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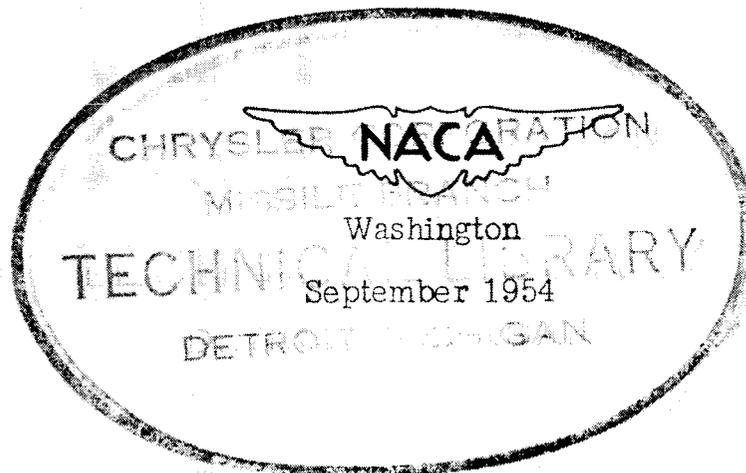
# NATIONAL ADVISORY COMMITTEE FOR AERONAUTICS

TECHNICAL MEMORANDUM 1374

KINETIC TREATMENT OF THE NUCLEATION  
IN SUPERSATURATED VAPORS

By R. Becker and W. Döring

Translation of "Kinetische Behandlung der Keimbildung in übersättigten  
Dämpfen," Annalen der Physik, Folge 5, Band 24, 1935.



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## INTRODUCTION AND SYNOPSIS

The "nucleation in supersaturated systems" (such as the formation of fog in supersaturated water vapor, for example) was originally made amenable to quantitative treatment by Volmer and Weber (ref. 1). To every saturation there corresponds a certain critical droplet size of the new phase of such a type, that the vapor is supersaturated only with respect to those droplets which are bigger than the critical droplet, but not to those which are smaller. The formation of fog is therefore contingent upon the origin of "kernels" or nuclei, i.e., droplets of precisely that critical size by a typical phenomenon of fluctuation. The frequency of such processes is, according to the relationship between entropy and probability, proportional to  $e^{-\frac{A_{crit.}}{KT}}$ , where  $A_{crit.}$  is the energy required for the reversible creation of such droplet. Volmer's treatment is briefly reviewed in section 1. The proportionality factor  $K$ , as yet indeterminate (in our equation (5)), was calculated by Farkas (ref. 2) for the case of droplet formation by a kinetic treatment, the results of which are fully confirmed (in section 2) by a more lucid method of calculation. The drawback of Farkas' calculations, as well as the arguments advanced by Stranski and Kaischew in connection with it (ref. 3), is that these writers' first convert the elementary equations of the kinetic theorem, each of which refers to the evaporation and condensation of a single molecule, in a differential equation which, when integrated, produce new and not always lucid constants. The change to the differential equation is risky because the ensuing functions of the molecule number  $n$  are at first defined only for integral values of  $n$  and at the transition from  $n$  to  $n + 1$  change frequently so much that the differential quotient loses its significance. By disregarding this risk Kaischew and Stranski obtained an incorrect result which differs from that of Farkas. On the other hand, the change into differential equation is entirely unnecessary (as will be shown in section 2). The algebraic equations for the individual processes give the wanted result by a simple, purely algebraic process of elimination. This method is shorter and less subject to errors than that of Farkas. Furthermore, the appearance of indeterminate

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\*"Kinetische Behandlung der Keimbildung in übersättigten Dämpfen,"  
Annalen der Physik, Folge 5, Band 24, 1935, pp. 719-752.

integration constants is completely avoided. Thus Farkas' final formula, for example, still contains a constant which he himself designates as indeterminate, while in reality, an accurately estimable value corresponds to it, which is in optimum agreement with the Volmer and Flood measurements.

The next three sections deal with the origin of critical nuclei, to which the general thermodynamic analysis of section 1 is applicable as for the droplets.<sup>1</sup> The first kinetic calculation of the thermodynamically indeterminate quantity  $K$  for crystals was made by Kaischew and Stranski (ref. 4). This important investigation prompted the present study. With regard to the highly idealized crystal model, use is made of the simple cubic lattice, utilized by Kossel as well as by Stranski, which consists of nothing but cubic basic elements, which are in energetic reciprocal action only with its six nearest neighbors. However, our results are largely independent of this special model conception. The kinetic analysis, like that of Stranski and Kaischew, results in a confirmation of Volmer's formula. On top of that, we succeeded in defining the absolute value of  $K$  for this case too.

Our algebraic method of eliminating the intermediate states not of direct interest affords an instructive representation suitable for the discussion of the particular nucleation process on the passage of an electric current through a network of wires of specific electric potential differences at the ends of the network and given ohmic resistances of the individual wires forming the network.<sup>2</sup>

The whole discussion of the system of algebraic equations is then equivalent to an investigation of the conductivity properties of this network. This method produces in sections 4 and 5 a comparatively simple and clear calculation of nucleation frequency for two- and three-dimensional nuclei.

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<sup>1</sup>Kossel's contrary opinion (Ann. d. Phys. (5), 21, p. 457, 1934) stems from a misconstrued conception of the nature of thermodynamic considerations, which never refer to individual molecules but to those average values which in technically feasible experiments, come under observation. For example: the work of separation of the single molecules in a lattice plane may jump back and forth arbitrarily; but in the evaporation of the total lattice plane, only the mean separation work enters the balance of the thermodynamic process as heat of evaporation.

<sup>2</sup>The possibility of such a representation was originally voiced by R. Landshoff in a conversation. Another, even more instructive representation is that of a diffusion process. (Cf. Volmer, Z. f. E., 35, p. 555, 1929.) But for the purposes of a quantitative treatment, our electrical pattern should be superior to the diffusion pattern, especially when a change from droplet to crystal is involved.

As an example for the application of the obtained results, the explanation and limits of validity of Ostwald's step rule are discussed in section 6. Lastly (section 7), mention is made of the unusual and rather general fact that in our electrical representation of the process of growth the resistances of all separate wires, which start from a specific state in the direction of growth, are given exact by  $\text{Constant} \times e^{+\frac{A}{kT}}$ , where  $A$  is thermodynamic potential of this state with respect to the initial state (vapor, for instance). The kinetic interpretation of Volmer's formula (5) amounts then to indicating that the total resistance of the network is dependent solely on those pieces of wire which lie in the region of the point related to the critical droplet or crystal.

### 1. THERMODYNAMICS OF NUCLEATION

If  $n$  denotes the number of molecules contained in a droplet,  $F$  its surface and  $\sigma$  its surface tension, the relationship between its vapor pressure  $p_n$  and that of a flat fluid surface ( $p_\infty$ ) reads

$$dnkT \ln \frac{p_n}{p_\infty} = \sigma dF \quad (1)$$

where  $dn$  is the increase in the number of molecules corresponding to the surface increase  $dF$ . With the radius  $r_n$  of the droplet for spherical shape

$$n = \frac{4\pi}{3} r_n^3 \frac{\rho}{m} \quad \text{and} \quad F = 4\pi r_n^2$$

hence

$$\ln \frac{p_n}{p_\infty} = \frac{2\sigma m}{kT\rho} \frac{1}{r_n} \quad (2)$$

$r_n$  is the critical droplet radius corresponding to the pressure  $p_n$ . At given pressure, droplets with smaller radius evaporate, those with larger radius grow. A droplet which is exactly in equilibrium with a given pressure, according to equation (2), is hereinafter also designated as critical droplet or as nucleus corresponding to the particular pressure. A condensation of the supersaturated vapor can therefore take place only when a nucleus originates as a result of a fluctuation phenomenon associated with entropy decrease.

According to the Boltzmann relationship between entropy and probability, the probability for the appearance of such a droplet is

proportional to  $e^{-\frac{S}{k}}$ , where  $S$  is the entropy decrease associated with the formation of a droplet of radius  $r_n$  from a vapor of pressure  $p_n$  at constant volume and constant energy. If the number of molecules contained in the vapor space is excessively great with respect to  $n$ , this entropy decrease is equal to  $1/T$  times the work  $A$  that must be performed in order to produce such a droplet in the vapor space isothermally and reversibly. This work can be determined, according to Volmer, by the following process:

1. Removal of  $n$  molecules from the vapor space
2. Expansion of  $p_n$  to  $p_\infty$
3. Condensation on a flat fluid surface
4. Formation of droplet from the fluid

The sum of these four operations must give the wanted quantity  $A$ ; but (1) and (2) compensate one another, which leaves

$$A = -nkT \ln \frac{p_n}{p_\infty} + \sigma F$$

Hence, with equation (1) borne in mind

$$A = \sigma F \left( 1 - \frac{n}{F} \frac{dF}{dn} \right) \quad (3)$$

Since  $F = \text{Constant} \times n^{2/3}$ , it follows that  $\frac{n}{F} \frac{dF}{dn} = \frac{2}{3}$ , that is

$$A = \frac{1}{3} F \sigma \quad (4)$$

For the number of fog droplets produced per second, denoted hereafter by the letter  $J$ , we therefore expect

$$J = K e^{-\frac{\sigma F_n}{3kT}} \quad (5)$$

where  $F_n$  is the surface of the critical droplet corresponding to the given pressure  $p$ . The factor  $K$  still remains indeterminate in the thermodynamic study, and must be defined by kinetic analysis as originally made by Farkas. The subsequently chosen method of computing  $K$

is clearer from the methodical point of view. Aside from that, the origin of crystal nuclei is to be treated also for which this equation (5) must, naturally, be applicable too. It will be seen that the factor  $K$  for fluid nuclei and crystal nuclei of equal order of magnitude is given by the gas kinetic collision factor.

Regarding the differential quotient  $dF/dn$  in equations (3) and (1), it should be noted that  $dF/dn$  is the mean growth of surface in the development of a molecule. For in the thermodynamic equation (1),  $dn$  still must always contain a multiplicity of molecules, although the equation is inapplicable as yet to single molecules. If this averaging of surface growth per molecule is not carried out over a greater number of molecules, the surprising result is that the concept of vapor pressure loses its simple meaning for crystals, as shown by Kossel (ref. 5), because the increase of crystals in the growth of a molecule is mostly zero, but now and again very great too.

## 2. FLUID NUCLEI

Consider the following quasi-stationary condensation process. The vapor pressure  $p$  in a very large tank is kept constant by addition of single molecules. Droplets are then produced continuously which would increase infinitely without outside interference. To prevent this, each droplet, as soon as a certain number  $s$  of molecules is reached, shall be removed from the tank and counted.

