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A geometric–probabilistic approach to heterogeneous chemical kinetics with respect to the IKP ambiguity

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Abstract

The widely used geometric–probabilistic formalism, which is rigorous with respect to nuclei impingement simulation, is shown to be essentially ambiguous for the inverse kinetic problem (IKP) solution. This holds true for all particular models derived within its framework. The nature of this ambiguity is made explicit. A partial solution of this is suggested, by a more detailed interpretation of the scheme through its restatement in mathematical terms of tessellations.

Keywords: Geometric–probabilistic approach; Inverse kinetic problem; Kinetics; Model; Tessellation

1. Introduction

Broadly speaking, the ultimate aim of the inverse kinetic problem (IKP) is to understand and, therefore, to explain observed macroscopic regularities on a microscopic scale. By its nature IKP is always ambiguous. But when solid-phase reactions are concerned, one more problem, in addition to the numerous objective causes of IKP ambiguity, is that different authors have different approaches to macro–micro relations. Not infrequently, this gives rise to various misunderstandings, disagreements with respect to the estimation of formality, etc. Two main related points here seem to be the problem of diffusion and the problem of chemical individuality.

When real disperse or porous systems are studied, one is normally considering diffusion-controlled solid-state processes, and accordingly diffusion mechanisms are

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implied. In this case a solid reagent is represented not as a chemical individual but as a "sample" characterized by its prehistory (rather than by chemical structure and composition) and oversimplified in the course of formalization. This determines the meaning attached to the word "micro" [1]. But if we want to talk about the chemical regularities of solid-phase reactions alone, diffusion must be eliminated (excluding, of course, single-barrier activated diffusion). Now the intrinsic logic of the problem becomes relevant, along with considerations concerning the derivation of the mathematical models with which the abstract kinetic behaviour is interpreted. This logic determines, in particular, the choice of a single crystal face to play the role of the chemical individual [2] and thus the meaning of the term "micro". (See also ref. 2 for a discussion on the definition of meaningful simulation versus formal approximation.)

And in this context, the geometric–probabilistic formalism, derived from the classical works of Johanson and Mehl [3], Kolmogorov [4], and Avrami [5], occupies, in the author's opinion, a more important place in the modern logical framework of heterogeneous chemical kinetics than is commonly believed.

2. Geometric–probabilistic formalism as a scheme

It is noteworthy that modern geometric–probabilistic formalism, now completely separate from chemistry, is partly of chemical origin. In examining the thermal decomposition of solids it was noted that whatever the chemical nature of a reaction, the corresponding kinetic $\alpha(t)$ curve is practically always sigmoid, i.e. the only type of kinetic curve corresponds to various types of chemical interactions. In addition, $\alpha(t)$ curves obtained for different reactions may be quite similar, whereas $\alpha(t)$ curves obtained for similar reactions may be quite different [6]. This has led to the idea that some universal geometrical regularities are superimposed on the chemical regularities and mask them, thus determining the shape and similarity of the $\alpha(t)$ curves.

In this way the concepts of nuclei formation and growth, borrowed from biology by MacDonald and Hinshelwood [7], have become the basic concepts of heterogeneous kinetics. The central problem in formalizing these concepts is connected with an accounting of the nuclei impingements. Its solution in refs. 3–5 gave birth to the discussed geometric–probabilistic formalism. It should be noted that refs. 3–5 themselves are devoted to phase transitions (crystallization of steel melt) and assume no chemical transformations.

This mathematical formalism, which has been widely discussed in the literature from various viewpoints [8–13], describes the origination and evolution of the boundary between two phases in terms of the origin, growth and impingement of nuclei, without discussing the causes and nature of the corresponding nucleation and growth processes. By using the word "scheme" we will emphasize that this formalism is free from both chemistry and physics, admitting various physical and chemical interpretations.

In this context, what is the interrelation between this scheme and the numerous particular models now in use in heterogeneous kinetics?

It must be noted that practically all mathematical models are represented in terms of the degree of conversion α or the rate $\dot{\alpha}$, or both. In the framework of the geometric–probabilistic approach, these main variables acquire a definite meaning (see next section). And it is rarely recognized that in describing particular systems by means of particular models in terms of α or $\dot{\alpha}$, one either makes use of their geometric–probabilistic interpretation or is unconsciously influenced by this interpretation. (This is illustrated in part in section 4 below.)

