

Review article

Geometrical probabilities in heterogeneous kinetics: 60 years of side by side development

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In developing the theory of heterogeneous chemical kinetics, the use of ideas and methods of geometrical probabilities provided the explanation of the universal kinetic regularities inherent in solid state reactions conjugated with first-order phase transitions. But in the course of time it is becoming clearer and clearer that the other side of the universality of the conventional geometric-probabilistic approach in terms of coverings is the set of discrimination issues which find no adequate resolution within this phenomenology. Meanwhile another mathematical language, the language of tessellations, had been worked out in the framework of the theory of geometrical probabilities and, later, stochastic geometry. It is more promising with respect to deeper interpretation and chemical differentiation of models. The interplay between these two languages is discussed from the angle of essential issues concerning the mathematical description of solid state reaction kinetics.

The veritable logic of our world is the count of probabilities
J.C. Maxwell

1. Introduction: feedforwards and feedbacks

The accumulation of various issues and controversial results needs, from time to time, a backward look for getting a keener insight into the present state of events and sketching a way forward. This is the case now for heterogeneous chemical kinetics, and this year provides an opportunity to approach in a historical retrospection some key points of the mathematical description of solid state reaction kinetics: in 1997 it is just 60 years to the paper [1]. This commonly known paper in the field is written by the outstanding mathematician, the author of the generally accepted system of axioms of probability theory, A.N. Kolmogorov. Chronologically, it was the first stone in the building of the geometric-probabilistic approach to heterogeneous chemical kinetics. Together with the works [2] and [3], it has played a decisive role in the transition from deterministic to stochastic description.

The penetration of the ideas and methods of geometrical probabilities into heterogeneous chemical kinetics appears to be very fruitful, and the geometric-probabilistic

approach performs nowadays an important conceptual role. The discussion of its various aspects may be found, in particular, in [4–11]. But there is also another important result, the strong feedback that influenced considerably the progress of the theory of geometrical probabilities and integral geometry, in particular the evolution of stochastic geometry into a separate branch [12–19].

Recently, considerable progress was made in a relevant field of stochastic geometry, namely, the theory of random tessellations [20–25], and the obtained results are promising for breaking the vicious circle of numerous essential issues that have accumulated meanwhile in heterogeneous chemical kinetics.

For the present, these results remain mainly the property of mathematicians. To attract to them the attention of chemists and to include them into the context of heterogeneous chemical kinetics is one of the aims of this paper. However, this aim is not the main one. The new language, the language of tessellations, provides a new look at the old issues which have found no adequate resolution for quite a long time. This determines the structure of the paper. In section 3 these issues are discussed using the usual language, the language of coverings, and an attempt is made to trace them back to the original works [1–3] and thus to get at their roots. In section 4 these problems are approached again in terms of tessellations from the angle of new possibilities to resolve them. Section 2 provides some preliminary information. The chronological description in no case assumes a historical study, as well as the 60-year anniversary of the geometric-probabilistic approach is nothing more than an opportunity for a brewed discussion of the accumulated issues.

The number of references is restricted to a possible minimum on the principle of an intersection rather than a combination of two sets representing the fields of heterogeneous kinetics and stochastic geometry. But the majority of the necessary additional references “in depth” as well as “in breadth” may be found in them. The use of a new language for overcoming existing problems implies not only changes in the mathematical formalism but also a different approach to experimental design. Accordingly, the main points under discussion may be of interest not only for theorists but also for experimenters, which determines to a certain degree the style of the paper.

2. Some preliminaries

The geometric-probabilistic approach to heterogeneous chemical kinetics has a purely geometrical precursor, and a number of issues considered below involve no probabilistic aspects. To make the further discussion a bit subtler, it is expedient to separate the main issues into a probabilistic part and a non-probabilistic one. The next section deals with the deterministic geometrical part of the formalism. In this respect, the word “before” in its title should be understood to have the logical rather than the chronological meaning.

2.1. Before geometrical probabilities

The purely geometrical aspects may seem at first glance not only well-known but also too simple to be discussed again, even in brief. But, nevertheless, they are considered here, and not only for consistency and completeness. There are at least three more reasons. (i) To show how volatile this simplicity is and how quickly it disappears when the geometry of the problem becomes a bit more involved. (ii) To realize the extent to which the interpretational ability of the models now in use is restricted with this simple geometry. (iii) To emphasize that, in spite of apparent simplicity, the unrestricted growth admits another representation, more deep in conceptual respect.

2.1.1. Reaction is localized within the active interfacial zone

Chronologically, this statement was the first influential penetration of geometry into chemical kinetics. Its simple but convincing “argumentation by contradiction” belongs to Langmuir [26]: otherwise a solid solution would be formed instead of separate individual phases. Thereby the local enhancement of reactivity within the active interfacial zone is implied implicitly. Such localized reactions are termed topochemical reactions. Contrary to this “logical origin”, the further progress is due mainly to experimental studies; and nowadays one may notice some gap between the experimental and theoretical views of the reaction zone. Note in this connection the following points.

- (i) According to the recent (mainly local) experimental results, the reaction zone is considered at present as a three-dimensional one. Although its width is small, it is admissible to say that events different in nature may occur at the same time within its different “layers”. Examples may be found, in particular, in [27,28].
- (ii) The experimentally observed front is not necessarily identical to the reaction zone. Thus, in the case of visual observations an experimenter registers the boundary between regions with different optical properties which does not necessarily coincide with the front of chemical transformations [29].
- (iii) The possible anticoincidence of several fronts, as well as the three-dimensionality of the reaction zone, found no adequate representation in the theory. The reaction front is considered as a strictly two-dimensional surface separating two three-dimensional phases. As a rule it is termed reaction front (or boundary) without any subdivision into the main and accompanying processes.

2.1.2. Reaction starts at the nuclei

The conception of nuclei borrowed from biology had a considerable impact on the theory of both first-order phase transitions and heterogeneous chemical reactions. This conception has come to chemistry through physics. An interesting historical review may be found in [30]. The adaptation of the conception of nuclei for describing the thermal decomposition of solids is associated by Young [9] with the work [31]. There are examples of the earlier use of the term “nucleus” [32], but before the

above-mentioned work of Langmuir the use of this conception might hardly have been efficient. The main ideas and terminology concerning the conception of nuclei are discussed in detail in [32]. In the present context the following points are worth mentioning.

- (i) The idea that a reaction starts from the formation of stable nuclei immediately leads us to the picture of the ensemble of growing nuclei, which means that at beginning stages the reaction zone is multiply connected.
- (ii) Subcritical and critical nuclei are small, and it is extremely difficult (if at all possible) to observe them experimentally. Accordingly, the considerations concerning the mechanism and peculiarities of nucleation are mainly speculative. On the other hand, the geometric-probabilistic formalism under discussion is adapted for operating with stable nuclei alone: the intensity of their appearance with time is described by a function $L_n(t)$ which is termed the nucleation law.
- (iii) In the majority of cases, the term “nucleus” (tacitly) means the nucleus of a product, and it is far from being always recognized that in this case the process of the demolition of the original phase is not taken into account [33].

2.1.3. Nucleation–growth processes

Gradually the nucleation and growth scheme strengthened itself as a basis for further development of theoretical views. First of all, it was due to

- (i) experimental observations of the figures of growth which agreed with the crystal chemical structure of samples [34], and
- (ii) acceptable coincidence of experimental data and theoretical calculations for early stages (when the absence of impingements is assumed) and late stages (when the boundary is assumed to be simply connected) [35]. At the same time, it was noted that this satisfactory fitting is partly because of mutual compensation of two simplifying assumptions: the absence of impingements and the constant number of nuclei.

In this way, the simultaneous proceeding of various conjugated chemical and physical steps is formalized in terms of geometry as a process of formation and growth of nuclei, i.e., as the appearance and evolution of the multiply connected reaction zone. In the framework of the geometric-probabilistic approach, all models are constructed on this basis, though it is not always recognized and explicitly stated to what extent this determines the capability and adequacy of these models. Some relevant aspects become explicit in discussing the interrelation between “internal” and “external” definitions of the rate.

Whatever involved the process is, it always may be characterized by the quantity of the rate as a function of time, which provides some integral representation of the internal peculiarities of this process and their dependence on external conditions. In our context, this is some experimentally registered quantity (the loss on ignition, heat

release, etc.) with which the results of theoretical simulations are compared. Sometimes such a rate definition is termed “external” [36]. In this connection the question arises which theoretical function of formation and growth of the ensemble of nuclei may be compared with this quantity. In answering this question some material nuances concerning the description of the *ensemble* of growing nuclei become explicit (there are no difficulties in the case of a separate nucleus).