With regard to  $s$  it is simply stipulated that it shall be greater than the critical number  $n$ . The number of droplets per second counted under these conditions is termed "nucleation frequency."<sup>3</sup> In this procedure, a steady distribution of droplets of various sizes will occur within the tank, which must be examined a little closer. Suppose that  $Z_v$  is the number of droplets containing exactly  $v$  molecules. The number of free vapor molecules kept constant in our tank by addition is then  $Z_1$ , while  $Z_s$  is held to zero. If  $J$  is the number of droplets counted per second,  $J$  may be regarded as a constant current that passes through all  $Z$ .

Next, assume that:

$q_v dt$  is the probability that in time interval  $dt$ , one molecule will leave  $1 \text{ cm}^2$  of the surface of a drop of  $v$  molecules,  $a_0 dt$  on the

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<sup>3</sup>This term coined in the literature is somewhat misleading insofar as the actual number of nuclei formed per second is exactly twice as great because there is precisely a 50 percent probability for each nucleus to continue to grow or to evaporate.

other hand is the probability that one molecule from the vapor space condenses on a surface of  $1 \text{ cm}^2$ ,  $F_v$  is the surface of a droplet with  $v$  molecules, and  $Z_v' = Z_v F_v$  is the total surface of all droplets with  $v$  molecules.<sup>4</sup>

Applied to the constant current we get

$$J = a_0 Z_{v-1}' - q_v Z_v' \quad (\text{for all } v).$$

Indicating

$$\beta_v = \frac{a_0}{q_v} \quad (6)$$

the initial conditions read then

$$Z_v' = Z_{v-1}' \beta_v - \frac{J}{a_0} \beta_v \quad (7)$$

The factors  $\beta$  introduced by equation (6) increase monotonic with increasing  $v$ . For the critical molecule number  $v = n$ ,  $\beta_n = 1$ . If  $r_v$  denotes the radius of the droplet with  $v$  molecules, then, by equation (2)

$$\beta_v = \frac{p_n}{p_v} = e^{\frac{2\sigma M}{\rho RT} \left( \frac{1}{r_n} - \frac{1}{r_v} \right)} \quad (8)$$

The factor occurring in the exponent is indicated by

$$\alpha = \frac{2\sigma M}{\rho RT} \quad (8a)$$

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<sup>4</sup>Unfortunately, the notation  $Z_v'$  and  $Z_v$  in the Stranski and Kaischew article are enterchanged relative to Farkas' report. We follow Farkas' notation.

In order to eliminate from the equations

$$\left. \begin{aligned}
 Z_{v+1}' &= Z_v' \beta_{v+1} - \frac{J}{a_0} \beta_{v+1} \\
 Z_{v+2}' &= Z_{v+1}' \beta_{v+2} - \frac{J}{a_0} \beta_{v+2} \\
 &\dots \dots \dots \dots \dots \dots \dots \\
 Z_s' &= Z_{s-1}' \beta_s - \frac{J}{a_0} \beta_s
 \end{aligned} \right\} \quad (7a)$$

the factors  $Z_{v+1}'$ ,  $Z_{v+2}'$ , . . .  $Z_{s-1}'$ , the first is divided by  $\beta_{v+1}$ , the second by  $\beta_{v+1}\beta_{v+2}$ , etc., the last one by  $\beta_{v+1}\beta_{v+2} \dots \beta_s$ . When all the thus obtained equations are added up, all the  $Z'$  values lying between  $Z_v'$  and  $Z_s'$  cancel out leaving

$$\frac{Z_s'}{\beta_{v+1}\beta_{v+2} \dots \beta_s} = Z_v' - \frac{J}{a_0} \left( 1 + \frac{1}{\beta_{v+1}} + \frac{1}{\beta_{v+1}\beta_{v+2}} + \dots + \frac{1}{\beta_{v+1}\beta_{v+2} \dots \beta_{s-1}} \right)$$

With it the nucleation frequency  $J$  is known as soon as one of the values of  $Z'$  is given. In view of the calculations for the crystal nucleus this method of solution is somewhat modified as follows: Through the multiplications equation (7a) takes the form

$$\Phi_{i+1} = \Phi_i - JR_i \quad (9)$$

with

$$\Phi_i = \frac{Z_i'}{\beta_2\beta_3 \dots \beta_i} \quad \text{and} \quad R_i = \frac{1}{a_0\beta_2\beta_3 \dots \beta_i} \quad (9a)$$

The quantity  $\Phi_i$  arises from the corresponding  $Z'$  values by division by the product of all the  $\beta$  values which occur during the successive growth of the droplet characterized by subscript  $i$  from single molecules. (By this method the equations are divided by the common factor  $\beta_2\beta_3 \dots \beta_v$ .) The style of writing (equation (9)) of the equation

system indicates that the current  $J$  flows from point  $i$  toward point  $i + 1$  under the influence of the voltage difference  $\phi_i - \phi_{i+1}$  by overcoming the ohmic resistance  $R_i$ . Visualizing a series connection of resistances  $R_1, R_2, \text{ etc.}$ , the entire nucleation current  $J$  can be regarded as a current driven by a given potential difference through this chain

$$J(R_v + R_{v+1} + \dots + R_{s+1}) = \phi_v - \phi_s$$

Now  $\phi_1$  is directly equal to  $Z_1'$  and  $\phi_s$  equal to zero. The whole problem therefore consists in adding the separate partial resistances. Now it is seen that the individual  $\beta_v$  values increase in such a way that  $\beta_n$  is exactly equal to unity, while the preceding ones are all smaller and those that follow all greater than unity. Up to the value  $R_n$  the partial resistances consist, therefore, of a product of integral factors which are greater than unity; on above  $R_n$  the additive factors appearing are all less than unity. As a result the  $R_i$  values plotted against  $i$  have a distinct maximum at  $i = n$ . Owing to the importance (8) of the quantities  $\beta$  the exact term for a partial resistance  $R_i$  reads

$$R_i = \frac{1}{a_0} e^{\alpha \left( \frac{1}{r_2} + \frac{1}{r_3} + \dots + \frac{1}{r_i} - \frac{i-1}{r_n} \right)}$$

The sum of the reciprocal radii occurring here in the exponent is replaced by an integral with respect to the quantity

$$x_v = \frac{r_v}{r_n} = \left( \frac{v}{n} \right)^{1/3} \quad (10)$$

The integration variable  $x$  indicates, therefore, the ratio of a particular droplet radius to the critical radius. By solution of equation (10) with respect to  $v$

$$v = n(x_v)^3, \quad dv = 3nx^2 dx$$

hence

$$\left( \frac{1}{r_2} + \frac{1}{r_3} + \dots + \frac{1}{r_i} \right) \approx \frac{1}{r_n} \int_{v=1}^i \frac{dv}{x_v} = \frac{3n}{r_n} \int_{x_1}^{x_i} x dx = \frac{3}{2} \frac{n}{r_n} (x_i^2 - x_1^2)$$

In addition

$$i - 1 = n(x_i^3 - x_1^3)$$

Indicating for abbreviation

$$A' = \frac{\alpha n}{2r_n} = \frac{\sigma F_n}{3kT}$$

the term for partial resistance  $R_i$  reads

$$R_i = \frac{1}{a_0} e^{A'} \left\{ (3x_i^2 - 2x_i^3) - (3x_1^2 - 2x_1^3) \right\} \quad (11)$$

Replacing the summation over the partial resistances also by an integration, leaves

$$\int_1^3 R_v dv = 3n \int_{x_1}^{x_s} R(x) x^2 dx = \frac{3n}{a_0} e^{-A'(3x_1^2 - 2x_1^3)} \int_{x_1}^{x_s} e^{A'(3x^2 - 2x^3)} x^2 dx$$

At  $x = 1$  the integrand has a steep maximum of the order of  $e^{A'}$ . Therefore we put  $x = 1 + \xi$ , i.e.,  $3x^2 - 2x^3 = 1 - 3\xi^2 - 2\xi^3$ , and get the integral

$$e^{A'} \int e^{-A'(3\xi^2 + 2\xi^3)} (1 + \xi)^2 d\xi$$

The variation of the integrand is represented in figure 1. The factor  $A'$  is fairly high, say about equal to 20 to 50, in practical cases, as will be shown later. So, without appreciable error the above integral can be replaced by

$$\int_{-\infty}^{+\infty} e^{-3A'\xi^2} d\xi$$

Then, the total resistance ( $3x_1^2 - 2x_1^3$  compared to unity being disregarded in the exponent) reads

$$R = \frac{3n}{a_0} \sqrt{\frac{\pi}{3A'}} e^{A'} \quad (12)$$

With this the thermodynamically obtained expression for the nucleation frequency of the indeterminate constant  $K$  is defined.

The final result is

$$J = \frac{a_0 Z_1'}{n} \sqrt{\frac{A'}{3\pi}} e^{-A'}, \quad A' = \frac{\sigma F n}{3kT} \quad (13)$$

Against this calculation the objection might be raised that the formula (1) had been applied to droplets of as low as two or three molecules, for which the concept of surface tension is certainly perfectly meaningless. But, when considering the curve of the partial resistances in figure 1, it is clear that the resultant total resistance is definitely defined by the partial resistance in the neighborhood of  $\nu = n$ . Therefore it is practically immaterial whether the partial resistances at the start of the chain had been chosen by a factor 100 too great or too small. Equation (13) is exactly identical with Farkas' formula (ref. 2), when bearing in mind that his constant  $C$  on the basis of its introduction (p. 239) has the significance  $Z_1'$ . Since Farkas did not notice that the extrapolation of his formula to droplets of only two or three molecules is positively unobjectionable, he failed to recognize the significance of this constant.

In comparison, the calculation of Kaischew and Stranski (ref. 3) does not seem to be entirely acceptable. They replace  $Z_{\nu-1}' - Z_{\nu}'$  by  $\frac{dZ_{\nu}'}{d\nu}$ , which serves no useful purpose in the subsequent calculation, since no integration along this differential quotient is ever made. It merely obscures the significance of their constant  $C$  which simply is  $-Z_1'$ . But, contrary to Farkas, they use the calculating method of logarithms and subsequent substitution of the differential quotient for the difference quotient for great  $\nu$  also. This certainly is inadmissible in the range of small  $\frac{dZ_{\nu}'}{d\nu}$ , where the logarithmic term changes rather considerable even at minor changes in  $\frac{dZ_{\nu}'}{d\nu}$ .