In this connection the following is worth emphasizing. The equation of a homogeneous elementary monomolecular reaction may be written as $\dot{\alpha} = \kappa(1 - \alpha)$. But it must be stressed that in this case α means the extent of reaction (expressible in terms of concentrations) rather than the geometric–probabilistic degree of conversion. In particular, the above term $(1 - \alpha)$ and the co-factor $(1 - \alpha)$ relating conventional and extended degrees of conversion (see section 4) have completely different meanings. Of course, in a definite sense the degree of conversion is an analogue of the extent of reaction in the case of more complicated heterogeneous systems. But it is possible to discuss the interrelation of these two quantities, avoiding their erroneous identification.

Therefore, if the main variable α has the geometric–probabilistic meaning, the discussed scheme sets four requirements to particular models which were formulated explicitly in ref. 3, the impossibility of relaxing them being demonstrated rigorously in ref. 12. Within these requirements the discussed scheme admits various interpretations, and particular models now in use do not cover all possibilities.

(i) The scheme implies that the dimension of each growing nucleus is small in comparison with the total reaction space.

(ii) The scheme admits various nucleation laws, requiring only that they must be according to Poisson.

(iii) The scheme admits various growth laws, requiring only that the law applied must be one and the same for all growing nuclei at a given instant of time. (Without this, the notion of a common rate for the whole system cannot be defined.)

(iv) The scheme admits any convex form of nucleus, requiring only that this form must be the same for all nuclei and all nuclei must be oriented in the same manner. The scheme is also invariant with respect to the dimensionality of a nucleus, and integer dimensionality is assumed, i.e. a nucleus may be either two-dimensional or three dimensional. When applying the fractal approach [14], this gives rise to additional essential controversy, namely whether the fractional exponent of a particular model derived from experimental data is the result of the fractal nature of the macroscopic system, or of the approximate calculations, or both.

When real, complicated systems are concerned, it is extremely hard or even impossible to meet simultaneously the above requirements. As a result, considerable effort is directed towards the set of problems succinctly characterized as "diagnostic limits" [15, 16], and the use of the epithets "empirical" and "effective" becomes even more frequent.

One faces the problems of diagnostic limits in the discrimination of particular models. And, of course, far from all of them are connected with the discussed

geometric–probabilistic scheme. A priori, the numerous failures in the discrimination of particular models may be attributed, in addition to the general philosophical misconception of discrimination procedures [17], to the essentially ambiguous interrelation between the mechanism and the kinetic behaviour [11, 18], to the misinterpretation of the scheme [12], etc. In this context the question arises: does the geometric–probabilistic scheme itself make a contribution to the IKP ambiguity? And, if so, what is the nature of this ambiguity and in what way may it be overcome?

3. Ambiguity on the phase plane $\dot{\alpha}-\alpha$

The inherent nature of the ambiguity of the geometric–probabilistic scheme in respect to the IKP solution becomes explicit when the problem is considered on the phase plane, rate ($\dot{\alpha}$)–degree of conversion (α), and rests on the fact that essentially different sets of growing nuclei may correspond to the same point (α, $\dot{\alpha}$) on the phase plane. This may be shown in the following way.

In the framework of the geometric–probabilistic scheme, the set Q of growing and impinging nuclei is characterized by two quantities, the nucleation law $L_n(t)$ and the growth law $L_g(\tau, t)$, depending not only on the current time t but also on the instant of nucleus appearance τ:

$$L_g(\tau, t) = \gamma \left(\int_\tau^t v(\xi)\, d\xi \right)^n$$

where γ is the form factor (for spherical nuclei, $\gamma = \pi$), $v(t)$ is the linear rate of nucleus growth, ξ is the integration variable, and n is the dimension [12]. Starting from the advantage that the results obtained within the geometric–probabilistic scheme are independent of the dimension n [3, 12], we will consider for simplicity the formation, growth and impingement of nuclei on a plane ($n = 2$), all conclusions also being true for $n = 3$.

L_n and L_g are two independent quantities. Accordingly, a description of the given set of nuclei by only the function $\alpha(t)$ is certainly ambiguous. It is not so obvious whether the pair of quantities (α, $\dot{\alpha}$), determining at fixed t, a point on the phase plane, may provide an unambiguous description for our set Q. From the formal viewpoint, the unambiguity requires that no other set of nuclei Q' may correspond to the same (α, $\dot{\alpha}$) point and, consequently, the system

$$\begin{cases} \alpha = \alpha' & (1a) \\ \dot{\alpha} = \dot{\alpha}' & (1b) \end{cases}$$

is incompatible (superscript ′ refers to the set Q').