- (i) *The form* of growing nuclei. Though initially the form of growing nuclei was naturally compared and correlated with the crystal chemical structure of a sample [34], the current practice is mostly the default assumption of the spherical form. It is worth noting that, on the one hand, this poorly agrees with symmetry considerations and, on the other hand, this is not at all required by the theory. The only requirement of the theory at this stage is that all nuclei must have the same form (in passing to the probabilistic part of the problem, this requirement will become more involved).
- (ii) *The orientation* of all growing nuclei must be the same. Only under this condition a linear dimension (radius) r may be used for describing the ensemble of these nuclei. The choice of the radius may be arbitrary (figure 1) but one and the same for all nuclei. The spherical form is the only case when there is no problem of orientation, and perhaps this largely elucidates the expressed preference of this form.
- (iii) *The growth rate* of a separate nucleus $\nu(t)$ must not depend on the instant τ of its appearance. In other words, at any instant t all growing nuclei must have the same growth rate independently of their “age”. This requirement enables one to characterize the whole ensemble of growing nuclei with a single quantity of rate; otherwise this quantity is ambiguous. The use of any particular geometric-probabilistic model implies that this requirement is satisfied. To what extent this theoretical requirement is adequate to reality will be discussed below.

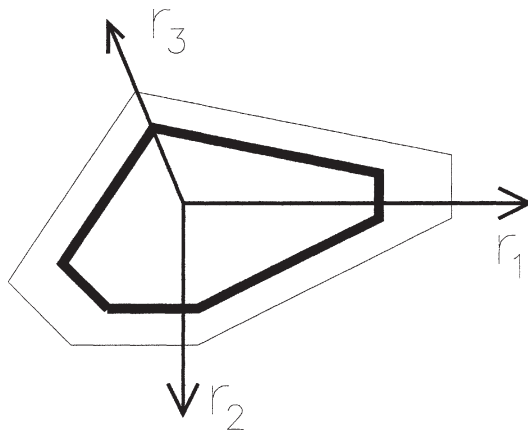


Figure 1. The radius of a nucleus may be chosen arbitrarily.

A more detailed treatment of these and some other related points may be found in [4].

Within the above framework the evolution of the ensemble of separate nuclei is described in the following way. The total rate $w(t)$ of the growth process is assumed to be directly proportional to the total measure $M(t)$ of the interface (interface length in the two-dimensional case or interface area in the three-dimensional case). The radius of a separate nucleus appeared at instant τ may be calculated as $r(\tau, t) = \int_{\tau}^t \nu(\xi) d\xi$, where t is the current time and ξ is the integration variable. The corresponding interface measure $\mu(\tau, t) = cr^{d-1}$, where c is the form factor (equal to 2π for circles) and d is the dimensionality of a nucleus (either 2 or 3). Until the ensemble of separate nucleus is concerned (i.e., there is no impingements), $M(t) = \int_0^t L_n(\xi)\mu(\xi, t) d\xi$ and the total rate is

$$w(t) = k \int_0^t L_n(\xi)cr^{d-1}(\xi, t) d\xi, \quad (1)$$

where k is the proportionality factor. Thus, the main variables have purely geometrical meaning, leaving for chemistry only the factor k .

2.2. Nucleus impingements: the need for and two ways of probabilistic approach

To take the impingements of growing nuclei into consideration is the most involved and non-trivial part of the problem. In reality the first impingements occur at fairly small t , and to calculate the rate correctly one needs to know the actual total length of the boundary with the account of impingements.

Two sources of randomness are connected with the impingements of growing nuclei:

- (i) Nuclei appear at random instants of time.
- (ii) New nuclei are situated in a random manner with respect to old nuclei.

This is just the point at which we face the need to resort to the ideas and methods of probability theory.

If we restrict ourselves to the planar case and allow nuclei to grow up to the end, we will get a picture similar to that shown in figure 2. A picture like this one will be seen, for example, if peering into a metallographic lapping. *Informally, the problem is to find appropriate regularities in this involved picture.* From the standpoint of contemporary mathematics, there are two essentially different possibilities to approach this problem. In two subsequent sections they will be discussed with respect to the issues of heterogeneous kinetics. Conventionally they may be named as the approach in terms of coverings and the approach in terms of tessellations.

Chronologically, the approach in terms of coverings was the first one that determined to a considerable extent the phenomenology of heterogeneous kinetics, the main trends of its development, and the present-day situation (section 3). This conventional geometric-probabilistic description has been used in heterogeneous kinetics

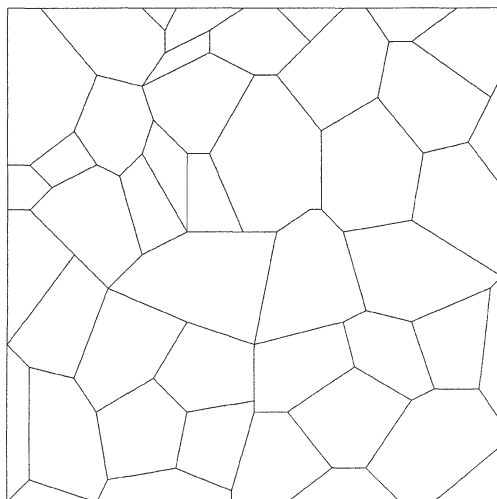


Figure 2. An example of the random tessellation: a nucleation and growth process is completed.

for 60 years. During this period stochastic geometry has developed another language, the language of tessellations. Only relatively recently the development of this language has reached the level sufficient for discussing essential issues of heterogeneous kinetics. This line is traced in section 4.

The first solution in terms of coverings to the problem of nucleus impingements was given by Kolmogorov [1] soon after he had presented his system of axioms of probability theory [37]. A bit later and completely independently the work of Johnson and Mehl [2] appeared, which, in its turn, inspired the series of works of Avrami [3]. These works gave birth to the geometric-probabilistic approach to heterogeneous chemical kinetics. Though the final equations obtained in these works are similar, they differ essentially in methods and rigour. In historical retrospection [4], the very first work [1] appears to be the most rigorous one in mathematical respect. In the work [2] an elegant “fictitious mechanism” is suggested which is more visual and due to this it provides the possibility to discern some essential nuances. In [3] the combinatorial aspects of the problem are considered in detail, but a number of compromises as to the mathematical rigour were admitted.

In the available literature on heterogeneous kinetics, the discussion of theoretical aspects is practically never based directly on the work [1]. Besides the obvious language barrier, this is likely because it is purely mathematical in style and concise presentation of the material. But when it comes to the questions concerning the essential issues accumulated in heterogeneous kinetics (the discussion of which may be found, in particular, in [5–8,38–42]), it is the work [1] and the further development of the method [4] that provide a deeper understanding of their roots, as well as possible ways out.

3. Conventional geometric-probabilistic approach to heterogeneous chemical kinetics

3.1. Note concerning dimensionality

The independence of the main results from the particular dimensionality of the reaction space is characteristic and essential in the present context peculiarity of the discussed geometric-probabilistic approach [1,4]. This makes it possible to restrict our considerations to the two-dimensional case only. In a later section we will see that this is done not only for the reasons of simplicity and visuality: in the case of chemical reactions in which a solid reagent participates, the two-dimensional approach has much deeper substantiations.

3.2. The parent dependent variable

The structure of the theory, its capability and restrictions are determined to a considerable extent by the particular manner in which the concept of the rate of a chemical reaction is formalized as a function of time. For heterogeneous reactions this problem is considerably more involved than for homogeneous reactions. One of the reasons is that chemical changes are always conjugated with first-order phase transitions.

In the framework of the geometric-probabilistic approach, the *degree of conversion* $\alpha(t)$ serves as the parent dependent variable. It is defined as a (geometrical) probability of the event that an arbitrary point A of the initial phase will be “consumed” at instant t by the phase of a product.

On the plane the picture is as follows. Let the area of the initial surface be S_0 . Figure 3 shows the picture at some moment t when a part $S(t)$ of the plane has undergone a transformation. One throws by chance a point on this plane. The probability $\alpha(t) = S(t)/S_0$ that it will fit one of the hatched regions is identified with the degree of conversion.

