METHORICS OF THE PRECIPITATION PROCESSES. I. SOME CONCEPTS OF THE CRYSTAL GROWTH FROM ELECTROLYTIC SOLUTIONS

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It is emphasized that in discussing the elementary process of ionic crystal growth, the structure of the region between the crystal phase and the ionic solution must be duly considered. These intermediate structures are influenced by both well defined phases of the boundary region, and have many specific properties. In order to visualize the principal elements of these transitional, typically methorical structures, some elements of Bjerrum's theory of ionic association are used, and the concept of the probability spheres and probability shells indicating the probability of free, dissociated or associated ionic states respectively, is introduced. For neutral, symmetrical electrolytes when calculating mutual distances between the centres of spheres, the whole volume of the solution was divided by the total number of ions; the thickness of the probability shell is given by the distance at which the coulombic becomes twice the thermal energy. The greater thickness of the probability shell is taken in the chemically active ions. It was shown that the methoric spaces occurring in the process of building up one ionic sheet on the crystal face may exceed the thickness of several thousands of angströms. In this way some periodic phenomena, especially those of the layer formation during the crystal growth, were discussed.

Introduction

It is a generally recognized fact that there is no direct method for the determination of the surface structure. It is known that in electron diffraction experiments, space lattice regions of considerable thickness are always involved. For the discussion of the structure of the boundary region of the crystal, especially during crystal growth, we have usually to rely on cases of the growth of homopolar crystals or of the growth from vapour phase. The theories of the three-and two-dimensional nucleation, of the rôle of repeatable steps in the crystallization, etc. (Kossel, Stranski, Volmer and others), are limited to experimentally ideal conditions which are rarely met with in practice. However, we have good reasons to expect that the phenomena of adsorption, coagulation, crystal growth, and precipitation performed under systematically varied conditions, may facilitate experimental investigations of the structure of the region between the two well defined phases: the more or less fixed ions of the crystal latice, on one side, and the statistical distribution of the ions in the bulk of the solution on the other.

It seems that the difficulties in the structural interpretation of the immense number of experimental facts which are observed in relatively simple ionic systems were due principally to the difficulties to visualize, semiquantitatively at least, such elements, as the ionic atmosphere, the activity, and the ionic strength involved in the mathematical theory of Debye and Hückel. As the starting point the elements of Bjerrum's theory of the ion-pair and cluster formation have therefore been taken.

We have developed some elementary concepts of the processes in the boundary state: the ionic crystal — the electrolytic solution[1]) and it seems worth while to attempt the use of these concepts as a general and very simple tool in discussing the experimental material which we are acquiring, in the hope to find some of the essential elements operating in the complex structure of the heteropolar methoric spaces.

The structural elements of ionic solution

In order to draw a simple and idealized picture we shall take into consideration such an ionic solution where 1—1 valent ions are differing only by their opposite charge. The interactions

