Kinetics of Phase Change. I General Theory

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The theory of the kinetics of phase change is developed with the experimentally supported assumptions that the new phase is nucleated by *germ nuclei* which already exist in the old phase, and whose number can be altered by previous treatment. The density of germ nuclei diminishes through activation of some of them to become *growth nuclei* for grains of the new phase, and ingestion of others by these growing grains. The quantitative relations between the density of germ nuclei, growth nuclei, and transformed volume are derived and expressed in terms of a *characteristic time scale* for any given substance and process. The geometry and kinetics of a crystal aggregate are studied from this point of view, and it is shown that there is strong evidence of the existence, for any given substance, of an *isokinetic* range of temperatures and concentrations in which the characteristic kinetics of phase change remains the same. The determination of phase reaction kinetics is shown to depend upon the solution of a functional equation of a certain type. Some of the general properties of temperature-time and transformation-time curves, respectively, are described and explained.

A. INTRODUCTION

IN the appearance of a new phase from a previous one upon change of temperature, concentration, or other controlling factors, there is almost always the possibility of a lag or "metastable" condition beyond the equilibrium point. If, for the sake of specificity, we suppose temperature to be the controlling factor, and maintain other external conditions constant, we may describe the general phenomena as follows. Upon lowering the temperature slightly below the equilibrium point, and maintaining it there, the new phase sets in at a rate first slow, then faster, and finally toward the end of the transformation, slow again. The general S-shape of the transformation-time curve is characteristic of such changes at lower "supercooling" temperatures also, and any adequate theory must account for it quantitatively. As the temperature at which the transformation-time curve is determined is progressively taken lower, the time required for any given amount of transformation is found to be shorter until a minimum is reached. This temperature of very rapid rate, in the case of crystallization from solutions and melts, probably corresponds with the temperature of "supersolubility" and "superfusion" considered by Ostwald[1] and Miers.[2] Whether, upon

further lowering of the supercooling temperature, the time for the transformation is increased again depends upon other factors, primarily, as we shall see below, upon the "rigidity" of the phases involved with respect to the movements of the constituent particles. As an instance, with industrial importance, of the temperature-time curves of this sort, we may take the upper part of the hardenability governing "S curve" (not to be confused with the S-shape of the general transformation-time curves) of a simple carbon steel given in Fig. 1.[3] The lower part of this curve depends upon other complex factors which will be considered in detail elsewhere.

Two other groups of experimental data bearing on phase transformation are sometimes available. First, the number of growth nuclei of the new phase formed as a function of time may be observed. For transparent media this may often be done by direct count; for opaque media, by "freezing" the situation at a given stage of the transformation, cutting through the material, and, with the aid of polishing or etching techniques (as in metallography), determining the nuclear count in the exposed surface. Second, in similar ways, the frequency of grains of a given size at any stage of the transformation may be determined. In all the experiments in which the data are taken by inspecting the surface of a cut through the material, it must

[1] W. Ostwald, *Lehrbuch der Allgemeinen Chemie*, Vol. II, Part 2, p. 780.
[2] H. A. Miers, J. Chem. Soc. **89**, 413 (1906); Proc. Roy. Soc. **A79**, 322 (1907).
[3] E. S. Davenport and E. C. Bain, Trans. American Institute of Mining and Metallurgical Engineers, Iron and Steel Division **90**, 117 (1930). E. C. Bain, **100**, 13 (1932).
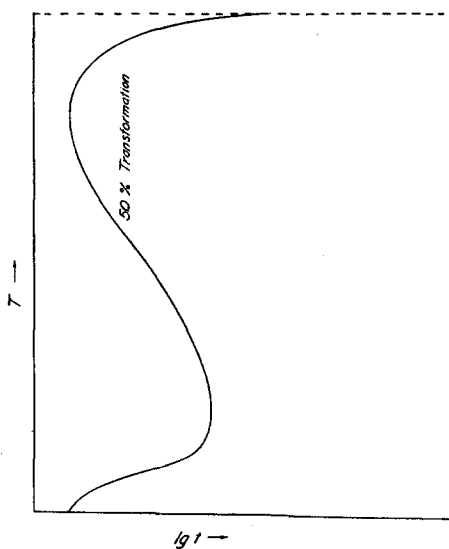
50 % Transformation

lg t →

FIG. 1.

be remembered that the surface is a random one, and the actual space frequency-size distribution must be deduced by statistical methods from the observed one. Methods for doing this have been given by Huber[4] and Scheil.[5]

Numerous investigations, both theoretical and experimental, have been made of the mechanism of phase change. There is an overwhelming amount of evidence pointing to the conclusion that the new phase is nucleated by tiny "germ nuclei," or "ultra-nuclei," which already exist in the old phase, and whose effective number can be altered by temperature and duration of superheating. These may consist of heterogeneities of any type, e.g., foreign particles with an adsorbed layer of the new phase, or tiny "blocks" or "crystal molecules" of the new phase (if solid) of the sort contemplated in one form or another by Zwicky, Smekal, Goetz, and many others.* In accord with the Gibbs-Thomson relation between vapor pressure and particle

size, such germ nuclei will have a lower transition temperature than grains of larger size. Nevertheless, the kinetic reasoning of Bloch, Brings, and Kuhn[7] (in the case of crystals) indicates that, for given supercooling or superheating, they grow or diminish considerably more slowly than grains of visible size. It would be highly desirable to have this theory placed on a more fundamental basis.