In homogeneous kinetics there is a quantity that plays a similar role and it is termed also as the degree of conversion (see, for example, [43]). It must not escape one's attention that in spite of the same terminology and designation these quantities are considerably different. The “homogeneous degree of conversion” is expressed through the number of moles of a reagent and thus it has a chemical meaning. The “heterogeneous degree of conversion” is expressed through the area (or volume) and has no direct connection with chemistry. The fact that in both cases one deals with the dimensionless variable $\alpha(t)$ varying between 0 and 1 must not mask these conceptual distinctions. To emphasize them, note that in the case of a non-stoichiometric homogeneous reaction a separate degree of conversion may be defined for each component, which is not the case for a non-stoichiometric heterogeneous reaction. There exists an even more fundamental distinction: the “homogeneous degree of conversion” is connected with another quantity, the extent of reaction (introduced by De Donder [44]), which is the property of a system [43]. The “heterogeneous degree of conversion”

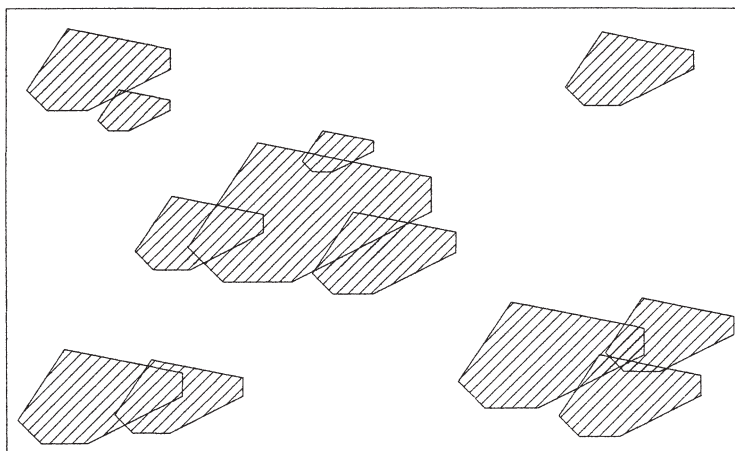


Figure 3. In contrary to figure 2, a nucleation and growth process is not yet completed.

provides an ambiguous description of a system in the sense that the same magnitude may be realized in a variety of ways (various sets of nuclei) [11].

We are interested in the rate of a reaction. It is determined as the derivative of the “heterogeneous degree of conversion” with respect to time. And this determines to some extent the structure and the interpretational ability of the approach under discussion.

3.3. The main scheme

As was rightly noted in [4], the main contribution of the work [1] to the theory is not so much the final relationships as the precise formulation of the method and conditions under which the results rigorously follows.

Our aim is to follow in what way the degree of conversion $\alpha(t)$ defined in terms of geometrical probabilities may be connected with the ideas of formation, growth and impingements of nuclei and calculated in terms of two quantities termed nucleation law $L_n(t)$ (see section 2.1.2) and growth law $L_g(\tau, t) = c(\int_{\tau}^t \nu(\xi) d\xi)^d$.

Consider a point A chosen by chance within the original phase (figure 4(a)). The sufficient condition for being consumed at instant t by a new phase is the appearance at some earlier instant $\tau < t$ of a nucleus at such a distance r from A that in the course of growth this nucleus will be able to reach the point A at the instant t or before. For brevity such a nucleus will be termed “aggressor” (following the terminology accepted in [4]). For the given values of t and τ , the value of r is determined by the growth rate in the given direction. The form of nucleus shown in figure 4(a) is chosen to emphasize that generally it may be arbitrary; the only requirement for the nucleus form is convexity. A centrally symmetric figure is termed “imaginary nucleus” [4]; figure 4(b) shows four concentric imaginary nuclei with point A as their center.

The appearance of an aggressor at any point of the boundary of the imaginary nucleus with the center in the point A and radius r (figure 4(b)) will obviously result

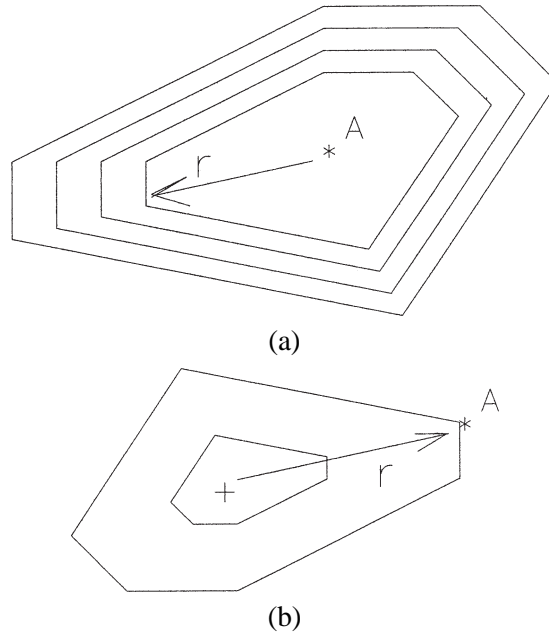


Figure 4. Will the point A be consumed at the instant t by a growing nucleus or not? The answer is in the text.

in the consumption of the point A by the new phase up to instant t . The point A may also be consumed by an aggressor that appeared inside this imaginary nucleus at some earlier instant τ , the distance from A being determined by the value of τ . Note that the appearance of an aggressor in one of these points is a sufficient but not a necessary condition for the point A to be consumed. For this reason the calculation of $\alpha(t)$ is based on the inverse statement: if up to instant τ there will be no aggressors within imaginary nucleus (including the boundary) with corresponding radius r (figure 4(b)), the point A will not be consumed by the new phase up to instant t . This enables one to pass to the system of independent events, the probabilities of which may be multiplied. The time interval $[0, t]$ is subdivided into N equal parts. Accordingly, space around the point A is subdivided into the enclosed concentric negative nucleus (figure 4(b)). The nucleation is assumed to proceed according to a Poisson process. This means that the probability of the appearance of one nucleus within the region with the area $S(\tau, t) = L_g(\tau, t) = c(\int_{\tau}^t \nu(\xi) d\xi)^2$ is equal to $p_i = L_n(\tau_i)L_g(\tau_i, t)\Delta\tau + o(\Delta\tau)$, whereas the probability of the appearance of more than one nucleus is $o(\Delta\tau)$. The probability that no nuclei will appear is $q_i = 1 - p_i$. The probability $Q(t)$ that a point A will not be consumed by the new phase up to instant t is calculated as the product of the probabilities q_i corresponding to the subsequently widening regions in figure 4:

$$Q(t) = \prod_{i=1}^N q_i(\tau). \quad (2)$$

Further calculation steps are as follows. By taking the logarithm, one passes from the product to the sum

$$\ln Q(t) = \sum_{i=1}^N \ln q_i \tag{3}$$

and, after expanding it into a series and substituting the expression for q_i 's, one gets

$$\ln Q(t) = - \sum_{i=1}^N L_n(\tau_i) L_g(\tau_i, t) \Delta\tau + o(1). \tag{4}$$

Letting $N \rightarrow \infty$, one gets

$$\ln Q(t) = - \int_0^t L_n(\tau) L_g(\tau, t) d\tau. \tag{5}$$

The sought-for probability that a point A will be consumed by the new phase up to instant t is

$$\alpha(t) \equiv 1 - Q(t) = 1 - \exp\left(- \int_0^t L_n(\tau) L_g(\tau, t) d\tau\right), \tag{6}$$

which is the central relationship connecting $\alpha(t)$ with the idea of growing nuclei.

It was emphasized above that the ideas and methods of geometrical probabilities are employed for taking the *impingements* of growing nuclei into account, which is the most difficult part of the problem. But from the above considerations, the particular way in which this can be done is not obvious. Some details, important in the present context, become explicit in terms of the visual approach of Johnson and Mehl [2].

The expression for the rate may be obtained by differentiating (6) with respect to t . Taking into account that $L_g(t, t) = 0$ and $[L_g(\tau, t)]'_t = 2c\nu(t) \int_\tau^t \nu(\xi) d\xi$, one gets

$$\begin{aligned} \dot{\alpha}(t) &= \nu(t) 2c \int_0^t \left[L_n(\tau) \int_\tau^t \nu(\xi) d\xi \right] d\tau \\ &\times \exp\left(- \int_0^t L_n(\tau) L_g(\tau, t) d\tau\right). \end{aligned} \tag{7}$$

Note that in this particular case, $d = 2$, the second factor in (7) coincides (within the proportionality factor) with (1). In terms of unrestricted growth, this is the total length of the interface. In terms of the approach of Johnson and Mehl, this is the extended length l_{ext} of the interface calculated under the assumption that all nuclei are growing "ignoring each other" (figure 5). The third factor in (7) is equal to $1 - \alpha(t)$ which is the probability for an arbitrary point to fit the original phase. With this account, the expression for the rate may be rewritten in the form

$$\dot{\alpha}(t) = \nu(t) l_{\text{ext}}(t) (1 - \alpha(t)). \tag{8}$$

This provides an idea about the essence of the Johnson–Mehl approach: first the extended length of the interface is calculated, which presents no difficulties, and

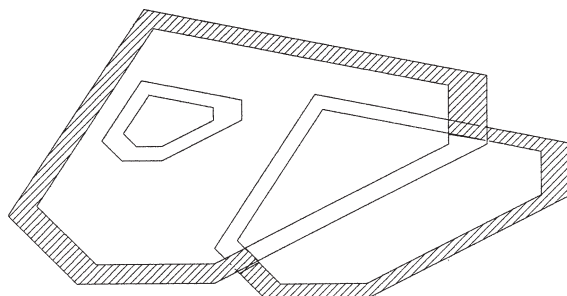


Figure 5. Illustration to the “fictitious mechanism” of Johnson and Mehl.

then the regions of overlapping (unhatched in figure 5) are taken into account through multiplying l_{ext} by $1 - \alpha(t)$. Thus, it may be said that the approach under discussion makes it possible to “avoid” the detailed treatment of impingements. It is due to this fact that the rigorous final solution is obtained in a relatively simple and elegant manner: each step of the calculations described above guarantees the unoccupied space for new nuclei to appear. This is a great advantage from the viewpoint of the final result. On the other hand, this poses some restrictions on the interpretational ability of the scheme. We will return to this point below.

