

Kinetics of Phase Change. II Transformation-Time Relations for Random Distribution of Nuclei

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hydrogen bromide than for hydrogen iodide. We surmise that in hydrogen chloride, the sensitivity of the barrier height to the lattice parameter is the cause of a transition of the first kind instead of one of the second kind. In the case of hydrogen bromide, the behavior of the dielectric constant in the transition is qualitatively described. The theory is subject to corrections of two types. The first of these would involve taking into account energy fluctuations in states of the same orientational distribution. The second relates to deviations from classical statistical

mechanics. The present theory must be regarded as inadequate when the separation between neighboring rotational energy levels in the crystal becomes large relative to kT . Evidence for the necessity of a quantum-mechanical theory of cooperative phenomena in the case of molecules of low moment of inertia at low temperatures is provided by the differences in the heat capacity curves of methane and the deuterio-methanes, which cannot reasonably be attributed to differences in intermolecular forces between neighbors in the lattice.

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Kinetics of Phase Change. II

Transformation-Time Relations for Random Distribution of Nuclei*

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Following upon the general theory in Part I, a considerable simplification is here introduced in the treatment of the case where the grain centers of the new phase are randomly distributed. Also, the kinetics of the main types of crystalline growth, such as result in *polyhedral*, *plate-like* and *linear* grains, are studied. A relation between the actual transformed volume V and a related *extended volume* $V_{1\text{ex}}$ is derived upon statistical considerations. A rough approximation to this relation is shown to lead, under the proper conditions, to the empirical formula of Austin and Rickett.

The exact relation is used to reduce the entire problem to the determination of $V_{1\text{ex}}$, in terms of which all other quantities are expressed. The approximate treatment of the beginning of transformation in the isokinetic range is shown to lead to the empirical formula of Krainer and to account quantitatively for certain relations observed in recrystallization phenomena. It is shown that the predicted shapes for isothermal transformation-time curves correspond well with the experimental data.

A. RESUMÉ

IN the previous paper¹ we have developed some of the general theory of phase change with the following assumptions strongly supported by experiment.

(I) The new phase is nucleated by tiny "germ nuclei" which already exist in the old phase and whose effective number \bar{N} per unit nucleation region can be altered by temperature and duration of superheating. These germ nuclei, which may be heterogeneities of any sort, usually con-

sist of small particles of the subcritical phase or tough films of the latter surrounding foreign inclusions.

(II) The number of germ nuclei per unit region at time t , $N \equiv N(t)$ decreases from \bar{N} in two ways: (a) through becoming active growth nuclei, with number $N' \equiv N'(t)$, as a result of free energy fluctuations with probability of occurrence n (a function of temperature, concentration, etc.) per germ nucleus; (b) through being swallowed by grains of the new phase whose linear dimensions are growing at rate G (also a function of temperature, concentration, etc.). Letting $V \equiv V(t)$ represent the volume of the new phase per unit volume of space we are led to

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¹J. Chem. Phys. 7, 1103 (1939). Referred to hereafter as K.P.C. I.

the relation

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

between the density of germ nuclei and transformed volume. For the density of growth nuclei we find

$$N'(t) = \bar{N} \int_0^t e^{-nz} [1 - V(z)] dz.$$

It is very useful to express these relations as well as the others in terms of the *characteristic time scale* of the substance and process, defined by changing the unit of time so that $ndt = d\tau$. This gives

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

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

Beyond $\tau = \bar{\tau}$, roughly corresponding to the time when the germ nuclei are exhausted, i.e., where

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

these expressions are to be replaced by*

$$N = 0,$$

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

(III) Besides (5'), we found another relation in that V is a functional $V[N(\tau)]$ of N , i.e., at any time τ , it depends upon the values of $N(\tau)$ throughout the interval 0 to τ . Assuming, as is usually true in crystalline growth, that where one grain impinges upon another, growth ceases, we found the form and significance of the terms $V_{m \text{ ex}}$ in the expansion of the functional

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

(IV) If now it is assumed, as is plausible from the underlying mechanisms and as the experiments verify, that

$$G/n \equiv \alpha$$

* If we wished to be meticulous we should add to the above the contribution of the last germ nucleus. This is most likely to nucleate at ordinary time $t+1/n$ or characteristic time $\bar{\tau}+1$.

is approximately independent of temperature and concentration in a given "isokinetic range," for a given substance and crystal habit, we have

$$V_{m \text{ ex}} = \int_0^\tau N(z_1) dz_1 \int_0^{z_1} N(z_2) dz_2 \cdots \times \int_0^{z_{m-1}} N(z_m) \bar{v}_m [\alpha(\tau - z_1), \cdots \alpha(\tau - z_m)] dz_m. \quad (6'')$$

In particular

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

for pseudospherical or polyhedral grains, where σ is a shape factor, equal to $4\pi/3$ for spherical grains. \bar{v}_m , $V_{m \text{ ex}}$, and therefore the transformed volume V , in the characteristic time scale depend upon n and G only through the ratio α , which has been supposed constant. Therefore, the relative internal history of the transformation is independent of temperature, concentration, or other variables (in the range in which n and G are proportional); or, to restate our conclusion: *For a given substance and crystal habit, there is an "isokinetic range" of temperatures and concentrations throughout which the kinetics of phase change in the characteristic time scale remains unchanged.* This observation enables us to translate results of isothermal reaction curve analysis to the description of phenomena under conditions of varying temperature and concentration.

The calculation of $V_{m \text{ ex}}$, and the determination thereby (with Eqs. (9) and (5')) of the complete kinetics of the process, was shown to depend upon complex statistical considerations. Fortunately, in the important case of *random* distribution of the grain centers, we may use a general method which, expressing all quantities in terms of a suitably defined $V_{1 \text{ ex}}$ alone, enables us to avoid these detailed statistical calculations. We note that the assumption of random distribution of grain centers throughout the volume should be applicable with good approximation to cases where the germ nuclei tend to segregate at the boundaries of a fine grained structure in the old phase, as with many solid-solid phase changes, especially in metals. The results of this

TABLE II.

