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Granulation, Phase Change, and Microstructure

Kinetics of Phase Change. III*

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The theory of the preceding papers is generalized and the notation simplified. A cluster of molecules in a stable phase surrounded by an unstable phase is itself unstable until a critical size is reached, though for statistical reasons a distribution of such clusters may exist. Beyond the critical size, the cluster tends to grow steadily. The designation "nuclei" or "grains" is used according as the clusters are below or above the critical size. It is shown that a comprehensive description of the phenomena of phase change may be summarized in Phase Change, Grain Number and Microstructure Formulas or Diagrams, giving, respectively, the transformed volume, grain, and micro-

structure densities as a function of time, temperature, and other variables. To facilitate the deduction of formulas for these densities the related densities of the "extended" grain population are introduced. The extended population is that system of interpenetrating volumes that would obtain if the grains granulated and grew through each other without mutual interference. The extended densities are much more readily derivable from an analysis of the fundamental processes of granulation and growth. It is shown that, under very general circumstances, the densities of the actual grain population may be expressed simply in terms of the extended population.

A. NUCLEI AND GRAINS

IN the previous papers¹ we have developed a treatment of the transformation mechanism which we may now generalize. At the same time, it is desirable to simplify some of the previous notations. To recapitulate: It appears that the grains of a new phase generally originate at certain centers or heterogeneities in the old phase. In these it is desirable to distinguish between two stages. For even though, in the supercooled (or superheated) condition, the *internal* free energy of the new phase is lower than in the old, the additional opposing free energy change, involved in the creation of an interface, makes a cluster of the new phase below a certain critical size (function of the thermodynamic conditions) incapable of steady growth. Only if a cluster larger than the critical size occurs, e.g., through spontaneous or stimulated fluctuations, will it grow steadily.

Now, in previous investigations,¹ we have used the name "germ nuclei" to refer to such activable regions before they reach the critical size, and "growth nuclei" for those which have reached and passed the critical size. It is possible, and perhaps desirable for psychological reasons, to

simplify the terminology by calling the former simply "nuclei" and the latter "grains" (or "new grains" if necessary for specificity).

This we shall do in the future, *confining the term "nucleus" to a cluster of the new phase smaller than the critical size, the term "grain" to a cluster larger than the critical size.* The region (originally a nucleus) around which a grain has grown may be referred to as the "*grain center*." A nucleus or grain may have foreign matter (inclusion) as a core, or it may form on a foreign surface and thus not be entirely surrounded by the old phase, but, in any case, the specifications for the critical size may be worked out.^{1(a)} It has been suggested that the process of passing from the nucleus to the grain stage shall be termed "granulation."[†] The "*granulation rate*" is the number of nuclei, per unit time and unit volume, which "pop," i.e., pass through the critical size, and, becoming grains, embark upon a career of steady growth.

Several recent investigators² have discussed the necessary existence, in equilibrium, of clusters of one phase in another before the temperature

[†] This replaces the term "nucleation" which was used in K.P.C. I in conformity with the current somewhat vague terminology. It seems logical, to confine the term nucleation to the process of becoming a nucleus.

² In particular J. Frenkel, J. Chem. Phys. 7, 538 (1939); W. Band, *ibid.* 7, 324 (1939); J. E. Mayer and S. F. Streeter, *ibid.* 7, 1019 (1939). A connection has also been established with the general statistical mechanical treatment given by Mayer and his collaborators.

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¹ (a) J. Chem. Phys. 7, 1103 (1939); (b) *ibid.* 8, 212 (1940); referred to as K.P.C. I and II, respectively.

