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Chemistry of Interfaces with Special Respect to Precipitation Phenomena*

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»Scientia est experientia«
Paracelsus

The general scheme of various investigations concerning the equilibrated, more static, or dynamical, frequently nonequilibrated solid/liquid/gaseous systems was pointed out approaching to the problems of interboundary states.

The schemes for steady state of the growing crystal at the boundary solid/liquid, the interferences in crystal growth, especially by aggregation of primary particles into secondary structures, the role of spacial distributions of reacting ions with concentration, and, in general, the complexity of the precipitation processes and structures, were discussed. It was emphasized that with the transformations from homogeneous electrolyte solutions to heterogeneous precipitating systems the equilibrium states are very rarely met. The 'solution aging' and 'aging of precipitates' may be taken as demonstration of this fact. Therefore the diagrams showing the time dependency of 'precipitation bodies' may be taken as a rational approach for the characterization of the systems in question.

For the interpretation of the phenomena as consisting of the formation of complexes, embryos, nuclei, direct crystal growth, and the stability/instability relationship of various entities it seems necessary to pay full attention to the different transition stages leading to the concentrational differences in the methorical layer and the solution in bulk.

It is assumed that such an interplay of genotypical and phenotypical factors primarily influencing the formation of 'new parts', in the Gibbs' sense, in the boundary region (methorical layer) between the solid and liquid phases is the controlling mechanism for the formation of specific structures and the resulting properties of emerging solids.

At our *First Conference of Solid/Liquid Interfaces* four years ago we started the General Introduction by discussing the stability/instability relationship of colloid particles. Now we can take one step further and put the emphasis on the problems of the appearance of the solid phase from the solution in general. Namely, we are sure that some deeper significance could be found in the analysis of the transition stages from homogeneous to heterogeneous systems in the study of such topics as Gas/Liquid, Liquid/Liquid, and

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Liquid/Solid systems, including the specific interfaces of polymers and biopolymers as well as the optical and spectroscopic techniques used in the investigation of interfaces and the study of the phenomena in physics and chemistry of the boundary state.

Therefore, we have reason to start from Gibbs' definition of 'Surfaces of discontinuity' characterized by the energy, entropy, volume, and quantity of the components of 'new parts' representing »infinitesimal masses . . . entirely different in state and composition from any initially existing«, and taking into account »the nature of the surfaces of discontinuity between solids and fluids with reference to the tendency toward solidification or dissolution of such surfaces, and also with reference to the tendencies of different fluids to spread over surfaces of solids«.

Applicability of Various Theories

Certainly, in the past and the present state of the physics and chemistry of formation and dissolution of solid phase in solution of electrolytes, there are some fundamental answers to the problems defined by Gibbs. But for a synthetic approach the chances are diminishing with the development of knowledge about various aspects of either 'new parts' or 'classical parts' representing the specific phases and compositions of solids, liquids or gases. For such convergent and also divergent trends with respect to our knowledge of 'new parts' in interboundary, interfacial, interphasial, or methorical layer between solid and liquid we have tried to establish a meeting place for those who belong to the 'invisible college' working on some of the dominating problems in this complex field.

We are aware of the difficulties because the current interpretations for some of the very important or most important processes and structures represent in reality a confusion of outlooks, concepts, models, theories, and principles. This happens also in limited sectors of the field in question. One of the signals of such a state is that Professor Matijević[1] [receiving the Kendall Reward at the *Symposium on Chemical Aspects of Interfacial Phenomena,* Boston, April 10—13, 1972.] put in a most prominent place the citation of Wo. Ostwald[2] from 1938:

> »If a professor is obliged to discuss this unsatisfactory condition of the theory of coagulation for thirty or more years, in every term of the academic year, then it may easily happen that he becomes more and more impatient. Either he becomes resigned or he commences to curse. The latter course is in general more fruitful.« [*J. Phys. Chem.* **42** (1938) 982.]

It is significant that we are in nearly the same situation nowadays although there were at least three approaches put forward immediately after the date of Wo. Ostwald's statement. These are those of Langmuir[3] (1938), Deryagin-Landau[4] and afterwards Verwey-Overbeek[5], now DLVO-theory (1941), and Težak[6] (1942).