τ	$E_3(-\tau)$	τ	$E_3(-\tau)$	τ	$E_3(-\tau)$
0.1	0.0000041	2.4	0.914	11	171.33
0.2	0.0000641	2.5	1.057	12	227
0.3	0.000318	2.6	1.223	13	293.67
0.4	0.000987	2.7	1.4025	14	372.33
0.5	0.00236	2.8	1.5995	15	464
0.6	0.00481	2.9	1.815	16	569.67
0.7	0.00874	3.0	2.050	17	690.33
0.8	0.01462	3.1	2.305	18	827
0.9	0.02307	3.2	2.582	19	980.67
1.0	0.0346	3.3	2.881	20	1152
1.1	0.050	3.4	3.204	25	2315.67
1.2	0.069	3.5	3.553	30	4079
1.3	0.095	3.6	3.923	35	6567.33
1.4	0.124	3.7	4.322	40	9905.67
1.5	0.161	3.8	4.748	45	14,219
1.6	0.205	3.9	5.202	50	19,632
1.7	0.258	4.0	5.685	60	34,259
1.8	0.317	5.0	12.34	70	54,786
1.9	0.387	6.0	23.00	80	82,212
2.0	0.468	7.0	38.67	90	117,539
2.1	0.560	8.0	60.33	100	161,766
2.2	0.666	9.0	89.00	\downarrow	\downarrow
2.3	0.783	10.0	125.67	∞	$\tau^3/3!$

theory should then check approximately with those of a theory which explicitly takes into account the distribution along grain boundaries.

Before proceeding, we should point out that the special formulae (12), (15), and (16) given in the preceding paper apply only to the case of pseudospherical or polyhedral grains, i.e., those growing at approximately the same rate in all directions. In the general case, where the growth is considerably unsymmetrical, we have to deal with an interesting and complex problem. We shall not study it here but merely note that besides the case, given above, of what we can call *polyhedral* growth, we may have two important situations: First, where growth is primarily along two dimensions so that the grain is *plate-like* in shape; and second, where growth is primarily along one direction when we shall call it *lineal*. In these two cases, the expressions corresponding to (16) are

$$V_{1\text{ ex}} = \sigma' \alpha^2 \int_0^\tau (\tau - z)^2 N(z) dz, \quad (16')$$

$$V_{1\text{ ex}} = \sigma'' \alpha \int_0^\tau (\tau - z) N(z) dz, \quad (16'')$$

respectively. Here α represents the ratio, in each case, of a suitably chosen G to n . Like (16), these formulae are applicable only if we are in a range

approximately isokinetic, i.e., for G/n constant. In general for most substances, as crystallization velocities are made higher the type of growth changes from polyhedral to lineal.

B. RELATION BETWEEN V AND $V_{1\text{ ex}}$ ²

1. Approximation. The Austin-Rickett formula as a special case

In any region, selected arbitrarily, let us designate as "nonoverlapped" that part of the volume in which there is no transformed matter, i.e., no grains or parts of grains of the new phase. Then we have that, *on the average, the ratio of nonoverlapped volume v' to extended volume $v_{1\text{ ex}}$ of a randomly selected region is equal to the density of untransformed matter $1 - V$ at that time, i.e.,*

$$\frac{v'}{v_{1\text{ ex}}} = 1 - V. \quad (17)$$

If now we suppose that the grains of the new phase themselves have formed at random during the reaction, we might hope to apply (17) to these on the average. We cannot, however, do this directly because any actual grain is not randomly located in the *entire* unit volume. Its position is subject to the restriction that its nucleus lay somewhere outside of the transformed volume $V(z)$ at the time z of its origin. We can circumvent this complication in one of two ways. In either case we get the same result. First we can restore complete randomness by including in our consideration all the "phantom" grains associated with germ nuclei which would have been activated into growth if they had not been absorbed by the growing new phase. At time z , the total rate of grain formation, including phantoms, is $\bar{N}e^{-z}$ (per unit volume), and it is this value of $N(z)$ which should be used in the calculation of the various extended volumes $V_{m\text{ ex}}$. In particular

$$V_{1\text{ ex}} = \bar{N} \int_0^\tau e^{-z} v(\tau, z) dz \quad (18)$$

where, as in (6) of the previous paper,

$$v(\tau, z) \equiv v_{1\text{ ex}}(\tau, z)$$

² R. F. Mehl and W. Johnson in *Metals Technology*, T.P. No. 1089 (1939), have used arguments similar to those in this section in the special case of spherical grains appearing at a constant rate per unit untransformed volume.

is the extended volume, at time τ , of a grain which started at z . The contributions of the phantom grains to the nonoverlapped and actual volumes, V_1' and V , respectively, are zero, so that there is no physical difference introduced by their consideration. Strictly, we should distinguish between $V_{m\text{ ex}}$ as defined in this way and as used before, but for brevity's sake we employ the same notation. From now on, unless otherwise specified, we shall work with the phantom-included population in calculating $V_{m\text{ ex}}$. This way of thinking is particularly useful in proving the theorem of the Appendix. Now we may apply (17) to the nonoverlapped volume of an average grain (over the phantom included population) in relation to its extended volume. Summing both numerator and denominator over all the grains (including phantoms) in unit volume we get

$$\frac{V_1'}{V_{1\text{ ex}}} = 1 - V$$

or

$$\frac{V_1'}{1 - V} = \bar{N} \int_0^\tau e^{-z} v(\tau, z) dz \quad (17')$$

An alternative approach, without the use of "phantom" grains, which leads to the same result is as follows: The nucleus or center of an actual grain originating at time z was, with equal likelihood, anywhere in the volume $1 - V(z)$ (and only in this region). Then, at a later time τ , when the untransformed volume has diminished to $1 - V(\tau)$, the ratio of non-overlapped to extended volume of the grain is, on the average, given by

$$\frac{v_1'}{v_{1\text{ ex}}} = \frac{1 - V(\tau)}{1 - V(z)} \quad \text{or} \quad \frac{v_1'}{1 - V(\tau)} = \frac{v_{1\text{ ex}}}{1 - V(z)}$$

If we multiply both sides of the equation by the number of (actual) grains forming in time interval dz , and integrate from 0 to τ , we get

$$\frac{V_1'}{1 - V} = \bar{N} \int_0^\tau e^{-z} v(\tau, z) dz$$

which agrees entirely with (17').