We have to examine the compatibility of the system (1). To avoid complications associated with nuclei impingements, it is expedient to use the notion of an extended degree of conversion α_{ext}, introduced in ref. 4, and to pass without loss of generality to sets of separate (not impinging) nuclei. The term α_{ext} is calculated under two assumptiions: (i) nuclei grow "ignoring each other"; and (ii) nuclei may

appear not only on the free surface but also on the surface occupied by the new phase. Note that the expression for the degree of conversion

$$\alpha(t) = 1 - \exp\left(- \int_0^t L_n(\tau) L_g(\tau, t)\, d\tau \right) \tag{2}$$

may be represented as $\alpha(t) = 1 - e^{-\alpha_{ext}(t)}$. This means that the equality (1a) may be replaced by the corresponding equality for the extended magnitudes. Analogous replacement is possible for the rate

$$\dot{\alpha}(t) = v(t) \times 2\gamma \int_0^t \left(L_n(\tau) \int_0^t v(\xi)\, d\xi \right) d\tau \times \exp\left(- \int_0^t L_n(\tau) L_g(\tau, t)\, d\tau \right) \tag{3}$$

The second co-factor in this expression is the extended (total) length of the boundary of all nuclei (l_{ext}); the exponential co-factor may be written with allowance for Eq. (2) as $(1 - \alpha)$, i.e.

$$\dot{\alpha}(t) = v(t) l_{ext}(t)(1 - \alpha) = \dot{\alpha}_{ext}(t)(1 - \alpha) \tag{4}$$

Taking into account Eq. (1a), we may pass finally from the system (1) for actual quantities to the system

$$\begin{cases} \alpha_{ext} = \alpha'_{ext} \\ \dot{\alpha}_{ext} = \dot{\alpha}'_{ext} \end{cases} \tag{5}$$

for the extended quantities and to an examination of the compatibility of this system.

In terms of the geometric–probabilistic scheme the main variable α indicates the probability that an arbitrary point in the original volume (on the original surface) will, at the instant t, be taken up by the growing nucleus of the new phase appearing at some earlier instant τ. In our two dimensional case this is the ratio of the total area occupied by new phase to the area of original surface. For the unit original surface, this is simply the total area of all (separate) nuclei: $\alpha = \gamma r_1^2 + \cdots + \gamma r_n^2$, where r_i is the radius of the ith nucleus. The rate is proportional (according to Eq. (3)) to the total boundary length: $\dot{\alpha} = \gamma v r_1 + \cdots + \gamma v r_n$. Thus, the possibility to replace our set Q consisting of n nuclei with radii $r_1, \ldots, r_n$ by a single nucleus with radius x is determined by the compatibility of the system

$$\begin{cases} x = r_1 + r_2 + \cdots + r_n \\ x^2 = r_1^2 + r_2^2 + \cdots + r_n^2 \end{cases} \tag{6}$$

(reduced coefficients γ and v are omitted). This system is incompatible at any x, and the replacement is impossible.

But even in the case of two nuclei (with radii x and y) the situation is changed. The system

$$\begin{cases} x + y = r_1 + \cdots + r_n & \text{(7a)} \\ x^2 + y^2 = r_1^2 + \cdots + r_n^2 & \text{(7b)} \end{cases}$$

is compatible at some values of x and y. And this represents the appearance of ambiguity.

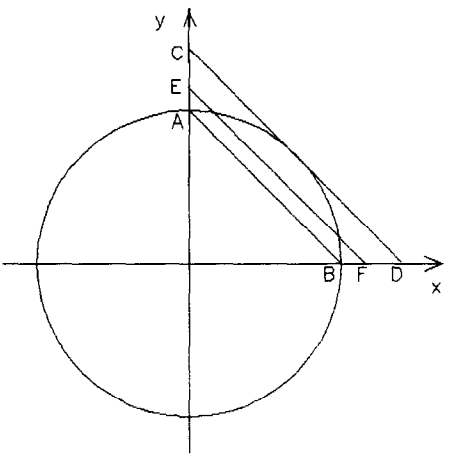

Fig. 1. Graphical representations of system of Eq. (5).

The conditions of the compatibility may be discerned from Fig. 1. Equation (7b) determines the circle with radius $\rho = \sqrt{r_1^2 + \cdots + r_n^2}$ on the (x, y) plane, whereas Eq. (7a) corresponds to the line EF cutting off the equal segments $\mathrm{OE} = \mathrm{OF} = l = r_1 + \cdots + r_n$ on the axis. Because the inequality $r_1 + \cdots + r_n > \sqrt{r_1^2 + \cdots + r_n^2}$, i.e. $l > \rho$, is true for any positive r_i, the line EF is always situated beyond the chord AB ($\mathrm{OA} = \mathrm{OB} = \rho$). Our system is compatible if the line EF crosses the circle. So, the corresponding values of x and y must fit the region between the chord AB and the tangent CD. Denoting the distance of EF from the origin by d, one gets for the lower boundary $d > \mathrm{OC} = \rho/\sqrt{2}$ and for the upper boundary $d < \rho$. Finally, taking into account that $d = l/\sqrt{2}$, one gets $\rho < l < \sqrt{2}\rho$.