Whatever the hypothesis as to their nature, the existence of these nuclei is so well established that to ignore it in a theory of the kinetics of phase transformation is to open the way to gross discrepancy with the experimental data. The two attempts to deal with the kinetics of isothermal crystallization and solid-solid phase change by Göler-Sachs†[8] and Mehl-Johnson[9] are open to this objection. They effectively assume, following Tammann,[10] a constant rate of spontaneous nucleation of the new phase either throughout (and proportional to) the volume, or upon the grain surfaces, of the old phase. This spontaneous rate of nucleation is a function of temperature and can be determined following Volmer and others,[11] from thermodynamic considerations. We shall discuss this matter more fully elsewhere. In the meantime we may note that the assumption of constant rate of nucleation (proportional to the transforming volume or surface) is in very many cases definitely contradictory to the experimental facts. The work of deCoppet,[12] Hammer,[13] Scheil-Lange-Weise[14] and

leads to the result that the apparent probability of nucleation n of such germ nuclei increases with time up to a maximum after which it becomes constant. This may account for the fact that sometimes the rate of appearance of growth nuclei seems first to increase to a maximum before dropping off in accord with the simple theory where n is supposed constant.

[4] A. Huber, Zeits. f. Physik **93**, 227 (1935).

[5] E. Scheil, Zeits. f. Anorg. allgem. Chemie **201**, 259 (1931); W. Bading, E. Scheil and E. H. Schulz, Arch. Eisenhüttenwes. **6**, 69 (1932/33); E. Scheil and H. Wurst, Zeits. f. Metallkunde **28**, 340 (1936).

* A review of the experimental work bearing upon the nature of such block structures of crystals can be found in a book by Desch (reference 6) and in the report on the Solid State at the International Conference on Physics (1934). *Note added in proof.*—An interesting possibility is that some of these germ nuclei are "heterophase fluctuations," present from above the equilibrium temperature, of the type recently considered by Frenkel (J. Chem. Phys. **7**, 538 (1939)). This possibility, examined quantitatively,

[6] C. H. Desch, *The Chemistry of Solids* (Cornell University Press, 1934).

[7] R. Bloch, T. Brings, and W. Kuhn, Zeits. f. physik. Chemie **12B** 415 (1931).

† See also Huber (reference 4).

[8] F. v. Göler and G. Sachs, Zeits. f. Physik **77**, 281 (1932).

[9] R. F. Mehl, "The Physics of Hardenability," Symposium on Hardenability, American Society of Metals, Detroit, October, 1938.

[10] G. Tammann, *Kristallisieren und Schmelzen* (Leipzig, 1903).

[11] M. Volmer and A. Weber, Zeits. f. physik. Chemie **119**, 277 (1926); M. Volmer and M. Marder, Zeits. f. physik. Chemie **A154**, 97 (1931).

[12] L. C. de Coppet, Ann. Chem. et phys. **8: 10**, 457 (1907).

[13] C. Hammer, Ann. d. Physik **33**, 445 (1938).

[14] E. Scheil and H. Lange-Weise, Archiv Eisenhüttenwesen **11**, 93 (1937/38).

others, indicates that, as transformation proceeds, the rate of observed nucleation decreases much faster than in proportion to the untransformed region, so that the total number of growth nuclei approaches a definite saturation value characteristic of the degree of undercooling. It is as though only a certain number of germ nuclei which, becoming activated, can serve as nuclei for growth to grains of observable size, are originally present, and as transformation proceeds these become used up. Why the total number of growth nuclei which appear depends upon the temperature of supercooling, we shall see later.

The second assumption, which Göler-Sachs and Mehl-Johnson make in their analyses, deriving also from Tammann, i.e., that of the constant rate (at a given temperature) G of linear increase of a crystal from a growth nucleus, is well verified by experiment for macroscopic crystals. It is evidently equivalent to the assumption that the rate of volume growth of the crystal is proportional to its surface area (for constant shape). For extremely small crystals this relation must probably be modified as suggested before.

Putting the two assumptions discussed above together, one can derive an expression for the rate of transformation of the matter from the old phase to the new. Göler-Sachs, working with the case of volume nucleation, derive an approximate expression assuming the growing grains to be spheres and neglecting the slowing down effect due to the impingement of grains upon each other and the cessation of growth in the overlapping regions. Mehl-Johnson claim to follow a similar method, though modified to the case of surface nucleation (for the austenite-pearlite transition in silicon killed steels) and corrected for the overlapping of the growing spheroids. They indicate only the results, the derivation to be published later. In both cases, however, as is to be expected from the incorrectness of one of the fundamental assumptions, the results do not fit experiment. Thus, for instance, one conclusion which should follow from the assumption of constant rates of nucleation and growth is that the distribution curve for frequency with grain size when the transformation is complete, should practically be a horizontal straight line. Instead, as the data of Tammann-

Crone[15] on cadmium and aluminum, and of Scheil-Lange-Weise on the austenite-pearlite transition show, the frequency-size curve is concave to the abscissa, rising from zero for the largest size to a maximum and dropping to zero again. Thus there are actually far fewer small crystals than is to be anticipated on the basis of the constant nucleation hypothesis. This fact is of course consistent with the idea that the germ nuclei which serve as the basis of the growth nuclei get used up as the reaction proceeds. The apparent abnormal smallness in the number of very large grains is probably due to the above-mentioned difference between the frequency-size distribution on a random surface and the actual space frequency-size distribution. We shall allow for this later.