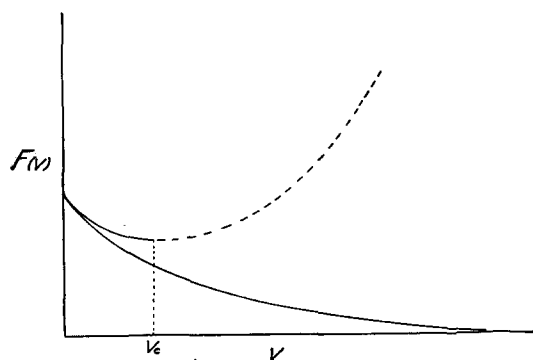


FIG. 1.

for macroscopic transition is reached.^{††} These “heterophase clusters” are nuclei in our sense of the word. In the case of a substance free from foreign particles, they are the only nuclei present. Their typical size-frequency density (i.e., number of given size per unit volume), at a certain temperature T_1 above the transition point, is indicated by the solid curve in Fig. 1. Below the transition point, the critical size diminishes from infinity to some finite value. Thus, if we quench suddenly from T_1 to a supercool temperature T_2 , for which the critical nucleus size is v_c , all clusters larger than v_c , present at T_1 , are effective grains and start growing steadily. Those below the critical size shift their frequency statistically and, it can be shown, generally increase in number, so that at a later time the frequency is given by a curve like the dotted one in Fig. 1. The general kinetics of the processes involved will be analyzed in a later paper. For the present, the underlying physical situation may be described as follows: Any particular nucleus below the critical size has a higher tendency to dissolve than to grow. But when we consider the entire group of a particular size, we find that the tendency of its majority to dissolve is more than balanced by the minority tendency of the *larger group* of next smaller size to grow. The granulation rate, at any time, is the number of clusters per unit volume which pass through the “bottleneck” v_c per unit time.

Sometimes, the distribution with which we start was not in equilibrium at the pretreatment

^{††} For simplicity of speech, and in conformity with the usual experimental conditions, we consider pressure kept constant and temperature as the controlling variable. Also, we take the new phase as the one stable at lower temperatures, and therefore speak of supercooling. The generalization can be made without difficulty.

temperature. Also, it may be non-uniform, so that the resulting density varies in space. The considerations in this paper will, however, apply generally to these and other industrially important cases where the transforming substance contains foreign heterogeneities which catalyze the reaction by providing adsorbing-activating surfaces on which nuclei and grains form. These, like the heterophase clusters, may be present from the beginning of the reaction, and are therefore determined by its “prehistory”; or they may be introduced physically, or formed chemically, during the reaction, and are therefore functionals of its history.

B. VOLUME, GRAIN, AND FREQUENCY DENSITIES

We may arrange observations on the kinetics of transformation under the following headings. First we consider the *volume density* V of the new phase (i.e., fraction of unit volume of space occupied), as a function of time t , position P , initial temperature T_0 , and as a functional of the prehistory and of the subsequent type of thermal treatment $T(t, T_0, P)$. For given prehistory and type of history (e.g., isothermal, linear cooling, “seeding” at a certain time, etc.), and for the unit volume around a given point, a three-dimensional diagram relating V , t , and T_0 may be constructed. We shall call this the “*Volume Diagram*” or “*Phase Change Diagram*” in contrast with the familiar Phase Equilibrium Diagrams to which it reduces in the cross section at infinite time (system with isothermal history). The analytical representation of

$$V \equiv V(t, T_0, P)$$

will be called the “*Phase Change Formula*.” It is to be remarked that V corresponds to the variable, “degree of advancement” of a reaction, used by De Donder-Rysselbergh³ and Guggenheim⁴ in various thermodynamic studies.

A second important type of relation is that giving the *grain density* N (i.e., number of grain centers per unit volume)* as a function of t , T_0 ,

³ De Donder-Rysselbergh, *Affinity* (Stanford University Press, 1936).

⁴ Guggenheim, *J. Chem. Phys.* 7, 103 (1939).

* This is a reversal of the notation in the two earlier papers, where N' was used to designate grain density and N was used for nucleus density. Since we shall deal

P , $T(t, T_0, P)$, and the prehistory. Again, for given prehistory, type of history, and location, we may construct a three-dimensional "Grain-Number Diagram" between N , t , and T_0 . The analytical representation of

$$N \equiv N(t, T_0, P)$$

will be called the "Grain-Number Formula."