The formula obtained for  $J$  is now compared with the Volmer-Flood measurements on fog formation at adiabatic expansion of water vapor. The factor  $Z_1'$  is, by assumption, equal to the total surface of the free molecules;  $a_0 Z_1'$  signifies thus twice the number of gas kinetic collisions per second between the  $Z_1'$  vapor molecules. From the mean free path length  $\frac{\lambda}{2}$  and the mean molecular velocity  $v$  the number of collisions per  $\text{cm}^3$  of vapor space follows at

$$a_0 Z_1' = N \frac{v}{\lambda}$$

Since  $\underline{l}$  is inversely proportional to the concentration  $N$ , we get

$$\begin{aligned} a_0 Z_1' &= N^2 \frac{v}{\underline{l}_0 N_0} \\ &= L \sqrt{\frac{8}{\pi R}} \frac{T_0}{p_0 \underline{l}_0} \frac{1}{\sqrt{M}} \frac{p^2}{T \sqrt{T}} \\ &= 5 \times 10^{22} \frac{1}{\underline{l}_0 \sqrt{M}} \frac{p^2}{T \sqrt{T}} \end{aligned}$$

where

$N$  number of vapor molecules per  $\text{cm}^3$

$L$  Loschmidt number

$p$  vapor pressure mm Hg

$\underline{l}_0$  free path length at  $0^\circ \text{C}$  and standard pressure

For the number of molecules in the critical droplet we get

$$\begin{aligned} n &= \frac{4\pi}{3} r_n^3 \frac{\rho}{M} L \\ &= \frac{4\pi}{3} \left( \frac{2\sigma M}{\rho R T x} \right)^3 \frac{\rho}{M} L \end{aligned}$$

whereby  $\ln \frac{p}{p_\infty} = x$ .

For water ( $\rho = 1 \text{ g/cm}^3$ ;  $\sigma = 75 \text{ dyn/cm}$ )

$$n = 240 \left( \frac{T_0}{T} \right)^3 \frac{1}{x^3}$$

For the attainable supersaturations ( $x \approx 1.5$ )  $n$  amounts to about 100 molecules.

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$$A' = \frac{1}{3} \frac{\sigma F_n}{kT} = \frac{4\pi}{3} \frac{L\sigma}{RT} \left( \frac{2\sigma M}{\rho RT x} \right)^2$$

for  $A'$  the formula for  $J$  reads

$$\ln J = 49 + \ln \frac{p_\infty^2 \rho}{L_0 M^3 / 2 \sigma^{3/2}} + 2x + 2 \ln x - 17.7 \left( \frac{\sigma}{T} \right)^3 \left( \frac{M}{\rho} \right)^2 \frac{1}{x^2} \quad (13a)$$

$p_\infty$  in mm Hg

This result is then compared with the Volmer-Flood measurements on water at temperatures  $T$  of  $260^\circ$  and  $275^\circ$ . All measurements at  $T = 270^\circ$ ,  $p_\infty = 4$  mm Hg,  $l = 10^{-5}$  cm,  $\sigma = 75$  dyn/cm are entered below the logarithm. Hence

$$\ln J = 52.5 + 2x + 2 \ln x - 5.74 \times 10^3 \left( \frac{\sigma}{T} \right)^3 \frac{1}{x^2}$$

The curves obtained for  $\ln J$  are shown plotted against  $x$  in figure 2 for  $T_1 = 275.2^\circ$  and  $T_2 = 261.0^\circ$ . But there is a certain uncertainty as to which value of  $J$  is to be designated as condensation. According to the graph the curves intersect the  $x$  axis at such a slope that it is practically immaterial, when defining the critical supersaturation, whether  $J = 1$  ( $\ln J = 0$ ) or  $J = 10$  ( $\ln J = 2.3$ ) is plain fog. Choice of the intersection point of the curves with the straight line  $\ln J = 1$ , gives the following values for the critical supersaturation, which can be compared with the measurements

	T	$\sigma$ (dyn/cm)	x calculated	$\frac{p_n}{p_\infty}$	
				calculated	measured
Curve 1	275.2	75.23	1.46	4.30	4.21
Curve 2	261.0	77.28	1.64	5.14	5.03

$A'$  amounts to 55 to 56

Worthy of note is the insensitivity of the theoretically computed factors to errors in the calculation of  $a_0 Z_1'$ . Even a factor 10 would change the constant 52.4 only by 2, i.e., practically no change at all in the result.

Since all further measurements on other substances in the Volmer-Flood report have been compared with those measurements on water and gave a good confirmation of Farkas' formula, it is concluded that the present formula (13) reproduces the whole available test material very satisfactorily.

### 3. THE LINEAR CHAIN

Preparatory to the problems of the actual crystal growth, the following process is analyzed: It is assumed that the rectangular area ABCD is the base of a simple cubic crystal, on which as the beginning of a new surface, a layer of edge lengths  $z$  and  $l$  is available and on which the  $(l + 1)$ th chain of length  $z$  is included in the growth. The growth of this new chain is analyzed. Figure 3 represents the stage in which exactly  $k = 3$  atoms of the  $(l + 1)$ th chain are condensed. The difficulty of forming nuclei here is due to the fact that during the start of a new chain the first and possibly also the second and third atom are less solidly bound than those following, which are all bound with the same energy (repeatable steps, according to Kossel, bond at "half crystal" according to Stranski). So, unless there is too much supersaturation after a complete chain has formed, there is a considerable lapse of time before - as the start of a new chain - a linear nucleus capable of growing has formed. The energies, with which the single atoms are bound in the successive formation of the chain, are indicated with  $\Phi_1, \Phi_2, \dots, \Phi_k, \dots$ . Then the possibility  $q_k dt$  that the  $k$ -th atom evaporates as a result of the thermal motion in time interval  $dt$  on a chain consisting of  $k$  atoms, is given by

$$q_k = F(T)e^{-\frac{\Phi_k}{kT}} \quad (14)$$

On the other hand, the possibility  $a dt$ , that a further atom settles on the chain, is independent of  $k$  and solely given by the external vapor pressure. It is assumed that there is no slip of atoms at the crystal surface. In that event  $a$  is essentially equal to the number of vapor atoms per second arriving at the surface of a single crystal atom. The quantity  $a$  introduced here follows from the  $a_0$  (of section 2) by multiplication with the surface atom.

We put

$$a = F(T)e^{-\frac{\Psi}{kT}} \quad (15)$$

hence, where the energy  $\psi$  is the measure of the external vapor pressure.<sup>5</sup> The whole mechanism of growth is governed by the factors

$$\beta_k = \frac{a}{q_k} = e^{\frac{\varphi_k - \psi}{kT}} \quad (16)$$

which for normal growth at the beginning of the chain ( $k = 1$ ) are substantially smaller and for greater  $k$  a little above unity. In conjunction with Stranski and Kossel, this behavior is then schematized so that  $\beta_1$  is regarded as very small compared to unity and all other  $\beta$  values as equivalent and greater than unity. For the investigation of the growth of a chain the following steady process is analyzed: A space under constant vapor pressure contains a very large number of crystals which are in the stage of growth represented in figure 3. But the new chain in the process of formation may be of any possible length and assume any possible position on the raised side of the rectangle. The number of crystals on which the new chain has exactly the length  $k$  and is at a specific position at the growing edge is indicated with  $n_k$ ; correspondingly, the number of crystals arising from the crystals of the type  $n_k$  due to deposition of an atom at a certain end of the chain  $k$ , is indicated by  $n_{k+1}$ .

By partial current  $J'$  is meant the excess of the growth process per second which lead from the  $n_k$  crystals to those of the type  $n_{k+1}$ , through the evaporation processes, which lead from  $n_{k+1}$  to  $n_k$ . For this specific partial current

$$J' = n_k a - n_{k+1} q_{k+1} \quad (17)$$

Each chain has then two possibilities of adding an atom corresponding to its two free ends. In the two positions of chain  $k$  in which one end coincides with one end of the base, there is only one possibility of build-up. Since, for the chain  $k$ , there are  $(z - k + 1)$  various positions possible, there are altogether  $2(z - k + 1) - 2 = 2(z - k)$  partial currents  $J'$ , which collectively lead from all the crystals with chains of length  $k$  to those with chains of length  $k + 1$ . But in the case of transition from  $n_0$  to  $n_1$  there are only  $z$  partial currents corresponding to the  $z$  deposition possibilities of the first atom of the new chain. This branching of the current is represented in figure 4 for  $z = 6$ .

Now the not entirely exact assumption is made that all partial currents leading from  $k$  toward  $k + 1$  are equivalent. Since their sum

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<sup>5</sup>At absolute zero point the heat of vaporization would have to be used. As a rule,  $\psi$  signifies a thermodynamic potential.

gives the total current  $J$ , each is equal to

$$J' = \frac{J}{2(z - k)}$$

It is readily apparent from figure 4 that this assumption cannot be rigorously correct on account of the equations of continuity between the partial currents. Owing to equation (17) this assumption corresponds to the assumption that all positions of the chain  $k$  are identically frequent.

Thus, on this premise the steady state is described by the equations

$$\left. \begin{aligned} n_1 &= n_0 \beta_1 - \frac{J}{a} \frac{\beta_1}{z} \\ n_2 &= n_1 \beta_2 - \frac{J}{2a} \frac{\beta_2}{z - 1} \\ &\dots \dots \dots \\ n_{k+1} &= n_k \beta_{k+1} - \frac{J}{2a} \frac{\beta_{k+1}}{z - k} \\ &\dots \dots \dots \\ n_z &= n_{z-1} \beta_z - \frac{J}{2a} \beta_z \end{aligned} \right\} \quad (18)$$

These equations are treated the same way as those of the droplet formation (in section 2), by regarding them as equations for the passage of current through a series of specified partial resistances. By division of the  $k$ -th equation by the product  $P_{k+1} = \beta_1 \beta_2 \dots \beta_{k+1}$ , they take the form

$$\Phi_{k+1} = \Phi_k - JR_k \quad (19)$$

where the individual potentials and partial resistances indicate

$$\left. \begin{aligned} \Phi_k &= \frac{n_k}{\beta_1 \beta_2 \dots \beta_k}, & R_k &= \frac{1}{2a(z-k)\beta_1 \dots \beta_k}, \\ \text{but } \Phi_0 &= n_0, & R_0 &= \frac{1}{az} \end{aligned} \right\} \quad (19a)$$

Thus, in figure 4 the electric potential of a specific state is represented by the quotient of the number  $n_k$  of crystals in state  $k$  and the product  $P_k = \beta_1 \beta_2 \dots \beta_k$  of the  $\beta$  values of all atoms bound in this state. Specific experimental interrogatory forms are synonymous with the corresponding statements regarding the electric potential difference placed at the ends. However, it is to be noted that, in contrast to the electrical picture, the absolute value of the potential in the growth process itself has a well defined meaning

$$\frac{\Phi_k}{R_k} \quad \text{and} \quad \frac{\Phi_k}{R_{k-1}} \quad \text{respectively}$$

namely are the number of individual processes taking place in unit time from  $k$  to  $k+1$  and  $k$  to  $k-1$ .