The above and related considerations lead us to adopt the following simple picture, which, we shall show in the sequel, accounts quantitatively for many of the phenomena of phase change. We shall also see that it leads, in one extreme case, to the assumptions which underlie the Göler-Sachs analysis. It thus includes the latter as a special case.

B. Relation Between Germ Nuclei, Growth Nuclei and Transformed Volume

Let us suppose that there were $\bar{N}$ germ nuclei distributed in any manner whatsoever per unit volume and present from above the equilibrium temperature. These consist either of small blocks of the subcritical phase or tough films of the latter surrounding foreign inclusions. At any rate, $\bar{N}$ is a function of the time and temperature of superheating, generally decreasing with increase of either.

During transformation the germ nuclei get used up and their number per unit volume $N \equiv N(t)$ decreases from $\bar{N}$ in two ways. First, some of them become active growth nuclei (whose number we represent by $N' \equiv N'(t)$) in consequence of free energy fluctuations (which may come from size, concentration, or order fluctuations in the various possible cases) which enable them to jump over the boundary of the metastable region. The probability of this happening is given by nN where $n \equiv n(T)$, the

[15] G. Tammann and W. Crone, Zeits. f. anorg. Chemie **187**, 289 (1930).

probability of formation of growth nuclei per germ nucleus per unit time, may be calculated as a function of temperature by methods similar to those of Volmer, Stranski-Kaischew,[16] Borelius,[17] and Becker.[18] It will have the general form*

$$n(T) = Ke^{-Q+A(T)/RT},$$

where Q, a constant, is an energy of activation (per gram molecule), R is the gas constant, and $A(T)$ is the work per gram molecule required for forming a growth nucleus at temperature T. Volmer and Weber[11] have demonstrated that a growth nucleus forming at an interface requires less work than one forming within a phase. Thus A is smaller and n larger at such an interface. It is to this fact that we may ascribe the formation of growth nuclei about germ nuclei long before spontaneous nucleation within the phase is appreciable. In certain extreme cases, where there are almost no germ nuclei present and the substance is greatly supercooled, the spontaneous nucleation throughout the volume will effect phase change. Such cases may be treated by picturing them in terms of a very numerous and uniformly dense distribution of germ nuclei with a correspondingly small $n(T)$, as will be seen below.

The variation of $A(T)$ with temperature has been worked out by Borelius[17] and Becker[18] for solid-solid reactions of a certain type. The form of this variation is probably quite general. A is found to decrease very rapidly as T is lowered, finally leveling off to an almost constant value at low temperatures. Q, on the other hand, is generally constant for a given substance over a large range. The result of the operation of these two factors is that, as the temperature drops, n increases from a negligible value at the critical temperature to a maximum at some subcritical

[16] I. N. Stranski and R. Kaischew, Zeits. f. physik. Chemie **B26**, 317 (1934); Physik. Zeits. **36**, 393 (1935).

[17] G. Borelius, Ann d. Physik **33**, 517 (1938).

[18] R. Becker, Ann. d. Physik **32**, 128 (1938).

* Since, as the work of Volmer (reference 11) has shown, the growth of crystals is primarily governed by the appearance of two-dimensional nuclei of the right size on the faces of the crystal, an expression very similar to the one for $n(T)$ results for the dependence of the rate of grain growth G on temperature.[16] In fact, we shall see later that there is strong evidence that, for a given crystallizing substance, n and G are approximately proportional to each other. This is extremely important in enabling us to simplify the treatment of phase changes under conditions of changing temperature and concentration.
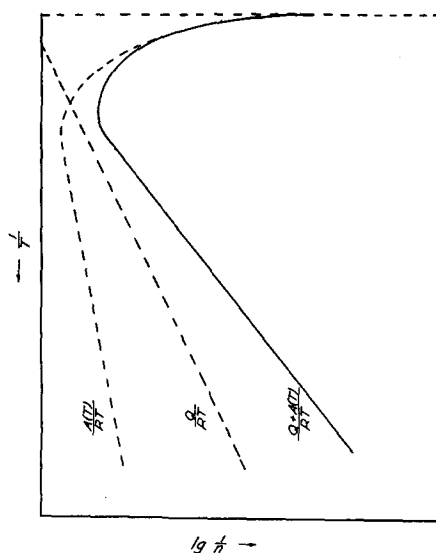

FIG. 2.

temperature and then decreases again. A plot of $\lg 1/n$ against $1/T$ in a typical instance is indicated in Fig. 2. The two terms $A(T)/RT$ and Q/RT, as well as their sum, are separately indicated. As we shall later see, the importance of this chart is that, in certain common circumstances, it represents the temperature-time relation for a given degree of transformation of a substance, e.g., that represented in other coordinates in Fig. 1.

