

CRYSTAL GROWTH

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A GENERAL DISCUSSION
ON
CRYSTAL GROWTH

12th - 14th April, 1949

A GENERAL DISCUSSION on Crystal Growth was held in the Department of Physics, Bristol University (by kind permission of the Vice-Chancellor) on the 12th, 13th and 14th April, 1949. The President, Prof. Sir John Lennard-Jones, K.B.E., F.R.S., was in the Chair and over 300 members and visitors were present.

Among the distinguished overseas members and guests welcomed by the President were the following :—

Prof. R. Becker (Göttingen), Dr. G. Berkhoff (Geleen, Netherlands), Dr. H. de Bruijn (Geleen, Netherlands), Prof. C. Correns (Göttingen), Dr. P. H. Egli (Washington, D.C.), Dr. P. Franzen (Delft), Dr. W. Gaade (Amsterdam), Mr. I. J. Haven (Eindhoven), Prof. R. Hocart (Strasbourg), Ir. Th. J. J. Hoek (Geleen, Netherlands), Dr. A. N. Holden (Murray Hill, N.J.), Prof. A. Juliard (Brussels), Dr. D. W. van Krevelen (Geleen, Netherlands), Dr. W. C. McCrone (Chicago), Ir. W. May (Delft), Mr. W. M. Mazee (Overleen, Netherlands), Mlle. M. Michel-Lévy (Paris), Dr. S. O. Morgan (Murray Hill, N.J.), Dr. M. H. R. Plusjé (Geleen, Netherlands), Dr. and Mrs. A. H. Spong (Cape Town), Dr. E. W. R. Steacie (Ottawa), Prof. D. C. Stockbarger (Cambridge, Mass.), Prof. I. N. Stranski (Berlin), Dr. C. E. Sunderlin (U.S. Navy, London), Ir. E. Sweep (Amsterdam), Miss M. G. Ter Horst (Leeuwarden, Netherlands), Mr. R. S. Titchen (Paris), Mr. H. P. J. Wijn (Eindhoven), Dr. J. Willems (Krefeld) and Dr. S. Zerfoss (Washington, D.C.).

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GENERAL INTRODUCTION ON CRYSTAL GROWTH

BY W. E. GARNER

Received 31st January, 1949

In the earlier investigations the two aspects of the growth of crystals, the initiation of crystallization and the rate of growth, were developed independently. It is now realized that each plane of atoms or molecules added to the crystal may involve a fresh initiation of crystallization, and that the rate of crystallization is dependent on the rate of nucleation on the crystal surface. This means that in the fundamental treatment of crystal growth, the two sections are inseparable, and this has been recognized in the grouping of papers for this Discussion.

In this introduction, which is mainly historical, the gradual evolution of the present outlook is indicated. Interest in this field has been accentuated by important applications in industry and a brief survey of these applications is included.

Initiation of Crystallization. Throughout the nineteenth century there was much interest in the crystallization of supersaturated solutions, for example, of solutions of Glauber's salt, magnesium sulphate, vitriols, etc. Boisbaudron found that spontaneous crystallization took place only in strongly supersaturated solutions and de Coppet, by cooling solutions, determined the limits of solubility at which spontaneous crystallization begins. Ostwald developed the idea of a metastable zone on the solubility diagram showing the limits within which no crystal nuclei could form spontaneously. This theory proved to be of considerable practical importance at the time in explaining some of the phenomena of precipitation and of Liesegang rings.

Much attention was paid to the limiting size of particle needed to start crystallization in the metastable zone, and rough estimates gave a minimum size of 10^{-9} – 10^{-12} g. The thermodynamic criteria developed by Willard Gibbs in 1878 which were applicable to this problem were not very early appreciated, with the result that for a long period the approach to the subject was empirical in character.