As application of (19) the actual linear nucleation as well as the growth of the rectangle layer about a whole chain is now analyzed.

#### A. Linear Nucleation

The procedure for defining the nucleation frequency is the same as for the droplet formation. All the crystals for which the chain has reached a certain arbitrarily chosen length  $s$  are removed;  $s$  is to be very small compared to the length  $z$  of the edge. The number of crystals removed per second is called linear nucleation frequency. Hence we put  $\Phi_s = 0$  and find

$$J = \frac{1}{R} \Phi_0, \quad \text{with } \Phi_0 = n_0$$

and

$$\begin{aligned} R &= R_1 + R_2 + \dots + R_{s-1} \\ &= \frac{1}{2a} \left( \frac{2}{z} + \frac{1}{(z-1)\beta_1} + \frac{1}{(z-2)\beta_1\beta_2} + \dots + \frac{1}{(z-s+1)\beta_1 \dots \beta_{s-1}} \right) \end{aligned}$$

With the specialization  $\beta_2 = \beta_3 = \dots = \beta$  and because  $s \ll z$

$$R = \frac{1}{2az} \left[ 2 + \frac{1}{\beta_1 \beta^{s-2}} (\beta^{s-2} + \beta^{s-3} + \dots + 1) \right]$$

$$= \frac{1}{2az} \left( 2 + \frac{\beta^{s-1} - 1}{(\beta - 1) \beta_1 \beta^{s-2}} \right)$$

is applicable also.

Disregarding the 1 next to  $\beta^{s-1}$  and the 2 next to  $1/\beta_1$ , leaves  $R = \frac{1}{2az} \frac{\beta}{(\beta - 1) \beta_1}$ , hence the frequency of the linear nucleation at one of the  $n_0$  edges, independent of  $s$

$$\frac{J}{n_0} = 2az \frac{\beta - 1}{\beta} \beta_1 \tag{20}$$

The factor  $2 \frac{\beta - 1}{\beta} \beta_1$ , small compared to unity, is regarded as a probability that one of the atoms striking the edge (their number per second amounting to  $az$ ) grows up to a new chain.

#### B. Deposition of a Whole Chain of Length $z$

In this event all the partial resistances from  $R_0$  to  $R_{z-1}$  must be added up

$$J(R_0 + R_1 + \dots + R_{z-1}) = \Phi_0 - \Phi_z$$

or

$$\frac{J}{2a} \left( \frac{2}{z} + \frac{1}{(z-1)\beta_1} + \frac{1}{(z-2)\beta_1\beta_2} + \dots + \frac{1}{\beta_1\beta_2 \dots \beta_{z-1}} \right) = n_0 - \frac{n_z}{\beta_1\beta_2 \dots \beta_z}$$

The first partial resistance  $2/z$  in comparison with  $\frac{1}{(z-1)\beta_1}$  can always be disregarded. Putting  $\beta_2 = \dots = \beta_z = \beta$ , we get with the abbreviation

$$S_z = \left( \beta + \frac{\beta^2}{2} + \frac{\beta^3}{3} + \dots + \frac{\beta^{z-1}}{z-1} \right) \quad (21)$$

$$n_z = n_0 \beta_1 \beta^{z-1} - \frac{J}{2a} S_z \quad (22)$$

The sum  $S_z$  does not lend itself to elementary evaluation. The approximate value

$$S_z(\beta) \cong \frac{\beta^z}{z \ln \beta} \quad (21a)$$

used in the following is obtained by the following consideration: Replacing the sum (21) by an integral gives

$$S_z \cong \int_1^z \frac{\beta^x}{x} dx$$

hence, with the substitution  $x = z - \frac{y}{\ln \beta}$

$$S_z \cong \frac{\beta^z}{z \ln \beta} \int_0^{\ln \beta(z-1)} \frac{e^{-y}}{1 - \frac{y}{z \ln \beta}} dy$$

The approximate value is obtained by disregarding  $\frac{y}{z \ln \beta}$  which is small compared to unity, which, however, presents only a rough approximation near the upper limit of the integral. Equation (22) enables the deposition of a whole chain  $z$  to be treated as an elementary process. The equation (17a), valid for the actual elementary process, is simply replaced by the relation

$$J = n_0 A_z - n_z B_z \quad (23)$$

whereby

$$\left. \begin{aligned} A_z &= \frac{2a\beta_1\beta^{z-1}}{S_z} \cong 2az \ln \beta \frac{\beta_1}{\beta} \\ B_z &= \frac{2a}{S_z} \cong 2az \ln \beta\beta^{-z} \end{aligned} \right\} \quad (23a)^6$$

$A_z$  is slightly dependent on  $z$ , while  $B_z$  decreases exponentially with  $z$ . Both quantities become equivalent at a critical value of  $z$ , which is denoted by  $m$ , and is defined by

$$\beta_1\beta^{m-1} = 1 \quad \text{or} \quad \frac{\beta}{\beta_1} = \beta^m \quad (24)$$

$m$  is that chain length which is precisely in equilibrium with the external pressure. According to (16) the definition (24) of  $m$  is equivalent to

$$\begin{aligned} \varphi_1 + (m - 1)\varphi &= m\psi \\ \text{or} & \\ \varphi - \psi &= \frac{1}{m} (\varphi - \varphi_1) \end{aligned} \quad (24a)$$

The mean evaporation energy of the "critical chain  $m$ " is equal to the energy  $\psi$  characterizing the external vapor pressure.

#### 4. TWO-DIMENSIONAL NUCLEUS

Equation (22) makes it possible to analyze a chain of length  $z$  as an element, through whose deposition or evaporation the growth of plane nuclei or of whole rectangular plates is controlled. In this instance the growth of a plane nucleus on a given base of edge lengths  $i$  and  $k$  is involved. A specific stage of this growth is represented in figure 3. The bonding energy of a single atom on the smooth base ("bond to one neighbor") is denoted with  $\varphi_0$ ;  $\varphi_1$  and  $\varphi$  have the same meaning as in section 3. Accordingly, there are

$$\beta_0 = e^{\frac{\varphi_0 - \psi}{kT}}, \quad \beta_1 = e^{\frac{\varphi_1 - \psi}{kT}}, \quad \beta = e^{\frac{\varphi - \psi}{kT}} \quad (25)$$

The energy required to detach the whole plate ( $i$ ,  $k$ ) from the base is then

$$\varphi_0 + (i + k - 2)\varphi_1 + (i - 1)(k - 1)\varphi$$

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<sup>6</sup>In this calculation it is assumed that at no time two nuclei are simultaneously existent on the same chain and then grow together to one chain. When  $z$  is not extremely great, this assumption is well justified.

From the assumption that  $\beta_2 = \beta_3 = \dots = \beta$  are all equivalent and independent of the position of the deposited molecule on the base, inevitably follows the condition

$$\varphi_0 + \varphi = 2\varphi_1$$

hence also

$$\beta_0\beta = \beta_1^2 \quad (25a)$$

The total bonding energy of a structure must be independent of the manner in which the growth takes place. Applied specifically to a system of 3 atoms on the base as in figure 5, the binding energy for growth in the order of 1, 2, 3, is  $\varphi_0 + \varphi_0 + \varphi$ , but for the sequence 1, 3, 2, it is  $\varphi_0 + \varphi_1 + \varphi_1$ . The equality yields the above relationship. The evaporation energy of the whole plate ( $i, k$ ) is therefore

$$ik\varphi - (i + k)(\varphi - \varphi_1)$$

Visualize a column of cross section  $i \times k$  consisting of  $l$  whole atom layers, the deposit of the  $(l + 1)$ th layer being located on a rectangle  $s \times z$ . In analyzing the full growth of this deposit into a whole layer the procedure is the same as in section 3. A multiplicity of columns and rectangles of every possible size and position is assumed, with  $n_{s,z}$  denoting the number of those at which the nucleus  $(s,z)$  has a specific position on the base. The number of the possible positions is, obviously  $(i - s + 1)(k - z + 1)$ . The total number  $Z_{s,z}$  of the columns with a plate  $(s,z)$  would then be  $n_{s,z}(i - s + 1)(k - z + 1)$ , if it is assumed, as in section 3, that each position of the rectangle  $(s,z)$  on the base occurs with the same frequency. For the current  $J_{s,z}$ , leading from  $s,z$  to  $s + 1,z$ , there are altogether  $2(i - s)(k - z + 1)$  possibilities, namely, two each for each specific position of the rectangle  $(s,z)$ , with exception of those positions at which it lies to the left or right at the edge. In these cases there is only one possibility for depositing a new chain. It is assumed again that these  $2(i - s)(k - z + 1)$  partial currents, all of which lead from  $s,z$  to  $s + 1,z$ , are equivalent.

Now, in order to describe the growth of the plane crystal after the foregoing arguments with the above equation (22),  $n_z$  is replaced by  $n_{s+1,z}$ ,  $n_0$  by  $n_{s,z}$  and  $J$  by  $\frac{J_{s,z}}{2(i - s)(k - z + 1)}$ , while  $J_{sz}'$  is

to denote the current from  $(s, z)$  to  $(s, z + 1)$ . In the steady state the plane growth is then governed by the equations

$$\left. \begin{aligned} n_{s+1,z} &= n_{s,z} \beta_1 \beta^{z-1} - \frac{J_{s,z}}{4a(i-s)(k-z+1)} S_z \\ n_{s,z+1} &= n_{s,z} \beta_1 \beta^{s-1} - \frac{J_{s,z'}}{4a(i-s+1)(k-z)} S_s \end{aligned} \right\} s, z = 1, 2, \dots \quad (26)$$

On the other hand

$$n_{11} = n_{00} \beta_0 - \frac{J}{aik} \beta_0 \quad (26a)$$

is applicable.