Maybe it will not be taken as presumptuous that the qualification of these theories, after thirty years of possibility of their checking, belong to various categories; namely, as to theories of description (Težak), of prediction (Langmuir), and of unchecked assumption (DLVO). The main criteria for such judgment should be those of Paracelsus from the beginning of the era of modern science about 500 years ago. Thus, there is an answer to the question expressed by Overbeek[7] again nearly twenty years ago, how to »... deduce from the lack of agreement that present theories are on the wrong track? And if so, what is the right track and how do we know it is?« The answer is that the experimental data alone, and the agreement between experiments and concepts and expressions which reflect some general experiences in at least such a number of cases which can be taken as representative for the corresponding phenomena, have to represent arguments for the choice of the right track.

General Approach to the Problems of Interboundary States

Accordingly, in treating interfaces, the whole spectrum of physical and chemical interactions should be taken into account. It may be said, and I will allow myself to say it, that the supposition that for the stabilization/coagulation processes there are only Debye-Hückel interactions responsible for repulsion, and cumulative van der Waals forces as the main component for attraction between particles in solution, has been shown, to be a futile attempt in spite of a large amount of work and a seemingly generally accepted theory. For the interpretation of real systems and processes in the formation of a new, especially solid phase from an electrolytic solution, there is a great variety of physical, and chemical factors playing part in kinetics and thermodynamics, and all of them have to be applied, sometimes simultaneously, to the various stages as well as to the resulting products. But in spite of the multitude of these factors one principle seems to be of quite exceptional influence for aggregation (embryonation, nucleation, multistage crystallization, coagulation, flocculation, and agglomeration of various kind) which in general terms could be expressed as concentrational or osmotic differences of microcomponent species in the methorical layer (number of interfaces, interphasial region between bulk phases) and the solution in bulk.

From the point of view of such a general statement we have to look for further steps in the synthesis of results which have been gathered through investigations along the five paths mentioned in our first International summer school and conference on the topics of solid/liquid interfaces[8]. Moreover, for the general treatment of the systems where the gas phase is present the schematic approach to the most important paths of research may be analogously represented by Fig. 1.

The complex character of the phenomena, when two or more phases are interacting, may be studied along the lines interconnecting solid, S, liquid, L, and Gas, G, areas; sometimes, however, the most appropriate indicators of the controlling processes are reflected in stability/instability conditions of the emerging stages of 'new parts' in the transition subsystem of colloid dispersions. Considering that there are a large number of subsystems through which proceed the formation of a new, solid phase from the electrolyte solution, the experiencies of an enormous number of investigators from whom especially Wo. Ostwald[9], P. P. v. Weimarn[10], S. Odén[11], V. Kohlschütter[12], and L. G. Sillén[13] should not be ignored. Concerning the composite parts of the ion pair and cluster, mononuclear and polynuclear complex formation, embryogenesis, nucleation, crystal growth, and various other processes of aggregation[14], as well as structural and chemical transformations expressing the tendency towards more equilibrated states under given circumstances[15], the controlling mechanism is usually represented by a stability/instability relationship of the smaller units from which the larger ones are composed. For this reason the formation of precipitates and crystalline aggregates, either induced or spontaneous, may be taken as a testing ground for many or nearly all experiences either with experiments or theories independently or interdependently developed as our knowledge of behavior of separate or composite, amorphous or crystalline solid phases in solution. Consequently, this point of view should be taken when looking upon the many papers of this collection, as well as on the concluding paper under the title: »Precipitation processes in concentrated electrolytic solutions and temperature effects on silver halide sols *in statu nascendi*«.