The grain-number diagram or formula is of great importance in the theory of microstructures resulting from given treatment. For a given type of crystal habit, a quantitative description of microstructure may be given by the *volume-frequency density* $F(v)dv$, i.e., the number, per unit volume, of centers of grains (or nuclei) with volume between v and $v+dv$. This, too, is a function of time, position, initial temperature, etc. Fixing the prehistory, history, and location, we still have one more variable here, and it would be necessary to use a four-dimensional plot to represent the frequency density as a function of both time and temperature. If, however, we fix the initial temperature, we may set up a three-dimensional diagram between F , v , and t . This may be called the microstructure-time diagram. A more important diagram will be that giving the volume-frequency density, after infinite (or very long) time, as a function of initial temperature. This we shall designate the "Microstructure Diagram." The general formula for F will be called the "Microstructure Formula." By definition, the relations

$$N = \int_{v_c}^{\infty} F(v)dv \quad (1)$$

and

$$V = \int_0^{\infty} vF(v)dv \quad (2)$$

must subsist.[†]

In some cases (crystalline aggregates), the orientation η (abbreviation for the two direction-specifying coordinates) of the individual grains with respect to some fixed direction in space may be distinguished. In others, where the grains are

primarily with grain density, it is desirable to make this simplification even at the risk of some difficulty in comparing with I and II.

[†] The "nucleus density" has the obvious correlative definition $\int_0^{\infty} F(v)dv$. Formula (2) is correct only if the unit volume is large compared with the grain sizes or the space gradient of grain density; see Eq. (5) below.

isotropic and possess complete spherical symmetry (drops and bubbles), this distinction is lost. In the anisotropic grain case, a more detailed description of the system may be given by taking into account the distribution in orientation of the grains. This leads to an orientation-dependent grain density

$$N(\eta, t, T_0, P)d\eta,$$

and an orientation-dependent frequency density

$$F(\eta, v, t, T_0, P)d\eta.$$

The previously given N and F may be regarded as orientation-averaged densities, and it is with these that we shall work in the following unless otherwise specified. We note that all the subsequent analysis may be carried through equally well with the orientation-dependent densities.

The deduction of formulas for V , N , and F is considerably facilitated by the conception of related "extended densities" which we shall now develop. As a transformation proceeds, two phenomena occur: (1) Some nuclei are reached and enveloped by growing grains and become inoperative for production of new grains. (2) The growing grains impinge upon one another and interact; the possible forms of this interaction will be discussed later. Those grains which would have appeared up to any given time, if their nuclei did not lie in occupied regions, will be referred to as "phantom grains."^{1(b)} The grains (phantoms included), taken in the fullest extent they would have, had their growth been unimpeded and unmodified by impingement upon one another, will be referred to as "extended grains." To visualize the extended-grain population, we may imagine a representative geometrical system of interpenetrating volumes obeying exactly the same laws as the physical system except that the volumes *granulate and grow through each other*. For brevity, we shall use the adjective "extended," and the superior symbol \sim , to designate any attribute of the representative geometrical system.^{††} Thus, the "extended volume-frequency density" $\tilde{F}(\tilde{v})d\tilde{v}$ is the number per unit volume of (phantom-included) grains or nuclei of extended volume between \tilde{v} and $\tilde{v}+d\tilde{v}$. The "extended grain density" \tilde{N} is the total number

^{††} This is a simplification of the notation in the previous papers in which the subscript αx was employed.

larger than \bar{v}_c in the unit volume, i.e.,

$$\bar{N} = \int_{v_c}^{\infty} \bar{F}(\bar{v}) d\bar{v}. \quad (1')$$

Similarly, the *extended volume density* \bar{V} is the fraction of unit volume of space occupied by the extended population. By definition then, over a volume large compared with the size of an average grain

$$\bar{V} = \int_0^{\infty} \bar{v} F(\bar{v}) d\bar{v}. \quad (2')$$

Evidently \bar{V} can become larger than unity.

