for counter ions at the critical concentration of coagulation (ion-pair formation), and for large molecules at the critical concentration of flocculation and stabilization. Shaded portions show the precipitation side.

M = K^+ ($x = 1$), Mg^{2+} ($x = 2$), La^{3+} ($x = 3$), Th^{4+} ($x = 4$).

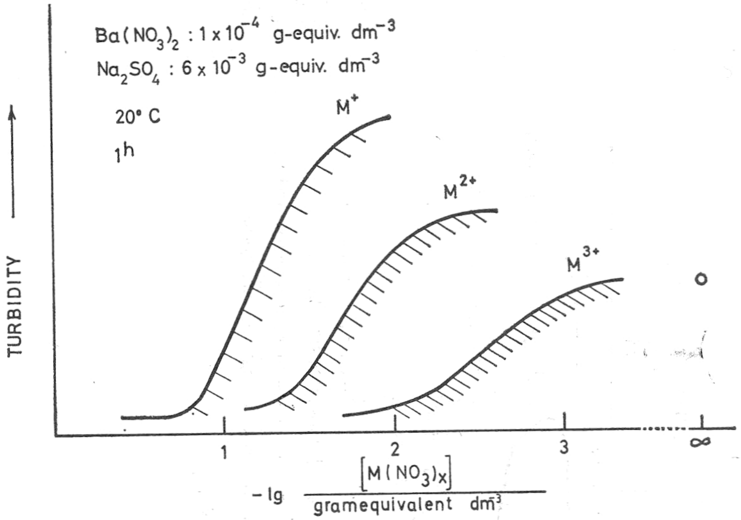


Figure 9. Counter-ion suppressing effect on formation of $BaSO_4$ precipitates.

M = K^+ ($x = 1$), Mg^{2+} ($x = 2$), La^{3+} ($x = 3$).

Quite in contrast to the coagulation effects of the systems with relatively stable primary particles are the suppressing effects of "neutral electrolytes" on the formation of embryos and nuclei as it is demonstrated in the case of sparingly soluble sulfates. Figure 9 illustrates[15] the delaying action of higher concentrations of monovalent, divalent and trivalent cations in the formation process of $BaSO_4$-precipitate in an excess of SO_4^{2-}-ion.

Since the solubilities of $BaSO_4$ and AgCl are nearly the same, v. Weimarn's criteria cannot explain the differences, and the only other solution is to start the analysis from characteristics of the interacting ionic and molecular species, where the 1—1 and 2—2 valency relationship of precipitating ions are certainly among many others the basic ones.

7. *Interactions Between Ions*

Starting from the homogeneous, ideal solution of electrolytes, it should be remembered that changing the concentrations and composition of components causes great changes in the relationship of interactions between all ionic, molecular, mononuclear and polynuclear complexing, pairing and clustering, and some other subultramicroscopic species. In this respect it is necessary to consider the dynamic equilibria caused by the interplay of at least three parts of the composite ionic potential, namely: μ_{solv}, $\mu_{stereochem}$, and μ_{coul}; expressing ion-solvent molecule complex, stereochemical (chemical, lattice energy, and van der Waals), and coulombic interactions. The schematic presentation of such a spatial and structural dynamic distribution is given in Figures 10 and 11.