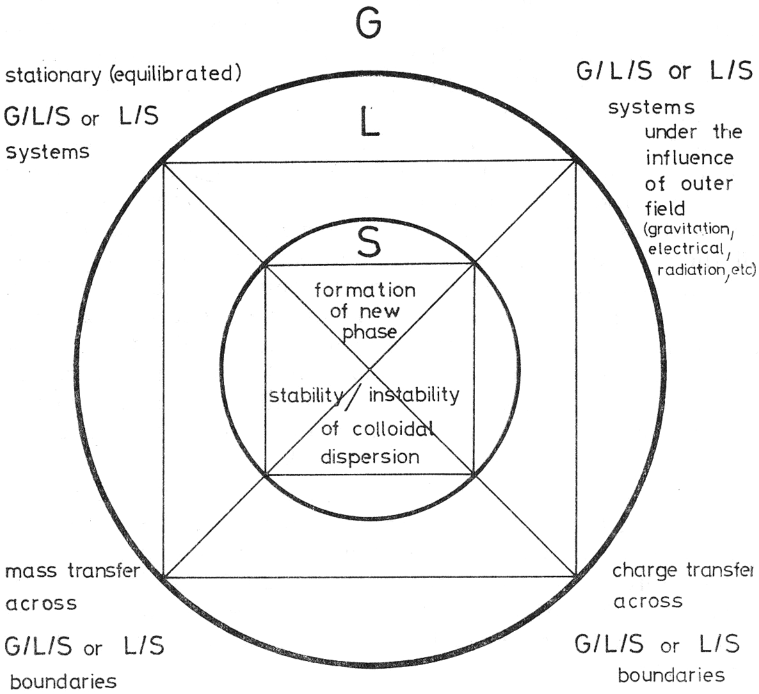


Fig. 1. Scheme of the five complementary approaches to the study of methorical layers (interfaces, 'new parts').

The reason for using such a presentation as especially significant to our conference is the need to try to find not only a syntesizing approach but also to point to the necessary corrections of the practice of forcing the experimental findings into narrow channels of special and sometimes improved theories.

In elucidating a complex natural phenomenon which could be defined as an experimentally conceivable system there are two different approaches; one, by carefully observing the changes which are caused by the systematic variation one by one of the parameters controlling the state of the system, or on the contrary, by preparing a large number of model systems or subsystems, and putting them into the composite interrelationship and thus constructing the totality of the system under investigation.

Nevertheless, for the final proof of the validity of the conceptual schemes used we have to find the true correspondence between both approaches. In the search for such a common frame which may embrace the majority of facts connected with 'new parts' of the methorical, that is, a number of interfaces[16] between regular more static solid structure and dynamical more statistical arrangements of solution constituents, including some excursions to the gaseous phase interacting with other phases through various films, we have to look upon the subjects of our conference.

Therefore, by starting from the discussion of isolated phenomena we are trying to emphasize the need to consider the separate experiences from a more general system approach. The other reason for concentrating our attention to stability questions, at least as we have done in the introduction to our First Conference, is that all four other paths of investigation of interfaces, represented by Fig. 1, are reflected in the stability or instability of the emerging phase from a previously homogeneous system. Moreover, there are a number of spontaneous signals, especially the discontinuities in composite kinetics of changes which could be used in elucidating the complex phenomena encountered. In connection with such reasoning we have pointed out the necessity to look at the interplay of at least five subsystems[14] in transition from a homogeneous solution to a heterogeneous precipitating system.

Interference to Crystal Growth

Besides appearence of ion pairs, clusters, mononuclear and polynuclear complexes, embryos, nuclei, primary particles, and higher aggregates, probably the most intriguing steps are connected with the direct growth of the solid particles. Although there are a large number of theories of crystal growth it seems that necessary attention has not been given to some important elements. The time-dependent character of the steady state condition in the methorical layer of the growing crystal phase in relationship to stability conditions of the particles belongs to such a neglected field.

As we have already given the fundamental concepts for stability/instability relationships of the so called sols *in statu nascendi,* it seems appropriate to outline at this occasion some schemes which will enable us to see the controversial points more easily.