Tammann's work on the initiation of crystallization in undercooled organic liquids and inorganic glasses was of the greatest significance and settled many doubtful points. By making counts of nuclei under controlled conditions, he showed that the formation of nuclei obeyed the laws of probability and that the maximum probability occurred at temperatures 40° – 120° below the melting point, where the liquids begin to lose their mobility and show marked changes in viscosity. There was a zone of about 20° , below the melting point, where nuclei formation was very slow, which corresponded to the metastable zone found with supersaturated solutions. Tammann showed that nuclei could be formed in this zone if the observer would wait long enough for them. He thought, however, that there might be a metastable region a few tenths of a degree below the melting point, due to an increase in solubility resulting from a decrease of particle size. He also found that the rate of nuclei formation became very slow in the glassy state of undercooled liquids, where the viscosity was very high.

Tammann considered that since the formation of a nucleus was a very rare event, a large number of molecules must meet under limiting conditions o

velocities, orientation and direction of movement, before a nucleus can be formed. The process was so complicated that any simple relations between the probabilities and the stabilities of the forms produced were not to be expected. He concluded that Ostwald's Law of Stages was not universally applicable.

Willard Gibbs showed that a spherical particle of phase II, $p = p''$, was in equilibrium with a continuous phase I, $p = p'$, when $r = \frac{2\sigma}{p'' - p'}$. The equilibrium is, however, unstable, for if r is slightly reduced, the particle will decrease in size and finally disappear, and if it be slightly extended it will grow until phase I completely disappears. The work done in the creation of a particle of phase II in phase I is always positive up to the value of $r = \frac{2\sigma}{p'' - p'}$, so that phase I is stable with respect to nuclei formation so long as r is of such magnitude for the surface tension equation to apply. It will break down as r approaches molecular dimensions and $p'' \gg p'$. It would be expected, therefore, that for an undercooled liquid there would be a metastable region for phase I, where spontaneous nuclear formation could not occur, and a metastable limit below which the system became labile owing to r approaching molecular dimensions.

Haber employed the Thomson equation,

$$\frac{T_s - T_r}{T_s} = \frac{2\sigma M}{rQ_s\rho}$$

in a theoretical examination of the crystallization of supercooled liquids. T_s is the melting point, T_r the melting point of a nucleus of radius r , σ the interfacial energy, Q_s the heat of crystallization, ρ the density of the solid phase, and M the molecular weight. He postulated a *Spurenschmelzpunkt* as the melting point of the smallest ordered aggregate, which determined the temperature of the metastable limit.

These considerations of Gibbs and Haber will, however, be modified if there be taken into account the local fluctuations of energy which occur in any fluid and which have been demonstrated in the phenomena of critical opalescence. These local fluctuations will facilitate the formation of nuclei and render the metastable limit less sharp, although the conception of a metastable zone is still of some practical value.

Rate of Growth. Tamman's researches on the crystallization of supercooled liquids show that the rate of crystallization is very slow down to about 30° below the melting point, increasing to a maximum which is often flat, and falling off as the viscosity increases to that of a glass. The maximum for the rate of crystallization lies at higher temperatures than for nucleation. The low values just below the melting point are due to the slow removal of heat of crystallization. Tamman concludes that the rate is at its maximum when the temperature of the melt is

$$T = T_0 - q_0/c_m,$$

where T_0 is the melting point, q_0 the heat of crystallization, and c_m the mean specific heat.

Surface Flow. Studies of the growth of crystals from the gaseous phase indicate that the flow of molecules over the surfaces of the crystals plays an important role in the rate of crystallization. Volmer and Estermann showed that mercury crystals formed from the vapour consist of very thin flat plates, and that the rate of extension of the main faces can only be accounted for if the molecules colliding over the whole surface of the crystal are available for the growth of the very small areas at right-angles to the basic planes. This requires that the surface flow of a molecule during its

lifetime on the surface is of considerable magnitude. The work of Becker and of Taylor and Langmuir on adsorbed caesium on tungsten, and of Bosworth on potassium on tungsten, at temperatures where the evaporation of the adsorbed atoms is low, shows that the atoms undergo activated diffusion along the surface. For caesium the number of sites covered during the lifetime is at least 10^8 . Also, Newman has demonstrated that activated diffusion occurs on the surface of heated sodium chloride crystals. The experiments of Volmer and Adikari on the surface flow of benzophenone on glass and of Kowarski on *p*-toluidine over a crystal of the same substance illustrate the same principle.