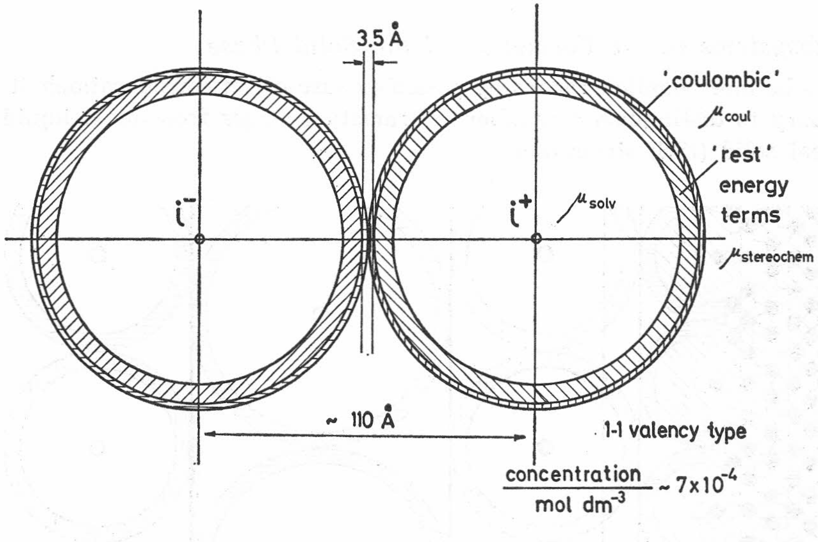


Figure 10. Ionic distribution spheres with association shells of 1-1 interactions (concn. $\approx 7 \times 10^4$ mol dm^{-3}).

The ionic and molecular interactions are not limited to the solution phase only, but are responsible for special structures and textures in the region between the liquid and emerging solid bulk phases, giving the possibility of quite specific equilibria differing strongly from those which are expected in the case of ideal phases in contact. Supported by such facts Balarew[14] has gone as far to assume that the true thermodynamic equilibria give exclusive preference to colloid dispersions.

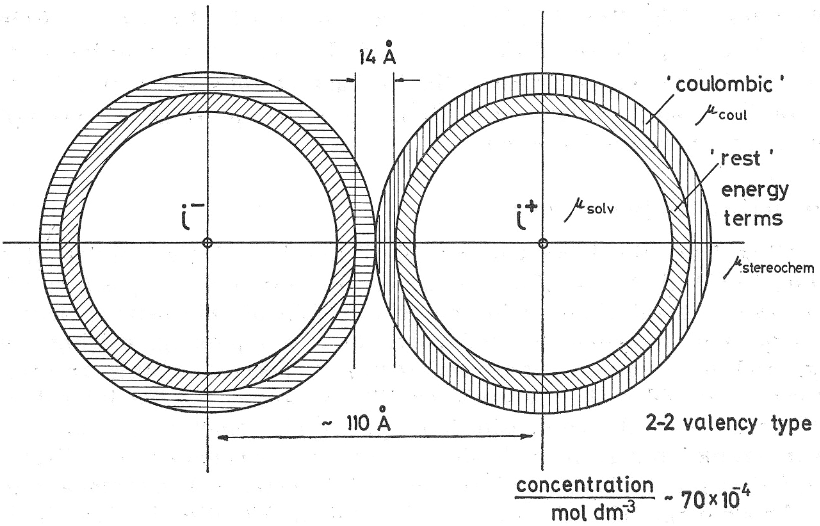


Figure 11. Ionic distribution spheres as in Figure 10 but for 2-2 ionic interactions.

8. *Subsystems in the Formation of the Solid Phase*

To be more explicit regarding possible cause-effect considerations, it seems necessary to distinguish a number of transition stages from ideal liquid (ILS) to ideal solid (ISS) structures.