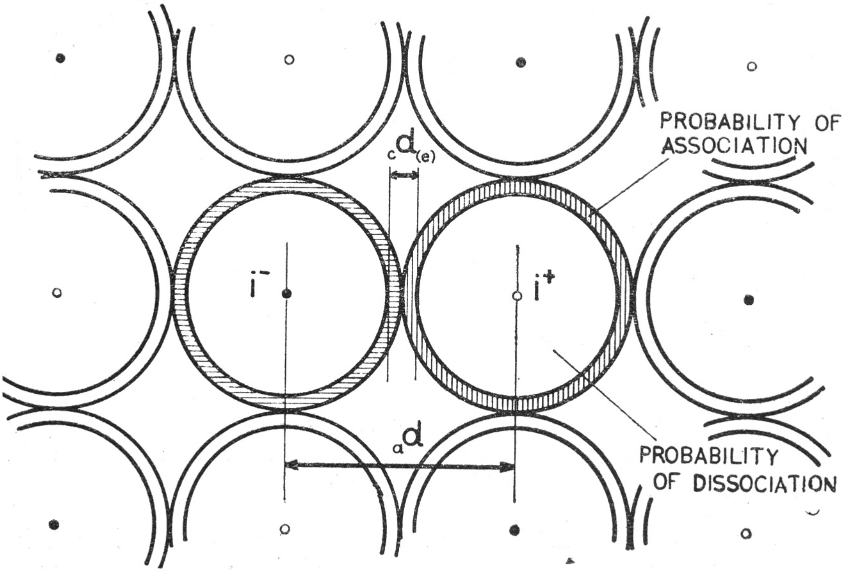

Fig. 1. Schematic presentation of the relationship between the mean interionic distance, $_ad$, and the Bjerrum distance of electrostatic interaction, $_cd$. Circles correspond to the ionic distribution spheres of 1—1 electrolyte (conc. 0.06 M).

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[1]) B. Težak, Z. physikal. Chem. **191** A, 270 (1942); Arhiv kem. **19,** 19 (1947).

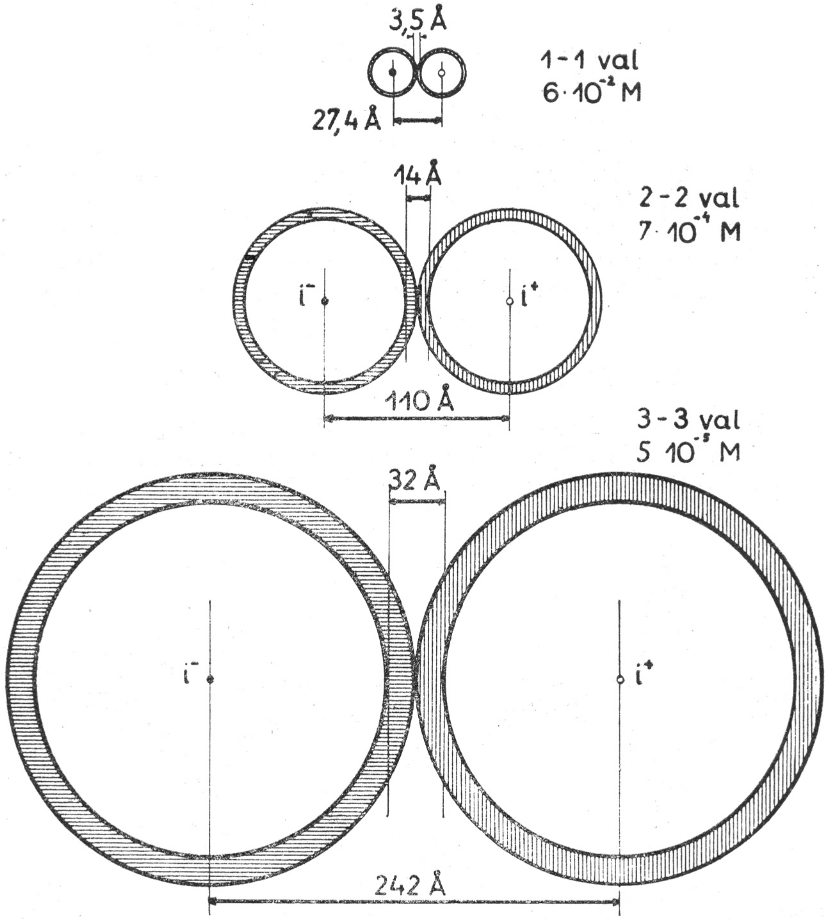

Fig. 2. Schematic presentation of the relationship between the ionic distribution spheres of 1—1, 2—2 and 3—3 valent electrolytes of the same coefficient of activity.

between ions, assuming their ideal distribution through the whole volume of the solution, can be described in the following way. Each ion may be statistically found in a sphere, the radius of which is obtained by dividing the whole volume of the solution by the total number of the ions. Such spheres may be taken as distribution elements of the statistical-kinetical structure of the solution. The probability that an ion may be found in the vicinity of the boundary of its sphere will be a function of the energy of thermal agitation, and of many factors, such as viscosity of the medium, the solvation, etc., which, for the same solution may be taken as constant. The ions attract or repel each other by coulombic interaction of their charges, the potential function being e^2/Dd, where e is charge in electrostatic units, D dielectric constant of the solvent and d distance between the ions.