We shall now consider an interesting special case: For transformations in which the new phase is very fine grained, and therefore the overlapping is small, we may write as a rough

approximation

$$V_1' = V$$

and, combining with (17'), this gives

$$V/(1 - V) = V_{1\text{ ex}}. \quad (17'')$$

Under isothermal conditions, and for phases which remain uniform in concentration, growth of linear dimensions is frequently at a constant rate G . n too is constant and as before, with $\alpha \equiv G/n$ and polyhedral growth, we get

$$V_{1\text{ ex}} = \sigma \alpha^3 \bar{N} \int_0^\tau (\tau - z)^3 e^{-z} dz. *$$

In assuming the constancy of G under isothermal conditions, we have supposed that, once activated, the germ nucleus soon passes the region of slow growth beyond which its rate becomes constant. This amounts to neglecting any "incubation period" in the growth nucleus. Integrating, we get

$$V_{1\text{ ex}} = \frac{6\sigma G^3 \bar{N}}{n^3} \left[e^{-\tau} - 1 + \tau - \frac{\tau^2}{2!} + \frac{\tau^3}{3!} \right] \equiv \beta E_3(-\tau) \quad (18')$$

where we have introduced the convenient abbreviations

$$\beta \equiv 6\sigma G^3 \bar{N} / n^3, \quad (18'')$$

$$E_m(-x) = \frac{1}{m!} \int_0^x (x - z)^m e^{-z} dz = (-1)^{m+1} \times \left[e^{-x} - 1 + x \cdots (-1)^{m+1} \frac{x^m}{m!} \right].$$

TABLE III.

τ	$E_1(-\tau)$	$E_2(-\tau)$
0.1	0.0048375	0.0001625
0.5	0.10653	0.01847
1.0	0.36788	0.13212
2	1.13534	0.86466
3	2.04979	2.45021
4	3.01832	5.98168
5	4.00674	8.49326
6	5.00248	12.99752
7	6.00091	18.49909
8	7.00034	24.99966
9	8.00012	32.49988
10	9.00005	40.99995
20	19	181
100	99	4901
\downarrow	\downarrow	\downarrow
∞	τ	$\tau^2/2!$

* The generalization to the nonisothermal case as in quenching, and to that of varying concentrations (as in precipitation from noneutectic solutions), has the same form in the isokinetic range, but the unit of τ in ordinary time is variable.

(18') is valid only up to $\tau = \bar{\tau}$, the time corresponding to the exhaustion of the germ nuclei. Beyond this, the upper limit of the integral should be replaced by $\bar{\tau}$, and we may express the result of integration by

$$V_{1\text{ ex}} = \beta \{ E_3(-\tau) - e^{-\bar{\tau}} E_3[-(\tau - \bar{\tau})] \}. \quad (18''')$$

Formulae similar to (18') and (18'''), with E_3 replaced by E_2 and E_1 , respectively, are obtained when we suppose the grain growth to be plate-like or lineal as in (16') and (16''). For brevity's sake we shall use the designation $E(\tau)$ with the understanding that

$$E(\tau) = \begin{cases} E_3(-\tau) & \text{for polyhedral growth} \\ E_2(-\tau) & \text{for plate-like growth} \\ E_1(-\tau) & \text{for lineal growth.} \end{cases}$$

$E_3(-\tau)$, $E_2(-\tau)$, and $E_1(-\tau)$ are tabulated as functions of τ in Tables II and III.

For n very large, (18') goes over to

$$\beta \tau^3 / 3! = \sigma G^3 \bar{N} t^3.$$

For τ small, i.e., t small compared with $1/n$, it goes into

$$\beta \tau^4 / 4! = \sigma G^3 \bar{N} n t^4 / 4.$$

In either case, and for different types of crystal growth, it approximates the form Bt^k , where B is a function of temperature only and k is a constant. (17'') gives then

$$V(t) / (1 - V(t)) = Bt^k \quad (17''')$$

and this is exactly the formula for isothermal transformation of super-cooled austenite into bainite found empirically by J. B. Austin and R. L. Rickett.³ The reasons for the approximate independence of temperature of k are now clear. Any observed deviations from (17''') can be understood as due to the approximations involved in deriving it from (17').

2. Exact relation

To obtain the exact relation between V and $V_{1\text{ ex}}$ we may employ the following argument: Applying the same reasoning as in the previous section, not to the volumes of the single grains, but to the nonoverlapped and extended portions of the *increments* of these grains in an element of

time, we get for the average grain (including phantoms)

$$dv_1 / dv_{1\text{ ex}} = 1 - V$$

since the nonoverlapped increment of a grain is nothing other than the increment in transformed volume of that grain. For the unit volume

$$\frac{dV}{dV_{1\text{ ex}}} = 1 - V. \quad (19)$$

Integrating, and rearranging, this gives

$$V = 1 - e^{-V_{1\text{ ex}}} \quad (20)$$

as the desired fundamental relation, which is applicable in the case of random distribution of the grains.

The derivation of (20) is entirely independent of any assumption about isothermal or isokinetic conditions. Thus even in the case where the distribution of grain centers is not uniformly random, as for instance in solidification in an ingot mold where there is a temperature gradient, as long as the distribution is fine grained and *locally random*, we may expect to be able to apply (20). $V_{1\text{ ex}}$ and V are then functions not only of the ordinary time t , but also of the space coordinates which, together with t , determine the thermal history and the local characteristic time at any point.

Substituting (20) into (5) and (5'), we get

$$N = \bar{N} e^{-(\tau + V_{1\text{ ex}})}, \quad (21)$$

$$N' = \bar{N} \int_0^\tau e^{-[z + V_{1\text{ ex}}(z)]} dz. \quad (22)$$

Thus the entire problem of determining the kinetics of reaction has been reduced to finding $V_{1\text{ ex}}$ from (18) in any particular case. The isokinetic case will be examined in detail in this and the next paper.

Considerable doubt might have been raised as to the validity of (19), on the following grounds chiefly. The fraction $1 - V$ measures the ratio of nonoverlapped to extended volume of any *volume region* selected at random. We cannot too easily assume that it also measures the corresponding ratio in what is effectively a *selected surface region*, i.e., the layers of grain increments in an element of time. The assumption requires

³ J. B. Austin and R. L. Rickett, Metals Technology, September 1938, T.P., No. 964.

therefore more rigorous justification. It does turn out to be correct, primarily because of the complete randomness which we assume. The rigorous justification given in Appendix I brings out a number of very interesting relations. Expressions, which are valid in our case of random nucleation, for all $V_{k\text{ ex}}$, V_k , and V_k' in terms of $V_{1\text{ ex}}$ alone, are also derived there.