The second way in which germ nuclei can get used up is through being swallowed by growing grains of the new phase, and thereby rendered inoperative for growth themselves. If we let the number per unit volume thus ingested up to time t be designated by $N'' \equiv N''(t)$, we have during any short time interval dt (and, as always in statistical laws, for the N's not too small)

$$dN = -dN' - dN'', \tag{1}$$

where

$$dN' = nN dt \tag{2}$$

and

$$dN'' = \bar{N} dV. \tag{3}$$

dV is the increase in time dt of the volume of the new phase per unit volume of space. It might be thought that (1) should be further corrected by subtracting from dV, in the second term (dN''), the contribution made by the dN' growth nuclei formed in dt, since these have already been allowed for by the first term.

It is, however, easy to verify that this correction is of the order $(dt)^3$ and therefore negligible by comparison with the other terms which are of the order dt.

Looking at (1), (2), and (3) we see that the total number of effective growth nuclei which appear throughout the phase change will depend upon the temperature of supercool because this alters the relative number of germ nuclei used for growth and those swallowed up. If we consider the case where n is relatively so large that almost all of them start growing before any ingestion can occur, the second term in (1) may be neglected by comparison with the first and we get

$$dN/dt = -dN'/dt = -nN. \qquad (1')$$

Therefore, for n constant with time (i.e., under conditions of constant temperature and concentration), $N = \bar{N}e^{-nt}$. The number of growth nuclei at time t would be

$$N' = \int_0^t nN dt = \bar{N}(1 - e^{-nt})$$

and the total number appearing $\bar{N}' = \bar{N}$. This does not give the dependence upon temperature of supercooling of the upper limit of the number of growth nuclei. But we can get a rough indication of the effect of varying supercooling temperatures upon the beginning of the process. If $n(T)$ is large, as it is for lower T, t can be still fairly small when an appreciable number of growth nuclei appear. Hence we get earlier intersection upon the abscissa and steeper slopes of the nuclei-time curves for lower, i.e., more critical supercooling. This is in general accord with experiment. Comparisons with the more exact theory will be given later.

If the other extreme be taken where n is small and the germ nuclei are so numerous and densely packed that the number which become activated for growth can be neglected by comparison with those which become ingested, (1) becomes

$$dN/dt = -dN''/dt = -\bar{N}dV/dt \qquad (1'')$$

and in the resultant formulae we have to put $N \to \infty$ $n \to 0$ $nN \to$ a finite rate of spontaneous nucleation per unit untransformed volume. This is equivalent to the Göler-Sachs assumption, and it is thus seen that the latter's analysis is included in ours as an approximation which is valid only in certain special cases.

It is convenient to simplify the analysis of (1) and (2) in the general case by changing the unit of time so that

$$ndt = d\tau \quad N(t) \to N(\tau) \quad V(t) \to V(\tau). \qquad (4)$$

In this way we get, by substituting (2) and (3) in (1),

$$dN/d\tau + N(\tau) + \bar{N}dV/d\tau = 0$$

which when integrated gives

$$N(\tau) + \int_0^\tau N(z)dz = N(\tau) + N'(\tau)$$
$$= \bar{N}[1 - V(\tau)],^* \qquad (5)$$

an expression which is valid only up to $\tau = \bar{\tau}$, corresponding to $t = \bar{t}$ when the germ nuclei are exhausted and the number of growth nuclei becomes constant. At that moment $dV/d\tau$ may still be different from zero and so also $dN/d\tau$. But N becomes and remains zero and the relation derived from (1) can no longer be used. V can then be found from the functional $V|[N(\tau)]|$ as explained below.

In case n varies with time according to some known dependence $n(t)$ we may still make the substitution (4) with

$$\int_0^t n(y)dy = \tau,$$

and (5) is again valid though the unit in which we measure time is variable; i.e., it is itself a known function of the time depending upon the nature of the substance and how we vary its environment (e.g., temperature or concentration) during phase change. We may call the time scale defined by (4) the *characteristic time scale* of the substance and process. The phenomena, as described in it, may be called the *characteristic phenomena*. From now on, unless otherwise specified, we shall use this characteristic time which has the effect of removing n from our formulae. We shall later (Section D) see an additional very remarkable consequence of the introduction of the characteristic time scale.

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* We may note that in the case where the nuclei are distributed solely upon a surface S, considerations similar to the foregoing may be carried through and we get an equation like (5) but with $V(\tau)$ replaced by $S(\tau)$. The theory will be dealt with in a subsequent paper.

The functional equation (5) relating N and V may be described physically as follows: $1 - V(\tau)$ is the yet untransformed volume (per unit volume of space) at time τ, and $\bar{N}[1 - V(\tau)]$ the corresponding number of germ nuclei *had these retained their original density*. But, since the (changing) untransformed volume has been drained throughout its history by spontaneous growth nuclei forming to the total extent of $N'(\tau)$, we must subtract the latter from $\bar{N}[1 - V(\tau)]$ to get the number of still effective germ nuclei.