3.4. The main applicability conditions and particular cases

Relationship (6) is the *rigorous solution* of the problem only if four applicability conditions are satisfied. They were clearly stated in [1] and analyzed in detail in [4].

- (i) The original parent phase must be unlimited; in other words, a growing nucleus must be small in comparison with the total reaction space.
- (ii) The nucleation must proceed according to a Poisson process. (The possibility to extend this condition through taking into account the dependence of the probability of nucleation on the distance from the reaction front is discussed in [4].)
- (iii) The form and orientation of all nuclei must be the same, and the nuclei must be convex (comparing this with section 2, we see that the requirement of convexity is added, i.e., it concerns the probabilistic aspects of the problem).
- (iv) The growth rate of a nucleus must not depend on its “age”; i.e., it must be one and the same for all nuclei.

If the convexity requirement or condition (iv) is violated, then

$$\alpha(t) \leq 1 - \exp\left(-\int_0^t L_n(\tau)L_g(\tau, t) d\tau\right). \quad (9)$$

The use of a particular geometric-probabilistic model without discussing the above conditions, which is not infrequently the case in the current literature, introduces an additional ambiguity into the interpretation of results.

Whereas conditions (i) and (ii) usually raise no objections, the two other conditions seem at first glance to be in poor agreement with reality. Perhaps for this reason, condition (iii) is often “avoided” through the default acceptance of the spherical form of nuclei.

In connection with condition (iv), the incompatibility of the geometric-probabilistic description with the diffusive control of a process must be emphasized. Under diffusive control, the radius of a separate nucleus, $r(\tau, t) \sim \sqrt{t - \tau}$, and hence the growth rate, depends on the age of a nucleus. This is in direct contradiction with condition (iv). The impossibility to relax this condition was rigorously shown in [4]. This means that geometric-probabilistic models may be used only if the kinetic regime is proved or supposed. Nevertheless, they are not infrequently used for describing processes controlled by diffusion. It is worth noting that in these cases one deals with a formal approximation rather than with meaningful simulation, i.e., no definite meaning may be assigned to model parameters.

In the present context, the emphasis on the applicability conditions is of particular interest. The possibility to satisfy them rigorously in a natural way through taking the crystal chemical structure of a solid reagent into considerations will be discussed below.

The nucleation law $L_n(t)$ and the growth law $L_g(\tau, t)$ are initial hypotheses, the substantiation of which is beyond the phenomenological geometric-probabilistic approach. Among others, the following two particular cases are most frequently used in heterogeneous kinetics.

- (i) The constant intensity of nucleation $L_n = \gamma$ and the constant growth rate ν . In this case,

$$\alpha(1) = 1 - \exp(-c\gamma\nu^d t^{d+1}/(d+1)). \quad (10)$$

- (ii) The instantaneous nucleation at the very beginning of a process with the density β nuclei per unit surface; $\nu = \text{const}$. In this case,

$$\alpha(t) = 1 - \exp(-c\beta\nu^d t^d). \quad (11)$$

3.5. Homogeneous chemical interpretation of the main scheme

Talking about the rate of a chemical reaction, we consciously or subconsciously keep in mind the rate equations for unimolecular and bimolecular reactions as a reference examples of the most simple and well-studied cases in chemical kinetics. The conventional way to derive them is to write down the mass action law and to integrate the corresponding expression (see, for example, [45]).

It was emphasized by Erofeev [46] that the same equations may be obtained without integrating the mass action law. In formal respect, his approach repeats “word to word” the above scheme (section 3.3). Let q_i in equation (2) have the meaning of the probability of an elementary event that a molecule of a particular reagent chosen at random will not react within the i th subinterval of the time interval $0 = t_0 < t_1 <$

$\dots < t_{i-1} < t_i < \dots < t_n = t$. Then the above calculation steps will lead to the equation

$$\alpha^*(t) = 1 - \exp\left(-\int_0^t p(\xi) d\xi\right), \quad (12)$$

in which $p = 1 - q$. Putting $p = k$, where k is constant, one immediately arrives at the commonly-known equation of a unimolecular reaction

$$\alpha^*(t) = 1 - e^{-kt}. \quad (13)$$

It must be emphasized again that in these equations we deal with the “homogeneous degree of conversion” expressible through the number of moles of a component (which is shown by asterisk). Putting $p = (k/\nu)(b - \alpha a)$, where a and b are the initial concentrations of the reagents A and B, respectively, and V is the volume, one arrives at the relationship

$$\alpha_A^*(t) = 1 - \exp\left(\ln \frac{a - b}{a - b \exp(k/V)(b - a)t}\right), \quad (14)$$

which is equivalent to the conventional equation for a bimolecular reaction [46]. But in passing to the kinetics of solid-phase reactions, that was the central subject of paper [46], Erofeev assigned to p a geometric-probabilistic rather than a chemical interpretation and arrived at the equation similar in essence (and form) to the equations of Kolmogorov, Johnson–Mehl, and Avrami. Along with spherical nuclei, he also considered cylindrical and plane nuclei.

3.6. The main trends of development

Pure mathematics deals only with what may be done by rigorous means, whereas applied mathematics deals with what is necessarily done by available means [47]. Not infrequently, the many-year development of one or another theory is the attempts to put these both extremes together. In heterogeneous chemical kinetics, this tendency is fairly expressed and far from being completed.

The work [1] belongs for sure to the realm of pure mathematics: this is the rigorous work with clear statement of the applicability conditions for the results obtained. But with respect to reality, represented by polydisperse polycrystalline systems consisting of poorly characterized (by prehistory instead of composition and structure) samples, the developed scheme may seem at first glance fairly “lean” with the applicability conditions being unreal. Accordingly, immediately after the problem of nucleus impingements had been solved, attempts followed to describe “what is necessary”. Gradually they were split into two directions, the extension of the general scheme and the modification of particular models.

The main step in developing the general scheme is the attempt to solve the problem for spherical particles with the subsequent transition to polydisperse systems. The random nucleation at the surface of a spherical particle was considered practically

simultaneously in the works of Mampel [48] and Todes and Bogutskiy [49], though the two approaches differ in some essential details. In [48], the spherical particle is subdivided into concentric shells, and the appearance, growth and impingements of nuclei are considered first for the outer shell only. The appearance of a nucleus within one or another internal shell is determined by the time required for a nucleus appearing at the outer shell to reach this internal shell. Finally, the degree of conversion $\alpha(t)$ is calculated through integrating over all spherical shells. The problem is thus solved “shell-by-shell”. The result is as follows:

$$\begin{aligned} \alpha(t) = & \frac{3}{4\pi R^3} \int_{\Delta_1}^{\Delta_2} 4\pi(R-Z)^2 \\ & \times \left\{ 1 - \exp \left[-\frac{R}{R-Z} \left(k_1 N_0 k_2^2 \pi t^3 / 3 - k_1 N_0 \pi Z^2 + \frac{2}{3} \pi Z^3 k_1 N_0 / k_2 \right) \right] \right\} dZ \\ & + \frac{3}{4\pi R^3} \int_{\Delta_3}^{\Delta_4} 4\pi(R-Z)^2 \\ & \times \left\{ 1 - \exp \left[-4k_1 N_0 \pi R^2 t + \frac{4k_1 N_0}{3k_2} \pi R(4R^2 - 2RZ + Z^2) \right] \right\} dZ. \end{aligned} \quad (15)$$

Here R is the radius of the external shell, Z is the distance of an internal shell from the external surface, N_0 is the average number of nuclei per unit square, k_1 is the nucleation constant, k_2 is the growth constant, and the integration limits are as follows: for $0 \leq t \leq R/k_2$, $\Delta_1 = 0$, $\Delta_2 = k_2 t$, $\Delta_3 = 0$, $\Delta_4 = 0$; for $R/k_2 \leq t \leq 2R/k_2$, $\Delta_1 = 0$, $\Delta_2 = 2R - k_2 t$, $\Delta_3 = 2R - k_2 t$, $\Delta_4 = R$; for $2R/k_2 \leq t$, $\Delta_1 = 0$, $\Delta_2 = 0$, $\Delta_3 = 0$, $\Delta_4 = R$.