According to Bjerrum for an effective ion-pair formation it may be put that

$$e^2/2D_c d = kT, \quad \text{and} \quad {}_c d = e^2/2DkT\,;$$

$\frac{1}{2}\,{}_c d$ is approximately the thickness of the shell of the ionic distribution sphere which may be correlated to the probability of association of the oppositely charged ions. The volume of the internal sphere would then be a function of the probability that the ion is in a free, dissociated state. Thus, to a given activity coefficient of the electrolytic solution, corresponds a given ratio between the volume of the inner and outer sphere. These relations are given in Fig. 1 for a 1—1 electrolyte of $c = 6 \times 10^{-2}$ N. When the ions are 2—2 or 3—3 valent, the corresponding ratio of the shell to the sphere may be found only at much lower concentrations; e. g., in Fig. 2 the distribution of 1—1, 2—2 and 3—3 valent electrolytes are given supposing that their activity coefficients are equal. On Fig. 2 the distances were calculated assuming a

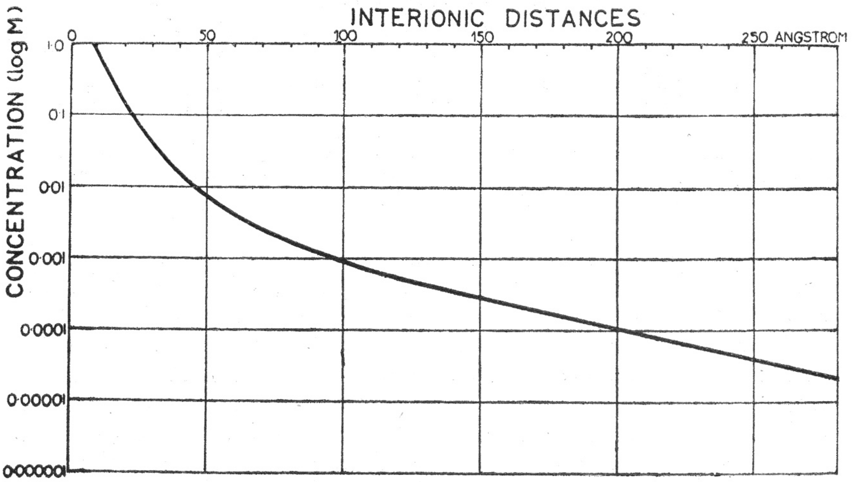

Fig. 3. The relationship between the logarithm of molar concentration and the mean interionic distances (assuming the uniform distribution of 1—1 valent electrolyte).

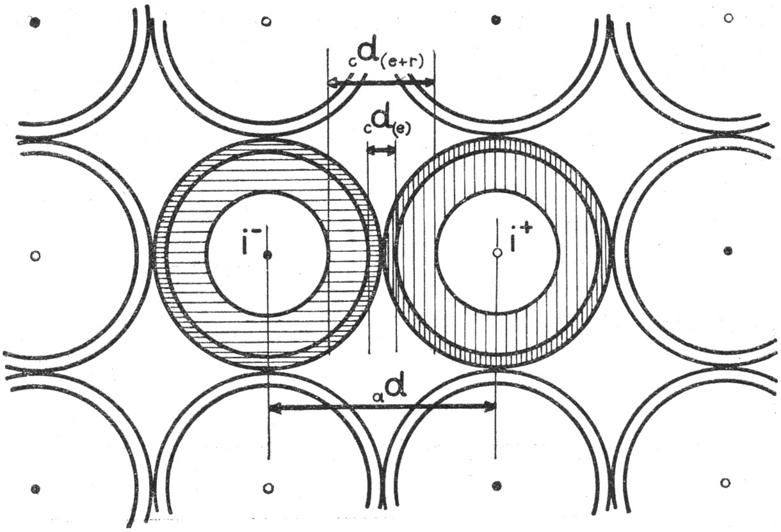

Fig. 4. Schematic presentation of the ionic distribution spheres with shells indicating the associating probabilities: (1) of electrostatic character (dense shading) and (2) of chemical character (light shading).