In the case of the set Q' consisting of three nuclei, the final inequality will be the same, ρ designating the radius of a sphere in the (x, y, z) coordinates and l designating the segments intersecting the axis by the corresponding plane. Whatever the number of nuclei in the set Q' (more than one), the obtained conditions of compatibility may be represented in terms of r_i as

$$\sqrt{r_1^2 + \cdots + r_n^2} \leq r_1 + \cdots + r_n \leq \sqrt{2}\sqrt{r_1^2 + \cdots + r_n^2} \tag{8}$$

and, accordingly, in terms of the extended quantities in the form of inequality

$$\frac{\sqrt{\alpha_{\mathrm{ext}}}}{\sqrt{\gamma}} \leq \frac{\dot{\alpha}_{\mathrm{ext}}}{2\gamma v} \leq \frac{\sqrt{2}\sqrt{\alpha_{\mathrm{ext}}}}{\sqrt{\gamma}} \tag{9}$$

Taking into account the above-mentioned interpretation of extended quantities and comparing this inequality with the well-known isoperimetric inequality [19], we conclude that inequality (9) is satisfied. Reverting finally to the actual variables α and $\dot{\alpha}$ we get the inequality

$$\sqrt{4\gamma\alpha(1-\alpha)} \leq \frac{\dot{\alpha}}{v} \leq \sqrt{8\gamma\alpha(1-\alpha)} \tag{10}$$

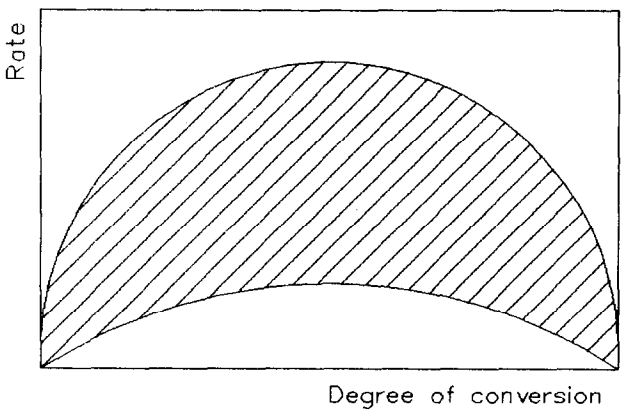

Fig. 2. Schematic representation of the ambiguity region on the phase plane.

which enables one to sketch (up to v and γ) the region of ambiguity on the phase plane (Fig. 2).

Thus, we arrive at the conclusion that essentially different sets of growing and impinging nuclei may correspond to the same (α, $\dot{\alpha}$) point of the phase plane, and this means that the discussed geometric–probabilistic scheme is ambiguous with respect to the IKP solution. In this context some interrelations between the problems concerning the interpretation and discrimination of particular models, both conventional and generalized, become more clear.

4. Geometric–probabilistic interpretation of particular models

Each particular model results from the formalization of more or less detailed concepts concerning the reaction mechanism. Some of these details are lost during model derivation and simplification. On being applied for discrimination, models are compared in a formal rather than a conceptual respect because of the purely statistical nature of the discrimination procedure. The discussed ambiguity introduces additional material complications into the controversial question [18] as to which way the results of the discrimination may be interpreted in a conceptual respect. We will concentrate on the peculiarities of the geometric–probabilistic interpretation of conventional and generalized models to show that limitations in this interpretation represent one of the causes of the discussed ambiguity.

4.1. Conventional models

It is worth emphasizing again the geometric–probabilistic interpretation of the main variables α and $\dot{\alpha}$. 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 alone. 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: this is obviously insufficient for non-linear models and has two related manifestations.

(i) Quite different original concepts concerning the reaction mechanism may lead to the same equation in terms of α. For example, the well-known equation

$$\ln(\alpha/(1-\alpha)) = \kappa t \tag{11}$$

may be obtained by assuming [20] 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 ref. 20.

(ii) When considered in total from some common viewpoint, models may acquire an interpretation different from the original one which is accompanied by a considerable reduction of the variation in their conceptual meaning. In terms of functional analysis, this was examined in ref. 21. We are interested in the geometric–probabilistic interpretation of the models listed in Table 1, independent of the manner of their derivation (diffusive models are not considered).

Note that the main co-factors of these models have the following interpretation in the framework of the geometric–probabilistic scheme: α is the degree of conversion, the fraction of the original unit surface occupied by new phase; $(1-\alpha)$ is the fraction of the free surface. However, another interpretation of this quantity is no less important, i.e. it determines the interconnection between actual and extended magnitudes $(d\alpha/d\alpha_{ext} = 1-\alpha)$ where $-\ln(1-\alpha) \equiv \alpha_{ext}$ is the extended degree of conversion.