Todes and Bogutskiy [49] considered simultaneous nucleations of two types: random formation of nuclei and activation of randomly situated potential nuclei. For the point A chosen at random inside the spherical particle, the probability is calculated that at time t this point will be consumed by the new phase. The result is identified with the degree of conversion

$$\begin{aligned} \alpha(t) = & \frac{1}{R^2} \int_{R-\nu t}^R \left[1 - \exp \left\{ -\frac{\pi R}{r} \left[N_0 (\nu^2 t^2 - (R-Z)^2) \right. \right. \right. \\ & \left. \left. \left. + \frac{a}{3} \left(\nu^2 t^3 - 3(R-r)^2 + 2\frac{(R-r)^3}{\nu} \right) \right] \right\} \right] r^2 dr. \end{aligned} \quad (16)$$

Here N_0 is the average density of potential nuclei and a is the probability of nucleation per unit surface per unit time, r is the polar radius.

These results for a single spherical particle are the first step on the way from “what is possible” to “what is necessary”. And even this first step has led to the involved integrals which cannot be expressed in the closed form. The more so, attempts to estimate the influence of the particle size on the kinetics of a transformation and to pass to the analysis of polydisperse systems [50] faced the considerable computational difficulties that led to simplifications, the acceptability of which is not simple

to substantiate. The situation is aggravated because of the difficulties connected with the direct experimental check of the obtained results [9]. Note also that though in both papers chemical reactions are mentioned along with first-order phase transitions, no distinction between them is drawn. The original particles are considered to be homogeneous and isotropic; the form of nuclei is spherical.

Much later the elaborated analysis has shown that even in the most simple planar case of the layer-by-layer growth, with all the four applicability conditions given above being satisfied, the problem has no rigorous solution in closed form [4].

The sharp increase of difficulties in modifying the general scheme, on the one hand, and unsatisfactory description of experimental data by rigorously derived particular equations (10), (11), on the other hand, resulted in attempts to modify these particular equations proceeding from various empirical considerations. Thus, it was suggested in [51] to use the equation

$$\alpha(t) = 1 - e^{-kt^\nu - kt^{\nu+1}} \quad (17)$$

instead of equation (11), i.e., to add one more term to the exponent (in contrast to d in equation (11), ν is a formal adjustment parameter). This was motivated by the need to describe the bend of the experimental straight line in the logarithmic scale. Modification of another type consists in the change of factor $1 - \alpha(t)$ to factor $(1 - \alpha(t))^\mu$, where μ is one more formal parameter; $\mu > 1$ [52]. As a result, instead of equation (11) one gets the (totally dissimilar) equation

$$(1 - \alpha(t))^\mu = \frac{1}{1 + kt^\nu}. \quad (18)$$

The next step in this direction was done in [53], where the following equation with formal parameters λ , μ and ν was suggested:

$$\dot{\alpha}(t) = k\alpha(t)^\lambda (1 - \alpha(t))^\mu [-\ln(1 - \alpha(t))]^\nu. \quad (19)$$

This equation is a generalized one in the sense that many of the particular equations now in use may be obtained from it under definite values of parameters. However, it must be stressed in this connection that any choice of $\mu \neq 1$ negates the fundamental assumption of the equiprobability of nucleus formation discussed above [11].

In all mentioned works, the spherical form of both nuclei and original particles was explicitly or implicitly assumed. Along with this, from the very beginning there were attempts to enrich the set of models in other ways, through considering different forms of nuclei (e.g., [54]) and also different forms of original particles (e.g., [55]). In the latter case three possibilities for a reaction to start were considered, on the faces, edges or vertices of a particle. These elements may enter a reaction either simultaneously or according to the law of chance. But in these ways the difficulties appeared to be even much greater, and nowadays the majority of works deal with the spherical form.

The above considerations provide an idea about the ways in which the set of geometric-probabilistic models now in use in heterogeneous chemical kinetics was

formed. The discussion of various relevant aspects may be found in modern treatises, reviews and papers [4–11,27–29,38–42,56–60].

3.7. The main problems; the role of the geometric-probabilistic approach

The above main trends of development have resulted in two extremes with practically no “golden mean”. On the one hand, we have too complicated models like (15), (16); the other extreme is the set of oversimplified models such as (10), (11) and (17)–(19). Whereas the former models have found practically no utilization, the latter ones have been widely employed for describing and analyzing experimental results. In the course of long intensive practice of using these models, various discrimination problems arose that gradually formed a fairly stable circle. During the last two decades they were discussed from various angles [5–8,38–41,58–60]. The following problems belong to the most representative ones.

- (i) Statistical indistinguishability of models: one and the same set of experimental data may be described equally well by several different models [61].
- (ii) Quite different original concepts concerning the reaction mechanism may lead to the same equation in terms of α . For example, the well-known equation

$$\ln(\alpha(t)/(1 - \alpha(t))) = kt \quad (20)$$

may be obtained by assuming [62] the mechanism of autocatalytic reactions, the chain mechanism of “outstripping” self-dispersion, the radical-chain mechanism, and the diffusion mechanism. A number of other similar examples may be found in [62].

- (iii) When considered in totality from one or another common viewpoint, models may acquire an interpretation different from the original one which is accompanied by a considerable reduction of the variation of their conceptual meaning. In terms of functional analysis, this was shown in [59,60]. Twenty particular models widely used in heterogeneous kinetics were selected for analysis. This set was considered as a space, and the scalar product was introduced in the usual way for its vectors. Thus, the emphasis was placed on the form rather than on the meaning of models: the bigger the angle between two models the greater distinctions between them. The analysis of this space provides four classes of kinetic models, characterized by similar properties; some models being intermediate between these classes. One of the conclusions made by the authors is that some models different in mathematical form give practically very close values of the kinetic parameters, i.e., they actually characterize very similar processes, but describe them in a different mathematical form. In terms of geometrical probabilities, various models are compared in [11].

Among other discrimination issues, the problem of fractional values of exponents in particular models deserves special attention. During recent years this fairly old problem has taken new interesting aspects. This is due to the wide penetration of

the theory of fractals [63,64] into heterogeneous chemistry [65]. In this connection it is worth emphasizing that within the conventional geometric-probabilistic approach an integer dimensionality of the reaction environment is implied. Accordingly, numerous cases of fractional values of this parameter obtained from experimental data have always been a considerable problem of interpretation. At first glance, fractals suggest themselves in this situation as a direct way out. However, the following points should be taken into account. (i) It is not a simple task to reconcile the notion of fractal with the convexity requirement. The possibility to relax this requirement in the framework of discrete description has been shown in [66]. But within the conventional continuous description this requirement cannot be relaxed [4]. (ii) In many cases fractals appear as a result of diffusion-control processes. Recall in this connection that the geometric-probabilistic approach is not adapted for taking these processes into account (see section 3.4). (iii) In computational respect, fractional exponents may well result from violation of the above applicability conditions. No doubt, the fractal approach to heterogeneous chemistry is interesting and promising. But the question of whether a fractional exponent of a particular geometric-probabilistic model indicates the formation of a fractal remains open for the present and requires further development of the geometric-probabilistic approach with respect to chemical interpretation.

The discrimination problems give rise to the question to what extent they are specified by particular models and to what extent they are inherent to the general geometric-probabilistic scheme. In [11] it was shown that the geometric-probabilistic scheme is essentially ambiguous with respect to inverse kinetic problems. In this connection it is worth emphasizing again the geometric-probabilistic interpretation of the main variables. The consequence of this is that all conceptual details of the mechanism which do not fall within this interpretation are represented on the stage of formalization by the model coefficients only. As a result, they participate in the discrimination procedure not through the form of the function but only through the numerical values of the coefficients. Note also that a single phase transition and, therefore, the complete coherence of all processes are implied by conventional equations now in use, which is not the case for the majority of reactions.

We saw that, along with the geometric-probabilistic interpretation, the formal scheme admits also a chemical interpretation. But in the framework of the conventional continuous approach, EITHER a chemical OR a geometric-probabilistic meaning may be assigned to the probabilities q_i in (2). Perhaps this is the main reason why there was no progress in developing the theory in the direction of chemical interpretation and differentiation of models, and such an important characteristic of the chemical individuality of a solid reagent as its crystal chemical structure was not represented in the theory at all. Accordingly, symmetry considerations appear to be inapplicable.