Now the content of these equations is described by a discussion in the  $s$ - $z$  plane (fig. 6):

Suppose that a certain lattice point  $s, z$  represents the crystallite defined by the edges  $s$  and  $z$ . Thus, in figure 6, for example, the point A corresponds to the crystallites  $3 \times 2$ . The current  $J_{s,z}$  flows then horizontally from  $s, z$  toward  $s + 1, z$ ,  $J_{s,z'}$ , but vertically upward from  $s, z$  toward  $s, z + 1$ . The whole lattice extends to  $s = i$  and  $z = k$ . The problem then consists in computing a total current  $J$  that enters at  $(0,0)$  and branches off in partial currents  $J_{s,z}$  and  $J_{s,z'}$ , according to equation (26). The obvious method is to regard the entire figure 6 as the image of a material network through which passes a current  $J$  under the effect of a certain electrical direct current voltage. To complete the picture, the several equations of (26) must be expressed in the form of Ohm's law

$$\begin{aligned} \Phi_{s+1,z} &= \Phi_{s,z} - J_{s,z} R_{s,z} \\ \Phi_{s,z+1} &= \Phi_{s,z} - J_{s,z'} R_{s,z'} \end{aligned} \quad (27)$$

which describes the current in the separate pieces of wire of the network in figure 6. It can be accomplished by dividing the first equation of (26) by the product  $P$  of all the  $\beta$  values occurring in the build-up of the plane  $(s + 1, z)$ , that is,

$$P_{s+1,z} = \beta_0 \beta_1^{(s+z-1)} \beta^s (z-1)$$

The potential  $\phi_{s,z}$  and the partial resistances  $R_{s,z}$  and  $R_{s,z}'$  become then

$$\phi_{s,z} = \frac{n_{s,z}}{P_{s,z}} = \frac{n_{s,z}}{\beta_0 \beta_1^{(s+z-2)\beta} (s-1)(z-1)}; \quad \phi_{0,0} = n_{0,0} \quad (27a)$$

$$\left. \begin{aligned} R_{s,z} &= \frac{1}{4a(i-s)(k-z+1)} \frac{S_z}{P_{s+1,z}}; \\ R_{s,z}' &= \frac{1}{4a(i-s+1)(k-z)} \frac{S_z}{P_{s,z+1}} \end{aligned} \right\} \quad (27b)$$

The whole problem now consists in the discussion of the electrical properties of the network built up of partial resistances (27b).

Introduction of the approximate value (21a) for  $S_z$  gives

$$R_{s,z} = \frac{1}{4a(i-s)(k-z+1)z \ln \beta} \frac{1}{\beta_0 \beta_1^{s+z-1} \beta^{sz-s-z}}$$

Introduction of the critical edge length  $m$  defined by equation (24) and with the relation  $\frac{\beta_1}{\beta_0} = \frac{\beta}{\beta_1} = \beta^m$  following from equation (25a), the second factor of the above  $R_{s,z}$  becomes

$$\beta^m \beta^m (s+z)^{-sz} = \beta^{m+m^2-(s-m)(z-m)}$$

With a system of axes turned through  $45^\circ$  ( $\sigma$  along the diagonal,  $\zeta$  at right angle to it)

$$\left. \begin{aligned} s &= \sigma + \zeta \\ z &= \sigma - \zeta \end{aligned} \right\} \quad (28)$$

becomes

$$(s-m)(z-m) = (\sigma-m)^2 - \zeta^2$$

hence the factor of  $R_{s,z}$  in question

$$\beta^{m+m^2} \beta^{-(\sigma-m)^2} \beta^{\zeta^2}$$

The relationship of  $\zeta$  implies: if the partial resistances  $R_{s,z}$ , which are met by a normal to the diagonal, are examined, they are seen to have a sharp minimum on the diagonal itself (at  $\zeta = 0$ ). One, two, three lattice points away from the diagonal, the resistances increase by the factors  $\beta$ ,  $\beta^4$ ,  $\beta^9$ , etc. Thus practically only the diagonal  $s \cong z$  of this lattice is conductive, while along the diagonal (change of  $\sigma$  at  $\zeta = 0$ ), the resistance has the same sharp maximum at  $\sigma = m$ , i.e., at the critical edge length. There the partial resistances drop with the distance from this point to the  $\beta^{-1}$ ,  $\beta^{-4}$ ,  $\beta^{-9}$ -th fraction, when the distance from  $\sigma = m$  amounts to one, two, three lattice points. Therefore, the entire current must flow along the diagonal in a narrow gorge, characterized by the factor  $\beta^{\zeta^2}$ , which in turn leads over a very steep "pass" at  $\sigma = m$ .

The over-all resistance  $R$  of the entire network is practically concentrated on the resistance

$$R \approx R_{m,m} = \frac{1}{4a(i-m)(k-m+1)m \ln \beta} \beta^{m+m^2} \quad (29)$$

at the height of the pass. Naturally, it is assumed then that the spot  $s = z = m$  still lies substantially within the lattice. A further discussion of the branching conditions in the immediate vicinity of the spot  $m,m$  could contribute to the expression  $R$  no more than a factor close to unity, which, however, would be useless for the purposes involved here. Now the two questions concerning the frequency of plane nucleations, as well as the growth of the rectangular column  $i \times k$  around a whole layer, can be answered exactly as for the chain in section 3.

#### A. The Formation of Plane Nuclei on a Rectangle Base

To determine the nucleation frequency, all the columns for which the sum of the edges  $s + z$  has reached an arbitrarily specified value  $s + z = n$  are withdrawn from the vapor space and counted, that is, the lattice points lying on the straight line  $s + z = n$  are grounded. The saddle point  $s = z = m$  is found to be located still within the thus out-off triangle and also that  $n$  and hence  $m$  itself should be very small with respect to the edges  $i$  and  $k$  of the base. The result is the satisfactory approximation:  $R = \frac{1}{4aikm \ln \beta} \beta^{m+2}$ , hence, the nucleation

current for a single one of the  $n_0$  crystals is

$$\frac{J}{n_0} = 4aikm \ln \beta \beta^{-m-m^2} \quad (30)$$

The two factors  $\beta$  and  $m$  still remaining are tied to one another by the relation  $\beta^m = e^{\frac{\varphi - \varphi_1}{kT}}$ , according to equation (24), with the aid of which one of the two can then be eliminated from equation (30).

Elimination of  $\beta$  leaves

$$\frac{J}{n_0} = 4aik \frac{\varphi - \varphi_1}{kT} e^{-\frac{m(\varphi - \varphi_1)}{kT}} e^{-\frac{\varphi - \varphi_1}{kT}} \quad (30a)$$

Here, as it should be,

$$\frac{\text{half the free-edge energy}}{kT}$$

is in the first  $e$  power, because  $\frac{1}{2}(\varphi - \varphi_1)$  is the free-edge energy per atom,  $4m\frac{1}{2}(\varphi - \varphi_1)$  is, therefore, the total free-edge energy. The plane energy accompanying the formation of the chain (at both of its ends!) is in the second  $e$  power. The factor before the already thermodynamically required  $e$  function is extremely simple: its order of magnitude is defined by the number  $aik$  of the vapor atoms per second impinging upon the plate  $ik$ . The then still remaining factor  $\frac{4(\varphi - \varphi_1)}{kT}$  is nearly equal to  $\frac{\text{evaporation heat}}{RT}$ . It has no significance for the only interesting order of magnitude of  $J$ .

On the other hand, when  $m$  substitutes for  $m + 1$ , the elimination of  $m$  from equation (30) gives

$$J = 4aik \frac{\varphi - \varphi_1}{kT} e^{-\frac{(\varphi - \varphi_1)^2}{(kT)^2 \ln \beta}} \quad (30b)$$

This equation gives the dependence of current  $J$  on the experimentally directly defined supersaturation  $\beta$ .

B. At the formation of a whole plane  $i \times k$  it is necessary to analyze the entire rectangular network on which the current  $J$  is introduced at point  $(0,0)$  and channeled off at  $(i,k)$

$$\Phi_{0,0} - \Phi_{i,k} = J\bar{R}_{i,k}$$

where  $\bar{R}_{i,k}$  is the over-all resistance of the entire rectangular network.

Here, also, the only case of interest is that where the point  $(m,m)$  lies still within the net;  $\bar{R}_{i,k}$ , therefore, according to equation (29), may be replaced by  $R_{m,m}$ . If use is made of the relations  $\beta_0\beta = \beta_1^2$

and  $\frac{\beta}{\beta_1} = \beta^m$  in the product  $P_{s,z}$ ,  $P_{s,z}$  then becomes

$$P_{s,z} = \beta_0\beta_1^{s+z-2}\beta^{(s-1)(z-1)} = \beta^{(s-m)(z-m)-m^2}$$

Thus, by equations (27) and (29)

$$n_{i,k} = n_{0,0}\beta^{(i-m)(k-m)-m^2} - J \frac{\beta^{m+(i-m)(k-m)}}{4a(i-m)(k-m)m \ln \beta} \quad (31)$$

On the basis of this equation (31), the accumulation of a whole plane can henceforth be treated as elementary process. The equation applicable to it reads

$$J = n_{0,0}A_{i,k} - n_{i,k}B_{i,k} \quad (32)$$

where

$$\left. \begin{aligned} A_{i,k} &= 4a(i-m)(k-m)m \ln \beta \beta^{-m-m^2} \\ B_{i,k} &= A_{i,k}\beta^{m^2-(i-m)(k-m)} \end{aligned} \right\} \quad (32a)^7$$

Both quantities are equivalent at  $m^2 - (i-m)(k-m) = 0$  or  $ik = (i+k)m$ . For square plates, which are practically the only ones

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<sup>7</sup>Multiple nucleation is excluded again. At very great  $i$  and  $k$  the foregoing is therefore no longer applicable.

occurring at the subsequent growth of the spatial crystal, it results in  $i = k = 2m$ . The probability for evaporation and condensation will not be identically great until the edge length of the plane is twice as great as the critical chain length  $m$ . Naturally, this result was to be foreseen by reason of the fact that the equilibrium vapor pressure is defined by the mean evaporation energy, as already predicted by Stranski and Kaischew. It is to be noted that  $A_{i,k}$  is very slightly dependent on  $i$  and  $k$ , while  $B_{i,k}$  decreases rapidly with increasing size of the plane.