Table 1
Mathematical models widely used in heterogeneous chemical kinetics

kt	No.	$\dot{\alpha}$	
Acceleration			
$2\alpha^{1/2}$	1	$k\alpha^{1/2}$	Power law
$3/2\alpha^{1/3}$	2	$k\alpha^{2/3}$	
$4/3\alpha^{1/4}$	3	$k\alpha^{3/4}$	
$\ln\alpha$	4	$k\alpha$	Exponential law
Sigmoid			
$2(-\ln(1-\alpha))^{1/2}$	5	$k(1-\alpha)(-\ln(1-\alpha))^{1/2}$	KEKAM
$3(-\ln(1-\alpha))^{1/3}$	6	$k(1-\alpha)(-\ln(1-\alpha))^{2/3}$	
$4(-\ln(1-\alpha))^{1/4}$	7	$k(1-\alpha)(-\ln(1-\alpha))^{3/4}$	
$\ln(\alpha/(1-\alpha))$	8	$k(1-\alpha)\alpha$	Prout–Tompkins
Retardation			
$2(1-(1-\alpha)^{1/2})$	9	$k(1-\alpha)^{1/2}$	Tightened area volume
$3(1-(1-\alpha)^{1/3})$	10	$k(1-\alpha)^{2/3}$	
$-\ln(1-\alpha)$	11	$k(1-\alpha)$	First order
$(1-\alpha)^{-1}$	12	$k(1-\alpha)^2$	Second order
$(1-\alpha)^{-2}$	13	$k(1-\alpha)^3$	Third order

Note that Table 1 is symmetrical about its centre line: replacing α by $(1-\alpha)$ in Eq. Nos. (1), (2) and (4) for $\dot{\alpha}$, one gets Eq. Nos. (9), (10), (11). Thus, it is reasonable to start with Eqs. (5)–(7) (the abbreviation KEKAM in the table represents the equations of Kolmogorov, Erofeev, Kazeev, Avrami, and Mampel). Taking the definitions of the co-factors mentioned above, they may be interpreted as follows. The co-factor $(-\ln(1-\alpha))$ is the extended degree of conversion; the corresponding exponent gives this quantity the meaning of the extended boundary length; when multiplied by $(1-\alpha)$ this extended magnitude is converted into an actual one. In other words, the rate is proportional to the boundary length with coefficient κ, and no further interpretation is attached to these equations within the geometric–probabilistic scheme.

The same simple interpretation may be discerned for Eq. Nos. (1)–(3) (Table 1) in the limit of small α, when there are no impingements. Equation No. (8) may be treated as the less strong limit $(-\ln(1-\alpha)) \approx \alpha$. The exponential law (Eq. No. (4)) in this context is the particular case of Eq. No. (8), by mathematical form as well as by the logic of derivation. Concerning the equations of reaction-order type (Eq. Nos. (11)–(13)), taken from homogeneous kinetics, the corresponding exponent deprives the co-factor $(1-\alpha)$ of the meaning of length. This is to be expected as a result of the difference between concentration and α stressed above. So, the use of the notion of reaction order is hardly substantiated within the geometric–probabilistic interpretation.

4.2. Generalized models

One of the most frequently used generalized models is the Šesták–Berggren model [22]

$$\dot{\alpha} = \kappa\alpha^{l}(1-\alpha)^{m}[-\ln(1-\alpha)]^{n} \tag{12}$$

which is the product of all three co-factors mentioned above. Accordingly, from formal viewpoint, many models used in heterogeneous chemical kinetics are particular cases of Eq. (12), its approximation ability being considerably greater due to its larger number of variables. But here we face again the "contradiction" between formalism and interpretation.

(i) In the framework of the geometric–probabilistic scheme the exponents l and n must give the meaning of boundary length to the co-factors α^{l} and α^{m}_{ext}.

(ii) This length occurs twice in Eq. (12) (calculated with and without accounting for nuclei impingements), but finally it may be included only once.

(iii) Any choice of $m \neq 1$ negates the fundamental assumption of the equiprobability of nuclei formation [12].

Thus, being derived from experimental data, model parameters will hardly fit automatically the specified "logical interval". But if the appropriate restrictions are imposed on the parameters a priori, the model is no longer a generalized one.

Comparing these considerations with the successful use of the model in thermal analysis kinetics [15], we face again the need to pass the limits of geometric–probabilistic interpretation.