uniform distribution of the ions as in the case of the 1—1 electrolyte (Fig. 3). Such relations between ions may be typical for the neutral strong electrolytes; when the mutual interactions between ions are not only the result of potential energy of coulombic interactions, other terms of the chemical potential must be taken into acount. Although such energies are specific and differ from one ion-pair to another manifesting themselves in a different attractivity between the ions, we shall represent the behaviour of such ions simply by an additional shell thickness added to that of our coulombic association probability. Thus the total thickness of the shell will be a function of the mutual coulombic energy, of the exchange energy, of the van der Waals term, and of other energy factors influencing a desolvation in the system at a given temperature. On Fig. 4 these »rest« energy terms are represented by another shell which is closer to the centre of our distribution volume than the shell of coulombic interactions.

All these relationships are taken assuming the simple cubic »lattice« of the quasi-crystalline structure of the electrolyte.

The boundary region: ionic crystal — ionic solution

It is clear that if we have to deal with such a boundary region where a varying number of ions is adsorbed at the face of the heteropolar crystal, the distribution of these ions in the adsorbed state would be a factor of primary importance for the distribution of all the other ions in the neighbouring region of the solution. As shown by experimental evidence the charged surfaces on ionic crystals are the most frequent phenomenon, and the distribution of one kind of the »lattice« ion in the adsorbed state must be taken as a starting point for the discussion of all of the complex processes of adsorption, coagulation or crystal growth.

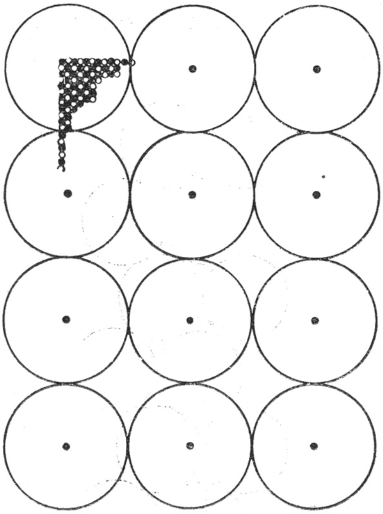

Fig. 5. Schematic presentation of the distribution of potential determining ions on the surface of the ionic crystal (density is about 1 ion on 1,600 Å²).

In spite of the fact that the »lattice« ions are adsorbed in preference to all other ions which may be present in a solution, the »density« of such ions in the adsorbed state which manifest their »free« ionic charge is usually not great. According to the experiments on silver halides²), their number is so small that only about 1% or less of the exposed adsorption surface could be covered. This is approximately one charge on 400 — 1,000 Å². Such findings suggest that the distribution of the adsorbed »lattice« ions is similar to that of the ions in electrolytic solution of a concentration of about 0·1 to 0·01 N. Fig. 5 shows a schematic representation of such a surface, where only 1/200 of the possible sites are occupied by one »lattice« ion (one ion on ca 1 600 Å²). This drawing is an orthogonal projection of the adsorption plane. The whole methoric system is shown in Fig. 6. For reasons of simplicity it was supposed that the distribution spheres of all

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²) E. J. W. Verwey and H. R. Kruyt, Z. physikal. Chem. **167 A**, 137 (1933); A. Basinski, Rec. trav. chim. **59**, 331 (1940).

the ions, including those in an adsorbed state, are equal. Under such circumstances the methoric layer which is directly engaged in building up one layer of ions into the actual crystal lattice will be at least 2,000 Å thick, or, in general, dimensions of 40 Å to 2,000 mμ as the range of the influence of the forces operating in the crystal growth through the expanded arrangement of the adjacent ions, should be considered as normal (according to the solubility between 5 to 0,01 M respectively).