The ambiguous interrelationship between kinetic behaviour and mechanism is, of course, the problem not only of heterogeneous kinetics. This is the general problem of chemical kinetics [5,6,36,67]. When fairly involved reactions are concerned, it is impossible to elucidate the mechanism proceeding from the mathematical treatment of the observed kinetic behaviour only. In the case of a more developed theory (in

the contiguous fields such as heterogeneous catalysis), kinetic analysis is accomplished with various additional measurements and considerations [36]. That is why the question whether or not the chemical interpretation of the geometric-probabilistic scheme is possible is so important: one may hope to resolve the above problems only in the way of overcoming the “chemical facelessness” of the conventional approach [40,58].

All what was said about the problems and difficulties must not disparage the important conceptual role of the geometric-probabilistic approach for contemporary heterogeneous chemical kinetics. Whereas phase transitions may occur without chemical transformations, any solid state chemical reaction is always conjugated with the disappearance and formation of phases that proceed through the formation, growth and impingements of nuclei. This point cannot be avoided, and the rigorous solution of the direct problem in terms of the geometric-probabilistic approach provides the reliable ground for further development of the theory.

In thinking about the ways of adequate chemical interpretations of the geometric-probabilistic scheme and the possibility to describe correctly “what is necessary”, new mathematical tools naturally attract attention of those who are dealing with the theoretical problems of heterogeneous kinetics. Some of them are due to the recent development of the theory of random tessellations.

4. Nucleation–growth–impingement processes in terms of tessellations

The works [1] and [2], classical in heterogeneous chemical kinetics, are also cited in the literature on stochastic geometry among the origins of one of its important parts, the theory of random tessellations. On the background of unsatisfactory dynamics in resolving the above discrimination issues, especially during recent years, this affinity naturally attracts one’s attention as a potential possibility to approach them from a new angle. There are comprehensive treatises and reviews on stochastic geometry among which references [12–20,72–75] seem to be most appropriate to the subject of this paper. The aim of the subsequent section is to follow briefly the evolution of the theory of random tessellations emphasizing interconnections and parallels essential in the present context.

4.1. Random tessellations: from geometrical probabilities to stochastic geometry

The problem of nucleus impingements was rigorously solved in [1] in terms of geometrical probabilities, and practically at the same time attempts to make more precise the statements and methods of the theory of geometrical probabilities itself gave rise to the appearance of a new mathematical discipline, integral geometry [68], in the framework of which stochastic geometry has later been crystallized [12–14]. From the viewpoint of stochastic geometry, figure 2 shows a random tessellation. Various problems connected with disparate by nature random tessellations are typical problems of stochastic geometry [16–18]. It is also worth emphasizing that the study of

random tessellations, in particular Voronoi tessellations and Johnson–Mehl tessellations, contributed considerably to the formation of stochastic geometry as a separate branch [12].

Along with the work [2], the works [69–71] should be mentioned as the original works dealing with random tessellations. In these works the first results have been obtained and the main trends and issues have become explicit. Later a considerable progress was reached in the series of works of Miles (summarized, in particular, in his review [72] where other references may be found). The two-dimensional case was considered separately, which is essential in the present context (see section 3.1). As was noted by Santalò [12], these works of Miles have played an important role in the formation of stochastic geometry by introducing ideas and methods of the theory of random processes into integral geometry. The term “stochastic geometry” was suggested in 1969 by Kendall, Krickeberg, and Miles at a Symposium on Integral Geometry (Germany) [12]. The review of Miles on random tessellations [72] appeared even later, in 1972. Note that at this time the conventional geometric-probabilistic approach to heterogeneous chemical kinetics had been used for quite a long period of time, had found the representation in the main treatises [6,7,9], and also gave rise to some of the issues which make one to resort today to the ideas and methods of stochastic geometry.

Initially integral geometry dealt with finite sets of geometrical elements and with measures spaces of these sets. The transition to countably infinite sets provides the possibility of using the methods of the theory of random point processes [71]. The systematic use of the theory of random sets inspired, in particular, a considerable progress in the statistics of geometrical objects [74]. In its turn, results of stochastic geometry gave positive impact to the theory of random point processes, which is noted in [75]. In the preface of the book [12], this dynamics of events is characterized as the renaissance of the interest in this beautiful bewitching brunch of mathematics. This development is promising, in particular, for heterogeneous chemical kinetics, and random tessellations form in this respect a “conceptual cross-road”.

4.2. Voronoi tessellations and Johnson–Mehl tessellations

During the recent 10–15 years, a general theory of random tessellations has been established in the framework of stochastic geometry [20–23]. The growth models have found their place in stochastic geometry along with intersection models (connected with random line processes and plane processes) and fracture models [17,18] and, together with them, such terms as “birth–growth processes”, “nuclei”, “crystals”, etc., have entered stochastic geometry. The characteristic feature of the theory is that the majority of models are developed based on Poisson processes, since non-Poisson models in general seem to be analytically intractable [22]. Though a number of important results are obtained for arbitrary dimensions, we will be interested, as before, in the two-dimensional case only.

A planar random tessellation is characterized by its *typical element*, and a possibility to approach the above issues of heterogeneous kinetics from a new angle is connected with the use of this notion. The typical element is characterized by its area, perimeter length, typical edge length, number of edges, etc. [12–14]. Note that each cell of a random tessellation has six neighbors on average; in other words, the typical element has six edges. The purely topological character of this fact (interesting and essential in the present context) was proved in [76] before the work [2] had appeared.

A Voronoi tessellation appears as a special case where all nuclei are born at the same instant. But even in this relatively simple case the closed expressions of distribution functions or densities are unknown for the majority of random variables. Concerning the second-order moments, the variances and covariances of the cell area, edge length, perimeter length, and number of vertices have been calculated, but generally results of this kind are very complicated to evaluate [21]. The main characteristics of a typical element are as follows [14] (λ is the intensity of a Poisson point process): the average number N of edges of a typical element is 6; the average area S is $1/\lambda$; the average perimeter length P is $4/\lambda^{1/2}$; the average length L of a typical edge is $2/3\lambda^{1/2}$; the average number N' of edges outgoing from a typical vertex is 3; the average total length L' of edges outgoing from a typical vertex is $2/\lambda^{1/2}$.

In examining the Johnson–Mehl tessellations, the role of numerical simulation increases considerably. In [22] the algorithm for simulating spatially and temporally inhomogeneous Poisson processes and the general procedure for generating a typical crystal are given. For the particular case of the Johnson–Mehl tessellations in two dimensions, 10000 independent realizations have been obtained for estimating the area, perimeter length, number of vertices, number of full neighbors, and minimal and maximal angles of the typical vertex. Also, histograms for the empirical distributions of these quantities are given. The main characteristics of the typical element are as follows [22]: the average number N of edges and vertices is 6; the average area S is λ^{-1} ; the average length L of a typical edge is $2\mu_1/\lambda$ (where μ_1 is the density of 1-interfaces); intensities I_d of d -interfaces (where d is the dimensionality) are λ for $d = 2$ and 3λ for $d = 1$.

In the background of the deficiency of closed expressions for the majority of distribution functions, the well-known distribution of the distances of the nearest neighbors in the Voronoi case [15],

$$f_j(r) = 2(\lambda\pi)^j ((j-1)!)^{-1} \exp\{-\lambda\pi r_j^2\} r_j^{2j-1}, \quad (21)$$

where j is the subsequent number of a neighbor, provides an interesting possibility to progress in describing and analyzing solid state reaction kinetics in the way of explicit account of nuclei impingements.

4.3. The explicit account of nuclei impingements

Upon acquaintance with the literature on random tessellations, one of the first (and, perhaps, the most indisputable) conclusion is that in describing solid state reaction

kinetics no simplifications of the formalism may be expected. It is understandable from the very beginning that essential computational problems cannot be avoided. The interest in the possibility to pass from the description in terms of coverings to the description in terms of tessellations is, thus, due to essential conceptual novelties, some of which are discussed below.

4.3.1. Deterministic growth versus stochastic nucleation and impingements

It follows from section 2 that the description of the unrestricted growth of both separate nuclei and ensemble of nuclei is purely deterministic. The requirements of the same form, same orientation and independence of the growth rate from the nucleus age are of this origin. In solving the problem of nucleus impingements in terms of coverings, this deterministic part is incorporated into the stochastic one in such a way that the former is practically “dissolved” in the latter, which is illustrated by the “fictitious mechanism” of Johnson and Mehl (section 3.3). This interconnection between deterministic and stochastic parts of the problem ensures a relative simplicity in obtaining the final result. But the price for this simplicity is the loss of some informative details.