One more example of the contradiction between formalism and interpretation will be given. According to ref. 23 the KEKAM equation may be represented as the linear combination of three different models, one of which is of diffusive type. Because of this, it is considered as the generalized model, being also suitable for describing experimental data in diffusive regimes. But in a diffusive regime the growth rate is not the same for all nuclei [12], which is in contradiction with the derivation and substantiation of the equation in the framework of the geometric–probabilistic approach.

Therefore, in addition to being ambiguous in respect to the IKP solution, the geometric–probabilistic scheme does not seem to be sufficiently adapted to take into account the wide variety of original concepts concerning the mechanism of heterogeneous chemical reactions. Consequently, with the allowance for (i) the indubitable advantage of the scheme as being the rigorous formalization for the important concepts of nuclei appearance, growth and impingement, and (ii) the impossibility of avoiding the ambiguity connected with the solution of the first kind of integral equations (like Eq. (2)), one has to think of a way of developing the scheme with respect to a more subtle interpretation.

5. Geometric–probabilistic scheme in terms of coverings and in terms of tessellations

Thus, we shall attempt a (partial) overcoming of the ambiguity of the geometric–probabilistic scheme by an amplification of its "interpretative ability". The appropriate step is prompted by Eq. (4). One of two ambiguity conditions, the equality (1b), is satisfied under various combinations of v and l; l has a purely geometrical meaning, whereas v may be connected with the chemistry of a process (more concretely, with the single-barrier process) [24]. This would enable one to use chemical considerations for solving the discussed problem. In this connection, it is essential that the geometric–probabilistic scheme, represented in mathematical terms of coverings, may be restated without loss of generality in terms of tessellations. Changing nothing in the formalism itself, this makes it possible to overcome the limits of conventional interpretation.

The following describes how the geometric–probabilistic scheme can be represented in mathematical terms of coverings. Imagine that one throws, at random, circles of various (and small enough) radii on the unit plane. Some of them may be partly or completely covered by others, and the totality of all the circles forms a covering of our unit plane (Fig. 3a). We are interested in the part of the plane covered, α. The contribution σ_1 of the first thrown circle to the covering is equal to its area: $\sigma_1 = s_1$. According to general probability theory, the randomness of the throwings means that the contribution of the second circle σ_2 is proportional to the area of this circle s_2 and to the fraction of free (at this stage) surface $q_1 = 1 - s_1$

$$\sigma_2 = s_2 q_1 = s_2(1 - s_1) \tag{13}$$

Before the third throwing, the free area is equal to

$$q_2 = 1 - \sigma_1 - \sigma_2 = (1 - s_1)(1 - s_2) \tag{14}$$

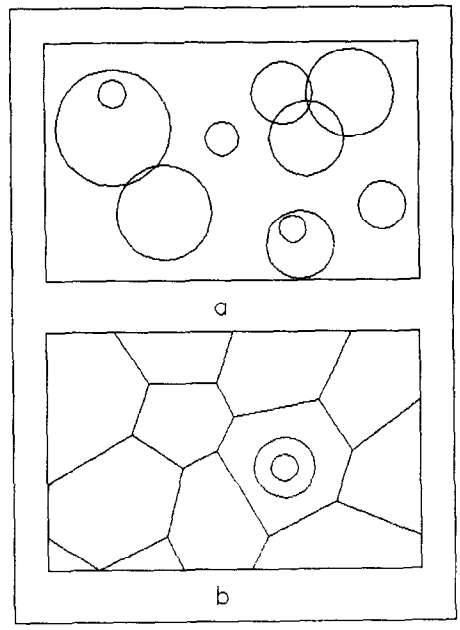

Fig. 3. Covering (a) and tessellation (b) of a unit plane.

and, accordingly, the contribution of the third circle to the covering is

$$\sigma_3 = s_3 q_2 = s_3(1 - s_1)(1 - s_2) \tag{15}$$

This is sufficient to notice the general regularity

$$q_n = \prod_{i=1}^{n} (1 - s_i) \tag{16}$$

and to calculate

$$\alpha = 1 - q_n = 1 - \prod_{i=1}^{n} (1 - s_i) \tag{17}$$

By taking the logarithm with the following expansion into the series, one gets

$$\ln(1 - \alpha) = \sum \ln(1 - s_i) \cong -\sum s_i \tag{18}$$

and thus, taking into account the aforementioned interpretation of extended quantities

$$\ln(1 - \alpha) = -\alpha_{\text{ext}} \tag{19}$$

and

$$\alpha = 1 - e^{-\alpha_{\text{ext}}} \tag{20}$$

It is worth emphasizing that the notion of rate is not used in these calculations. This enables one to separate the geometric–probabilistic formalism from its interpretation in terms of nuclei formation and growth, and to make explicit that the exponential form of the interrelation between actual and extended degree of conversion is the attribute of the formalism alone. In this or another form, the presented logic and calculations may be discerned in each of refs. 3, 4 and 5, which just means that the problem is considered in terms of coverings and that Eq. (2) may be treated in this context as the interpretation of Eq. (20) in terms of nuclei formation and growth, provided that the four aforementioned requirements are satisfied.