## 5. THE CRYSTAL NUCLEUS

After these preparations the quantitative treatment of the nucleation frequency for spatial crystals is easy. Again visualize in a vapor space a large number of box-like crystals of all possible edge lengths  $i, k, l$  in steady distribution so that the vapor pressure remains constant and that all crystals, as soon as they have reached a certain size, are removed from the space and counted. The number of crystals with the edge lengths  $i, k, l$  is assumed at  $Z_{i,k,l}$ . They may, for example, change to crystals  $(i+1, k, l)$  by gathering of a plane  $(k, l)$ , that is, this plane can be deposited on two different sides of the little box. The law for this process was defined in equation (31). Replacing  $n_{i,k}$  by  $Z_{i+1,k,l}$ ,  $n_{0,0}$  by  $Z_{i,k,l}$ ,  $i, k$  by  $k, l$  and  $J$  by  $1/2J_{i,k,l}$  results in

$$Z_{i+1,k,l} = Z_{i,k,l} \beta^{(k-m)(l-m)-m^2} - \frac{J_{i,k,l} \beta^{m+(k-m)(l-m)}}{8a(k-m)(l-m)m \ln \beta} \quad (33)$$

where  $J_{i,k,l}$  indicates the partial current that leads from  $i, k, l$  to  $i+1, k, l$ . By the method previously used several times, equation (33) can again be put in the form

$$\Phi_{i+1,k,l} = \Phi_{i,k,l} - J_{i,k,l} R_{i,k,l} \quad (34)$$

and identify it as the electrical current in a spatial network whose lattice points have the potential  $\Phi_{i,k,l}$  and in which  $R_{i,k,l}$  is the ohmic resistance of the piece of wire that leads from  $i, k, l$  to  $i+1, k, l$ . The transition from (33) to (34) is accomplished again by division of (33) by the product  $P_{i+1,k,l}$  of all the  $\beta$  values which occur during the successive development of the state  $(i+1, k, l)$  from  $(i+1)k, l$  single atoms. The factor for  $Z_{i,k,l}$  in equation (33) is precisely the product  $P_{k,l}$

of the  $\beta$  values for that plane  $(k, l)$  which is newly added in the particular reaction. The product  $P_{i,k,l}$  can be constructed as follows: On a single atom free columns of  $i - 1$ ,  $k - 1$ ,  $l - 1$  atoms are deposited along the coordinate axes, each of which gives the factor  $\beta_0$ . The spread-out rectangle sides are then filled out. It yields  $(i - 1)(k - 1) + (k - 1)(l - 1) + (l - 1)(i - 1)$  times the factor  $\beta_1$  and, in addition,  $(i - 1)(k - 1)(l - 1)$  times the factor  $\beta$ . Hence, altogether

$$P_{i,k,l} = \beta_0^{i+k+l-3} \beta_1^{(i-1)(k-1)+(k-1)(l-1)+(l-1)(i-1)} \beta^{(i-1)(k-1)(l-1)}$$

for which the relations  $\frac{\beta_0}{\beta_1} = \frac{\beta_0}{\beta} = \beta^m$  give

$$P_{i,k,l} = \beta^{-m(ik+kl+li)+ikl+3m-1}$$

and

$$P_{i+1,k,l} = P_{i,k,l} \beta^{(k-m)(l-m)-m^2}$$

By division with this quantity, we obtain in equation (34) as factor of  $J_{i,k,l}$  the final term for the partial resistance

$$R_{i,k,l} = \frac{1}{8a(k-m)(l-m)m \ln \beta} \beta^{m(ik+kl+li)-ikl+m^2-2m+1} \quad (35)$$

To clarify the behavior of the exponent visualize a perpendicular line dropped from the point  $i, k, l$  of the network on the space diagonal,  $\sigma, \sigma, \sigma$  to indicate the foot of this perpendicular.

Putting

$$\left. \begin{aligned} i &= \sigma + r_1 \\ k &= \sigma + r_2 \\ l &= \sigma + r_3 \end{aligned} \right\} \quad (36)$$

the construction given then

$$r_1 + r_2 + r_3 = 0 \quad (36a)$$

along with

$$r_1 r_2 + r_2 r_3 + r_3 r_1 = -\frac{1}{2} (r_1^2 + r_2^2 + r_3^2) \equiv -\frac{1}{2} r^2$$

By (36) and (36a)

$$ik + kl + li = 3\sigma^2 - \frac{1}{2}r^2$$

and

$$ikl = \sigma^3 - \frac{1}{2}\sigma r^2 + r_1 r_2 r_3$$

With this the exponent of equation (35) reads

$$m(ik + kl + li) - ikl = 3\sigma^2 m - \sigma^3 + \frac{1}{2}(\sigma - m)r^2 - r_1 r_2 r_3$$

Disregarding the practically nonessential term  $r_1 r_2 r_3$  (the surrounding of the diagonals being considered), the conditions for  $R_{i,k,l}$  are the same as before in section 4 for the plane lattice. The factor  $\frac{1}{\beta^2}(\sigma-m)r^2$  in the region  $\sigma > m$  solely considered here, effects such a rapid rise of the resistance on leaving the diagonal, that the current can flow practically only on the diagonal  $r = 0$ . On the diagonal itself the factors  $\beta^3 \sigma^{2m-\sigma^3}$  has such an enormously steep maximum at  $\sigma = 2m$ , that the entire voltage drop along the diagonal is practically defined solely by the partial resistance

$$R_{2m,2m} = \frac{1}{8am^3 \ln \beta} \beta^{4m^3+m^2-2m+1}$$

Owing to  $\phi_{1,1,1} = Z_{1,1,1}$  the nucleation frequency is therefore defined at

$$J = 8aZ_{1,1,1} m^3 \ln \beta \beta^{-4m^3-m^2+2m-1} \quad (37)$$

Elimination of  $\beta$  by means of

$$\beta^m = \frac{\beta}{\beta_1} = e^{\frac{\Phi - \Phi_1}{kT}}, \quad m \ln \beta = \frac{\Phi - \Phi_1}{kT}$$

leaves

$$J = 8a_{Z_{1,1,1}} m^2 \frac{\varphi - \varphi_1}{kT} e^{-\frac{4m^2(\varphi - \varphi_1)}{kT}} e^{-\frac{m(\varphi - \varphi_1)}{kT}} e^{-\frac{\varphi - \varphi_1}{kT} \left(2 - \frac{1}{m}\right)} \quad (37a)$$

The factors deciding the order of magnitude of  $J$  are  $a_{Z_{1,1,1}}$  and the first of the three e-functions;  $a_{Z_{1,1,1}}$  is essentially (like the factor  $a_{OZ_1}$  in equation (13) for droplet formation) the number of gas kinetic collisions per second. The first e-power is synonymous with the factor  $e^{-\frac{\sigma F \eta}{3kT}}$  of the thermodynamic formula (5). In fact,  $\frac{1}{2}(\varphi - \varphi_1)$  is the surface energy per atom; the total surface energy of the cube of critical edge length  $2m$ , therefore, is equal to  $(2m)^2 \times 6 \times \frac{1}{2}(\varphi - \varphi_1) = 12m^2(\varphi - \varphi_1)$ ; the third portion of it stands, as it should be, in the exponent. The exponent of the second e-function indicates, as shown in section 4,  $\frac{1}{2} \frac{\text{edge energy}}{kT}$  for a critical plane nucleus. This factor occurs in similar manner in the report by Stranski and Kaischew too. Admittedly, its appearance hinges on the exact knowledge of the factor  $m$ , as is apparent from the fact that in equation (37) the term with  $m^2$  can be made to disappear completely, if  $m$  is replaced by  $m - \frac{1}{12}$ . For the problem involving the critical supersaturation the second and third e-functions are ignored.

## 6. THE OSTWALD LAW OF STAGES

This law states that in the formation of nuclei from supersaturated vapor the liquid phase is separated first, as a rule, even when the temperature of the vapor is considerably below the freezing point. Our results on the nucleation of liquid (13) and solid (37) nuclei enable a theoretical foundation and a quantitative improvement of this law to be made.

Omitting the last two e-functions in (37a) and introducing the relation for Volmer's exponent of equation (5)

$$A'' = \frac{\sigma F}{3kT} = \frac{4m^2(\varphi - \varphi_1)}{kT}$$

we get by equation (37a) on the crystal nucleus

$$\text{Crystal: } J_{\text{crystal}} = 2aZ_{1,1,1}A''e^{-A''}$$

while equation (13) produced

$$\text{Droplet: } J_{\text{droplet}} = \frac{a_0Z_1'}{n} \sqrt{\frac{A'}{3\pi}} e^{-A'}$$

The factor  $Z_1'$  was, according to section 2, the number of vapor molecules multiplied by its surface. Since, according to section 3,  $a_0$  arises from  $a_0$  by multiplication with the atom surface,  $aZ_{1,1,1}$  and  $a_0Z_1'$  are identical in order of magnitude. Thus, the factor  $K$  of equation (5) for the formation of droplets appears smaller by  $1/n$  than for the formation of the crystal, where  $n$  denotes the molecule number of the nucleus. Although  $n$  is the order of magnitude of 100, this factor is not decisive in the problem involving the critical supersaturation. Moreover, it would be considerably overbalanced by the factor  $\beta^{-m^2}$  omitted at  $J_{\text{crystal}}$ . The factor  $A''$  and  $\sqrt{\frac{A'}{3\pi}}$  matter even less.

As long as no direct measurements of  $J$  are planned, but merely the order of magnitude of the critical supersaturation, the simple result is: The factor  $K$  in Volmer's nucleation formula is simply equal to the number of gas kinetic collisions, for the droplet as for the crystal. This statement applies, as seen in section 3 and section 4, to linear and plane nuclei; naturally, involved here is solely the number of collisions per second at the base.

The decisive reason for the validity of the law of stages remains then solely the fact that in the quantity  $\frac{\sigma F}{3kT}$  the surface  $F$  of the nucleus corresponding to a certain supersaturation is greater on the cube than on the sphere. The difference in shape is the deciding factor, not the crystalline structure. Its effect is computed on the assumption that the molecular volume  $v$  and the surface tension  $\sigma$  for fluid and crystal are equivalent.

If  $F = Cn^{2/3}$  is the surface corresponding to the molecule number  $n$ , then by equation (1), with  $x$  denoting the abbreviation of  $\ln \frac{p_n}{p_\infty}$ ,

$$kTx = \sigma \frac{dF}{dn} = \frac{2}{3} \frac{\sigma C^{3/2}}{F^{1/2}}$$

hence the surface corresponding to  $x$

$$F = \frac{4}{9} \frac{\sigma^2 C^3}{(kTx)^2}$$

The nucleus volume  $V$  for the sphere (radius  $r$ ) is

$$V = nv = \frac{4\pi}{3} r^3, \quad \text{thus,} \quad F = 4\pi \left( \frac{3}{4\pi} \right)^{2/3} v^{2/3} n^{2/3}$$

for the cube (edge length  $a$ ):

$$V = nv = a^3, \quad \text{hence,} \quad F = 6v^{2/3} n^{2/3}$$

Hence, for the sphere

$$C^3 = 36\pi v^2$$

and for the cube

$$C^3 = 6^3 v^2$$

The critical area corresponding to the same  $x$  is  $\frac{6}{\pi} = 1.91$  times greater for the cube than the droplet. To assure identical nucleation frequency, hence, equal values of  $F$ , it must

$$\frac{x_{\text{cube}}}{x_{\text{sphere}}} = \left( \frac{C^3_{\text{cube}}}{C^3_{\text{sphere}}} \right)^{1/2} = \sqrt{1.91} = 1.38$$

For the critical supersaturations themselves the condition would be

$$\left( \frac{p}{p_{\infty}} \right)_{\text{cube}} = \left( \frac{p}{p_{\infty}} \right)_{\text{sphere}}^{1.38} \quad (38)$$

As an illustration for applying this relationship, the supercooling at which crystalline and fluid nuclei occur with comparable frequency is analyzed. The saturation vapor pressure of the liquid phase is denoted

by  $p_1$ , that of the solid phase by  $p_2$ . By equation (38) the condition for comparable nucleation frequency reads

$$\frac{p}{p_2} = \left( \frac{p}{p_1} \right)^{1.38}$$

or

$$\ln p = \ln p_1 + 2.6(\ln p_1 - \ln p_2) \quad (39)$$

(The factor 2.6 is equal to  $1:(1.38 - 1)$ ). Figure 7 shows the vapor pressure curves  $\ln p_1$  and  $\ln p_2$  plotted against  $T$ . According to equation (39) the curve for  $\ln p$  would then have about the shape of that indicated by the broken curve. Below this limiting curve, more crystalline nuclei, above it, more fluid nuclei are to be expected. However, this theoretically interesting solution is meaningless in practice as long as the nucleation frequency lies below a limit amenable to observation. For that reason it is necessary to determine, in the same manner as in section 2, the curve of that pressure at which a formation of fluid nuclei occurs at all in observable amounts (dotted curve). The intersection point A of the two curves characterizes the temperature  $T_A$  at which an isothermal pressure rise would result in a simultaneous separation of fluid and crystalline nuclei. Below  $T_A$  only solid, above  $T_A$  only fluid nuclei would be observed.