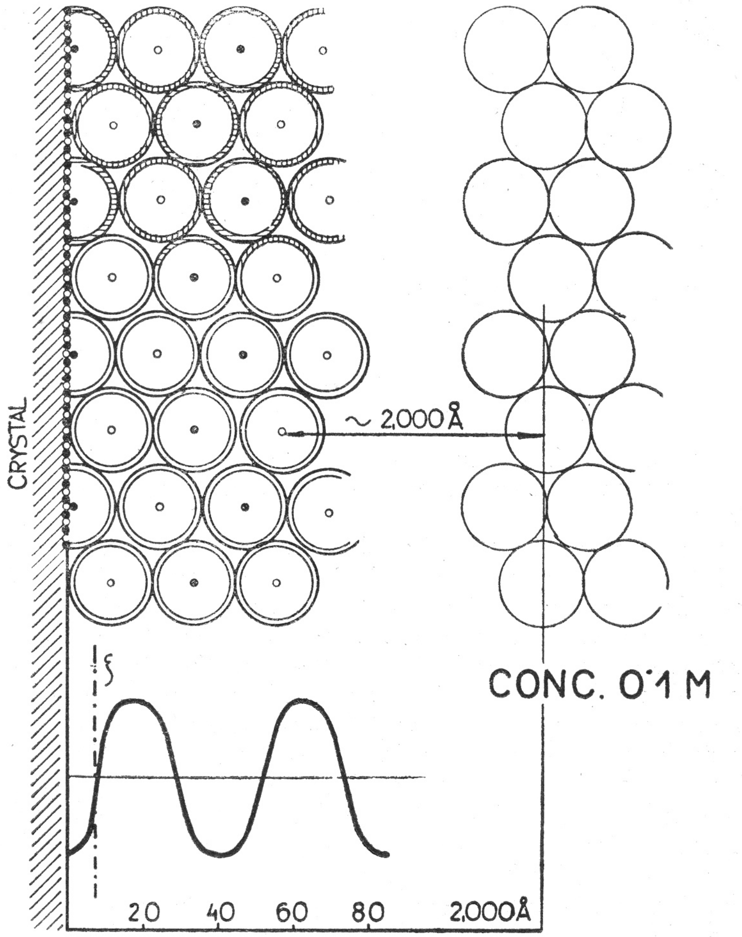

Fig. 6. Schematic presentation of the section perpendicular to the boundary: ionic crystal — electrolytic solution, showing the distribution of the potential determining ions and the ionic distribution spheres of 0.1 M 1—1 valent electrolyte.

This does not necessarily mean that in some systems the average thicknesses of the critical methoric layer cannot be much thinner in spite of the small solubility. Nevertheless, we may expect even in such cases a temporary formation of the condensed ionic layers of the same kind as those which we have used previously for the interpretation of the transition layers on the growing or coagulating crystal particles[3], but in the majority of experimental cases where the solubility and supersaturation are comparatively low, the expanded form of the ionic distribution is probably much more frequent.