The first notion which has to be made clear when we are dealing with transitions from homogeneous electrolytic solution to heterogeneous precipitating systems is the limited meaning of equilibrium states. By expressions of phase equilibria in such systems there is usually accentuated the tendency of change only, while the accompanying processes may represent a wide spectrum of nonequilibrated states with quite appreciable tenacity extending sometimes to geological periods of time. Therefore, we have to be aware of the succession of events in constructing the behavioral schemes. Besides more exceptional 'solution aging'[17] there are very frequent phenomena of 'aging' in solid state[18] which is a clear manifestation of nonequilibrated stages. Especially when we are dealing with the formation of sparingly soluble precipitates, the usual diagrams for phase equilibria are not appropriate. For this reason we have chosen the presentation of the processes and structures by so called time dependent 'precipitation bodies' in the 'cube of dilution'. By projection of the precipitating—nonprecipitating boundaries on the two-dimensional plot where the reacting ionic components are expressed by their concentrations in logarithmic scale, we have already in hand four very distinctive types[19] of 'precipitation bodies' of which the ionic solubility product principle represents only one.

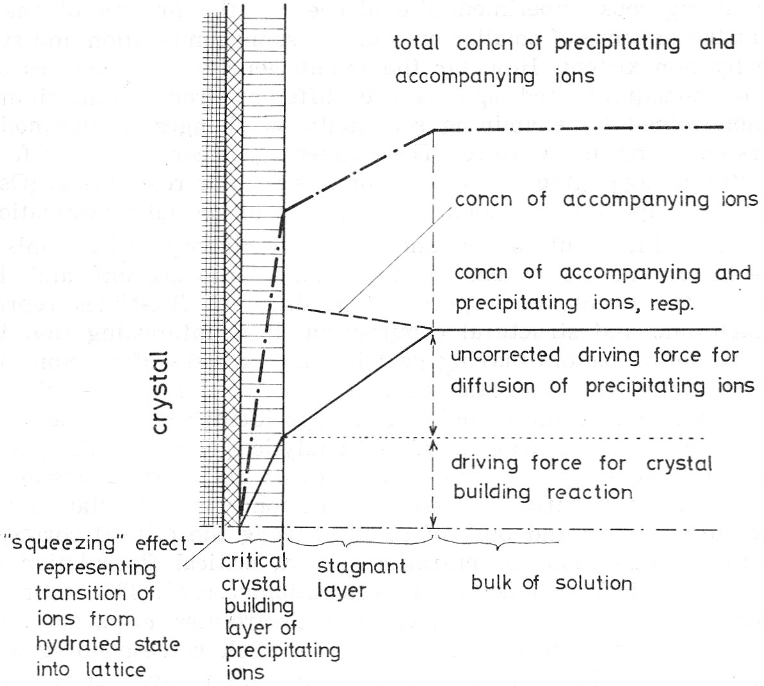
Although the phase rule is the basis for organizing and interpreting equilibrium states, the models themselves, as well as the principle of constancy of solubility product, may easily lead to oversimplifications of the complexities of real systems, where such factors as the interplay of usually unknown rates of important chemical reactions and consecutive physical steps have to be fully appreciated. Generally, by experimental determination of the 'precipitation bodies' it is possible to enter into the concentrational region where a qualitative and quantitative interpretation for the activity of ions, and for the thermodynamic behavior of concentrated solutions, are extremely difficult or sometimes impossible to construct.

In spite of the fact that boundaries for the appearance of the precipitate represent very different processes, the recognition of a common pattern may help enormously to systemize the large number of data. The first step in this direction is the full characterization of external and internal limits of the dinstinct discontinuities in precipitating phenomena and structures in relationship to the systematic variation of influencing factors..

While the trends of outer boundaries of the 'precipitating bodies' clearly indicate the dominating relationships between the reacting species in the formation of solid particles, the internal ones are much more complex. Thus, by keeping other parameters of the system constant it may be helpful to observe the effects of so called neutral electrolytes, and other foreign ionic or molecular species, as well as the various solvents, on the precipitation stages. The change in the kinetics of precipitate formation according to the Schulze-Hardy rule as well as reversal of this rule[20] in the case of monovalent, divalent and trivalent counter ions for silver chloride and barium sulfate, respectively, was already demonstrated. These quite contrasting effects are produced in spite of both substances having nearly the same solubility; the stages of silver chloride precipitation show the formation of typical sols *in statu nascendi* of the same behavior as hydrophobic colloids, while for the formation of barium sulfate precipitate it seems that counter ion effects are closely connected with preembryogenesis stages. Therefore, according to substantial composition of the system involved there are 'neutral' ion effects either in nearly final or in quite early stages of the emerging solid phase. However, in both cases the crucial point was association, probably ion pair formation in the methorical layer of coagulating particles in the case of 1-1 valent silver chloride, and again the ion pair or cluster formation in supersaturated solution in the case of 2-2 valent barium sulfate. The aggregation of quite different precipitating units in both cases was the next step.

