Thermochimica Acta, 224 (1993) 281–289
Elsevier Science Publishers B.V., Amsterdam

The rate of a heterogeneous chemical reaction as a measure of the random marked-point process[1]

A. Korobov

Kharkov University, P.O. Box 10313, Kharkov 310023 (Ukraine)

(Received 8 January 1993; accepted 2 February 1993)

Abstract

To adapt the formalism of heterogeneous chemical kinetics to a more subtle simulation of the chemical regularities, the reaction rate is represented as a measure of the random marked-point process. This is done in terms of the mathematical notions of planigons and random mosaics. The suggested approach permits one to preserve the existing geometric-probabilistic formalism for simulating the growing nuclei impingement and at the same time to attach a more precise meaning to the model parameters, thus making the discrimination procedure more efficient through checking the mathematical models for physical-chemical adequacy.

THE QUEST FOR HETEROGENEOUS KINETICS

The adequacy and efficiency of the various descriptions of chemical kinetics are determined, to a considerable extent, by the particular way in which the concept of rate is formalized. This is manifested more clearly in heterogeneous kinetics because in this case the general conceptual definition of rate is more abstract. There are at least three essential reasons that necessitate a more adequate formal representation of the rate of a heterogeneous chemical reaction.

(i) The numerous examples of failures of models to discriminate (long attributed mainly to particular reasons such as the polycrystallinity or polydispersity of solid particles, the irregularity of their form, the considerable errors in experimental data, etc.) have left no doubt that these failures are of fundamental origins that need to be addressed from quite different viewpoints. The negation (or, at least, the considerable restriction) of the discrimination procedure in its general philosophical aspect [1] (considered with respect to chemical kinetics in ref. 2) provides an unfavourable background for the problem under discussion. The interesting (although not, in all respects, indisputable) examination of the set of mathematical models currently in use in heterogeneous kinetics, by

---

[1] Dedicated to the memory of B.I. Rogovskaya.

functional analysis, has led [3] to the conclusion that these models have differences in mathematical form that are considerably greater than their differences in physical meaning. In our opinion the models subjected for discrimination must differ essentially in their physical (or more accurately their physico-chemical) meaning, which must be reflected in their mathematical forms. Therefore, an important problem is how to provide this in practice.

(ii) To achieve this, at least one condition is that the models subjected for discrimination should represent the *chemical transformations.* And because, at any rate, one solid reagent takes part in these transformations, this reagent must be represented in the models as an individual chemical, rather than as some monodisperse or polydisperse sample consisting of abstract geometric (as a rule spherical) particles. This implies, in its turn, that the appropriate formalism is adapted for operating not only with the concept of composition, but also with the *concept of structure,* which has no basis in homogeneous kinetics where one may pass directly from the composition to the kinetic behavior. This is the weak link in modern theory.

(iii) Usually the rate is defined as some derivative with respect to time. In homogeneous kinetics this is, as a rule, the derivative of concentration which may be replaced (provided that stoichiometry causes no additional complications) by the equivalent quantity of the extent of reaction ξ introduced by De Donder. In heterogeneous kinetics one operates with the degree of conversion α, and it must be stressed that the analogy between ξ and α in this case is quite superficial. The former is a generalized coordinate, i.e. a property of the system; it is associated with the chemical notion of stoichiometry, and no structure of the system is implied. In contrast, the latter (being determined by the geometric-probabilistic approach, i.e. by the concepts of nuclei formation and growth) implies the concept of structure; it has no explicit relations to any basic chemical notion, and the system is characterized ambiguously by this quantity, i.e. it is not a property of the system. These important distinctions are rarely taken into account and, as a result, α and ξ are identified implicitly. And this leads to additional problems concerning the discrimination procedure. One of the reasons why ξ may be used instead of concentration in homogeneous kinetics is that there is no need to take the structure into consideration. However, in heterogeneous kinetics this structural factor must be represented in the definition of rate.