The extension of this principle to crystallization from supersaturated solutions and from undercooled melts is unavoidable, since in general the work required to move a molecule or ion along the surface is less than that to transfer it to the liquid phase.

The Repeatable Step. The energies required to remove ions or molecules of sodium chloride from the surface of a crystal into the gaseous phase have been calculated by Kossel and Stranski for the corner, edge and various surface positions. Homopolar lattices have been dealt with similarly by the same authors and by Becker and Döring. The difference between the energies for the various sites is sufficiently great to have an important bearing on the kinetics of crystal growth.

In building up a plane of atoms on the surface of a crystal, the greatest energy is liberated at the repeatable step of an uncompleted edge of a covered area. The energy evolved on adsorption on such sites is approximately the same as that resulting from embedding the atom half-way in the crystal. The process of crystallization on surfaces large compared with the atomic diameter consists mainly in the repetition of the 'repeatable step.' The adsorption of atoms singly on the plane surface is much less strong than at the repeatable step. Over part of the range of temperatures for which atoms are firmly held at the repeatable step, those on the main surface are readily desorbed. The surface molecules, however, travel by surface flow considerable distances before they evaporate, and therefore it is to be expected that in favourable circumstances the whole surface of the crystal will act as a collecting ground for the repeatable step.

Two-dimensional Nuclei. The rate of evaporation is greatest if the adsorbed molecules are held singly on the surface and least when held at a repeatable step on a two-dimensional nucleus, the size of which is above a critical value. In the building-up of new crystal planes, the average time taken to complete a two-dimensional nucleus of this critical size may be considerably greater than that required to complete the plane of molecules by a succession of repeatable steps. Volmer, for iodine crystals growing from vapour, concludes that the formation of the two-dimensional nucleus is such a rare event that the probability of its occurrence determines the velocity of crystallization.

Crystals grow the more regularly the lower the supersaturation. At high supersaturations polymolecular sheets are built up, giving a series of steps on the faces of crystals which can be detected by interference colours (Marcellin, Perrin, Kowarski). These phenomena are of frequent occurrence and are of special interest. Stranski, studying the growth of polished spherical surfaces, shows that the planes with high indices of even simple lattices give uneven surfaces during growth, built up of steps of various heights. It should, however, be borne in mind that some of these phenomena may be due to the discontinuities caused by polishing. It is clear, however, that the mechanism of crystal growth, with complex molecules from strongly supersaturated solutions, can become an involved problem. Phenomena make

their appearance which have not been unambiguously elucidated. It is possible that some of these may be due to Smekal, Zwicky or other types of discontinuity, as suggested by Frank. However, under the simplest conditions, with low supersaturation, the conception of the formation of two-dimensional nuclei aided by surface flow may prove to be adequate for the calculation of rates of growth.

Crystal-Crystal Interface. The nuclei formation in solid phases obeys similar temperature relationships to supercooled melts, giving maxima at temperatures considerably below the melting point. Volume changes on crystallization, producing cracks, are, however, an added complication. Nuclei formation in processes which are accompanied by gas evolution are one step more complicated, but the phenomena obey the same general rules. In a number of cases in which gas evolution occurs, the activation energy is approximately the same as the thermodynamic heat for the process, which implies a close fit between the lattices of the two phases and a very close coupling between the disappearance of the old and the building-up of the new lattice. This may well be the case, in favourable circumstances, for the growth of one crystal phase out of another.