Besides (5) we may find another relation between V and N, in that V is a *functional* $V|[N(\tau)]|$ of N (in the sense of Volterra[19]), i.e., at any time τ, it depends upon the values of $N(\tau)$ throughout the interval 0 to τ. Like any analytic functional, V can be represented in a Taylor-like expansion by a series of simple functionals (integrals), the first linear, the second quadratic, etc. In the next section we shall see the simple physical interpretation of these terms. When computed, the expression for $V|[N(\tau)]|$ may be inserted into (5) and the resultant functional equation determines $N(\tau)$. From this, $N'(\tau)$ and $V(\tau)$ are readily computed, and the kinetics of the transformation found. We shall illustrate by various cases in the following papers.

C. Geometry and Kinetics of a Crystal Aggregate

We may easily see the physical significance of the various order terms in the expansion of $V|[N(\tau)]|$ by considering the geometry of a crystal aggregate. We shall first derive some general relationships which will be independent of any assumptions about the distribution of the centers of the grains. Later we may specialize this distribution in various ways corresponding to important physical situations.

Suppose, at any fixed time, we consider an aggregate of grains of various shapes and sizes, the result of growth from centers beginning at various times in the past. The assumption we make is that where one grain impinges upon another growth ceases.* We may denote by the

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[19] V. Volterra, *Theory of Functionals* (Blackie and Son, London, 1930).
* This is usually true for cystalline growth. In other cases, as for instance in the condensation of vapor where

adjective "extended" the volume of any grain had its growth been unimpeded by impingement upon any other grain. Let the volume at time τ of any grain which began growth from a nucleus (of negligible size) at time z be $v(\tau, z)$. The number of such grains beginning at z is given by $N(z)$. Thus the total extended volume (per unit volume) at time τ, which is the total transformed volume if we neglect overlapping of growing grains, is

$$V_{1 \text{ ex}} = \int_0^\tau v(\tau, z)N(z)dz. \qquad (6)$$

This then is the linear term in the expansion of the functional $V|[N(\tau)]|$. For any particular case (e.g., constant linear growth) and shape of grain, an explicit function may be inserted for $v(\tau, z)$. We shall give examples later.

We may think of the actual pattern of grains of the new phase as made up of the extended grains overlapping each other in various groups, the overlapped regions being counted only once in getting the transformed volume $V(\tau) \equiv V_1$. Let V_1' denote the total transformed volume lying solely in the single grain (or nonoverlapping) regions of the extended volumes. This is indicated by dotted areas for a group of spherical grains in Fig. 3. Similarly let V_2' denote the transformed volume lying solely in double grain regions
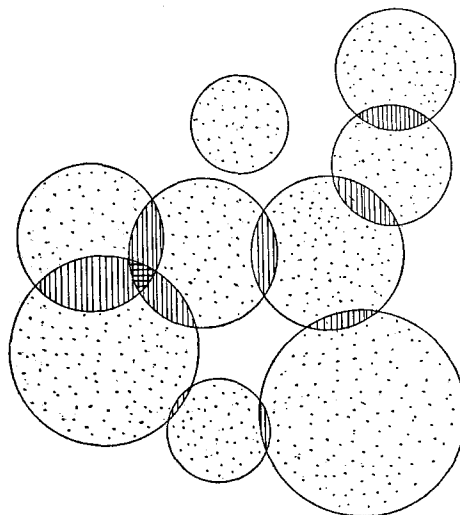

Fig. 3.

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there is coalescence of the liquid drops which are the "grains" of the new phase, the analysis would have to be modified accordingly.

(singly hatched areas), V_3' in triple grain regions (doubly hatched areas), and so on. Since each V_m' should be counted m times to get V_1 ex we have

$$V_{1 \text{ ex}} = V_1' + 2V_2' + \cdots mV_m' + \cdots, \qquad (7)$$

whereas the actual transformed volume .

$$V_1 = V_1' + V_2' + \cdots V_m' + \cdots. \qquad (8)$$

(7) and (8) may be seen to be special cases of a more general set of relations as follows. Let the total volume of overlapping of all groups of k grains counted and added separately without regard to higher overlapping be designated $V_{k \text{ ex}}$. Thus, for instance, in Fig. 3 $V_{2 \text{ ex}}$ is the sum of the singly hatched areas and three times the doubly hatched areas (plus six times the triply hatched areas, etc., in the case of higher overlapping). In general $V_{k \text{ ex}}$ is equal to a sum of terms in which V_m' is multiplied by the number of combinations of m things taken k at a time. Thus

$$V_{k \text{ ex}} = \sum_{m=k}^{\infty} C_k^m V_m'$$

$$= \frac{1}{k!} \sum_{m=k}^{\infty} m(m-1) \cdots (m-k+1) V_m', \quad (7')$$

of which (7) is a special case. On the other hand, let V_k denote the total volume of overlapping of all groups of k grains where each element of volume is counted only once. In Fig. 3 V_2 is merely the sum of the singly hatched areas and the doubly hatched areas (plus the triply hatched areas, etc.) taken only once. In general

$$V_k = \sum_{m=k}^{\infty} V_m'. \qquad (8')$$

It is $V_1 \equiv V(\tau)$ which we wish to determine and, since it is the $V_{k \text{ ex}}$ rather than V_k' that are most easily determined from statistical or other considerations (see below), we should like to get an expression for V_1 in terms of the $V_{k \text{ ex}}$. Supposing that this is of the form