Scheme for Direct Crystal Growth

Such or similar processes of aggregation interfere with developing stages of direct crystal growth. Again, not to repeat the schemes of the structures of the methorical layer (*Solid/Liquid Interfaces,* pp. 4, 22 and 28, Figgs. 1, 25 and 31, resp.)[8] it seems advisable to draw the schematic situation in the vicinity of the growing crystal as it is presented in Fig. 2.



Steady state concentrational scheme for crystallization from electrolytic solution

Fig. 2. Concentrational scheme in the boundary layer of the growing ionic crystal.

Such a steady state ionic transfer system with input and output concentrations may be very sensitive or sometimes quite insensitive to environmental conditions; the controlling factors belong either to the composition of the critical layer determining the stages of entering of ions into the crystal lattice represented by 'squeezing' layer, or to the resulting concentrational gradient in the so called stagnant layer including all possible interactions between species which may be present there. The steady state situation for most stable structures is usually found in competition with the formation of embryos and nuclei from much more rapidly formed species. Afterwards, when time allows for the nucleation of the final product, the recrystallization or real chemical change of the embryonal species into lattice constituents may take place.

Especially, such processes are common in systems which are represented by 'precipitation body' of so called unsymmetrical ionic activity type, where water as a chemically reactive solvent plays a very prominent role. Metal hydroxides with all their hydrolyzed species[21] are the main representatives of such a group. Again, the formation of hydrolytic species may be reflected in their specific behavior in solution (solution 'aging') and in the methorical layer resulting in specific growth, coagulation, reversal of charge, and flocculation effects. Concerning the effect of particle size on solubility it should be said that rigorous experimental evidence for the growth of the larger particles at the expense of smaller ones of the same composition and structure is practically nonexistent. How far the inhomogeneity in structures and the presence of nonequilibrated species are different from equilibrium states may be determined by examining sensitivity to changes in thermodynamic parameters (*e. g.*, the temperature). The coarsening or complete transformation of the crystalline aggregate into a more or less regular real crystal (Ostwald's and Tammann's ripening) represents a vast field of special investigations.

As it was pointed out earlier, and especially elaborated by Kohlschütter, the whole history of the system has to be taken into account, and thus the succession of the events and species with different life-times represent a special diachronic and structural composition. It is interesting that in spite of the multitude of factors playing part in the processes of precipitation and crystall growth the characteristics of four types of our precipitation bodies, or clear combination of these could be always identified. Also, according to a large number of experiences, mainly of analytical chemists, the phenomena of the stability/instability of primary particles or sols *in statu nascendi* allow us to enter into the essential discussion of the ionic or molecular interactions in the methorical layer and bulk of solution using the critical corresponding states (critical coagulation concentration, c. c. c., critical flocculation concentration, c. f. c., critical stabilization concentration, c. s. c.). The interpretation of the antagonistic effects of the mixture of electrolytes, *e. g.*, may be taken as one very convincing proof for the role of such corresponding states as expressed by c. c. c. Also, by using critical coagulation effects it is possible to enter into mechanism of special relationships where dynamic electrostatic, ion pairing and other equilibria play a dominant role.

The shapes of 'precipitation bodies' in their formation steps may be used as analytical and synthetic indicators for a number of essential reaction stages which very profoundly influence the properties of solids. They reflect in reality something of the 'internal environment' composed of the 'new parts' in the sense of Gibbs, and the dynamics of interventions of many steady state situations where the phenotypical factors interfere with genotypical[22] ones in the formation of real crystals.