In this respect, an alternative case is the simulation of the process as the growth of a single nucleus inside the typical cell of the corresponding random tessellation [11,77] (figure 6). This provides the possibility to separate the deterministic description of unrestricted growth from the stochastic description of nucleation and nucleus impingements and to take into consideration some geometrical details of impingements which are simulated in these terms as the impingements of the single nucleus with the edges of the typical cell. This change of the problem structure touches a number of conceptual points, in particular the choice of the parent dependent variable.

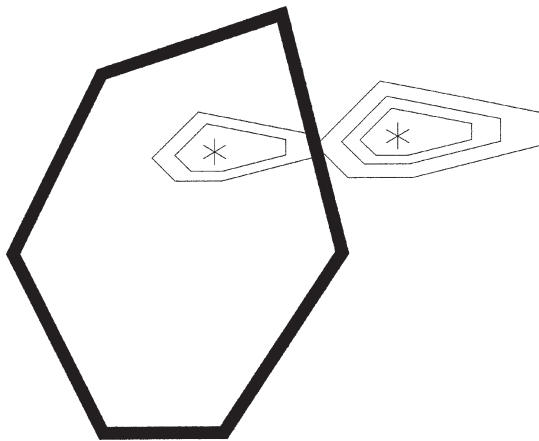


Figure 6. The nuclei impingements may be simulated as the impingements of separate nuclei with the boundary of a typical hexagon.

4.3.2. The parent dependent variable

In terms of coverings, the parent dependent variable $\alpha(t)$ has actually the meaning of area (see section 3.2), and the stochastic description of reaction kinetics is based on its interpretation as a probability. For random planar tessellations, the closed expression for the distribution function or density of area is unknown even for the relatively simple Voronoi case [20,21]. However, the exact density function is known for the distances to nearest neighbors (cf. (21)). As was noted above, this is one of the few available closed expressions relevant in the present context. From this viewpoint, and also keeping in mind the aim to give an adequate “internal definition” for the rate, it is appropriate to deal directly with the efficient boundary length. In terms of tessellations it may be estimated as a fraction of the perimeter length of a growing nucleus which falls within the interior of a typical cell [11]. (It is easy to see that for unrestricted growth, i.e., before the first impingement, this will be the total perimeter length.) In this way the role of two main variables, the degree of conversion $\alpha(t)$ and the rate $w(t)$, is exchanged: the latter becomes the parent dependent variable.

4.3.3. A second note concerning dimensionality

The conventional geometric-probabilistic approach is invariant with respect to the dimensionality [1,4]; the same is the case for the majority of results for random tessellations [21,22]. The main reasons of favoring the two-dimensional approach to describe solid state reaction kinetics are determined by conceptual rather than formal considerations [33,58]. Among them the symmetry considerations should be put at the first place: in terms of the crystal chemical structure of a sample normal and tangential directions are not equivalent with respect to the reaction front advance. Symmetry considerations cannot be referred directly to a disperse polycrystalline sample which naturally leads to the need of dealing with single crystals [40]. This is in line with the modern trends in experimental research [27–29,39,78]. Quite a number of examples may be provided that one and the same reaction may proceed on different faces of the same crystal under the same conditions in different manners, performing disparate localization forms as well as kinetic behaviour [29]. The adequate tool to this is the representation of a single crystal as a set of crystallographic planes [79]. This provides the possibility to describe a bulk process “layer-by-layer”, the events within each layer being considered separately (figure 7) [33].

In a formal respect, however, there are also some important nuances. The above closed expression for the density function (21) is one of them. Another one is connected with the correct understanding of the statement that conventional geometric-probabilistic approach is independent of the dimensionality. This independence means that this formalism is equally applicable to describe the appearance, growth and impingements of nuclei both at a surface and within a volume, provided that the applicability conditions are satisfied. But if nuclei are formed at a surface alone and then a process proceeds into the bulk, the second applicability condition will be violated and, accordingly, the simple three-dimensional description will no longer be rigorous [11]. In the next section one more sound formal argument will be mentioned in the con-

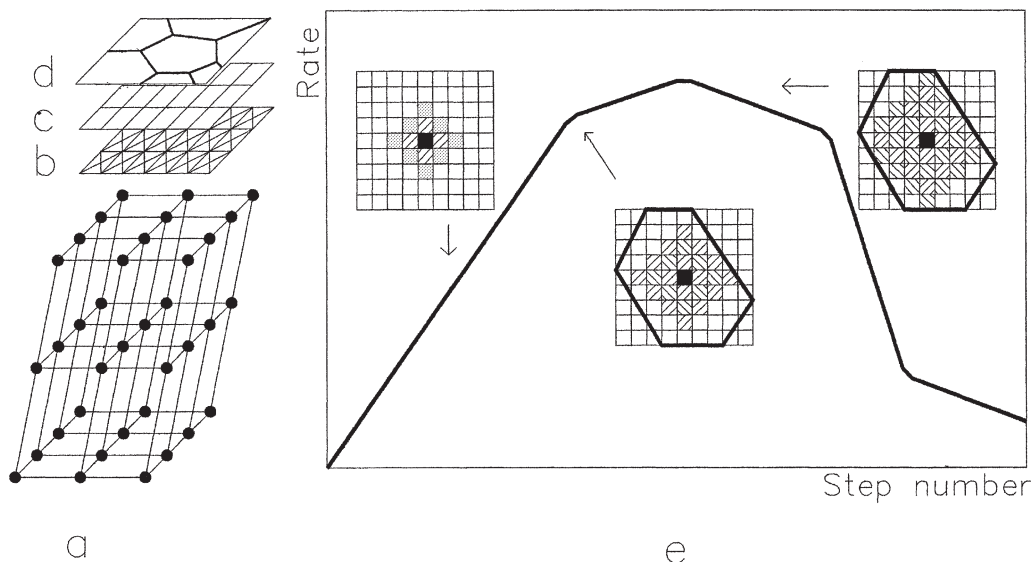


Figure 7. Genesis of the rate-time curve. A single crystal is represented as a set of crystallographic planes (a). For each plane, three tessellations are constructed: planigon tessellation (b), Wigner-Seitz tessellation (c), and random tessellation (d). In terms of the superposition of these Dirichlet tessellations, the appearance of singular points on the $w(s)$ curve may be followed step-by-step (e).

text of the interconnection of the geometry of the crystal space of a sample with the dynamics of the reaction front advance. It touches, in particular, the essential point concerning the chemical variable in the structure of the theory.

4.3.4. The chemical interpretation of the parent variable

In the structure of the conventional continuous formalism there is no chemical variable, i.e., such a variable which is capable of characterizing directly chemical changes in the system. It is implied that chemistry is represented by the coefficients of the models only. But one may notice that these coefficients multiply variables which are geometric-probabilistic in meaning and, in addition, usually include several factors of different nature. This “chemical facelessness” is one of the main roots of the discrimination issues which considerably aggravate the ambiguity of the inverse kinetic problem [11,33]. This rises the question whether an additional chemical variable should be introduced into the theory or, alternatively, a way to assign the chemical interpretation to the existing variable should be thought over (which means to interrelate the geometric-probabilistic and chemical degrees of conversion). In a formal respect, this is a question about the agreement of measures: for interpreting the existing variable some external extensional measure needs to be associated with the single-barrier elementary act [41].

In the framework of the essentially two-dimensional approach referred to a single crystal face, this may be done in terms of planigons [80]. A planigon is a convex planar polygon such that congruent planigons form a regular tessellation of the plane.

Any movement (symmetry operation) transforming one planigon into another transforms the whole tessellation into itself. Each planigon tessellation corresponds to one of the 17 two-dimensional Fedorov groups. The complete theory of planigons has been developed in the series of works of Delone and co-authors [81] and of Grünbaum and Shephard [82]. (The conclusive works are referred to here in which the preceding references may be found.) With the complete symmetry being represented in terms of planigons, it is natural to characterize the translational symmetry in terms of Wigner–Seitz cells [83] and to associate in this way the advance of the reaction front with the translational symmetry [80]. This approach is based on the fact that three relevant tessellations may be constructed for a single crystal face: planigon tessellation (figure 7(b)), Wigner–Seitz tessellation (figure 7(c)), and random tessellation (figure 7(d)). Note that from a formal viewpoint all the above three tessellations are Dirichlet tessellations (see [81], [83] and [20], respectively).