Practical Applications. The need for large crystals free from flaws for spectroscopy, piezoelectric measurements and the various purposes of the electrical industry cannot be met from the diminishing natural resources, nor do these give a sufficient variety. This has led to researches on the methods of accurate control of crystallization from the vapour phase, the melt, from supersaturated solutions and by hydrothermal processes at high pressures simulating those in nature. In the natural processes whereby crystals are formed in the earth's crust, an infinitude of time is available for the manufacture, but on the industrial scale the time available makes it necessary to work at higher supersaturations, where irregularities are the more likely to occur in the crystallization processes.

The control of crystal shape and size by the addition of surface active substances is a requirement in many industries. In the explosives industry particles with as nearly spherical shape as practicable are advantageous from the point of view of flow properties, bulk density, pelleting properties, etc. It is also possible in cases where two solid modifications are produced to prevent the formation of the unstable modification by the use of suitable additives. The control of particle size distribution is also important in the manufacture of materials used as the basis of products with good plasticity. The tendency of hygroscopic substances to cake can often be reduced by paying attention to crystal shape, choosing that shape which gives a minimum of contacts between the grains.

The surface agents may operate by adsorption on one set of faces, either reducing or preventing growth, as is found by the use of certain dyestuffs. These agents may operate by retarding all growth except in one direction, thereby giving spherulitic growths. The detailed mechanism by which they act is not yet elucidated, although it can readily be seen from current ideas on crystal growth that the effects of adsorption at the repeatable step would have important consequences.

There are many processes in which crystallization is the final stage, giving the product its essential properties. Such are the manufacture of cements, bricks, ceramics, etc. Although in these cases the crystallization process is often accompanied by chemical change, the mechanism involves the nucleation by crystals and the growth of crystals such as occurs for the simpler processes, and their study will benefit by the development of the fundamental theory of crystal growth.

The University, Bristol.

I. THEORY OF CRYSTAL GROWTH

Introductory Paper

By N. F. MOTT

Received 7th March, 1949

The theory of crystal growth can, it seems to me, conveniently be divided into three parts. These are :

(a) The theory of the rate of growth of a surface in contact with a vapour or solution with a given degree of supersaturation. Or, in the case of a crystal growing from the melt, the theory of the rate of growth for a given degree of supercooling. This will include a discussion of the rates of growth of different crystal faces, and the effect on growth rates of impurities which may be adsorbed on the surface, and of imperfections in the crystals themselves. The solution of the problems under this heading depends, of course, on a knowledge of interatomic forces.

(b) The use of results obtained under the heading (a) to determine crystal forms in as far as they depend in the case of growth from solution, or diffusion of the ions or atoms to be deposited, or in the case of growth from the melt on conduction through the material of the heat liberated. Much of the theory of dendrite formation is included in this category. It forms a part of classical rather than atomic physics, depending as it does on the equations of diffusion and heat flow.

(c) Discussions of the crystal form of the deposit. This will include such problems as the formation during growth of screw or edge dislocations in the crystal ; a solution of these problems is very important for the theory of mechanical strength. Then there is the question of the possible pseudomorphic forms of crystalline films grown on a substrate of different composition ; a contribution to this subject is made by van der Merwe in a paper to be presented to this conference. And, finally, there is the question of the state of strain and possible cracking of the surface layer treated by Molière, Rathje and Stranski.

(a) Atomic Theory of Growth. The elements of a theory of crystal growth have been laid down by Volmer, Stranski, Becker and Döring, and new contributions made by Frank, Burton and Cabrera (for references, see the contribution of F. C. Frank to this Discussion). This theory applies explicitly to growth from the vapour ; but can probably be applied in principle to growth from solution. The problem of growth from the melt remains an open question.

The elements of the theory of growth are as follows : consider a flat crystalline surface of low indices (say, (100) for a simple cubic or (111) for a close-packed structure) in contact with a vapour. Suppose this surface is partly covered by another layer. Then if the pressure of the vapour is raised by a small amount Δp above the equilibrium vapour pressure, theory indicates that the layer will grow, with a speed proportional to Δp , until it covers the surface. But in order to start a new layer, a two-dimensional nucleus must be formed, and, like other nucleation phenomena, the rate of nucleation varies with Δp as $e^{-A/\Delta p}$, where A is a constant at given temperature. It follows that when Δp is below some critical value the rate is negligibly small.