(1') and (2') enable us to compute \bar{N} and \bar{V} when \bar{F} is given. If, on the other hand, \bar{N} and the law of growth of the individual extended grain is easily found (a frequent case), \bar{V} and \bar{F} may be calculated therefrom. V , N , and F may then be calculated, so that a knowledge of \bar{N} and the law of growth of the individual grain is all that is required for the determination of the kinetics of a granular aggregate (sections C and D).

The introduction of the extended densities considerably facilitates the theoretical treatment of transformation kinetics. The problem can now be split into two parts. First, an analysis of the microkinetic processes of granulation and growth leads to the determination of the extended densities as a function of position, time, initial temperature, and as a functional of the prehistory and type of history.* Then, by the formulas to be developed in this paper, the observable macrokinetic quantities, V , N , and F , of the *actual* grains of the new phase may be deduced.

C. AVERAGE DENSITIES AND THEIR RELATIONS

It is necessary at this point to refine our concepts somewhat. So far, we have applied the term "density" to numbers or quantities found

* We shall show elsewhere that information about prehistory and type of history corresponds to boundary conditions for the system of differential equations governing the nucleation and growth processes of the extended population. This system is also representable by a partial differential equation of the same form as that which appears in the theory of heat conduction in a heterogeneous bar or electric propagation in a non-uniform cable. When this is set up and solved under appropriate boundary conditions, it yields the extended densities. On the other hand, the latter may often be found directly by elementary methods, as in K.P.C. I and II, where assumptions holding in special cases are made.

in unit volume, without pausing to consider the dependence upon the absolute size of the unit volume. We obtain a useful, statistically suitable, definition of density for point distributions in the following manner: Subdivide the space containing the points or grain centers into "physically small" cells Ω with positions indicated by subscript capital letters. Each is further subdivided into "geometrically small" subcells $\Delta\omega$ (positions designated by small letters) which may become infinitesimal. Let N_Q denote the number of centers contained in Ω_Q . The average

$$N(Q) = N_Q / \Omega_Q$$

will be referred to as the "average density around Q " or, simply, the "*density around Q* ." The absolute size of Ω is arbitrary within the limits set by the following conditions: (1) It shall be large enough to contain sufficiently many centers so that changing its dimensions continuously alters the density within only slowly. (2) It shall be small enough so that the average number of centers in the subcells $\Delta\omega$ does not vary appreciably from one side of Ω to the other. A further analysis of the concept of average density leads to some very interesting questions which we shall not discuss here. For the present purpose, the rough verbal restrictions given in (1) and (2) will suffice. We merely note that, for a sufficiently fine-grained distribution, the Ω will be small enough to serve, approximately, as elements of integration. We shall assume this in the following, replacing the individual Ω by $d\Omega$ whenever a summation is required.

It is clear that, though the average density may vary in a complex manner from one region of space to another, the centers within a cell may be very simply distributed. A particularly important case, *which includes most physical situations*, is where the numbers in the subcells are distributed about the local average N according to the laws of chance; i.e., the probability of finding m centers in any $\Delta\omega$ is given by the Bernoulli distribution function:

$$\binom{N}{m} (\Delta\omega)^m (1 - \Delta\omega)^{N-m}.$$

The distribution is then said to be "*locally random*." This includes the many important

systems where the gradient of grain density is very sharp, even infinitely sharp, as when the nuclei are distributed upon certain surfaces (walls or grain boundaries of the old phase). We shall investigate the case of local randomness in detail below.