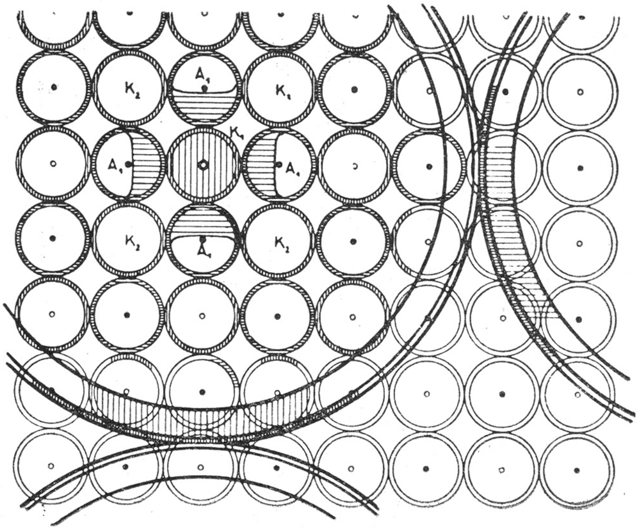

Fig. 7. Schematic presentation of the relationship between the ionic distribution spheres of the solution of 2×10^{-5} M silver chloride (large circles) and in the presence of 1×10^{-2} M of potassium chloride (smaller circles).

Until now we have not considered the rôle of the »rest-energies« in the association-dissociation balance of the ions. If in our solution there are also ions which are alien to the constituent ions of the ionic precipitate, the distribution would be quite different. An attempt to visualize the situation, with the silver ions ($AgCl : 2 \times 10^{-5}M$) in an aqueous solution of potassium chloride ($KCl : 8 \times 10^{-3}M$), is given in Fig. 7 where the greater probability of attraction between silver and surrounding chloride ions is shown by the corresponding deformation of the shells; as a

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[3] B. Težak, Kolloid Z. **59**, 158 (1932); Z. physikal. Chem. **190 A**, 257 (1942); **191 A**, 270 (1942).

consequence, the whole arrangement of the ions is changed, but this is not shown in our picture.

Special relations are encountered in the region of the higher ionic concentrations. Since the mutual interaction between ions increases with increasing concentrations, the critical phenomena of the »dynamical« complexes and the special solubility relations should be expected as a rule in the range of concentrations higher

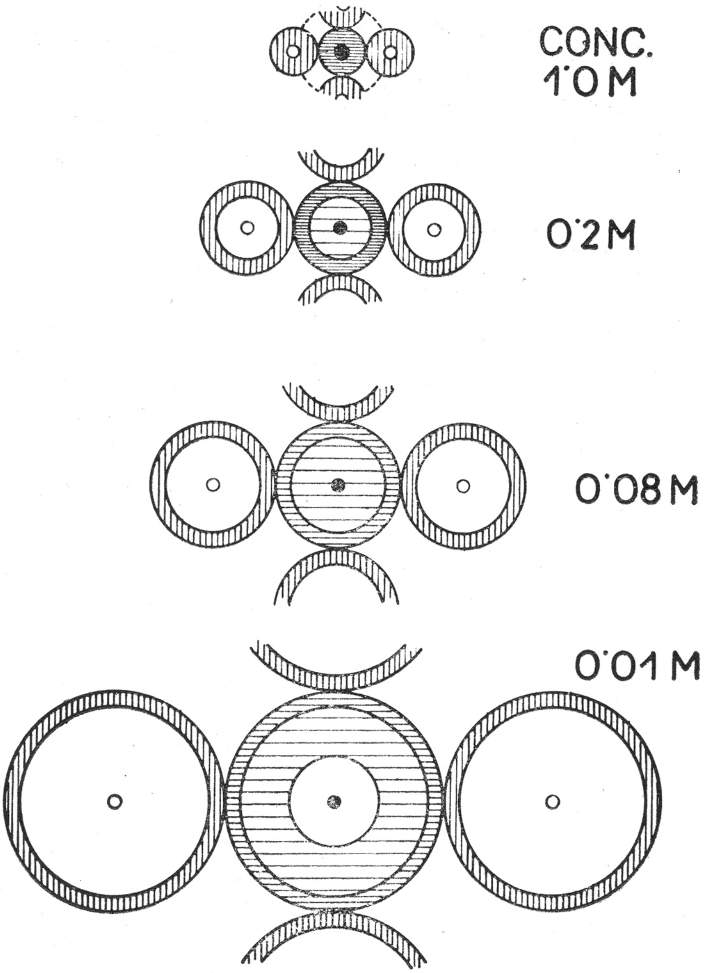

Fig. 8. Schematic presentation of the relationship between the probabilities of association due to coulombic and chemical interactions of the ions with increasing concentration (1—1 valent ions of the radius ~ 2 A).