It seems likely that the growth rate depends in general on the rate of nucleation, at any rate for surfaces of low indices ; for surfaces of high indices, having a step-like formation anyhow, nucleation is much easier.

But such surfaces of high indices will, of course, by growing quickly tend to disappear, leaving a crystal surrounded by planes of low index only.

It should be emphasized that a flat surface in contact with vapour will have a number of atoms adsorbed on it. Two-dimensional nucleation can occur whether or not these are mobile over the surface; it is not at present quite certain whether their mobility affects the rate of nucleation.

Among the papers presented to this Discussion, Becker gives a valuable account of the relation of his theory to Mayer's theory of condensation. Burton and Cabrera, in a paper to be published elsewhere, have made some refinements to the present theory by calculating the shape of the two-dimensional nucleus when it has reached the size beyond which it will normally spread. This puts the theory on a firmer footing, and does not alter the numerical values very much. Frank points out that the theory suggests a growth rate which is negligibly small unless the supersaturation of the vapour is of the order 1.5, and that this is contrary to experiment, in particular to the results of Volmer and Schultze on the growth of iodine crystals; the degree of supersaturation required is of the order 1.01. He suggests that the presence of dislocations is essential for growth at these concentrations, and that the growth rate depends essentially on the density of dislocations in the material.

Theory has at present made little contribution to our knowledge of habit modification. It does, however, follow that, if dislocations are essential for crystal growth, very small concentrations of impurity, which could be adsorbed preferentially at the "ledge" where the dislocation meets the surface, could profoundly affect growth rates and thus lead to habit modification.

(b) **Phenomena Depending on Heat Flow and Diffusion.** It is believed that dendrite formation in the solidification of liquid metals is due to the fact that a thin needle, growing into a supercooled solution, will need to get rid of less heat by conduction than a thicker one and so will grow faster. In the same way, in the formation of crystals from solution, a thin needle will grow more quickly than a thick one into supersaturated solution. Probably the clue to the step formation observed by Bunn will be found along these lines.

(c) **Physical State of the Crystal as a Consequence of the Mechanism of Growth.** Frank, in his paper, gives some reasons for believing that, at finite growth rates, dislocations will be formed in the crystal. They are in no sense present in thermodynamic equilibrium and ideally a long enough anneal would get rid of them; but, in practice, there appear always to remain a certain number.

Stranski and his colleagues reopen the very interesting question of the state of strain of the surface layer. The origin of the "Griffith cracks," responsible for the low stress for fracture of brittle materials, has never been explained, and it is possible that this work will provide a clue.

In a later section of the Discussion, van der Merwe discusses the crystal structure of thin films deposited on a substrate of differing crystal structure. He shows that the question, whether or not the deposit has a pseudomorphic form, depends on whether the first monolayer conforms to the structure of the substrate or not; and that this in turn depends on the degree of misfit.

Equilibrium Crystal Forms

The study of the shape of a crystal in equilibrium with a vapour forms an interesting field rather apart from the theory of crystal growth. Burton and Cabrera have found that the equilibrium form of the two-dimensional crystalline nucleus on a flat substrate is a rounded polygon, if only one

atomic or molecular unit is involved. For ionic forces, on the other hand, it appears that the two-dimensional nucleus may have sharp corners. In the case of three dimensions Stranski has shown that the corners of a crystal are rounded off through the presence of a *finite* number of planes of higher index, and so are not truly rounded.

The microstructure of the surface in equilibrium with vapour or solution is also of interest. As already stated, a flat surface will always contain some adsorbed atoms, and there will always be some vacant lattice points. Burton and Cabrera have made an investigation of the concentration of "Frenkel terraces" on a surface in equilibrium. For faces of low index, there will be practically none for a perfect crystal; any which exist depend on the presence of dislocations. A crystal temperature exists, however, at which they form, but this will in general be above the melting point.