C. TRANSFORMATION-TIME PHENOMENA IN THE ISOKINETIC RANGE

1. The beginning of transformation, isothermal and nonisothermal. Derivation of Krainer's formula. Recrystallization phenomena

The kinetics of phase change, as concerning transformation-time and nucleation-time relations are completely determined by (20) to (22), when $V_{1\text{ ex}}$ is known. In the isokinetic case, $V_{1\text{ ex}}$ is given by (18') up to $\tau = \bar{\tau}$, and we have

$$V(\tau) = 1 - e^{-\beta E(\tau)}, \quad (23)$$

$$N(\tau) = \bar{N} e^{-(\tau + \beta E(\tau))}, \quad (24)$$

$$N'(\tau) = \bar{N} \int_0^\tau e^{-[z + \beta E(z)]} dz \quad (25)$$

$\tau = \bar{\tau}$ is determined by

$$\bar{\tau} + \beta E(\bar{\tau}) = \lg \bar{N} \quad (26)$$

and for $\tau > \bar{\tau}$ we have, from (18'')

$$V(\tau) = 1 - e^{-\beta[E(\tau) - e^{-\bar{\tau}} E(\tau - \bar{\tau})]}, \quad (23')$$

$$N = 0 \text{ (or, more exactly, 1 up to } \bar{\tau} + 1), \quad (24')$$

$$N' = \bar{N}' = \bar{N} \int_0^{\bar{\tau}} e^{-[z + \beta E(z)]} dz. \quad (25')$$

In all cases when τ is very small, i.e., at the beginning of transformation, and for polyhedral grain growth, (23) goes over into

$$V = 1 - e^{(-\beta \tau^4/4!)} = 1 - e^{(-\sigma G^3 N n t^4)/4} \quad (27)$$

or, even more approximately,

$$V \simeq \frac{\beta \tau^4}{4!} = \frac{\sigma \alpha^3 \bar{N}}{4} \tau^4 = \frac{\sigma G^3 \bar{N} n}{4} t^4, \quad (27')$$

indicating that the $V-t$ curve begins like a fourth degree parabola. The physical significance of this is that in the early stages of transformation

the number of growth nuclei present is proportional to the first power of the time and their respective volumes to the third power giving for the total volume transformed a dependence on the fourth power of the time.

(27') shows that V begins to depart appreciably from zero, i.e., the transformation "begins" when $\beta \tau^4/4!$ becomes appreciably different from zero. Now, for ordinary magnitudes of β , this happens rather abruptly around $\tau = 1$. Thus we would expect that, generally, the time of "beginning" t_b of isothermal transformation would be approximately equal to $1/n$ at that temperature, i.e.,

$$t_b(T) \simeq 1/n(T)$$

or, if the circumstances under which transformation is taking place are nonisothermal, the condition for the "beginning" is

$$\tau = \int n(T) dt \simeq \int \frac{dt}{t_b(T)} \simeq 1$$

and this is precisely the result obtained empirically by H. Krainer⁴ in his experiments on the decomposition of austenite in steels. The root of the formula is seen to be the dependence of V upon the exponential of a high power of τ , a quantity which changes its value very considerably in the neighborhood of $\tau = 1$.

For constant β (isokinetic case), not only does the "beginning" time vary inversely with n at different temperatures, but also the temperature $-\lg$ time curves for different degrees of transformation are all parallel. We have indicated the form of these curves in the previous paper.

It is especially interesting to consider recrystallization phenomena in metals in the light of (27'). Here, even if α remains approximately constant (isokinetic range), we may vary \bar{N} considerably through the degree of deformation which the old phase is made to undergo. Now there is strong experimental evidence⁵ for believing that the "degree of deformation" in a polycrystalline material is measured by Nadai's "octahedral shear."⁶ This measure has the advantage of giving results which are independent of the mode of

⁴ H. Krainer, *Archiv f. Eisenhüttenwesen* **9**, 619 (1936).

⁵ H. F. Kaiser and H. F. Taylor, *Trans. A. S. M.* **27**, 227 (1939).

⁶ M. Nadai, *J. App. Phys.* **8**, 205 (1937).

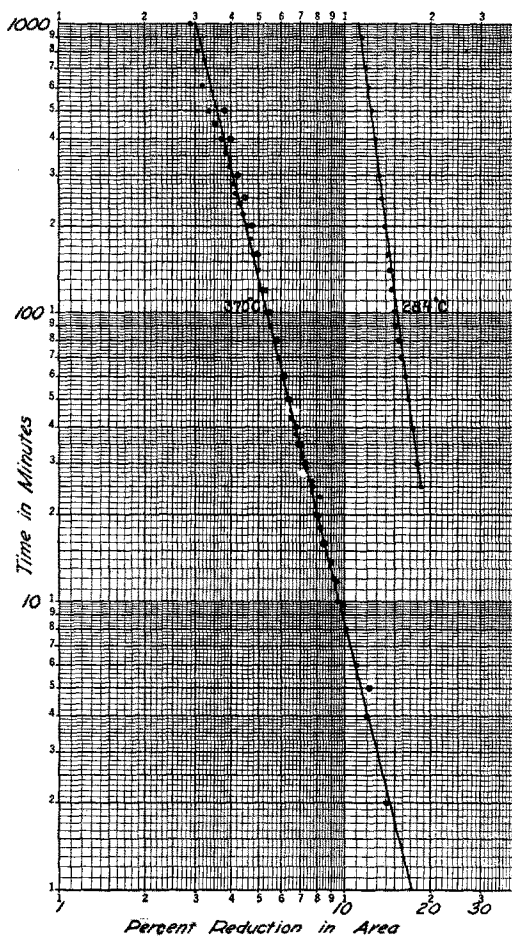


FIG. 4.

deformation, whether, for instance, tension, torsion or rolling. Nadai has given formulae whereby the octahedral shear may be computed, in any case, from the principal specific extensions or contractions. Thus, for instance, in deformation by elongation in tension, the octahedral shear γ_n is related to the specific reduction q through the formula

$$\gamma_n = \sqrt{2} \lg(1+q).$$

For small plastic deformations γ_n will evidently be proportional to q . For larger deformations, we must distinguish between the two.

Now, an inspection of the data on the number of nuclei which appear as a function of the deformation, e.g., that of Kornfeld and Pawlow,⁷

⁷ Kornfeld and Pawlow, *Physik. Zeits. der Sowjetunion* **6**, 537 (1934).

suggests a parabolic dependence of \bar{N} upon q , or γ_n , i.e.

$$\bar{N} \propto \gamma_n^2.$$

Since, by (27'), if we keep temperature and other things constant, t_b varies inversely as the 4th root of \bar{N} , we would expect to find

$$t_b^4 \propto \frac{1}{\gamma_n^2} \quad \text{or} \quad -8 \lg t_b \propto \lg \gamma_n \propto \lg \lg(1+q)$$

which for small deformations can be written

$$-8 \lg t_b \propto \lg q.$$

If the recrystallizing grains are growing lineally, instead of polyhedrally, t_b varies inversely as the 2nd root of \bar{N} and we would expect to find

$$-4 \lg t_b \propto \lg \lg(1+q) \sim \lg q$$

In the absence of data on the "time of beginning" we use, as a rough indication, the data on the so called "time of recrystallization." This is generally taken to mean the time $t_{0.5}$ required for approximately 50 percent transformation. As will be seen, this is not, by any means, always simply related to t_b . In many cases, however, it is found that the transformation, once started, proceeds rapidly, i.e., the rise of the S-shaped transformation-time curve is quite steep and $t_{0.5}$ does not differ very much from t_b . Here we may expect the data to fit an inverse fourth or eighth power relation depending on whether the growth is lineal or polyhedral.