than 0.01 M. In Fig 8 there are some illustrations of ionic distribution at the higher concentrations; as the ions are closer together, the spheres of dissociation dissappear, and the influence of the coulombic and »rest-energy« terms of the ionic attraction becomes prevalent while the average time of the ion-pair and cluster formation increases. Under such circumstances the greater part of the total number, or of one of the special kinds of ions, would be either ineffective or much more effective in respect to some reactions. With such relations it seems possible that the question of the special »complexes« of the ions in the region of the high ionic concentrations with special regard to the results of the solubility, the potentiometric and the conductometric measurements may find a ready interpretation.

Discussion

We are aware that the interpretation given may be too simple, but the processes encountered in heteropolar methoric systems are of such a complexity that such steps seem to be justified as a means of orientation. From recent discussions on crystal growth[4]) we have learned that the conceptions which we have put forward have been disregarded. Certainly, the very substance of such conceptions may be expressed in various ways, but we have not seen the full recognition of some of the principles which cannot be overlooked. For instance, the dependence of the medium, that is, the influence of the »internal environment« of the growing crystal, have in the majority of papers been completely overshadowed by the discussion of the first step in the series of the numerous »repeatable« steps of the continuous or discontinuous process of the crystal growth. It seems to us that too great an emphasis was laid on the presence of various Kossel-Stranski-Frenkel »kinks«, »dislocations« and »roughnesses« of the crystal surface compared with the actual rôle of the constituents in the methoric space. This may be especially true for the discussion of the growth of the ionic crystals from aqueous solutions. In such systems the dependence of the structure of the methoric space from the structure of the crystal phase on the one side, and of the statistical-kinetical arrangement of the ions in the bulk of the solution on the other, has to be taken into account. The arrangement of the constituents of the methoric layer may be of either fixed or kinetic character, and in such a dynamical system we have to look for the mechanism of ordering and exchanging the ions and molecules with special prefe-

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[4]) Crystal Growth, Discussions of the Faraday Society, **5** (1949)

rence to those constituents which may give to the whole system the transition structure of greatest stability. 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 properties of the medium in respect to the specific structure of the crystal lattice must also be recognized.

To illustrate our standpoint, we will refer to some experimental investigations communicated in the course of the discussions cited above.

Experiments by Davies and Jones[5]) show that the precipitation in the absence of seeds is extremely sensitive to the concentrations of the mixing components. The number of nuclei, their methoric layers, and their aggregation velocities as well as the velocities of direct growth, are all dependent upon small and sometimes only transient and local variations of the concentration of the precipitating ions during the mixture. Simultaneously with the direct crystallisation we may have the growth through oriented aggregation of ionic complexes as well as amicrons, submicrons and primary particles which have been formed at first. Naturally, it will be possible to apply a special treatment for the building up of the secondary crystals step by step from such smaller, primary units, supposing that the corners and edges are exerting some »vectorial« influence. Thus, the great variety of the »habitus« of the crystal forms (a result of the concentration ratio of the constituent ions, the presence of the foreign substances, or the solvent influences etc.) may find its explanation.

Apart from these considerations we have already shown that systematic variations of the disparity in the concentrations of chloride, resp bromide and silver ions have a very marked influence on the velocity of the precipitation of silver halides, and that there exists some periodicity which was interpreted by a periodic variation of the arrangement of the constituent ions in the transition layer[3]).

The behaviour of the systems composed of slightly soluble substances must not necessarily be more complex than the crystallisation of the soluble salts, where high concentrations must be reached to provoke a precipitation. In high concentration the ionic distribution spheres are so small that the ions are already under the influence of their coulombic interactions, and the first step in crystallisation 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

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[5]) C. W. Davies and A. L. Jones, Dis. Farad. Soc. 5, 103 (1949).

forms, especially of a transient character, must in such circumstances not be overlooked.