$$V_1 = \sum_k A_k V_{k \text{ ex}},$$

we may easily determine the coefficients A_k by substituting from $(7')$ and comparing with (8). We find

$$A_k = (-1)^{k+1}$$

and therefore

$$V(\tau) \equiv V_1 = V_{1 \text{ ex}} - V_{2 \text{ ex}} + V_{3 \text{ ex}} - \cdots + (-1)^{m+1} V_{m \text{ ex}} + \cdots, \quad (9)$$

an expression for which it is not difficult to give an intuitive justification, e.g., in writing $V_{1 \text{ ex}}$ instead of V_1 we add 1 superfluous V_2' and 2 superfluous V_3'; by subtracting $V_{2 \text{ ex}}$ we compensate for the superfluous V_2' but overcorrect for the V_3''s since there are $3V_3'$ in $V_{2 \text{ ex}}$; therefore we must add another $V_{3 \text{ ex}}$, but this requires further correction, etc. Again, (9) is a special case of a general formula for the V_j in terms of the $V_{k \text{ ex}}$. Setting

$$V_j = \sum_k A_k^j V_{k \text{ ex}} = \sum_{k, m} A_k^j C_k^m V_m'$$

and comparing with $(8')$, we may determine the coefficients A_k^j, and we get

$$V_k = \sum_{k=j}^{\infty} (-1)^{k-i} C_{j-1}^{k-1} V_{k \text{ ex}}. \qquad (9')$$

Similarly, by inverting $(7')$, or else by using the relation derivable from $(8')$

$$V_m' = V_m - V_{m+1}$$

in conjunction with $(9')$, we may express the V_m' in terms of $V_{p \text{ ex}}$

$$V_m' = \sum_{p=m}^{\infty} (-1)^{p-m} C_m^p V_{p \text{ ex}}. \qquad (10')$$

Formulas $(7')$, $(8')$, $(9')$, $(10')$, or their equivalents, may very likely be derivable alternatively to the above, from probability considerations. We shall not attempt such a discussion here.

(9) may be regarded as the expansion of the functional $V|[N(\tau)]|$. Let us study the structure of the general term $V_{m \text{ ex}}$ in greater detail. This will enable us to draw a very important conclusion. Let r, the "radius," be a measure of the linear dimensions of a grain. In case the growth is not purely radial but takes place by varying amounts in different directions so that the grain is not spherical, r may be regarded as a representative or suitably averaged quantity over the various directions. Similarly let G be the direction averaged rate of growth of r, in general varying with time due to changes in temperature, concentration, etc. Then r, at *ordinary* time t, of a grain

which began growth at *ordinary* time y is given by

$$r(t, y) = \int_y^t G(x)dx$$

or, if we introduce the characteristic time through the transformations

$$ndx = du \quad \tau = \int_0^t n(x)dx \quad z = \int_0^y n(x)dx,$$

$$G(x) \rightarrow G(u), \quad r(t, y) \rightarrow r(\tau, z),$$

we get

$$r(\tau, z) = \int_z^\tau \frac{G}{n} du \equiv \int_z^\tau \alpha du, \qquad (11)$$

where we have introduced the function α for G/n. The grain volume is

$$v(\tau, z) = \sigma r^3 = \sigma \left[\int_z^\tau \alpha du \right]^3, \qquad (12)$$

where σ is a shape factor, equal to $4\pi/3$ for a sphere.

Let us represent by $v(r_1, \cdots r_m, x_{12} \cdots x_{ij} \cdots)$ the volume of overlapping of m grains of "radii" $r_1, r_2, \cdots r_m$, when the centers of grains 1 and 2 are at distance x_{12} apart, of 1 and 3 at x_{13} apart, of i and j at x_{ij} apart, etc. If this volume is multiplied by the probability $D(r_1, \cdots r_m; x_{12} \cdots x_{ij} \cdots)$ of m such grains (of radii $r_1, \cdots r_m$) being found with mutual distances $x_{12}, \cdots x_{ij}, \cdots$, and integrated over all possible values of x_{ij}, we get the average volume of intersection of m grains of the given radii.

$$\bar{v}(r_1, \cdots r_m) = \int \cdots \int v(r_1, \cdots r_m; \cdots x_{ij} \cdots)$$

$$\times D(r_1, \cdots r_m; \cdots x_{ij} \cdots)dx_{12} \cdots dx_{ij} \cdots. \quad (13)$$

The form of the function D will naturally depend upon the distribution of the grain centers. For any particular type of distribution and grain shape, it may be worked out explicitly from statistical considerations, and $\bar{v}(r_1, \cdots r_m)$ may be evaluated.