THE GEOMETRIC-PROBABILISTIC MEANING OF RATE

In the framework of the existing approach, based mainly on the classical works of Kolmogorov [4], Avrami [5], Johnson and Mehl [6] and Erofeev [7] (recent presentations of this approach may be found, for example, in refs. 8–10), the rate of the heterogeneous process is expressed as

$$\mathrm{d}\alpha/\mathrm{d}t = v(t)\left\{2\kappa \int_0^t \left[L_\mathrm{n}(\tau)\int_\tau^t v(\zeta)\, d\zeta\right]\mathrm{d}\tau\right\}$$

$$\times\left\{\exp\left[-\int_0^t L_\mathrm{n}(\tau)L_\mathrm{g}(\tau, t)\,\mathrm{d}\tau\right]\right\} \tag{1}$$

where α is the degree of conversion, $L_\mathrm{n}(t)$ is the nucleation law, $L_\mathrm{g}(\tau, t) = \int_\tau^t v(\zeta)\,\mathrm{d}\zeta$ is the growth law, $v(t)$ is the nucleus growth rate, κ is the form factor, t the final time, τ the current time, and ζ is the integration variable. This expression, though somewhat cumbersome, has a simple geometric-probabilistic meaning and is obtained by differentiation of the corresponding expression for α

$$\alpha = 1 - \exp\left[-\int_0^t L_\mathrm{n}(\tau)L_\mathrm{g}(\tau, t)\,\mathrm{d}\tau\right] \tag{2}$$

which is the central relationship of the theory, in a mathematical as well as in a logical respect. This is the expression that was deduced rigorously and elegantly in terms of geometric probabilities by Kolmogorov [4] and, practically at the same time, was obtained independently (half-intuitively) by Mehl and Johnson [6] with the help of their convenient visual scheme. The latter work inspired Avrami to formulate the combinatorial analysis of the problem [5].

We are discussing here the geometric-probabilistic meaning of eqns. (1) and (2), because the deduction of these relationships is based on the following ideas.

(i) Reaction is localized at the interface.

(ii) Reaction proceeds through the formation and subsequent growth of nuclei.

(iii) Starting from some instant of time, the growing nuclei impinge.

The concepts of nuclei formation and growth determine the geometric nature of the problem; the probability approach is required to account for the growing nuclei impingement.

From this point of view the term

$$l(t) = 2\kappa \int_0^t \left[L_\mathrm{n}(\tau)\int_\tau^t v(\zeta)\,\mathrm{d}\zeta\right]\mathrm{d}\tau$$

in eqn. (1) represents the total length of the interface of all growing nuclei at the given instant t calculated assuming: (i) that these nuclei grow "ignoring each other", and (ii) that a nucleus may appear in regions occupied not only by original phase but also by new phase (the so-called extended length of the interface). The exponential factor in eqn. (1) is equal to $(1 - \alpha)$ which follows directly from eqn. (2). According to refs. 4 and 6, this determines the actual interface length. Thus, a simple description of eqn. (1) is that *the rate is proportional to the length of the interface.*

It must be stressed that it is not the content of this statement (hardly surprising to anybody) which is of interest in our context. It is essential that this intuitively obvious result is obtained *without any additional assumptions* in the framework of the discussed geometric-probabilistic approach. But at the same time this simple interpretation makes it clear that eqn. (1) is not adequate for simulating the chemical features of heterogeneous reactions. Hence, the question is whether this geometric-probabilistic scheme can be extended to apply to these aspects. In connection with this, the following comments can be made.

(1) The main relationship, eqn. (2), was obtained as a solution to the problem of the impingement of growing nuclei. But it must be emphasized that the same expression is obtained, in the equivalent form $\alpha = 1 - \exp(-\alpha_{\text{ext}})$, as a solution of a simpler (both in content and calculation) covering problem. Here the extended degree of conversion α_{ext} has the meaning mentioned above. And thus, this seems to apply to quite different model situations. From this viewpoint, the principal result of ref. 4 is the four conditions under which the onmipresent exponential relationship may be used to consider the growing nuclei impingement by expressing the actual degree of conversion through the (easily calculated) extended degree of conversion.

(i) The volume (area) of the original phase is to be unlimited.

(ii) The nucleation law is to be the Poisson one.

(iii) The form and orientation of all nuclei have to be the same.