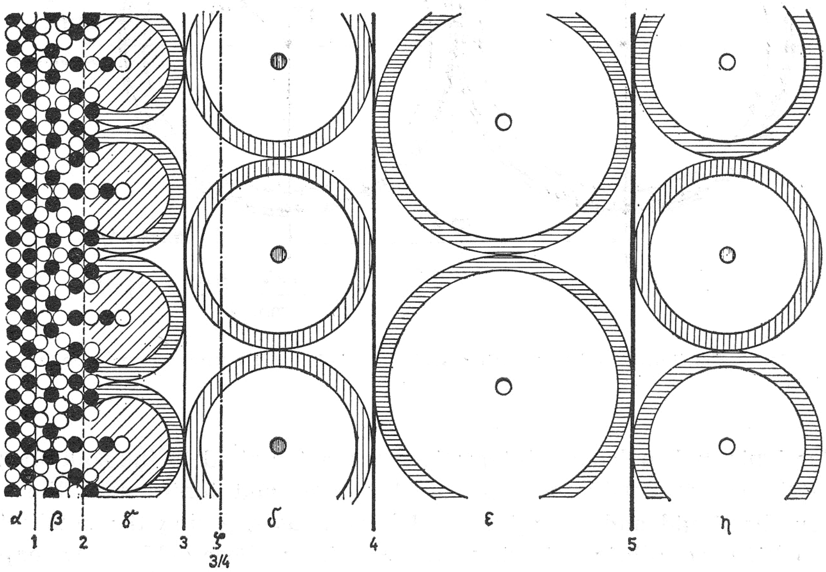
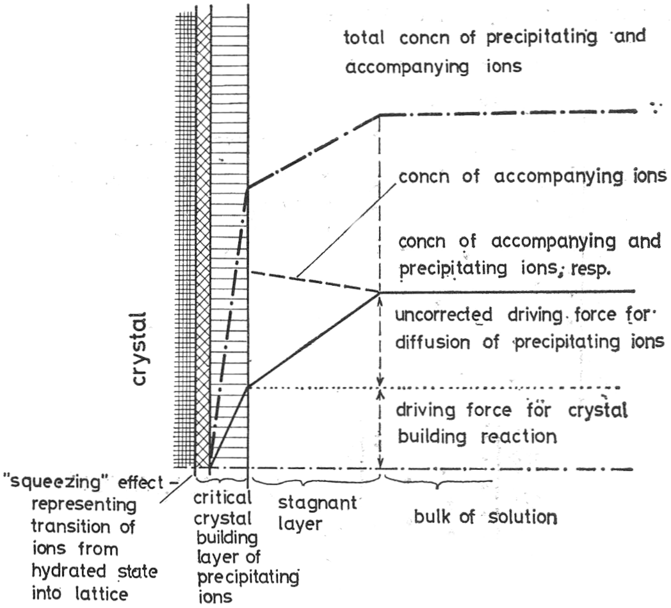


Figure 12. Scheme of "surfaces of discontinuity" within the methorical layer formed between ionic crystal and electrolytic solution; the distribution spheres and probabilities of ion-pair formation are shown (hatched portions of the circles).

Such stages are represented by at least five subsystems[15], namely: (*i*) the solution although homogeneous is in a saturated or supersaturated state and is thus very sensitive to concentration and temperature variations with respect to ion pairs, clusters, complex ions, polynuclear and polymer assemblies; (*ii*) the embryos as stable or unstable aggregates of precipitating species but without the formed core of the most stable ISS; (*iii*) the nuclei as growing units with a core of ISS; (*iv*) the primary particles as units with relatively well expressed colloidal individuality (micelles) owing to the development of a methorical layer with its peculiar composition, structure and texture (MS&T); and (*v*) the secondary aggregates which may be represented either as a sponge-like cluster of randomly agglomerated primary particles, or as oriented growing blocks of ISS units giving crystallites of more or less amalgamated but essentially regular habit. Recrystallizations, especially by changing thermodynamic parameters, may be the cause for approaching the more equilibrated systems. Those cases where the chemistry of the solvent such as water, is involved may be taken as a special group; e. g., the formation of metal hydroxides and oxides from aqueous solutions[16].



Steady state concentrational scheme for crystallization from electrolytic solution

Figure 13. Concentrational scheme in the boundary region of a growing ionic crystal.

9. *Methorical Layer and "Surfaces of Discontinuity"*

In all these systems and subsystems, from the moment of appearance of the first traces of heterogeneity, there is a need to apply Gibbs' critical remarks[17] about the "new parts" of the "surfaces of discontinuity" from which the methorical layer dividing solid or quasi solid and liquid phases in bulk is composed. Such a schematical presentation of five to seven "dividing surfaces" or interfaces in the methorical region is given in Figure 12.