In describing the reaction front advance in terms of the superposition of Dirichlet tessellations, we face one more advantageous peculiarity of the two-dimensional approach: in two dimensions there is the possibility to use the notion of *adjacency*. (In three dimensions there is no such possibility, and there exists no complete analog of the planigon theory [84].) The use of the notion of adjacency enables one to associate the dynamics of the reaction front advance with the geometry of the crystal space of a sample: at each step s a reaction is propagated with equal probability from converted regions to all translationally equivalent adjacent regions. In essence, this means the transition to a discrete description; the step s playing the role of the discrete time [80]:

$$\nu(s) = k\nu\eta(s - 1), \quad (22)$$

where η is the number of planigons comprised by a Wigner–Seitz cell and ν is the number of edges of this cell.

Each planigon is a “rightful domain” of its center of action, i.e., the particular atom of one or another chemical nature. This domain has definite form and dimensions which are unambiguously determined by the parameters of a crystal lattice. The corresponding tables may be found in [81]. Due to this, the change of the boundary length in passing from the step s to the step $s + 1$ may be expressed in terms of the usual geometrical measure with which, however, a definite number of atoms of a definite sort is associated. In this way the routine possibility to calculate geometrical probabilities as the ratio of measures is preserved and at the same time the parent variable acquires a chemical interpretation.

4.3.5. Restricted growth: genesis of the sigmoid α - t curve

Discrimination issues may be approached from the viewpoint of the statement of the inverse kinetic problem in the broadest sense as the interrelation between kinetic behaviour and mechanism. Whatever the chemical nature of a solid state reaction is, the corresponding $\alpha(t)$ curve practically always has the sigmoid form [9]. This contradiction between the wide variety of chemical reactions, on the one hand, and one and the same fairly simple form of the kinetic curve, on the other hand, determines

an important requirement for the formalism: to “discern” the chemical variety through the universal geometrical regularities that are responsible for the sigmoid form of the $\alpha(t)$ curve. It is impossible to do this in terms of coverings because the genesis of the curve with time cannot be followed step-by-step. The approach in terms of tessellations seems to be a more promising one in this respect due to the capability of taking the geometrical details of impingements into account.

The deterministic description of unrestricted growth in terms of planigons has one essential advantage from the standpoint of the stochastic aspects under discussion: the applicability conditions (section 3.4) are satisfied automatically. All nuclei have the same form corresponding to the crystal chemical structure of a crystal face; all of them are oriented in the same manner since Wigner–Seitz cells have the same orientation; the growth rate is independent of the nucleus “age” (cf. (22)). As a result, the applicability conditions look no longer as something artificial and incompatible with reality.

In these terms, the nucleus impingements are simulated as the impingements of a single growing nucleus with the edges and vertices of the typical cell of a random tessellation. The unrestricted nucleus growth (before the first impingement) is linear (cf. (22)). After the first impingement, the nucleus growth is restricted with one straight line. It was shown in [85] that in this case linearity is preserved but the slope is changed. As a result, a singular point appears on the $w(s)$ and $\alpha(s)$ curves. Similarly, each subsequent impingement of a growing nucleus with an edge or a vertex of the typical cell results in a new singular point. This enables one to follow the way in which the $w(s)$ curve is formed (figure 7(e)). Corresponding to this is the sigmoid $\alpha(s)$ curve.

The Voronoi case is simpler since a nucleus is growing within the typical cell invariable with time. In the general Johnson–Mehl case, the typical cell is tightened all the time due to the appearance of new nuclei. In both cases, as many as 11 singular points may be pointed out on the $w(s)$ curve corresponding to the impingements with 6 edges and 5 vertices of the typical cell. When the 6th, most distant, vertex is reached a process is completed and the rate is vanished.

This geometrical picture may be described in the general case by 12 difference equations corresponding to 12 line segments of $w(s)$ curve. For the reasons discussed in [85], it is convenient to write them in terms of $\mathbf{u}_s = (w(s), w(s+1))$ for each line segment:

$$\mathbf{u}_\sigma^{(j)} = A^\sigma \mathbf{u}_0^{(j)}, \quad (23)$$

where the consecutive number j of a line segment varies from 1 to 12 and

$$A = \begin{bmatrix} 0 & 1 \\ -1 & 2 \end{bmatrix}. \quad (24)$$

The step number σ is counted off the point next to the corresponding singular point $s_d^{(j-1)}$: $\sigma = s_d^{(j)} - s_d^{(j-1)} + 1$, i.e., $\sigma = 0$ for the first point of each line segment. The value $j = 1$ corresponds to unrestricted growth. In this case, $d^{(1)}$ in $\mathbf{u}_0^{(j)}$ is equal to the number of planigon edges, and $w^{(1)}(0) = 0$.

This description of the kinetic curve in terms of the superposition of Dirichlet tessellations of three types (planigon tessellations, Wigner–Seitz tessellations, and random tessellations) makes it possible to represent the rate of a solid-phase chemical reaction as a measure of the random marked-point process. This “internal definition” of the rate enables one to take the chemical individuality of a solid reagent into account and thus to make a step from the approximation which is formal in chemical respect towards meaningful simulations [40,73,86].

5. Conclusions: the interplay between the languages of coverings and tessellations

Every “rationally thinking person” understands that coincidences of dates and events mean nothing in the majority of cases. But, nevertheless, in facing such coincidences a doubt is inherent to the nature of a human being whether this is actually no more than a simple occasion. And sometimes unwitting ratiocinations on this subject make essential logical interconnections and parallels explicit.

Chronologically, the very first solution to the problem of nuclei impingements was given in 1937 [1]. And now it is clear that this solution is the most rigorous in mathematical respect. Practically simultaneously, the first book [68] on integral geometry appeared. And in the same year, 1937, it was proved in a purely topological manner that an average typical cell of a plane random tessellation has 6 edges [76]. Treating critically, as is appropriate to a “rationally thinking person”, the occasional coincidence of dates and events, the present author failed to escape the involuntary ratiocinations concerning the fact that these three events, completely independent at that time, have interlaced later in the context of heterogeneous chemical kinetics in connection with attempts to resolve the accumulated discrimination issues. This inspired to a degree the above considerations that lead to the following conclusions.

- (1) Starting from the works [1,2], two lines may be followed: (i) the development of the geometric-probabilistic approach to first-order phase transitions and heterogeneous chemical kinetics, and (ii) the development of the theory of random tessellations in the framework of the theory of geometrical probabilities and, later, stochastic geometry.
- (2) The conventional geometric-probabilistic formalism has played one of the key roles in the formation of contemporary heterogeneous chemical kinetics and remains one of the main theoretical grounds of this branch of science. This is determined by a number of reasons, the main one of which is that solid state reactions are always conjugated with first-order phase transitions, and the geometric-probabilistic approach is capable of providing the *rigorous solution* to the relevant direct problem. The absence of the expressed positive dynamics in resolving the accumulated issues connected with the inverse kinetic problem makes one think in essentially new ways. But however radical the changes may be, they will necessarily remain within the framework of the ideas of nucleation and growth.

- (3) In parallel with the development and employment of the conventional geometric-probabilistic approach in heterogeneous kinetics, the theory of geometrical probabilities itself has undergone important changes. The reconsideration of its grounds had led to the appearance of integral geometry. Later, the combination of ideas and methods of integral geometry with those of the theory of random processes gave birth to stochastic geometry. The theory of random tessellations, which has one of its roots in the work [2], has contributed considerably to the emergence of stochastic geometry and nowadays it is actively developed in the framework of this branch of mathematics.
- (4) The results obtained in the theory of random tessellations, especially during the recent 10–15 years, are promising from the standpoint of the discrimination issues of heterogeneous kinetics. The restatement of the “nucleation–growth–impingement” problem in terms of tessellations makes it possible to follow the genesis of the sigmoid α - t curve. In this framework, the description of the unrestricted growth in terms of planigons and Wigner–Seitz cells ensures the fulfillment of the main applicability conditions and enables one to attach a chemical meaning to the parent dependent variable preserving at the same time its properties of a geometrical measure. The latter is important with respect to overcoming the “chemical facelessness” of the existing formalism.
- (5) The two approaches, in terms of coverings and in terms of tessellations, are mutually complement rather than they exclude each other. At first steps, the use of the ideas and methods of geometrical probabilities made it possible to describe general universal features of solid state reactions avoiding the consideration of their particular features. The further progress is connected with the chemical differentiation on the basis of a keener insight into the mechanism. For this the language of tessellations seems to be more adapted. In this connection, the work [86] attracts attention as a bridge between the two approaches. It is devoted to limit theorems for the time of completion of Johnson–Mehl tessellations and, according to the words of its author, is “a continuation of the pioneering work [1]”. In solving the problems of heterogeneous chemical kinetics, the potential of the geometric-probabilistic approach is far from been exhausted, and a strong development may be expected in the way of using the language of coverings as a “limit language” with respect to the language of tessellations.

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