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FORMS OF EQUILIBRIUM OF CRYSTALS

By I. N. STRANSKI

Received 17th February, 1949

A knowledge of the forms of equilibrium of crystals is important for an understanding of the processes on crystal surfaces, independent of whether the crystal is immediately concerned in these, or merely functions catalytically. Furthermore, a comparison between theoretically and experimentally deduced forms of equilibrium makes it possible to check the assumptions used in the former, and supplies valuable clues to alteration in structure and changes within the individual lattice surfaces.

The following observation should first be made. The theoretical treatment falls into two parts. First the underlying ideas must be developed, then the mathematical work can be started. This is directed by the knowledge at the time of the force functions, and must of necessity bring new problems in its train. In the following I will confine myself to the part dealing with the underlying ideas.

The treatment of the forms of equilibrium of crystals has been developed on the basis of two fundamentally different ideas. The older one, historically, made use of an analogy to liquid surfaces. The surface tension here was replaced by the idea of the specific surface energy σ .

The values of σ for crystals are dependent upon direction, so that in general the form of equilibrium is a polyhedron which must satisfy Gibbs' condition:

$$\Sigma \sigma_i \cdot F_i = \text{minimum, at constant volume.}$$

If one ignores the edges and corners, it is known that here, also, one arrives at the same relation as for vapour pressure, which is completely analogous to Thomson's equation and has the following form¹:

$$\frac{kT}{2v_0} \ln \frac{p_r}{p_\infty} = \frac{\sigma_1}{r_1} = \dots = \frac{\sigma_i}{r_i} = \dots \quad (1)$$

¹ The following recent papers on the Thomson-Gibbs relation are mentioned:
Volmer, *Kinetik der Phasenbildung* (Dresden and Leipzig, 1939), p. 87 *et seq.*
v. Laue, *Z. Krist.*, 1943, **105**, 124.
Stranski, *Z. Krist.*, 1943, **105**, 91.
Honigsmann, Molière and Stranski, *Ann. Physik*, 1947, **1**, 181.

v_0 represents the volume of a crystal unit and r_i the centre distance, σ_i the specific surface energy of the i -th face. p_r and p_∞ are the sublimation pressures of the finite- and infinite-sized crystals respectively. Wulff's method for the construction of equilibrium forms of crystals follows directly from eqn. (1).

An exact relation, capable of general application, cannot be derived in this way. For if we wish to take into account the fact that the crystal also possesses edges and corners, and that the specific surface energy and the specific energy of the edges and corners which must further be introduced, possibly depend on the size of the crystal as well, a relation can only be derived at first for simplified models. This is to be shown in the following for the case where the form of equilibrium of the crystal is represented by a simple crystalline form, i.e., it is surrounded by only one kind of face. For this purpose let us refer to the definition of the specific surface energy, and give the definition of the specific edge and corner energies in reference to Born and Stern.²

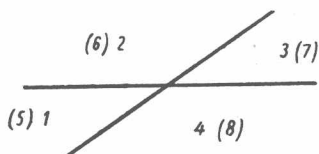


FIG. 1.—Division of a crystal by three planes. Two of these are shown as lines where they cut the plane of the diagram, the third lies in the diagram plane itself. The figures in brackets denote the sections below the plane of the diagram, those without brackets the sections above it.

The specific edge energy κ is defined as the work which must be done in order to separate the crystal sections 1 and 3, 2 and 4 respectively (see Fig. 1), divided by twice the length of the edge, and given a negative sign. Correspondingly, the specific corner energy ε is half the work required to separate two crystal sections situated diagonally in space, with their corners touching, e.g., 1 from 7, or 3 from 5 (see Fig. 1).

Assuming that these values are independent of the dimensions of the crystal, one obtains in place of eqn. (1):

$$\frac{kT}{2v_0} \ln \frac{p_r}{p_\infty} = \frac{\sigma}{r} + \frac{\kappa}{2r^2} \quad (2)$$

Thus, as a result of the existence of edges, an additional term appears as correction. The corners are without influence.