Using (11), we have for the average volume of overlapping at time τ of m grains which began at times $z_1, z_2, \cdots z_m$

$$\bar{v}(r_1, \cdots r_m)$$

$$\rightarrow \bar{v} \left[\int_{z_1}^\tau \alpha du, \int_{z_2}^\tau \alpha du, \cdots \int_{z_m}^\tau \alpha du \right] \equiv \bar{v}_m, \quad (12')$$

which may be regarded as the generalization of (12). The total number of overlappings due to grains starting during (characteristic) time intervals dz_1, dz_2, $\cdots dz_m$ is $N(z_1)N(z_2)\cdots N(z_m)dz_1 dz_2 \cdots dz_m$ where, so as not to count any m'th order overlapping more than once, we shall set $z_1 > z_2 > \cdots > z_m$. The total extended volume of overlapping at τ is then

$$V_{m\,ex} = \int_0^\tau N(z_1)dz_1 \int_0^{z_1} N(z_2)dz_2 \cdots$$

$$\times \int_0^{z_{m-1}} N(z_m)\bar{v}_m dz_m, \quad (6')$$

which may be regarded as the generalization of (6). It is now evident that $V_{m\,ex}$, and therefore the transformed volume V, in the characteristic time scale depends upon n and G only through the ratio α. This permits us to draw a very important conclusion as we shall see in the following section.

D. Invariance of the Characteristic Phenomena in the Isokinetic Range. Temperature-Time Curves

The factors which govern the tendency of the growth nuclei to grow out of the germ nuclei are similar to those which govern further growth, i.e., we may expect the variation of n and G with external conditions to be similar. As we have mentioned above, this is borne out in the special cases which have been worked out by the resemblance of the formulae for the two quantities.[11, 16]

It is thus plausible from our picture of the underlying mechanisms that n and G are approximately proportional throughout a considerable temperature and concentration range. Let us designate this the *isokinetic range*. We shall see below that the consequences of assuming the existence of an isokinetic range are well verified in experiment and explain some otherwise purely empirical observations.

If, therefore, we suppose that

$$G/n \equiv \alpha$$

is a constant for a given substance in the isokinetic range, we may write from (11) and (12)

$$r = \alpha(\tau - z), \qquad (14)$$

$$v(\tau, z) = \sigma \alpha^3 (\tau - z)^3 \qquad (15)$$

and from (6),

$$V_{1\ ex} = \sigma\alpha^3 \int_0^\tau (\tau - z)^3 N(z) dz. \qquad (16)$$

(6') becomes

$$V_{m\ ex} = \int_0^\tau N(z_1) dz_1 \int_0^{z_1} N(z_2) dz_2 \cdots$$

$$\times \int_0^{z_{m-1}} N(z_m) \bar{v}[\alpha(\tau - z_1), \cdots \alpha(\tau - z_m)] dz_m \qquad (6'')$$

and since α is independent of temperature and concentration, so also is the relative internal history of the transformation and the description of the kinetics of the process in the τ language. Here we have the justification for calling the phenomena, so described, the characteristic phenomena. To restate: *For a given substance and crystal habit there is an isokinetic range of temperatures and concentrations in which the characteristic kinetics of phase change remains the same.* The only difference in the phenomena at one temperature (concentration) or another is in the size of the unit of time. If the temperature (concentration) is varying during the phase change (nonisothermal), the description is still the same in terms of τ, but the unit of measure of τ in terms of t is variable during the process, and this must be watched in translating the description of the phenomena from the τ language to the t language. Thus, to lay the foundation for the solution of the entire range of reaction kinetics problems, we need to solve only the one problem in the τ language. We shall now examine some of the experimental consequences.

If the transformed volume for a given substance and grain shape is a function solely of τ then we may expect a parallelism of reaction curves taken at different constant temperatures and concentrations and plotted on a logarithmic *ordinary* time scale. This follows from the relation $\tau = nt$ whence

$$\lg t = \lg \tau - \lg n.$$

In other words, the $\lg t$ scale, on which each curve is separated from every other, is shifted from the single common master $\lg \tau$ scale by the temperature (concentration) dependent parameter n. The shift-coincidence, as we may call it, of reaction curves at constant temperature and concentration on a $\lg t$ scale has been indicated

here and there in the literature without its origin being understood. The curves by Bain and Davenport[3, 20] on the isothermal decomposition of austenite in various C, Cr, Ni, and Mn steels clearly show this effect. Another way of stating the conclusion is that if we use as abscissa the time *relative* to some definite degree of transformation, e.g., $t_{0.5}$ for 50 percent transformation, i.e.,

$$t/t_{0.5} = \tau/\tau_{0.5}$$

we get a single curve on which lie all the points of the different isothermal reactions. Tammann[21] has given curves in which Bain's data are plotted in this way. Upton[22] has drawn a similar curve to represent the original data of Bain and Davenport[3] on carbon and Cr steels.

Looking at the relation

$$\lg t = \lg \tau - \lg n$$

in another way, we note that, for a given degree of transformation, $\lg t$ is proportional to $-\lg n$. In other words, on a $1/T - \lg t$ plot, the temperature-time curves should all have the same shape as the resultant curve in Fig. 2, being shifted from each other by the parameter $\lg \tau$. We note that, because $A(T)$ becomes nearly constant at lower temperatures, $(Q + A(T))/RT$ then approaches a straight line. This result of the theory, which should be expected to hold for any substance in its isokinetic range, has been discovered empirically for austenite decomposition in steels by Austin-Rickett[23] working with the data of Bain-Davenport. It thus constitutes additional evidence that the phenomena in this range are isokinetic. The general formula for the temperature-time curves will be considered in the subsequent papers.