In the experiments of Karnop-Sachs⁸ on the recrystallization of stretched copper wires, the deformations were small enough to permit us to replace the octahedral shear by the specific reduction. In Fig. 4 we have plotted the logarithm of "time of recrystallization" against the logarithm of percentage reduction in area as obtained by Karnop and Sachs. We note that the data, over the entire range, all plot on straight lines with remarkable accuracy. The slope of the line passing through the points taken (from several wires) at 370°C is exactly equal to -4 , and the slope of the line through the points taken at 284° is equal to -8 . This tends to verify our assumption that the number of germ nuclei is proportional to the square root of the de-

⁸ R. Karnop and G. Sachs, *Zeits. f. Physik* **60**, 464 (1930).

gree of deformation, and suggests that the growth is lineal at the upper temperature and polyhedral at the lower temperature.

If we suppose α to be approximately constant and fix a definite time of annealing, (27) indicates that the \bar{N} required to produce appreciable recrystallization varies inversely as n^4 or, taking logarithms,

$$\lg \bar{N} \propto -4 \lg n = 4(Q+A)/RT$$

where, as shown in the first paper of this series, $Q+A$ is the total energy (per mole) required for a germ nucleus to become a growth nucleus. We shall suppose that we are in the temperature range where this has become constant. Now if we assume, as above, that

$$\bar{N} \propto \gamma n^{\frac{1}{2}} \propto [\lg(1+q)]^2$$

we may write, for a given time of anneal t_b ,

$$\lg \lg(1+q) \propto 1/T.$$

This proportionality is well satisfied over a wide range of deformation as may be seen from the straightness of the lines in Fig. 5, where we have plotted $1/T$ against $\lg \lg(1+q)$ for the data of Oberhoffer-Oertel⁹ on electrolytic iron and of Hanemann¹⁰ on hot forged mild steel. This result also constitutes evidence in favor of the assumption of proportionality of \bar{N} to some power of the degree of deformation

2. Transformation-time curves in the isothermal range

Let us consider the entire $V-t$ curve, for polyhedral grain growth as given by (23) and (23'). We first examine the case where \bar{N} is very large, i.e., exhaustion of the germ nuclei does not occur until the end of transformation. Under such conditions we may consider two limiting cases. When n is very small (τ small), (27) will be an adequate representation over the entire transformation, and this corresponds to the special case considered by Mehl-Johnson.² On the other hand, for n very large, τ will be large during most of the reaction, and (23) is repre-

sented by

$$V = 1 - e^{-\sigma G^3 \bar{N} t^3}. \quad (28)$$

For intermediate values of n the dependence of V upon t will lie between (27) and (28).

If \bar{N} is small so that exhaustion occurs near the beginning of transformation, i.e., for

$$\bar{\tau} \approx \lg \bar{N}$$

which (26) becomes in this case, most of the region of transformation is represented by

$$V = 1 - e^{-\sigma G^3 (\bar{N}-1) t^3} \quad (28')$$

which is practically the same as (28). The occurrence of the factor $\bar{N}-1$ instead of \bar{N} is due to the neglect of the last germ nucleus in the derivation of (23'). Had we included this we should have obtained a result identical with (28).

The physical interpretation of the two limiting cases is readily given. (27) was seen to be interpretable in terms of a linear increase in number and a third power increase in extended volume of the growth nuclei with time. (28) evidently corresponds to the case where the great majority of the growth nuclei start near the beginning of transformation, and the growth in total extended volume is due merely to their continued growth. A little analysis will show that all other cases, of nucleus exhaustion at intermediate stages of the reaction, give a dependence of V_1 on t somewhere in between t^3 and t^4 .

For plate-like and lineal growth an analysis similar to the above gives for limiting cases

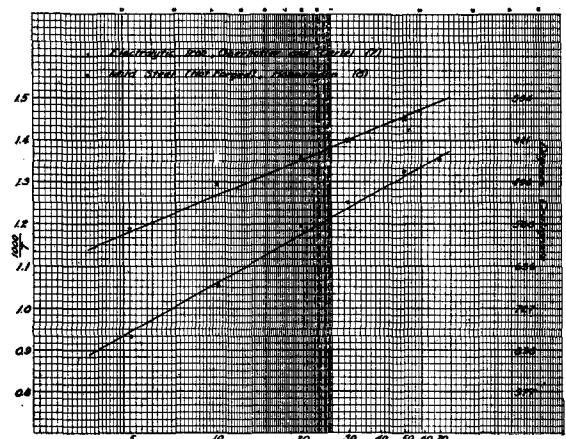


FIG. 5.

⁹ Oberhoffer and Oertel, *Stahl und Eisen* **44**, 560-561 (1924); *ibid.* **39**, 1061 (1919).

¹⁰ H. Hanemann and F. Lucke, *Stahl und Eisen* **47**, 1117 (1925). H. Hanemann, *Zeitschrift für Metallkunde* **17**, 316 (1925).

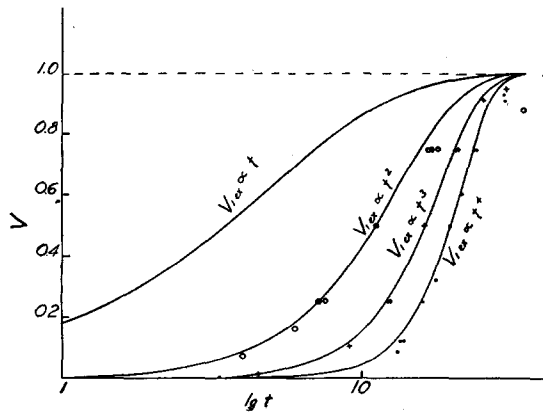


FIG. 6.