We return now to consideration of the quantities discussed in the previous section. It is clear that practically useful descriptions of frequency and grain distributions will be in terms of average densities. Also, a theoretical treatment is likely to yield information only about such average densities. In related fashion the probable or average "extended volume density around a point P " $\tilde{V}(t, P)$ may be defined by the average number of extended grains which have grown through $d\Omega_P$.† This may be expressed in terms of the integral of \tilde{N} over the entire region of influence of P

$$\tilde{V}(t, P) = \int \tilde{N}(t', Q) d\Omega_Q, \quad (3)$$

where t' is a retarded time something like that appearing in field theories (electromagnetism, etc.). The retardation $t - t'$ is the time required for the "propagation" or growth of a grain with linear velocity G from its origin at Q to its terminus P at time t . G is a function of temperature, concentration, etc., i.e., in general of position and time. Expressing Q in terms of spherical coordinates r, θ, φ about P as origin, we obtain the more explicit form (letting $d\psi = \sin \theta d\theta d\varphi$)

$$\tilde{V}(t, P) = \int_0^\pi \int_0^{2\pi} \int_0^{\tilde{r}} \tilde{N}(t', r, \theta, \varphi) r^2 dr d\psi, \quad (3')$$

where \tilde{r} denotes the radius of the region of influence for P (i.e., $t' = 0$). If external conditions remain constant in time so that G is a function only of position ρ, θ, φ then

$$t' = t - \int_0^{\tilde{r}} \frac{d\rho}{G}.$$

† It is evident that, upon integration over any macroscopic volume, the density so defined yields the correct total extended volume. Thus, for instance, the average extended volume in a macroscopic unit volume is the integral over the volume

$$\tilde{V} = \int d\Omega_P \int \tilde{N}(t', Q) d\Omega_Q.$$

This is the integral equivalent of formula (7) in K.P.C. I.

If the temperature is changing so that G is also a function of the time w , t' must be found from the conditions that, in the integral of the differential equation

$$d\rho = -G(\rho, \theta, \varphi, w) dw,$$

$w = t$ at $\rho = 0$ and $w = t'$ at $\rho = r$. This then expresses t' as a function of r , $t'(r, \theta, \varphi; t)$. On the other hand, if we so wish, the differential equation may be integrated to give r as a function of t' , $r(\theta, \varphi, t'; t)$, and r may be replaced in (3') by t' as an independent variable.

For anisotropic grains G depends also on the grain orientation, so that $\tilde{N}(t', Q)$ in the integral of (3) should be replaced by an average over the densities in the various orientations, each associated with a different value of the retarded time t' , i.e.,

$$\tilde{V}(t, P) = \int \int \tilde{N}(\eta, t'_\eta, Q) d\eta d\Omega_Q \quad (4)$$

or

$$\tilde{V}(t, P) = \int_0^\pi \int_0^{2\pi} \int_0^{\tilde{r}} \int \tilde{N}(\eta; t'_\eta, r, \theta, \varphi) d\eta r^2 dr d\psi. \quad (4')$$

This may be applied to various cases of distribution of the grain centers, e.g., uniformly random distribution in space;^{1(b)} random distribution on foreign surfaces (ingot walls in solidification, electrode plates in electrolytic deposition, etc.); random distribution on internal grain surfaces of the old phase as in grain boundary nucleation.

We shall not discuss the general problem of evaluating (4') here, but three limiting cases previously considered^{1(b)} recommend themselves to our attention. In the first, where the growth is polyhedral, i.e., approximately equal in all directions, t'_η is the same for all directions, and

$$\int \tilde{N}(\eta, t'_\eta, Q) d\eta = \tilde{N}(t', Q)$$

with G in t' representing the rate of radial growth of the pseudospherical grain. In this case, as is to be expected, (4) reduces to (3).

In the second case, that of *plate-like* growth, the grain grows primarily parallel to a single plane, i.e., its (small) thickness h does not change

appreciably while it grows planarly from its center with radial velocity G . If the plate grows in the shape of a circular sector with constant angle γ (radians), the cross section of the advancing face of the plate at distance r from its origin is γrh . Supposing, also, that the distribution of orientations is random, the probability of a grain with center at Q intercepting the element of volume $d\Omega_P$ at P , is the ratio of the area intercepted by the plate on the sphere of radius r to the area of the sphere itself, i.e.,