The Role of Spacial Distributions

In all these equilibrium and non equilibrium states a very important role belongs to the spacial distributions and spacial interactions of the microcomponents (ions, molecules *etc.*). It should be realized that dynamical equilibria expressed in relationships between resulting species of various life-time may lead to quite special space distribution, especially in cases when some constituents are more fixed in position as a part of the solid wall. Such situations as well as similar ones may appropriately be schematically presented as we have done for interacting spheres of coulombic and chemical influences between ions[23]. How much such interactions may be the cause of continuous or discontinuous functions in the case of changing concentrational parameters should be ascertained by corresponding experimental arrangements (ESR, NMR *etc.*).

The role of valency and chemistry of interacting ions may be demonstrated also by comparing the 'precipitation bodies' of 1—1, 2—2, as well as of assymetrical 1—2, 1—3 or 1—4 ionic, and especially the hydrolytical species.

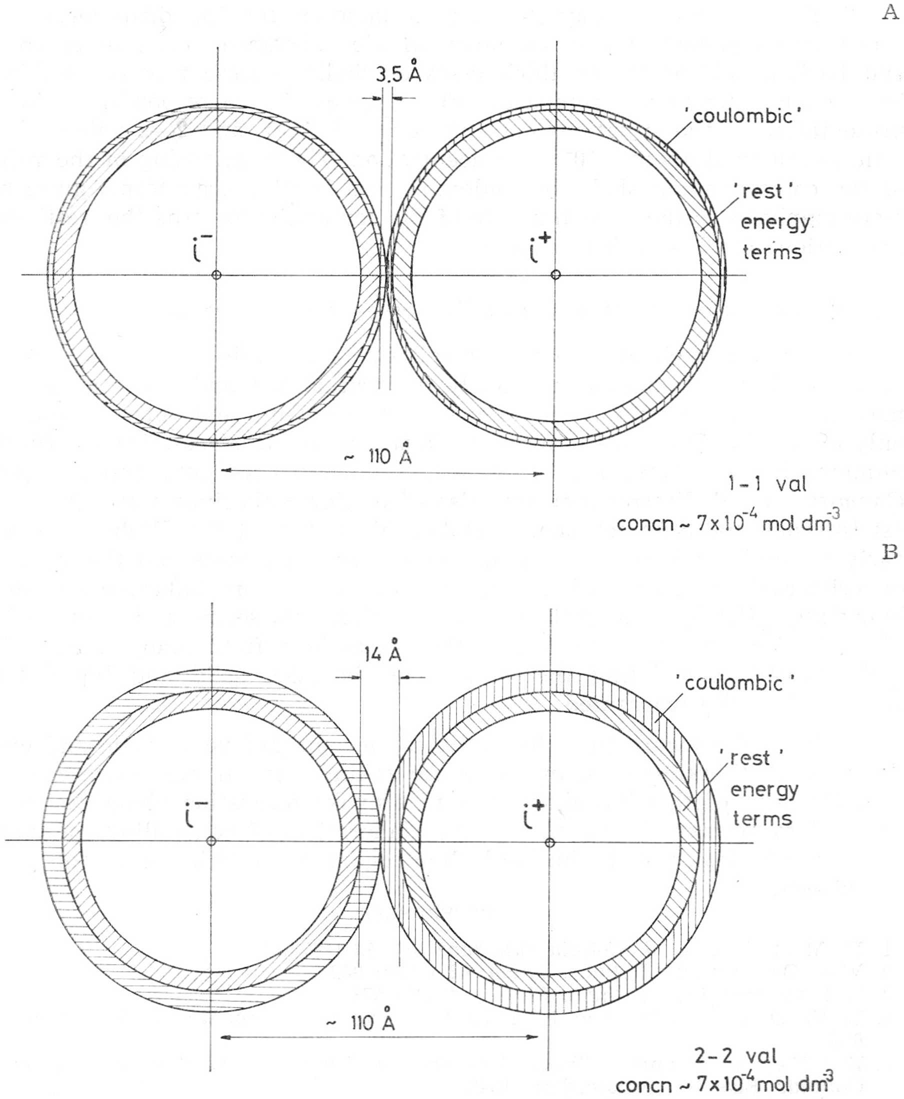


Fig. 3. Ionic distribution spheres with association shells of 1-1 ionic (A), and 2-2 ionic (B) interactions.