Plate-like, n small:

$$V = 1 - e^{-(\sigma' G^2 \bar{N} n t^3)/3}. \quad (29)$$

Plate-like, n large:

$$V = 1 - e^{-\sigma' G^2 \bar{N} t^2}. \quad (30)$$

Lineal, n small

$$V = 1 - e^{-(\sigma'' G \bar{N} n t^2)/2}. \quad (31)$$

Lineal, n large:

$$V = 1 - e^{-\sigma'' G \bar{N} t}. \quad (32)$$

all of which may be written, by analogy with the Austin Rickett formula,

$$V = 1 - e^{-B t^k}. \quad (20')$$

It is interesting to note that all of the cases (29) to (32) (except the last which has the shape of a first-order reaction curve) give the typical S-shape for V against t , starting slowly, rising rapidly, and then leveling off again. Since, in each, β and τ appear only in the combination $\beta \tau^k$ or $B t^k$ ($k=1, 2, 3, 4$), on a $V - \lg t$ plot all isothermal reaction curves for a particular value of k will have the same shape, differing only in position. Thus it will be convenient to designate as the shape of a $V-t$ curve the form which it takes in such a plot. We have plotted the four type curves in this fashion in Fig. 6. We note the increasing flatness of the reaction curves as the growth changes from polyhedral to lineal. This is in conformity with the available experimental data, which shows that when the habit changes from a polyhedral to an "acicular" needle-like, lineal type (e.g., for lowered tem-

perature), the transformation-time curves become flatter. The effect is quite apparent in the data of Bain and Davenport on various alloys.¹¹

For purposes of rough comparison with experiment, the difference in shape between the various limiting cases may be indicated by taking the ratio of times for two fixed degrees of transformation. A convenient representative index is the ratio of times for 75 percent and 25 percent transformation, respectively. This is equal in the various limiting cases to the fourth, third, second, and first roots, respectively, of

$$\frac{\lg(1-0.75)}{\lg(1-0.25)} = 4.82.$$

Thus we should expect to find observed values of the ratio lying between the corresponding limits for the various types of growth, i.e.,

$$1.48 \leq \frac{t_{0.75}}{t_{0.25}} = \frac{\tau_{0.75}}{\tau_{0.25}} \leq 1.69 \quad \text{for polyhedral growth.}$$

$$1.69 \leq \frac{t_{0.75}}{t_{0.25}} \leq 2.2 \quad \text{for plate-like growth.}$$

$$2.2 \leq \frac{t_{0.75}}{t_{0.25}} \leq 4.82 \quad \text{for lineal growth.}$$

TABLE IV.

STEEL	TEMPERATURE °C	$t_{0.75}$ IN SECONDS	$t_{0.25}$ IN SECONDS	$\frac{t_{0.75}}{t_{0.25}}$	TYPE OF GROWTH
A	340	500	365	1.37	Polyhedral, n small
	275	2000	1350	1.48	
	250	4900	3200	1.53	
	200	25500	17500	1.46	
B	340	110	60	1.83	Plate-like
	320	130	70	1.86	
	300	170	96	1.89	
	275	290	155	1.86	Lineal, n small
	260	420	180	2.33	
	250	540	220	2.45	
C	340	33	16	2.08	
D	340	69	41	1.68	Polyhedral, n large
E	340	245	145	1.69	Lineal, n small
	275	680	410	1.66	
	250	880	390	2.26	
F	340	650	480	1.35	
	275	4500	3300	1.36	
	250	10100	7400	1.37	

¹¹ Bain and Davenport, Trans. A.I.M.E. 90, 117 (1930); 100, 13 (1932).

To test these conditions, we have examined the ratios as observed in a set of different steels studied very completely by Bain and Davenport.¹² The results are tabulated in Table IV. We notice two things. First, the ratios for a given steel, at different temperatures within an appreciable range, are approximately the same. This is evidence that the phenomena in this range are isokinetic.[†] Second, except for A at 340°C and for F , all of the ratios lie within the theoretically predicted limits. What is more, the values for A lie approximately at the polyhedral— n small limit, i.e., where

$$V_{1\text{ ex}} \propto t^4$$

those for D and E above 250°C at the polyhedral— n large limit where

$$V_{1\text{ ex}} \propto t^3$$

and for C , B and E below 260° at the lineal— n small limit where

$$V_{1\text{ ex}} \propto t^2.$$

When we consider that the time dependences of $V_{1\text{ ex}}$ leading to the indicated limits were derived completely theoretically, these agreements are strong confirmation of the suggested mechanisms.

The values for B above 260°C are, of course, within the allowed range. They correspond to the 5/2th root of 4.82, and we have suggested that the growth is plate-like in this region. It may be, however, that plate-like growth is not common, and that this intermediate value is due to some other cause. The whole question will bear further experimental and theoretical investigation. It is interesting that the outstanding discrepancy, that of A at 340°C and F , corresponds almost exactly to the 5th root of 4.82. Whether this is connected with some time variation of n which leads to a 5th power dependence of $V_{1\text{ ex}}$ upon t we cannot at present say.

We have plotted the experimental data, associated by Table IV, with each of the limits, upon the corresponding limit curve in Fig. 6. We note the falling off of the experimental values from the

curve at the end of reaction in each case. A still more clearcut comparison of the data with the limit curves may be made on the basis of (20'), which implies that a plot of $\lg \lg 1/(1-V)$ against $\lg t$ should give a straight line with slope k . In fact, it is found that the experimental data plot even more accurately on these straight lines than on those given by Austin-Rickett. This is especially true at the beginning and end points. There is, however, the same falling off of the experimental points at the end of reaction as we observe in Fig. 6. We can trace this deviation to two factors both operating in the same direction: First, in writing

$$V_{1\text{ ex}} = Bt^k$$

with k constant, we have ignored the fact that the dependence of $V_{1\text{ ex}}$ upon t , as given by (18), occurs with a diminishing power of t as τ increases in $E(\tau)$. Second, as apparent in (18'''), there is an additional dropping off of $V_{1\text{ ex}}$ from the limit curve after the exhaustion of the germ nuclei. To obtain an exact fit for the experimental data we should use (23) and (23') with properly chosen values of β and $\bar{\tau}$. This, we have not attempted here. The deviation of experimental data from (17''') or (20'), always in the same direction (falling off), is important in affording strong additional confirmation of the whole germ nucleation mechanism, for if we assumed only a constant rate of spontaneous nucleation per unit untransformed volume we should obtain only the limit curves (27) to (31).