$$h\gamma r/4\pi r^2 = h\gamma/4\pi r,$$

where r is the distance PQ . Thus, out of the total $\tilde{N}(t', Q)$ of grains which had appeared around Q at t' , only the fraction

$$\frac{h\gamma}{4\pi r} \tilde{N}(t', Q)$$

is effective. Similarly, in the third case, that of *lineal* or needle-like growth at the rate G with approximately constant cross section a , the probability of a grain, originating at Q , intercepting $d\Omega_P$ is

$$\frac{a}{4\pi r^2}$$

and the effective orientation-averaged grain density is

$$\frac{a}{4\pi r^2} \tilde{N}(t', Q).$$

For brevity, let us designate the factor in front of \tilde{N} in (4') by $\sigma r^{k-1}/4\pi$ so that

$$\tilde{V}(t, P) = \frac{\sigma}{4\pi} \int_0^\pi \int_0^{2\pi} \int_0^{\tilde{r}} r^{k-1} \tilde{N}(t', r, \theta, \varphi) dr d\psi, \quad (4'')$$

where

$$\begin{array}{lll} \sigma = 4\pi & k=3 & \text{for polyhedral growth} \\ \sigma = h\gamma & k=2 & \text{for platelike growth} \\ \sigma = a & k=1 & \text{for lineal growth.} \end{array}$$

Integrating (4'') by parts with respect to r , and remembering that

$$\sigma r^k/k = \tilde{v}(t, t')$$

for the three types of growth, we have

$$\begin{aligned} \tilde{V}(t, P) = & -\frac{1}{4\pi} \int_0^\pi \int_0^{2\pi} \int_0^{\tilde{r}} \tilde{v}(t, t') \\ & \times \left(\frac{\partial \tilde{N}}{\partial r} + \frac{\partial \tilde{N}}{\partial t'} \frac{\partial t'}{\partial r} \right) dr d\psi \end{aligned}$$

or replacing r by t' as an independent variable

$$\begin{aligned} \tilde{V}(t, P) = & -\frac{1}{4\pi} \int_0^\pi \int_0^{2\pi} \int_0^t \tilde{v}(t, t') \\ & \times \left(\frac{\partial \tilde{N}}{\partial r} G + \frac{\partial \tilde{N}}{\partial t'} \right) dt' d\psi. \quad (4''') \end{aligned}$$

In the special case where \tilde{N} is independent of position in the region of influence of P (i.e., approximately uniform grain density), this reduces to

$$\tilde{V}(t, P) = \int_0^t \tilde{v}(t, t') \frac{\partial \tilde{N}}{\partial t'} dt', \quad (5)$$

which is equivalent to (6) of K.P.C. I with the mechanism of granulation assumed there.

(3) or (4) expresses \tilde{V} in terms of \tilde{N} (and t' , whose relation to t depends on the law of growth $\tilde{v}(t, t')$ of the individual grain). It remains to express \tilde{F} also in terms of \tilde{N} and \tilde{v} . This may be done as follows: A grain of volume \tilde{v} at time t comes from a nucleus which granulated at a previous time t' . This time can be determined from \tilde{v} and t when the law of growth $\tilde{v}(t, t')$ is known. Now $\tilde{F}(\tilde{v}, t) d\tilde{v}$ equals the number of grains which granulated at the earlier time t' in an interval dt' corresponding to $d\tilde{v}$, i.e.,

$$-\tilde{F}(\tilde{v}, t) \frac{\partial \tilde{v}}{\partial t'} dt' = \frac{\partial \tilde{N}}{\partial t'} dt'.$$

From this we obtain the extended microstructure formula

$$-\tilde{F}(\tilde{v}, t) d\tilde{v} = \left(\frac{\partial \tilde{N}}{\partial t'} / \frac{\partial \tilde{v}}{\partial t'} \right) d\tilde{v}. \quad (6)$$