The variety of dynamical species, mononuclear and polynuclear, from ion pairs and clusters to the embryonic aggregates, have to be considered in such systems. All of them, although expressing a statistical distribution and an interplay of many factors, may have the representative distribution visualized by spherical 'cages' and association shells making it possible to use critical distances and activities as well as concentrations in constructing the most important relationships. Following such illustrations, by continous variation of concentration of ions, the discontinous steps in ion pair or complex formation may be envisaged. For this purpose the schemes in an earlier publication[23] may be used.

Such an approach may give an explanation for the differences in the precipitation phenomena of similarly soluble substances, *e. g.*, silver chloride and barium sulfate, if the thicknesses of shells representing coulombic and 'rest' energy terms are compared. Fig. 3 gives the corresponding schematic presentation of the situations encountered with 1—1, and 2—2 valent electrolytic solutions of about 7.10^{-4} M concentration. The relationship of the volumes of the corresponding shells of coulombic and 'rest' energy terms gives much more emphasis to the predominance of the coulombic towards the 'rest' energy associations for 2—2 valent systems.

The Emphasis on Complexity of Processes and Structures

In general, such an approach emphasizing the role of complex interplay of nonequilibrated subsystems, steady state situations, and dynamic associates, may represent a common frame for some problems and their solutions not only of the 3rd Euchem Conference *Chemistry of Interfaces*, 3rd International Summer School *Chemistry of Solid/Liquid Interfaces*, and 2nd Symposium *Chemistry of Mediterraneum*, but also of earlier gatherings starting from our 1st International Summer School, Dubrovnik-Cavtat, 1969[8]. Probably, it is too early to predict where, when, and how the final concepts and the supporting experimental evidence will be put together in a more balanced complex of knowledge. However, in spite of the fact that this seems a distant goal, the effort in focusing the attention of the researchers from many more isolated paths toward elucidating the 'new parts' between solid and liquid phases seems to be fully warranted.

Being quite aware that the outlined concepts are very crude and outside the way of thinking of many who are taking part at our conferences, the principal aim of this introduction is to provoke discussion along the broader lines of experimental and theoretical elaboration of controlling mechanisms in the methorical, that is the borderline regions of solid/liquid or solid/liquid/gas phases.

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IZVOD

Kemija međupovršina s posebnim osvrtom na precipitacione pojave

B. Težak

Pristupajući problemima međugraničnih stanja, predložena je opća shema različitih istraživanja u pogledu ravnotežnih, više statičkih ili dinamičkih, učestalo neuravnoteženih čvrsto/tekuće/gasnih sistema.

Diskutirane su sheme za uspostavljeno stalno stanje (*'steady state'*) rastućih kristala na granici čvrsto/tekuće, interferencije u kristalnom rastu, posebno zbog agregacije primarnih čestica u sekundarne strukture, uloga prostorne raspodjele reakcionih komponenata u ovisnosti o koncentraciji i, općenito, kompleksnost precipitacionih procesa i struktura.

Istaknuto je da su kod transformacija iz homogenih elektrolitnih otopina u heterogene precipitacione sisteme vrlo rijetka ravnotežna stanja. 'Starenje otopina' i 'starenje precipitata' mogu se uzeti kao potvrda te činjenice. Međutim, dijagrami koji pokazuju ovisnost o vremenu i prikazuju 'precipitaciona tijela' mogu se smatrati kao racionalan pristup za karakterizaciju sistema u pitanju.

Za interpretaciju fenomena kao što su kompleksacija, embrionacija, nukleacija, direktni kristalni rast i odnos stabiliteta — nestabiliteta različitih jedinica, čini se da je neophodno obratiti punu pažnju različitim prijelaznim stadijima koji rezultiraju koncentracionim razlikama u metoričkom sloju i u unutrašnjosti otopine.

Pretpostavljeno je da je takva međuigra genotipnih i fenotipnih faktora, koja primarno utječe na stvaranje (formiranje) 'novih dijelova' u Gibbsovom smislu u graničnom području (metorički sloj) između čvrste i tekuće faze, prevladavajući mehanizam kod formiranja specifičnih struktura i rezultirajućih svojstava izlučene čvrste faze.

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