APPENDIX I

Expression of V_k , $V_{k\text{ ex}}$ and V_k' in Terms of $V_{1\text{ ex}}$

First we shall show how (20), and therefore (19), may be derived by taking into account all of the higher order terms in V . To do this we proceed as follows. Let $v_{m\text{ ex}}$ represent the extended volume of an average region in which m grains overlap, and let v_m' represent the volume of that part of the region in which *only* m grains overlap. Then, assuming complete randomness, we have by the same reasoning as that which leads to (17)

$$v_m'/v_{m\text{ ex}} = 1 - V.$$

Multiplying both numerator and denominator by the total number of regions of this sort in

¹² The compositions and descriptions of the steels are given in the Trans. A.I.M.E. 90, 117 (1930). I wish here to acknowledge my indebtedness, not only to Messrs. Bain and Davenport for making available their original data, but also to Dr. J. B. Austin of the U. S. Steel Research Laboratory for his help in reading the values off the charts.

[†] K.P.C. I.

unit volume, we get

$$V_m'/V_{m\text{ ex}} = 1 - V, \quad (\text{I}, 1)$$

where V_m' and $V_{m\text{ ex}}$ have the significance discussed in the previous paper. If we put this expression for V_k' into Eq. (10') of that paper

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

we get

$$(1-V) V_{m\text{ ex}} = \sum_{p=m}^{\infty} (-1)^{p-m} C_m^p V_{p\text{ ex}}$$

which, upon rewriting and putting down together with (9), gives us an infinite system of linear equations for the determination of the infinite set of $V_{p\text{ ex}}$ in terms of V .

$$-V = -V_{1\text{ ex}} + V_{2\text{ ex}} - \cdots (-1)^p V_{p\text{ ex}} \cdots \quad (\text{I}, 2)$$

$$0 = V V_{m\text{ ex}} + \sum_{p=m+1}^{\infty} (-1)^{p-m} C_m^p V_{p\text{ ex}}.$$

The determinants involved in the solution of this system do not seem to have been studied in the literature. They are connected with the rather remarkable type of continued fraction to be discussed below. Since the matter is largely of pure mathematical interest we shall confine ourselves here to the consideration only of the determinants which appear in the solution for $V_{1\text{ ex}}$.

$$\begin{vmatrix} -V & 1 & -1 & \cdots & (-1)^p & \cdots \\ 0 & -2 & 3 & \cdots & (-1)^{p-1} C_1^p & \cdots \\ & V & -3 & \cdots & (-1)^{p-2} C_2^p & \cdots \\ & & \cdots & \cdots & \cdots & \cdots \\ \cdots & V & -k & \cdots & (-1)^{p-k} C_k^p & \cdots \\ & & \cdots & \cdots & \cdots & \cdots \\ -1 & -1 & -1 & \cdots & (-1)^p & \cdots \\ V & -2 & 3 & \cdots & (-1)^{p-1} C_1^p & \cdots \\ & V & -3 & \cdots & (-1)^{p-2} C_2^p & \cdots \\ & & \cdots & \cdots & \cdots & \cdots \\ \cdots & V & -k & \cdots & (-1)^{p-k} C_k^p & \cdots \\ & & \cdots & \cdots & \cdots & \cdots \end{vmatrix}$$

Upon multiplying alternate rows and columns by -1 all the minus signs become plus. Expanding both numerator and denominator according to the elements of the first column, and dividing through, we get

$$V_{1\text{ ex}} = V/(1-fV), \quad (\text{I}, 3)$$

where f is the fraction

$$\begin{vmatrix} 1 & 1 & 1 & \cdots & 1 & \cdots \\ V & 3 & 6 & \cdots & C_2^p & \cdots \\ & V & 4 & \cdots & C_3^p & \cdots \\ & & \cdots & \cdots & \cdots & \cdots \\ \cdots & V & k & \cdots & C_k^p & \cdots \\ & & \cdots & \cdots & \cdots & \cdots \end{vmatrix} \div \begin{vmatrix} 2 & 3 & 4 & \cdots & C_1^p & \cdots \\ V & 3 & 6 & \cdots & C_2^p & \cdots \\ & V & 4 & \cdots & C_3^p & \cdots \\ & & \cdots & \cdots & \cdots & \cdots \\ \cdots & V & k & \cdots & C_k^p & \cdots \\ & & \cdots & \cdots & \cdots & \cdots \end{vmatrix}$$

The numerator and denominator of this fraction separately approach infinity, but the ratio is finite for values of V in the range of physical interest between 0 and 1. For $V=0$ f is evidently equal to $\frac{1}{2}$; for $V=1$ it goes over into a ratio of determinants of a type studied by Zeipel.¹² Terminating the rows and columns after any fixed number, e.g., $p-1$, the numerator and denominator have the values $p-1$ and $p+2$, respectively. For $p \rightarrow \infty$ the ratio approaches 1. f then varies between $\frac{1}{2}$ and 1 as V goes from 0 to 1, and we see how the Austin Rickett formula with $f=1$ can give an approximate representation of (I, 3). We shall now proceed to show how $V_{1\text{ ex}}$, and therefore f , may be obtained as a function of V .

If, by convention, we set $V_{0\text{ ex}}$, "the extended volume of no transformation," equal to 1, (I, 2) may be written in the compact form

$$0 = V V_{k\text{ ex}} + \sum_{m=k+1}^{\infty} (-1)^{m-k} C_k^m V_{m\text{ ex}}, \quad k=0, 1, \cdots \quad (\text{I}, 2')$$

Now let us arbitrarily cut off each of the equations after the term containing $V_{p\text{ ex}}$. We may later allow p to become infinite. Our system becomes

$$0 = V V_{k\text{ ex}} + \sum_{m=k+1}^p (-1)^{m-k} C_k^m V_{m\text{ ex}}, \quad k=0, 1, \cdots p-1. \quad (\text{I}, 4)$$

Let us add to each equation the last equation multiplied by

$$(-1)^{p-k} \frac{C_k^p}{C_{p-1}^p}.$$

Our system becomes

$$0 = V V_{k\text{ ex}} + \sum_{m=k+1}^{p-2} (-1)^{m-k} C_k^m V_{m\text{ ex}} + (-1)^{p-k-1} C_k^{p-1} \left[1 - \frac{V}{p-k} \right] V_{p-1\text{ ex}}, \quad k=0, 1, \cdots p-2, \quad (\text{I}, 4')$$

¹² V. v. Zeipel, *Lunds Universitets Arsskrift*, II (1865); VIII (1871).