Naturally, it may also happen that no intersection point appears. In that event, the law of stages holds unrestrictedly.<sup>8</sup>

## 7. THE GENERAL RESISTANCE ANALOGY

As already stated several times in the foregoing, the equations (17), (23), and (32), applicable to the elementary process, can be so transformed by extension with a suitable factor that they could be interpreted as the Kirchhoff equations of a suitably chosen network of wires. It can be proved that this electrotechnical analogy is possible in complete generality for the condensation and dissolution process of any structure consisting of atoms. Again it is assumed that, besides the vapor phase of a substance, some fractions of another phase are present in a container. These fractions are hereinafter called crystals, without in any way infringing upon the general character. An uninterrupted input or transport of vapor and removal or addition of crystals of random specific size assures the steady distribution of the crystals of various sizes and shapes.

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<sup>8</sup>Such a case seems to exist in the theoretical case treated by Stranski and Totomanow (Z. f. phy. Chem. (A), 163, p. 399, 1933).

Next, we consider any random specified type of crystals, say, of the shape represented in figure 8, for example. For a full description of such a crystal, a greater number of parameters are usually advantageous, a single one of which is, say, the number  $\nu$  of atoms in this crystal. By deposition of an atom at a well defined spot of this crystal, a crystal of type II with  $\nu + 1$  atoms is produced.  $J$  is the excess per second of the growth processes which lead from I to II, through the evaporation processes which lead from II to I. Then, if  $n_I$  and  $n_{II}$  are the number of crystals of type I and II in the steady state, the equation for this specific transition process reads

$$J = n_I a - n_{II} q_{\nu+1} \tag{40}$$

where  $a$  and  $q_{\nu+1}$  are the repeatedly employed deposition and evaporation probabilities of the atom at that particular spot. With the abbreviation  $\beta_{\nu+1} = \frac{a}{q_{\nu+1}}$  the result is again

$$n_{II} = n_I \beta_{\nu+1} - \frac{J}{a} \beta_{\nu+1} \tag{41}$$

Again  $q_{\nu+1} = F(T) e^{-\frac{\Phi_{\nu+1}}{kT}}$  and  $a = F(T) e^{-\frac{\Psi}{kT}}$ , are introduced, hence,  

$$\beta_{\nu+1} = e^{\frac{\Phi_{\nu+1} - \Psi}{kT}}$$

The energy of separation  $\Phi_{\nu+1}$  depends, as a rule, on all the parameters of state of the states I and II, rather than on  $\nu$  alone.

Now, visualize the crystal II built up successively from single atoms. To each one of the  $\nu + 1$  single processes, there corresponds a specific  $\beta_i$ . The individual  $\beta_i$  still will be dependent upon the sequence in which the atoms of the crystal are joined together. But the product  $P(II)$  of all  $\beta_i$

$$P(II)_{\nu+1} = \prod_{i=1}^{\nu+1} \beta_i = e^{\frac{\sum_{i=1}^{\nu+1} \Phi_i - (\nu+1)\Psi}{kT}} \tag{9}$$

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<sup>9</sup>Factor  $\beta_1$ , which by itself corresponds to no growth process, is put equal to 1; hence  $\Phi_1 = \Psi$ .

is solely dependent upon the configuration of crystal II, because the total work of growth  $\sum_{i=1}^{\nu+1} \phi_i$  can no longer depend upon the manner in which the growth took place.

Dividing equation (41) by  $P_{\nu+1}^{II}$  gives

$$\phi_I - \phi_{II} = JR_I \quad (42)$$

where, for abbreviation

$$\phi_I = \frac{n_I}{P_{\nu}(I)}, \quad \phi_{II} = \frac{n_{II}}{P_{\nu+1}(II)} \quad (42a)$$

and

$$R_I = \frac{1}{a} \frac{1}{P_{\nu}(I)} \quad (42b)$$

Every possible form of crystal can now be characterized by a point in the space of the parameters, which define this form. To every possible transition,  $I \rightarrow II$ , we then correlate a wire connection between the points of state I and II, to which the resistance given by equation (41b) is allocated. The equation (42) can then be regarded as the Kirchhoff equations of this wire netting and  $\phi$  as the corresponding potential of the nodes in this net. This interpretation is possible, because  $\phi$  is merely dependent upon the state, but not the manner in which a crystal is built up.

Obviously, this network of wires does not have to be multidimensional. Since the number of possible forms is finite, theoretically one parameter that counts the possible forms, may be sufficient. But for the representation the use of two or three parameters, as in sections 4 and 5, is more convenient so that the net becomes two or three dimensional.

This network itself is rather complicated even in simple cases. In the networks treated in sections 4 and 5, a large number of wires were consistently ignored because of their high resistance and complete wire systems combined into one resistance. For the actual calculation, this general analogy is therefore of little help. However, the purely qualitative distribution of the resistances will be indicated.

The resistance of a wire depends solely upon its initial point and has the form

$$R = \frac{1}{a} e^{\frac{\nu\psi - \sum_{i=1}^{\nu} \phi_i}{kT}} \quad (43)$$

where the quantity  $\nu\psi - \sum_{i=1}^{\nu} \phi_i$  in the exponent is the work to be performed to produce the system corresponding to the initial point of the wire by reversible process from the vapor. Of all the wire joints which lead from crystals with  $\nu$  atoms to those with  $\nu + 1$  atoms, the wires proceeding from the crystals with the least work of growth are therefore the wires of the smallest resistance. Whether this minimum is always as sharp in more general cases as on the model used above, requires further study. During the advance along the road of minimum resistance from smaller to larger crystals, the work of growth must, at some time, reach a maximum value, because, while for very small systems it certainly increases with  $\nu$ , it must, at very great  $\nu$  become proportional with  $\nu$  negatively arbitrarily great, so far as the vapor is supersaturated at all with respect to the very large crystals. The crystal on which the resistance reaches its (absolute) maximum with regard to advancing with  $\nu$  and a minimum in comparison to the other wires with the same  $\nu$ , is called the Volmer nucleus. The resistance at this point is

$$R_{\text{nucleus}} = \frac{1}{a} e^{\frac{A_K}{kT}} \quad (43a)$$

with  $A_K$  the work of nucleation. As is seen, the saddle-like character of the resistance distribution near the nucleus is completely independent of the model. The specific model representations merely yield information about the number of parallel wires of equal resistance in the saddle point, the distinct character of the saddle, and the extent to which any secondary maximums in the otherwise very jagged curve of the resistance become evident. The order of magnitude of the total resistance between two points with very small and very great  $\nu$  is, however, solely defined by  $R_{\text{nucleus}}$ .

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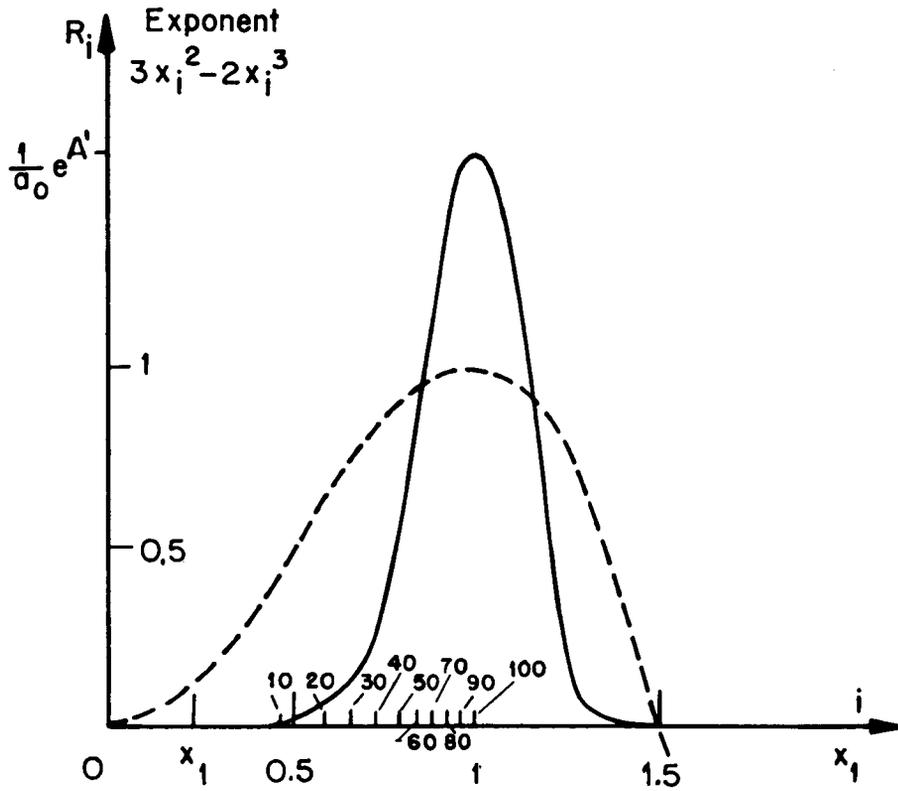


Figure 1.- Resistance  $R_i$  plotted against droplet radius  $x_1$  (case  $A' = 10$  and  $n = 100$ ). - - -: Curve of exponent  $3x_1^2 - 2x_1^3$ .