D. LOCALLY RANDOM NUCLEI

We shall now see that, for very general circumstances, it is possible to express V simply in terms of \tilde{V} . But first we must consider the possible types of grain interaction. When two grow-

ing grains of a new phase impinge, several things may happen. They may *coalesce* to form one larger grain, as frequently happens with gaseous bubbles and liquid drops. They may *adhere* to form a compound grain, ceasing growth at the common interface while continuing to grow normally elsewhere; this is usually true of crystalline grains. Again, a third mechanism may operate, especially if the surrounding phase is fluid, i.e., the interacting grains may *rebuff* each other, pushing away and continuing to grow as though there were no impingement. In this last case \tilde{V} will be a good approximation to V up to the last stages of transformation. In some situations, all three processes might operate to varying extents, together with motion of the grains (and nuclei) due to gravimetric or convective forces. This would complicate the transformation kinetics with considerations of mechanics. Here, however, we shall confine ourselves to stationary particles with the adhering-grain interaction alone. This assumption is usually valid for the growth of crystalline phases.

In the previous paper it was shown that, when the distribution of nuclei is uniformly random, V is given by

$$V(t, P) = 1 - \exp(-\tilde{V}(t, P)). \quad (7)$$

We shall here show that (7) is equally true when the distribution of nuclei (and initially present grains) is only locally random, and $\tilde{V}(t, P)$ is given by (3). With this generalization most of the important nucleated reactions encountered in practice are included.

Assuming the initial nuclei to be locally random, the extended grain population at any later time is also distributed with local randomness. Now, the ratio of non-overlapped to total volume of any random region, around any point P , is equal to the probability of untransformed volume there, i.e., $1 - V(t, P)$. As in K.P.C. II, let us choose for the random region the *increment* of transformed volume in an element of time. The non-overlapped part is dV , the total $d\tilde{V}$, and we have

$$dV/d\tilde{V} = 1 - V.$$

Integrating, we obtain Eq. (7).

An alternative derivation may be given as follows: Letting the average extended grain

density around Q , at time t' , be designated as above by $\tilde{N}(t', Q)$, we may calculate the probability that the element $\Delta\omega_q$, at q , does not contain any grain centers. By the Bernoulli distribution this probability ($m=0$) is

$$(1 - \Delta\omega_q)^{\tilde{N}(t', Q)}.$$

If we let $\Delta\omega_q$ become infinitesimally small, we get

$$\lim_{\Delta\omega_q \rightarrow 0} (1 - \Delta\omega_q)^{\tilde{N}(t', Q)} = \exp(-\tilde{N}(t', Q)d\omega_q).$$

This may be used to calculate the density of untransformed volume $1 - V$ around a point P , which is simply the probability that the volume element around P is completely untransformed. This probability is the product of probabilities of zero grain center content in each of the elements $d\omega_q$ (at its associated retarded time t') in the region of influence of P , so that we have

$$\begin{aligned} 1 - V(t, P) &= \prod_{\text{all } Q, q \text{ for } t' \geq 0} \exp(-\tilde{N}(t', Q)d\omega_q) \\ &= \exp(-\int \tilde{N}(t', Q)d\Omega_Q) = \exp(-\tilde{V}(t, P)) \end{aligned}$$

and we have justified Eq. (7).

We have now expressed V in terms of \tilde{V} . The latter, as we have seen, can be calculated from a knowledge of \tilde{N} and \tilde{v} . Likewise, assuming local randomness, N , v , and F may all be expressed ultimately in terms of \tilde{N} and \tilde{v} . Thus, taking unit volume around a given point, the ratio of actual to extended granulations in an element of time will evidently equal the fraction of untransformed volume at that time, i.e.,

$$\frac{\partial N}{\partial t} = (1 - V) \frac{\partial \tilde{N}}{\partial t} = \exp(-\tilde{V}) \frac{\partial \tilde{N}}{\partial t}$$

or, integrating,

$$\begin{aligned} N(t) &= \int_0^t \exp(-\tilde{V}(t)) \frac{\partial \tilde{N}}{\partial t} dt \\ &= \int_0^t \exp(-\int \tilde{N}(t', Q)d\Omega_Q) \frac{\partial \tilde{N}}{\partial t} dt. \quad (8) \end{aligned}$$