Another consequence of the invariance of the phenomena on the τ scale is that since

$$\alpha = G/n = Gt/\tau$$

is a constant, and τ is the same at all temperatures for a given degree of transformation, e.g., $\tau = \tau_{0.5}$, independent of temperature, for $V = 0.5$,

$$Gt_{0.5} = \alpha\tau_{0.5}$$

[20] E. C. Bain, Arch. Eisenhüttenw. **7**, 41 (1933).
[21] G. Tammann, Zeits. f. anorg. Chemie **214**, 407 (1933).
[22] G. B. Upton, Trans. A. S. M. **22**, 690 (1934).
[23] J. B. Austin and R. L. Rickett, Metals Technology, September, 1938, T.P. No. 964.

TABLE I.

TEMPERATURE °C	$t_{0.5}$ TIME IN SEC.	G RATE OF GROWTH IN CM/SEC.	$Gt_{0.5}$
717	30,000	$5 \cdot 10^{-8}$	1.5×10^{-3}
704	1050	$1.0 \cdot 10^{-6}$	1.05×10^{-3}
662	30	$3 \cdot 10^{-5}$	$.9 \times 10^{-3}$
620	4	$2.5 \cdot 10^{-4}$	1×10^{-3}
580	2	$5 \cdot 10^{-4}$	1×10^{-3}

should also be the same at all temperatures (in the isokinetic range). This conclusion is well verified by an examination of the work of Zimmerman, Vilella, and Guellich[24] on a eutectoid steel, from which Mehl[9] has calculated G approximately. The results, exhibited in Table I, show remarkably good agreement in the values of $Gt_{0.5}$ over the entire temperature range in which G itself varies ten thousand-fold. We shall later consider more detailed evidence for the constancy of α. In the meantime we merely emphasize that with its help the solution of the entire class of reaction kinetics problems of this type is reduced to the solution of Eqs. (5) and (9), using (6′).

We have seen that $V_{m\ ex}$ involves m-fold integration with $N(z_1)N(z_2)\cdots N(z_m)$ as a factor in the integrand. For any particular type of grain growth the remaining factor may be worked out from statistical considerations and written explicitly. When the expression (9) or an approximation thereto for $V(\tau)$ is inserted in (5) the resulting functional equation determines $N(\tau)$. From this $N'(\tau)$ and $V(\tau)$ may be computed, and the kinetics of the transformation known. This procedure is a lengthy and difficult one to carry out in general. We shall illustrate it in one special case in a subsequent paper by using the approximation

$$V(\tau) = V_{1\ ex} - V_{2\ ex}.$$

Fortunately, when the distribution of grain centers is random, we may avoid detailed statistical considerations by using the general method to be developed in the following paper. Later we shall compare the results of the two methods in the aforementioned special case.*

[24] J. G. Zimmerman, J. R. Villela, and G. E. Guellich, Metals and Alloys 22, January, 1937.

* We may again emphasize that the considerations we have hitherto advanced are independent both of the man-

In the subsequent papers we shall work out the kinetics of transformation for various cases where the regions of distribution of the germ nuclei are respectively the volume, internal surfaces of the old phase, and both the volume and surfaces. In general we find good agreement with the voluminous experimental data as well as additional insight into the physical processes involved.

ner in which the germ nuclei are distributed and the dimensionality of the regions considered, i.e., if the nuclei are distributed upon a surface S the V symbols throughout may be replaced by S symbols with analogous interpretations.

** *Note added in proof.*—Upon further consideration, it seems that (3) and therefore (5), should be replaced by a more accurate relation which also turns out to be simpler in its consequences. In (3) we have assumed that the number of germ nuclei per unit volume which the advancing front of the new phase encounters is the original density $\bar{N}$. But it will be seen that this is a valid approximation only when the density of growth nuclei is small compared with the density of germ nuclei. Otherwise, the actual density encountered, on the average, by the advancing front of the new phase is $N/1-V$, where $1-V$ is the fraction of untransformed volume per unit volume. (3) then should be replaced by

$$dN'' = \frac{N}{1-V}dV \qquad (3')$$

which, substituted into (1), gives

$$\frac{dN}{dt} = -nN - \frac{N}{1-V}dV.$$

Integrating, and introducing the characteristic time, we have instead of (5)

$$N(\tau) = \bar{N}e^{-\tau}[1 - V(\tau)] \qquad (5')$$

and the density of growth nuclei as a function of the time is given by

$$N'(\tau) = \bar{N}\int_0^\tau e^{-z}[1 - V(z)]dz. \qquad (5'')$$

An important result of this correction is that N drops off asymptotically to zero instead of vanishing of itself for some finite value of the time. To keep a correspondence between the statistical theory and experience when N becomes small, we should, however, assign a definite exhaustion time $\bar{\tau}$ when N becomes of the order of unity, i.e.,

$$N = 1 = \bar{N}e^{-\bar{\tau}}[1 - V(\bar{\tau})].$$

Beyond $\bar{\tau}$, N is taken to be zero and N', a constant, equals

$$\bar{N}' = \bar{N}\int_0^{\bar{\tau}} e^{-z}[1 - V(z)]dz.$$

$N/1-V$ and $\bar{N}$ are very nearly equal if N' (or n) is relatively small, and therefore the considerations in the limiting cases (1′) and (1″) remain unchanged. The subsequent discussion concerning the functional dependence of V upon N also remains unchanged.