Also, on the boundary of the growing crystal it is necessary to distinguish approximately five regions: (m) the undisturbed crystal lattice; (n) the transition region of ions from the solvated state into a lattice; (o) the adjoining solution layer where ions for building at least one complete layer of the crystal lattice can be found (this may be the cause of periodic pulsation[18]; (p) the more or less stagnant layer within which the concentrational drop occurs; and (r) the bulk of solution. Such a scheme, where the role of the foreign ions have also to be accounted for, is represented in Figure 13.

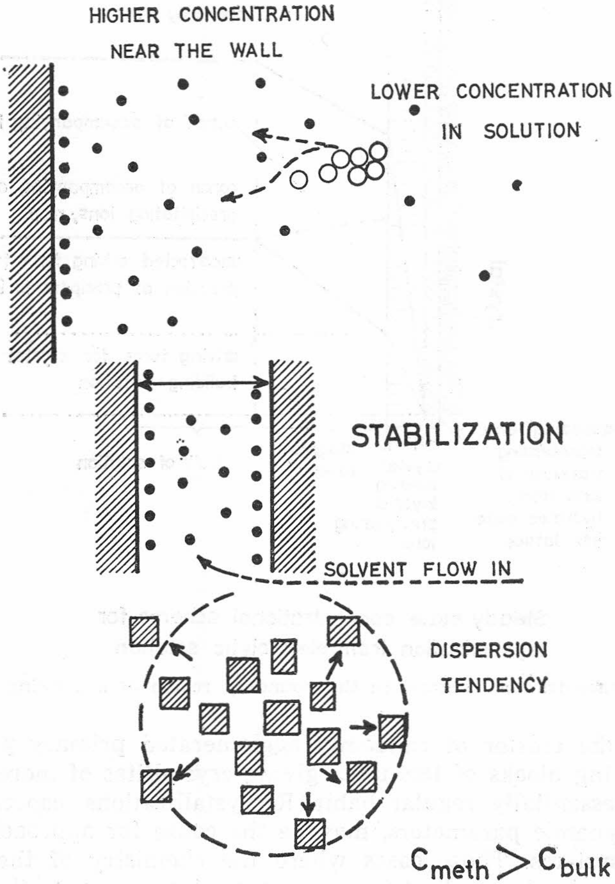


Figure 14. Stabilization caused by a higher concentration of microcomponents in the methoric layer with respect to the bulk solution.

10. *Stability/Instability Conditions for Primary Particles*

When the flux of the transferring ions across the boundary layer has ceased, then owing to the distribution of fixed ions of complexoides on the wall of the solid there is a higher or lower concentration of other ions in the methorical layer, and such a concentration may be different from that of the bulk solution. Just such differences are responsible for the stability/instability relationships of the emerging particles, as is schematically presented in Figures 14 and 15.