Again, as in deriving (7), the ratio of the non-overlapped increment dv of an *average* grain (of size v) to its extended increment $d\tilde{v}$, in an element

of time dt , equals the untransformed fraction at that time, i.e.,

$$\frac{dv(t, t')}{d\tilde{v}(t, t')} = 1 - V(t) = \exp(-\tilde{V}(t)).$$

Integrating, we get

$$v(t, t') = \int_{t'}^t \exp(-\tilde{V}(t)) \frac{\partial \tilde{v}(t, t')}{\partial t} dt, \quad (9)$$

where the values of the integrand are taken along the (space-time) route of growth of the grain around its center.

The expression for F may be obtained by reasoning similar to that used for (6). An average grain of volume v at time t comes from a granulating center at a previous time t' which can be determined as a function of v and t when the law of growth (9) of the actual (impinged) grains is known. $F(v, t)$ equals the number of actual grains which made their appearance at time t'

in the interval dt' corresponding to dv , i.e.,*

$$-F(v, t) \frac{\partial v}{\partial t'} dt' = -\frac{\partial N}{\partial t'} dt' = \exp(-\tilde{V}(t')) \frac{\partial \tilde{N}}{\partial t'} dt'.$$

Now, from (9)

$$\frac{\partial v}{\partial t'} = \int_{t'}^t \exp(-\tilde{V}(t)) \frac{\partial^2 \tilde{v}(t, t')}{\partial t' \partial t} dt,$$

so that the microstructure formula becomes

$$-F(v, t) = \frac{\partial \tilde{N}}{\partial t'} \exp(-\tilde{V}(t')) \int_{t'}^t \exp(-\tilde{V}(t)) \frac{\partial^2 \tilde{v}}{\partial t' \partial t} dt. \quad (10)$$

* Actually this is an approximation which is truer the more nearly t' corresponds to a unique volume in the actual grain population, i.e., the narrower the size frequency distribution of grains of the same "age," a function we have not analyzed here. This approximation makes (10) less and less valid toward the end of transformation. For a more detailed analysis of this and related points see a forthcoming paper in *Philosophy of Science* (Technical Supplement), January (1941).

Remarks on the Fluorescence, Phosphorescence and Photochemistry of Dyestuffs

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Many of the apparently conflicting facts of the photochemistry as well as of the phosphorescence and of the fluorescence quenching of dyes can be given a rational and unified interpretation if it be assumed that an electronically excited dye molecule can go over, by a process of internal conversion, to the electronic ground state of a reactive energy-rich tautomer. The endothermic reversion of such a tautomer to the electronically excited state of the original molecule would explain the weak, temperature dependent phosphorescence observed in some systems. In the presence of a suitable reducing agent the reactive tautomer may be reduced to a semiquinone. This process and the likely subsequent reactions are sufficient to explain the majority of dye-sensitized photo-oxidations as well as the photo-bleaching of dyes by reducing agents.

IT is well known that many dyestuffs which are able to fluoresce in solution are efficient sensitizers for photochemical reactions, while

In the case of chlorophyll, and possibly a few other dyes, it appears to be necessary to assume that the tautomer and a normal dye molecule can undergo a process of disproportionation. The assumption of this step leads directly and simply to an explanation of the rapid reversible bleaching of chlorophyll which is consistent with the other known photochemical and optical properties of this substance. In addition to the more familiar reaction steps which have been assumed as follow reactions in setting up the various mechanisms, it is necessary to include a step in which the HO_2 radical reduces a partially oxidized dye molecule (i.e., radical) back to the normal state. The several reaction steps assumed in these various schemes appear to be energetically feasible.

most of those which show no sign of fluorescence in solution are extremely inefficient sensitizers.¹

¹ Hurd and Livingston, *J. Phys. Chem.* **44**, 865 (1940).