In order to be able to discuss the dependence of the values σ , κ and ε upon the size of the crystal at all, the definitions of these values for finite crystals had first to be found. The definitions given by me at that time³ will be explained for a simple case with the aid of Fig. 2. If the form of equilibrium is represented by a cube, σ_a is equal to the work of separating such a small crystal from a cube face of the infinite crystal, divided by twice the area of one cube face of the small crystal. κ_a is correspondingly equal to the work of separating such a cube from the infinite crystal quadrant lying diagonally opposite divided by twice the length of a single edge and

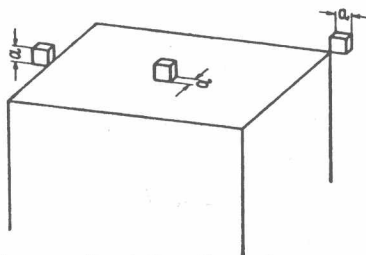


FIG. 2.—To define the values σ_a , κ_a and ε_a for a finite crystal cube with an edge-length a .

² Born and Stern, *Ber. Berlin Akad.*, 1919, 48, 91; Stranski, *Z. Krist.*, 1943, 105, 287.

³ Stranski, *Ber. Wien. Akad., math.-naturwi. Kl.*, 1936, IIb, 145, 840; *Mh. Chem.*, 1936, 69, 234.

with a negative sign. Lastly the corner energy ϵ_a is equal to half the work of separating a small crystal from the infinite crystal octant lying diagonally opposite in space. Thus the total surface energy of a small crystal with edges of length a is

$$\Phi_a = 6a^2\sigma_a + 12a\kappa_a + 8\epsilon_a. \quad (3)$$

In this case it is possible to obtain the form of equilibrium of a small crystal simply by taking an infinite crystal to pieces, and Φ_a can also be defined as the work of separating a small crystal from a crystalline half-crystal position (see Fig. 3). However, it should be mentioned that Φ_a is generally given in the following relation:

$$\Phi_a = N_a \cdot \varphi_{1/2} - \sum_{\nu=1}^{N_a} \varphi_{\nu}. \quad (4)$$

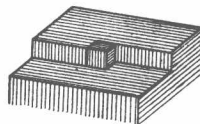


FIG. 3.—Crystalline half-crystal position. Φ_a is equal to the work of separation of the crystal cube with edge-length a , in the half-crystal position, as shown in the diagram.

$\varphi_{1/2}$ is the work of separating a crystal unit from the half-crystal position (see below). The second term is the work obtained in building up the small crystal from its N_a individual crystal units.

The example dealt with in the last section is especially simple. The important thing is, that this case already shows that it is not possible to specify the exact sublimation pressure of a small crystal from the forms of equilibrium, with the aid of the values σ_a , κ_a and ϵ_a , now assumed to be variable.

For this purpose, the differentiation of the eqn. (3) is necessary:

$$kT \ln \frac{p_a}{p_\infty} = \frac{d\Phi_a}{dN} = 12\sigma_a a \frac{da}{dN} + 6a^2 \frac{d\sigma_a}{dN} + 12\kappa_a \frac{da}{dN} + 12a \frac{d\kappa_a}{dN} + 8 \frac{d\epsilon_a}{dN}. \quad (5)$$

The values Φ_a , σ_a , κ_a and ϵ_a would thus have to occur as continuous functions of the number of crystal units N . That is not the case, however, for they present themselves as a series of isolated points.

The following possibilities can be discussed. (1) Curves are drawn through these points and differentiated. The result could give the sublimation pressure with sufficient exactitude. (2) The dependence of the values σ_a , κ_a and ϵ_a upon N can be found to be so small that it can be neglected. Neither possibility, however, can be proved for no standard of comparison exists at present, which gives us the correct pressure values. We will return to these questions below.