The interesting phenomena reported by Bunn and Emmet[6]) may also find a ready interpretation from our point of view. These authors have found that the spreading of crystallisation 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 2,000 to 4,000 Å. The substances on which layers were seen have moderate or high solubilities, and are either ionic or contain strongly polar groups. From our considerations of the distribution of ions in methoric spaces, the adjacent solution region where the number of ions necessary for the building up of successive layers is found must necessarily be put under the influence of each of the lattice layers in the formation state. Thus the layer of the solution, the thickness of which is about, say, 200 Å, 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 methoric space. This may afford the explanation that the observed layers of Bunn and Emmett became thinner with an increasing proportion of alcohol.

Thus the structure of the methoric space between the solid phase and the bulk of the solution shows the specificity governed by both phases beyond the boundary region, while the structure of the newly formed crystalline phase, or the possibility that the effective nucleation could be found at all, is conditioned by the dynamical arrangement of all the possible constituents, including all of the ions present as well as the molecules of the solvent.

In general, the crystallisation 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 cannot be directly compared with the condensation from vapour phase. The difference from the crystallisation of melts may also be manifested by comparing the phenomenology of Tammann's *nucleation* and *crystallisation* maxima with our *concentration, isoelectric, transition, crystallisation* and *secondary maxima*[7]). We are fully

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[6]) C. W. Bunn and H. Emmett, Dis. Farad. Soc. **5**, 119 (1949).

[7]) B. Težak, Kolloid-Z. **68**, 60 (1934); Z. physikal. Chem. **175 A**, 219 (1935); **190 A**, 257 (1942); **191 A**, 270 (1942); **192**, 101 (1943); Arhiv kem. **19**, 9 (1947); **20**, 1 (1948).

aware of the diversity of the properties of such systems, and we do not intend to look into their causes neither in the crystal nor in the solution alone. The answer to the questions open in this field could probably be found only in an appropriate recognition of the mutual interdependence between the rôle of the crystal, of the methoric layer and of the solution. From this point of view our research group has worked on many investigations which will follow under the same general title as this communication.

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[Received, December 9, 1949]

IZVOD

Metorika taložnih procesa. I.
Neke predodžbe o rastu kristala iz elektrolitnih otopina

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Diskutirajući o elementarnom procesu rasta jonskog kristala naglašena je uloga strukture prelaznog sloja između kristalne i tekuće faze. Ta struktura je pod utjecajem obih faza, te se za njenu karakterizaciju mogu djelomično iskoristiti obje granične faze, koje je moguće eksperimentalno definirati. Da se mogu predočiti bitni elementi tog prelaznog i tipično metoričnog sloja, upotrebljene su neke koncepcije Bjerrum-ove teorije o jonskoj asocijaciji, te je dana predožba o jonskoj raspodjeli pomoću sfera disocijacije i ljusaka asocijacije pojedinačnih jona u otopini. Za jednostavne, neutralne i simetrične elektrolite udaljenost između centara jonskih sfera može se izračunati jednostavnim dijeljenjem elektrolitnog volumena s ukupnim brojem jona, dok je za debljinu asocijacionih ljusaka predpostavljena ona udaljenost, kod koje je coulombsko privlačenje jona jednako dvostrukom iznosu energije jona s obzirom na termičku agitaciju. Kemijski aktivni joni karakterizirani su kod takovog načina prikazivanja većom debljinom ljuske, koja predstavlja vjerojatnost asocijacije.

Pokazano je, da debljina metoričnog sloja kod ugrađivanja samo jednog jonskog sloja u kristalnu rešetku može iznositi (već prema topivosti) od nekoliko desetaka do nekoliko tisuća ångströmovih jedinica. Takovim je prilikama moguće tumačiti neke periodičke pojave, koje su primjećene kod rasta kristala.

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Primljeno 9. prosinca 1949.