of which the last $(p-2)$ equation has the form

$$0 = V V_{p-2 \text{ ex}} - (p-1) \left[1 - \frac{V}{2} \right] V_{p-1 \text{ ex}}.$$

If now we add to each of the equations in (I, 4') the last equation multiplied by

$$\frac{C_k^{p-1} \left[1 - \frac{V}{p-k} \right]}{(-1)^{p-k-1} (p-1) \left[1 - \frac{V}{2} \right]},$$

our system becomes

$$0 = V V_{k \text{ ex}} + \sum_{k+1}^{p-3} (-1)^{m-k} C_k^m V_{m \text{ ex}} + (-1)^{p-2-k} C_k^{p-2} \left[1 - \frac{V}{p-k-1} \frac{1 - \frac{V}{p-k}}{1 - \frac{V}{2}} \right] V_{p-2 \text{ ex}},$$

$$k=0, 1, \dots, p-3. \quad (\text{I, 4''})$$

Continuing in similar fashion, we find that the last remaining term in the k th equation after the j th operation of this type is

$$(-1)^{p-k-j} C_k^{p-j} \left[1 - \frac{V}{p-k-j+1} \frac{1 - \frac{V}{p-k-j+2} \frac{1 - \frac{V}{p-k-j+3} \dots}{1 - \frac{V}{2} \frac{1-V/3}{1-V/2} \dots}}{1 - \frac{V}{2} \frac{1-V/4}{1-V/2} \dots} \right], \quad (\text{I, 5})$$

in which there appears a remarkable novel type of generalized ascending-descending continued fraction. It is characterized by the property that from each and every branch except the terminating ones there are two branches of higher order. We may perhaps describe it as a "tree fraction," and define its order as the order number of branchings, e.g., j in (I, 5). Upon letting the number of operations j equal $p-1$, the sole remaining equation for $k=0$ is

$$V = \left[1 - \frac{V}{2} \frac{1 - \frac{V}{3} \frac{1 - \frac{V}{4} \frac{1 - \frac{V}{5} \dots}{1 - \frac{V}{2} \frac{1-V/3}{1-V/2} \dots}}{1 - \frac{V}{3} \frac{1 - \frac{V}{4} \frac{1 - \frac{V}{5} \dots}{1 - \frac{V}{2} \frac{1-V/3}{1-V/2} \dots}} \right] V_{1 \text{ ex}} \quad (\text{I, 6})$$

and this determines $V_{1 \text{ ex}}$ in terms of V .

In general a tree fraction, like that in the brackets, defines a function which could be evaluated approximately for any value of the parameter by cutting off the "tree" after a certain number of branchings. In our case the function defined is a familiar elementary one as we shall now show. Let us designate the expression in the brackets by y . Then

$$V = y V_{1 \text{ ex}}. \quad (\text{I, 6'})$$

Since, for our infinite tree fraction, each successive *lower* branch is always exactly the same in structure as the entire tree, and is therefore equal to y , we have the relation

$$y = 1 - \frac{V}{2y} \left\{ 1 - \frac{V}{3y} \left[1 - \frac{V}{4y} (\dots) \right] \right\}$$

which may be rewritten

$$y = 1 - \frac{V}{2!y} + \frac{V^2}{3!y^2} - \frac{V^3}{4!y^3} + \dots = \frac{y}{V} (1 - e^{-V/y}),$$

from which

$$V = 1 - e^{-V/y}$$

and

$$y = -V/\lg(1-V).$$

Upon substituting into (I, 6') this gives

$$-\lg(1-V) = V_{1\text{ ex}} \quad (\text{I, 7})$$

which, upon rearrangement, gives

$$V = 1 - e^{-V_{1\text{ ex}}}, \quad (\text{20})$$

thus establishing the desired result.

Comparing (I, 7) with (I, 3), we find f in terms of V ,

$$f = \frac{1}{V} \left[1 + \frac{V}{\lg(1-V)} \right],$$

an interesting result for the ratio of the two infinite determinants given above.

Upon expanding (20) we get

$$V = V_{1\text{ ex}} - \frac{V_{1\text{ ex}}^2}{2!} + \frac{V_{1\text{ ex}}^3}{3!} - \dots (-1)^{m-1} \frac{V_{1\text{ ex}}^m}{m!} \dots \quad (\text{20}')$$

If we compare this with (9) the suggestion crops up that, in our case of complete randomness, the relations

$$V_{k\text{ ex}} = V_{1\text{ ex}}^k/k!$$

hold. That this is true can be seen as follows. From the previous paper

$$V_k = \sum_{m=k}^{\infty} V_m', \quad (\text{8}')$$

from which

$$V_k' = V_k - V_{k+1}$$

and, combining with (I, 1) and (20), this gives

$$V_k - V_{k+1} = V_{k\text{ ex}} e^{-V_{1\text{ ex}}}. \quad (\text{I, 8})$$

Now we must compare this with another relation, the generalization of (19), which we shall now obtain. Applying the same reasoning as above to increments in extended volume $dv_{k\text{ ex}}$ and volume

dv_k of the average k th-order region, we find

$$\frac{dv_k}{dv_{k\text{ ex}}} = 1 - V = e^{-V_{1\text{ ex}}}.$$

For unit volume

$$\frac{dV_k}{dV_{k\text{ ex}}} = e^{-V_{1\text{ ex}}}, \quad (\text{I, 9})$$

Differentiating (I, 8) and comparing with equations of the form (I, 9) we get

$$dV_{k+1\text{ ex}} = V_{k\text{ ex}} dV_{1\text{ ex}}$$

which is evidently equivalent to the desired result

$$V_{k\text{ ex}} = \frac{V_{1\text{ ex}}^k}{k!}. \quad (\text{I, 10})$$

To express the V_k also in terms of $V_{1\text{ ex}}$ we use the recursion formula (I, 8) successively to get

$$V_{k+1} = 1 - e^{-V_{1\text{ ex}}}(1 + V_{1\text{ ex}} + \dots + V_{k\text{ ex}})$$

and, substituting (I, 10) and rearranging, this becomes

$$V_{k+1} = (-1)^{k+1} e^{-V_{1\text{ ex}}} E_k(V_{1\text{ ex}}), \quad (\text{I, 11})$$

where E_k has the significance defined in (18''). Also

$$V_m' = \frac{V_{1\text{ ex}}^m}{m!} e^{-V_{1\text{ ex}}}, \quad (\text{I, 12})$$

which is evidently identical with (10') in our case, since

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

This completes the process of expressing all the other geometrical quantities in terms of $V_{1\text{ ex}}$ alone.