In our context, the central peculiarity of the formalism of coverings is that nuclei impingements are taken into account at the very last stage and in a purely probabilistic manner, without discussing the geometric details of these impingements. This being a considerable advantage from the viewpoint of the direct problem, there is a partial loss of information from the viewpoint of the inverse problem. This information will be used for a more subtle interpretation of the geometric–probabilistic scheme that determines its restatement in terms of tessellations.

Figure 3a corresponds to the well-known convenient model assumption [3] that a nucleus may grow through another one or even completely inside another one, a detailed combinatorial treatment of this being given in ref. 5. Now reverting to reality, the impingement of two nuclei stops their growth in the given direction without stopping growth in all other directions. Ultimately one will arrive at the picture sketched in Fig. 3b. Each cell of this picture is the "rightful domain" of a nucleus: it will be completely occupied by this nucleus when the process is completed. From the viewpoint of stochastic geometry, we are dealing with a random mosaic whose averaged cell is always characterized by a hexagon [25]. With time, new nuclei appear along with the growth of old nuclei. As a result the "rightful domain" of each nucleus is reduced, and the average hexagon cell decreases with time. In this way the above habitual picture is placed by another formally equivalent picture: a single nucleus grows inside the ever-decreasing averaged hexagon cell (the central part of Fig. 3b); the complicated picture of nuclei impingements is represented statistically as the impingements with the cell edges (see also ref. 24). This model representation has an obvious shortcoming: using it one would have more difficulties in representing α in terms of L_n and L_g. But the result is known, and this enables one to make use of some advantages of the suggested restatement with respect to the interpretation of the discussed geometric–probabilistic scheme. At present, three such advantages will be considered.

The process of nuclei formation acquires a spatial representation. This makes the scheme more homogeneous in comparison with conventional formalism, in the framework of which the nucleation process is treated as a purely temporal one, whereas nuclei growth proceeds in both time and space.

The main variables α and $\dot{\alpha}$ have a more detailed geometrical interpretation. The degree of conversion α is the fraction of the averaged hexagon cell occupied at the given instant of time by the growing nucleus. The rate $\dot{\alpha}$ is proportional to the nucleus boundary length, allowing for its impingements with the edges of the decreasing cell.

Each impingement of a nucleus with a cell edge, as well as each "filling" of a cell angle, results in a singular point on the $\alpha-t$ curve; as many as 11 such points may be indicated in the general case. This provides one with essentially new possibilities in analysing and classifying experimental curves. (More detailed discussion will be given elsewhere.)

The main advantage of the restatement is the wider possibility for interpreting the scheme in terms of chemistry, for example the use of planigons [27] (another variety of Dirichlet domains [26]) for representing the chemical individuality of a solid reagent. In ref. 24, the simultaneous use of planigons and random mosaics made it possible to define the rate of a heterogeneous chemical reaction as a measure of the random marked-point process. With this in mind, the further development of the scheme is connected with the use of planigons for taking chemical considerations into account.

6. Conclusions

Following the idea of separating, when possible, simultaneous processes [2], we have to agree that the geometric–probabilistic approach under discussion plays, in a conceptual respect, an important role in the logic of heterogeneous kinetics. In the present paper, this approach is shown to be essentially ambiguous with respect to the IKP solution and the nature of this ambiguity is made explicit. This means that even having created the strictly isothermal conditions, having eliminated diffusion, dealing with a single crystal alone (thus avoiding problems of polydispersity and polycrystallinity), and having satisfied, in addition, the four conditions mentioned above, one still does not completely eliminate the IKP ambiguity. This is obvious: the scheme admits various interpretations and therefore one has no grounds to expect unambiguity.

Accordingly, it is logical to attempt to progress by overcoming this unambiguity through the proper chemical (or physical) interpretation of the scheme. It is impossible and unnecessary to "struggle" against the geometrical aspect of the problem. One has to remember that geometrical regularities only mask the chemical regularities. However, the former are determined by the latter. Therefore, the aim is to bring chemical regularities into action. Among other things, "proper" means that a solid reagent must be represented as a chemical individual [24]. The scope of the present paper is restricted to showing that the scheme admits such an interpretation and may be adapted to it in terms of random mosaics.

The main conclusions concerning the geometric–probabilistic scheme under discussion may be summarized as follows.