The advantages of the method using the values σ , κ and ϵ are not to be denied, for by means of it, all considerations which had been made on liquid systems could be applied in a comparatively simple way, and with little alteration, to crystal systems. Special attention is here drawn to the fact that, on the whole, Volmer's theory on the frequency of nucleus formation⁴ also reproduces the conditions correctly for crystal systems. By continuing the nucleus idea, introducing, namely, the idea of a two-dimensional nucleus, the growth of a crystal could be submitted for the first time to a mathematical method. Many different questions could be answered comparatively simply. The interpretation of Ostwald's step-rule may be mentioned as an example.⁵

But the disadvantage of this method must also be enumerated. The values σ , κ and ϵ do not refer at all to elementary stages of growth and reduction, and the relations which are obtained with their aid can only be applied under certain conditions to kinetic considerations on crystals, and remain difficult to visualize. As is known, the application of Thomson-Gibbs'

⁴ Volmer and Weber, *Z. physik. Chem.*, 1926, **119**, 277; Volmer, *loc. cit.*

⁵ Stranski and Totomanow, *Z. physik. Chem. A*, 1933, **163**, 399.

equation has led to numerous, and often crass, misunderstandings. This method, by simulation of completion, has also prevented many equilibrium questions from being asked and answered at the right time.

The second treatment began to take form as a result of work by Kossel⁶ on the one hand, and myself on the other.⁷ The work of separating individual crystal units from the crystal surface was estimated, NaCl being taken as the first example, and with the help of this it was possible to draw a picture of the molecular processes connected with growth and solution. The logical starting point for these considerations is the determination of the length of time a crystal unit remains in the so-called half-crystal position.

The crystal unit in the half-crystal position possesses a work of separation which amounts to half of that of a crystal unit in the inside of the crystal. It is thus equal to the negative value of the lattice energy per crystal unit, and determines the vapour pressure of the infinite-sized crystal. Elementary reasons can be given for this conclusion if the position of growth of a repeatable growing crystal face is chosen as model of the half-crystal position. For, in this case, the position as such is retained after any number of separations or addition of crystal units. Thus the crystal would only be in equilibrium with its surroundings, if the probability of a separation of a crystal unit from the half-crystal position is found to be equal to the probability of an addition on this.

With the help of the different works of separation, it has already been possible to draw a series of conclusions which, at that time, were justifiably regarded as completely new-fangled. Only as a consequence of these was it asked whether certain faces in equilibrium can be retained as such, or whether their surface structures would have to undergo alterations of a coarsening nature.

It should be emphasized here that these questions could have been asked earlier, as a result of the determination of the values, or merely the signs, of the specific peripheral energies of the lattice surfaces concerned. That they have not been asked up to this time is to be explained exclusively by the fact that the older theories were difficult to visualize.

Because of its importance the criterion might be given here by reason of which one can decide whether a certain face appears in the equilibrium form of the infinite-sized crystal or can remain as crystal face. If the specific peripheral energy of this lattice face shows the value zero or a negative value, in one direction only, this face cannot appear as a form of equilibrium. Should this condition be fulfilled for one direction only, the face concerned will grow over one-dimensional nuclei and show a typical chain formation. A chain formation alone, on the other hand, is not sufficient argument against the face belonging to the equilibrium form. If this condition is fulfilled for two directions, the one-dimensional nucleus formation is also eliminated. An example of the first case is (011) on the NaCl crystal and of the second, (111) on the same crystal.

Another question could also be answered with the help of the work of separation, namely, with what kind of face must the infinite-sized crystal be surrounded? For it is evident that the only possible form of equilibrium is one in which all corner crystal units are bound at least as firmly as in the half-crystal position. So that by starting with a simple form, and systematically removing all crystal units which are less firmly bound, one could arrive at forms which no longer exhibit such crystal units, and which then mirror the equilibrium form, in that they possess all the faces of same.

In order to arrive at an expression which represents the sublimation

⁶ Kossel, *Nach. Ges. Wiss. Göttingen*, 1927, 135; *Leipziger Vorträge*, 1928, 1.

⁷ Stranski, *Z. physik. Chem.*, 1928, 136, 259.