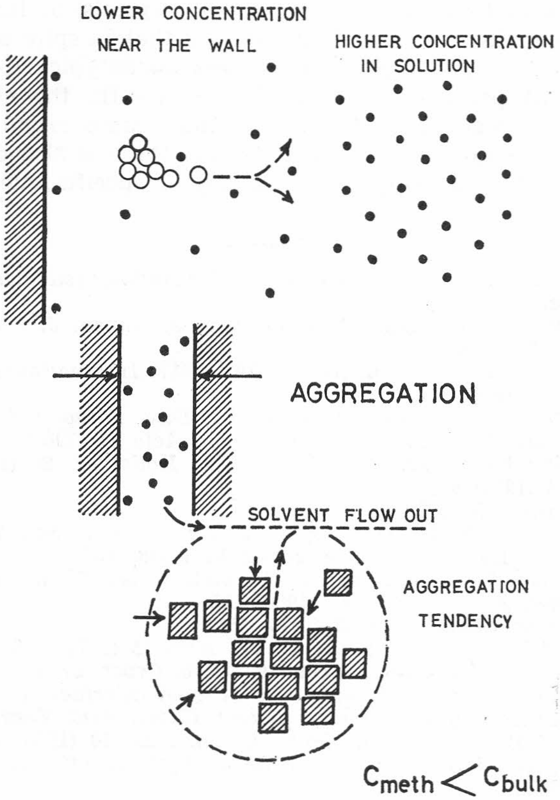


Figure 15. Aggregation caused by a lower concentration of microcomponents in the methoric layer with respect to the bulk solution.

11. *Competition Between Nonequilibrated and Equilibrated Subsystems*

Thus, we have to be aware of the succession of events when constructing behavioral schemes. Besides more exceptional "solution aging" there are very frequent phenomena of "aging" in the solid state which is a manifestation of the nonequilibrated stages which the system has gone through. Especially, when we are dealing with the formation of sparingly soluble substances from highly supersaturated solutions, the usual diagrams for phase equilibria are not appropriate. In such cases the composite processes may represent a wide spectrum of nonequilibrated states with a quite appreciable tenacity extending to geological periods of time. Also, when the critical situation in the critical moment has passed, new equilibria or quasi equilibria between new sometimes unexpected partners can be found. For this reason we have chosen, as a first approximation to the comparative analysis, the presentation of the processes and structures by time dependent "precipitation bodies" in the "cube of dilution".

As was very thoroughly elaborated by Kohlschütter[19], the whole history of the system has to be followed as closely as possible, since the succession of events and species with different life-times is controlling quite special diachronic and morphological compositions of real crystals, or individually structured so-called somatoids. But, it is interesting that in spite of the multitude of factors, some of the genotypical and others phenotypical[20], playing a part in the processes of precipitation and crystal growth, the characteristcs of four types of our "precipitation bodies" or clear combination of these could be identified in the majority of cases. Therefore there is already a finger-post for further approaches to many open, general or specific question in this of investigation.

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SAŽETAK

Teorija kristalizacije prema iskustvima s elektrolitnim sistemima

B. Težak

Čineći pregled starijih rezultata, posebno onih v. Weimarna i Odéna, na primjerima razlika između slabo topljivih sulfata i halogenida, korišteni su novi pristupi dijagramatskih prikaza karakterističnih pojava precipitacijskih i kristalizacijskih procesa i struktura. Naime, da bi se moglo uspoređivati, različiti sistemi su promatrani kod konstantne temperature i tlaka, u razvojnim stadijima prema njihovim

pozicijama u tzv. ”kocki razrjeđenja”, i prikazani kao specifična vremenski ovisna ”precipitaciona tijela”.

Istaknuto je da je pojavljivanje čvrste faze iz otopine kompleksna pojava, gdje veliki broj neravnotežnih stanja može interferirati jedan s drugim na takav način da već koncentracijski parametri različitih vrsta u preembrionacijskim stadijima, kao i u metoričkom sloju embrija, nukleusa, primarnih partikula i sekundarnih agregata u stvaranju, reflektiraju oboje: i direktni rast manjih jedinica, i njihovu agregaciju, uglavnom kontroliranu odnosima stabilnost/nestabilnost.

Za objašnjenje kritičnih stepena (uloga ”novih dijelova” i ”površina diskontinuiteta” prema Gibbsu) u transformaciji homogene otopine u heterogeni sistem, dane su sheme različitih udjela kemijskog potencijala u ionskim interakcijama ”površine diskontinuiteta” u metoričkom sloju, granice rastućeg kristala, i stabilnost/nestabilnost uvjeti embrija, nukleausa, ili primarnih partikula, koji se pojavljuju u otopini.

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ZAGREB
Yugoslavia

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