1. The discussed geometric–probabilistic approach results from the formalization of the concepts of nuclei formation, growth and impingements. In its framework, the main variables α and $\dot{\alpha}$ have geometrical rather than chemical meanings.

2. This formalization is rigorous with respect to the direct problem, provided that the four following conditions are satisfied: (i) the area of the original phase must be unlimited; (ii) the nuclei formation must be according to Poisson; (iii) the

form and orientation of all the nuclei must be the same; (iv) the rate of nucleus growth must be independent of the instant of its appearance. These conditions cannot be relaxed.

3. In respect to the IKP, the considered scheme is essentially ambiguous. This introduced additional complications into the problem of discrimination.

4. From a mathematical viewpoint, the discussed scheme may be considered as being represented in terms of coverings. This enables one to separate the geometric–probabilistic formalism from its interpretation in terms of nuclei formation, growth and impingement.

5. For a more detailed account of nuclei impingements, the geometric–probabilistic scheme may be restated without loss of generality in terms of random mosaics. The result is the possibility of representing nuclei impingements as the impingements of a nucleus with the edges of an averaged cell of a random mosaic, which is always a hexagon.

6. The geometric–probabilistic scheme itself describes the origination and evolution of the boundary between two phases without discussing the causes and nature of the corresponding nucleation and growth processes.

7. The discussed scheme admits various chemical and physical interpretations, and particular models now in use do not cover all of them. The restatement in terms of random mosaics provides for wider possibilities in this respect, e.g. the use of planigons to represent the chemical individuality of a solid reagent. This is a way of overcoming, to a degree, the discussed ambiguity.

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References

[1] V. Jesenak, Thermochim. Acta, 92 (1985) 39.
[2] A. Korobov, J. Therm. Anal., 39 (1993) 1451.
[3] W.A. Johanson and R.F. Mehl, Trans. Am. Inst. Min. Metall. Eng., 135 (1939) 416.
[4] A.N. Kolmogorov, Izv. Akad. Nauk SSSR, 3 (1937) 555 (in Russian).
[5] M. Avrami, J. Phys. Chem., 7 (1939) 1103; 8 (1940) 212; 9 (1941) 177.
[6] D. Young, Decomposition of Solids, Pergamon Press, Oxford, 1966.
[7] A. MacDonald and C. Hinshelwood, J. Am. Chem. Soc., 47 (1925) 2764.
[8] J. Šesták, Thermophysical Properties of Solids, Their Measurements and Theoretical Thermal Analysis, Elsevier, Amsterdam, 1984.
[9] B. Delmon, Introduction a la Cinétique Hétérogéne, Éditions Technip, Paris, 1969.
[10] P. Barret, Cinétique Hétérogéne, Gauthier-Villars, Paris, 1973.
[11] M.E. Brown, D. Dollimore and A.K. Galwey, Reactions in the Solid State, Elsevier, Amsterdam, 1980.
[12] V.Z. Belen'kiy, Geometric–Probabilistic Models of Crystallization, Nauka, Moscow, 1980 (in Russian).

[13] J.W. Christian, Theory of Transformations in Metals, Pergamon Press, New York, 1975.
[14] D. Avnir (Ed.), The Fractal Approach to Heterogeneous Chemistry, John Wiley, New York, 1989.
[15] J. Šesták and J. Malek, Solid State Ionics, 63–65 (1993) 245.
[16] J. Šesták, J. Therm. Anal., 36 (1990) 1997.
[17] K.R. Popper, The Logic of Scientific Discovery, Hutchinson, London, 1965.
[18] V.V. Nalimov, Zavod. Lab., 3 (1978) 325 (in Russian).
[19] G.A. Korn and T.M. Korn, Mathematical Handbook for Scientists and Engineers, McGraw Hill Book Company, New York, 1968.
[20] E.A. Prodan, Topochemistry of Crystals, Nauka and Technika, Minsk, 1990 (in Russian).
[21] S.V. Vyazovkin and A.I. Lesnikovich, J. Therm. Anal., 32 (1978) 249.
[22] J. Šesták and G. Berggren, Thermochim. Acta, 3 (1971) 1.
[23] A.I. Lesnikovich, S.V. Viazovkin and I.S. Romanovsky, J. Therm. Anal., 34 (1988) 85.
[24] A. Korobov, Thermochim. Acta, 224 (1993) 281.
[25] J. Mecke and D. Stoyan, Introduction to Stochastic Geometry, Academie Verlag, Berlin, 1984.
[26] G.L. Dirichlet, J. Reine Angew. Math., 40 (1850) 216.
[27] B.N. Delaunay, N.P. Dolbilin and M.P. Shtogrin, Proc. Math. Inst. Acad. Sci. SSSR, 147 (1978) 109 (in Russian).