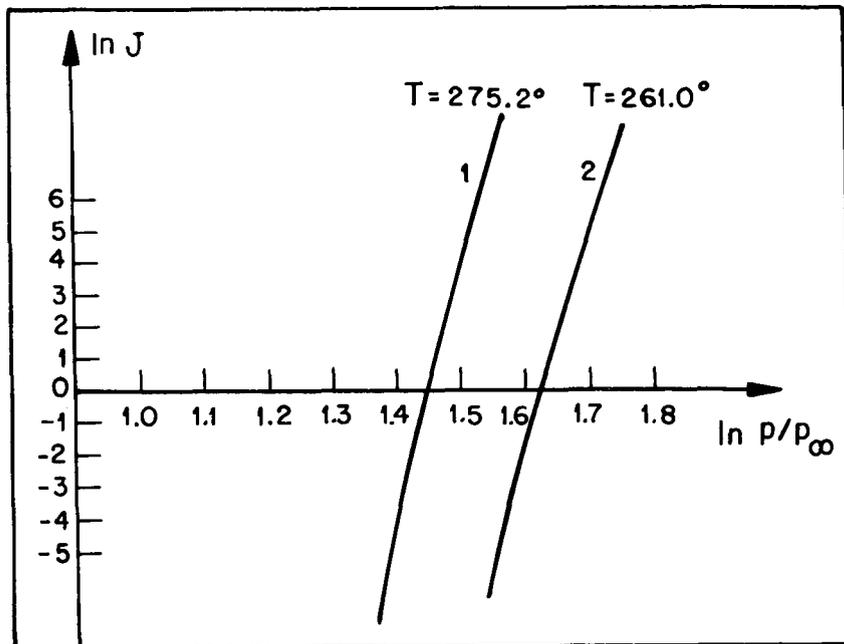


Figure 2.-  $\ln J$  plotted against  $x = \ln \frac{p}{p_\infty}$  at two temperatures, computed for water by equation (13a).

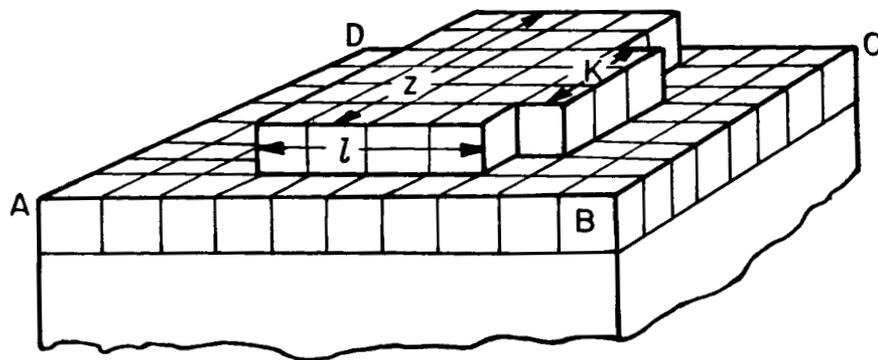


Figure 3.- A specific state of crystal growth.

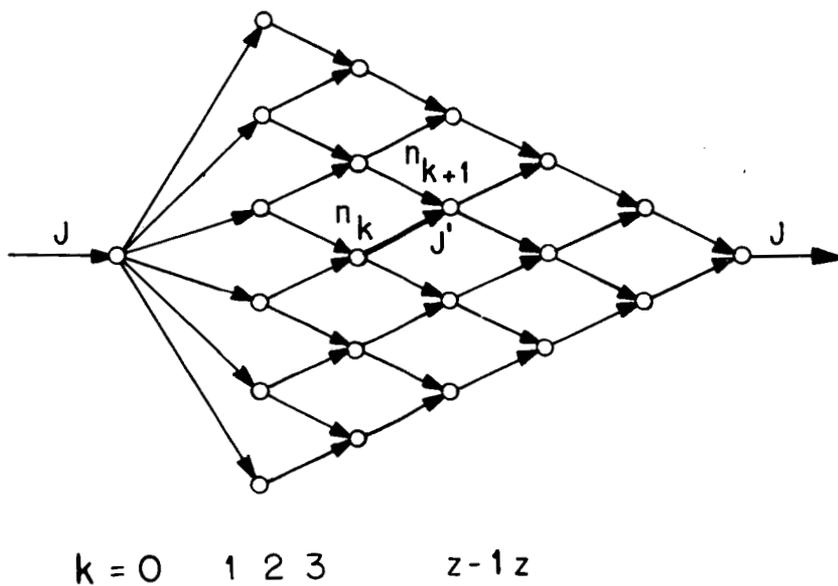


Figure 4.- Network of partial currents for the growth of the linear chain.

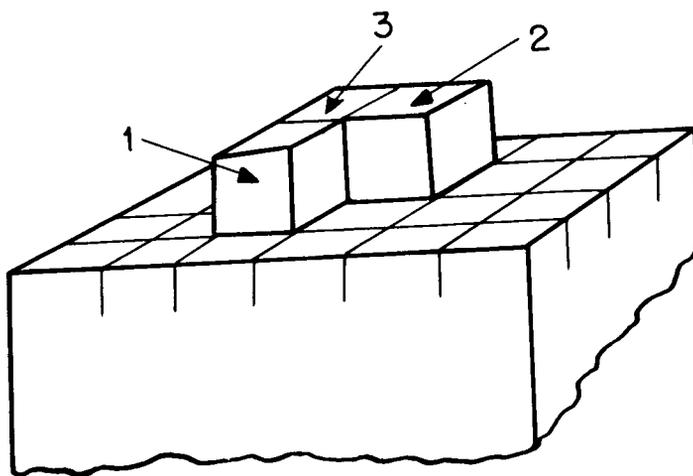


Figure 5.- Derivation of the relation  $\beta_0^\beta = \beta_1^2$ .

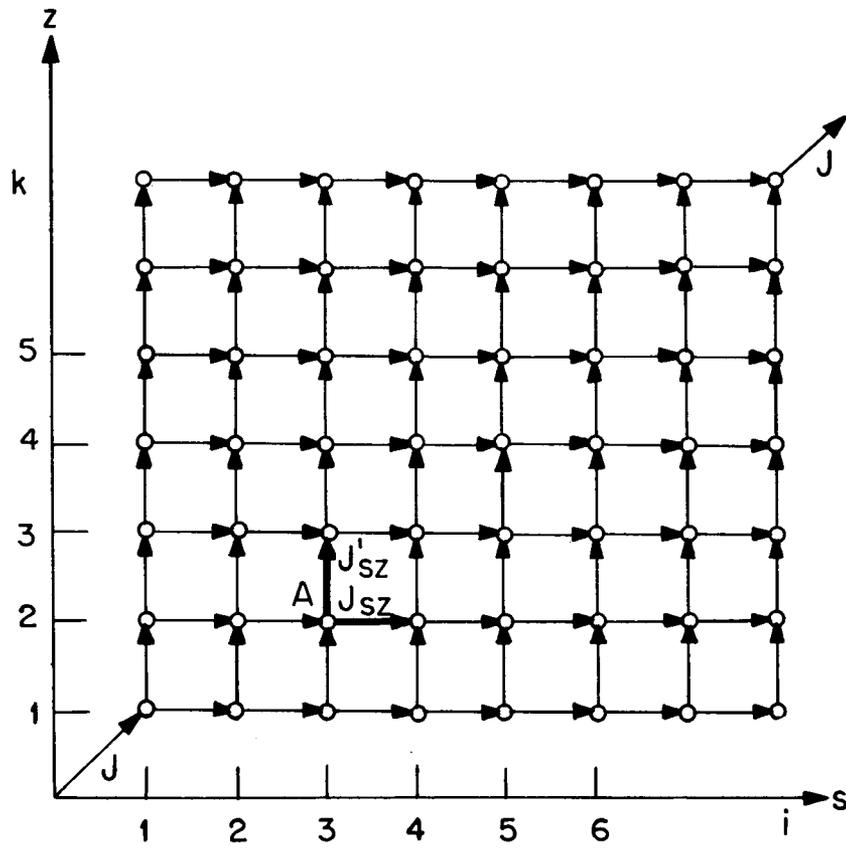


Figure 6.- Current network for growth of the plane. Point A:  
Rectangle: 3 x 2. Size of base: 8 x 7.

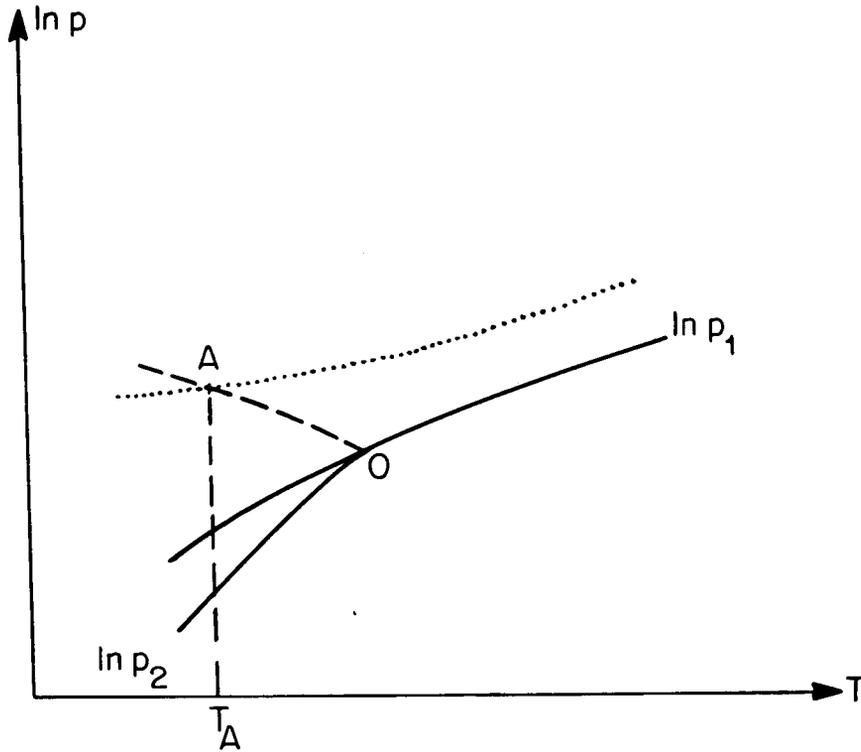
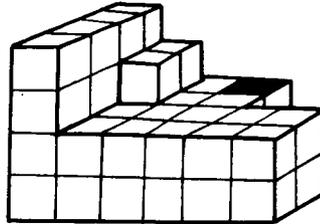
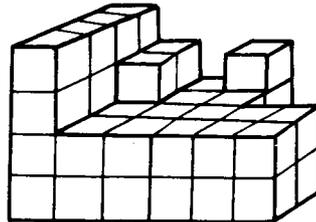


Figure 7.- Ostwald's law of stages. - - -: Curve of equal frequency of critical crystalline and fluid nuclei. Above  $OA$ : Excess of fluid nuclei. Below  $OA$ : Excess of crystalline nuclei. . . . Curve of nucleation frequency 1.



State I

a.



State II

d.

Figure 8.- The most elementary process of crystal growth. Deposition of one atom at the emphasized spot of state I leads to state II. Evaporation of raised atom on crystal II leads to crystal I.