(iv) The rate of nuclei growth is to be independent of the instant of its appearance.

A detailed analysis [11] has shown that these conditions cannot be relaxed, although a slight extension of (ii) is possible. The existing routine for considering mainly spherical (circular) growing nuclei is probably due to condition (iii), because otherwise the problem of orientation immediately arises.

(2) Phase transitions rather than chemical transformations were the subject of the studies by Kolmogorov, Mehl and Johnson, and Avrami. It was Erofeev [7] who showed that exactly the same geometric-probabilistic scheme may also be used to obtain the well-known homogeneous kinetics equations of monomolecular and bimolecular reactions, through the appropriate interpretation and assignment of probabilities in eqn. (2) alone (without integrating the equations of the action mass law). And here one may discern the premise for analyzing the chemical regularities in terms of geometric probabilities.

The problem under discussion is how this may be done in the case of chemical heterogeneous reactions. And it was the fundamental interrelation between the probability and the measure [12] that gave rise to the idea that rate has to be represented as some measure, which may then be brought into correlation with the basic chemical concepts in terms of measure assignment.

RATE AS A MEASURE

Following the decision to stay within the geometric-probabilistic formalism, one has to think in terms of nuclei formation and growth.

In terms of probability theory, it is logical to treat the formation of nuclei on the crystal face as a random temporal point process, because the appearance of each new nucleus is considered as an independent event. Two aspects are essential in connection with this.

(i) The point process determines the random Voronoi mosaic on the plane [13].

(ii) The point process may be interpreted as some random measure [14].

Being a mathematical notion of stochastic geometry, the Voronoi mosaic corresponds in our context to the following fairly realistic picture. Consider the growth of some nuclei of new phase appeared at $t = 0$ (their shape being immaterial at present). The impingement of any two nuclei stops their growth in the corresponding direction without stopping it in all other directions. After the whole crystal face is occupied with the new phase, one obtains the random Voronoi mosaic alone. In reality this mosaic is more complicated because additional nuclei may appear during the process.

The random mosaic is characterized by its averaged cell which is always a hexagon [13]. It is essential for us that from the geometric viewpoint the random mosaic is a particular case of Dirichlet fragmentations [15].

So if the nuclei grow on the crystal face rather than on an abstract plane, one has to find an appropriate way to formalize this. We will use planigons [16] for this purpose, rather than the more traditional notion of a crystallographic lattice. The main reason for this choice is that planigons are another variety of Dirichlet fragmentations. There are additional advantages. Planigons provide a more fractional, more detailed description of the surface structure due to the fact that 46 types of planigon correspond to only 17 two-dimensional Fedorov groups. A single planigon contains all the necessary information about the symmetry of the surface, which conforms with the tendency to local description. It should be noted, in particular, that using planigons one automatically satisfies the above-mentioned criterion of the same orientation of all growing nuclei. This makes it unnecessary to operate with spherical (circular) particles (which are poorly combined with basic crystallographic ideas).

And here one arrives at the non-trivial opportunity of using Dirichlet fragmentations for the simultaneous simulation of the nuclei formation processes (in the form of random mosaics) and of the nuclei growth processes (in the form of planigons) within the same geometric-probabilistic approach. This approach implies an essentially two-dimensional representation of the heterogeneous reaction, the bulk process being considered as the combination of the surface ones. The origination and evolution of the reaction front on a single crystal face may be represented in terms of Dirichlet fragmentations.

(1) The given crystal face is considered as the packing made up by planigons of a definite type corresponding to the symmetry and metric of the two-dimensional surface lattice. If the surface is formed by atoms of different elements, the choice of the center of action is determined by the particular reaction type, the atoms of the other elements being situated on the appropriate edges of the planigon.

(2) The random appearance of separate nuclei at the very beginning of the process due to one or other chemical interaction is treated as the "entering of some planigons (or, more accurately, their centers of action) into reaction." Depending on the particular type of chemical reaction, the nucleus may be represented by a single planigon or by a group of planigons. The nuclei appearance determines the random Voronoi mosaic on the crystal face.

The result is the superposition of the two considered types of Dirichlet fragmentations: the random Voronoi mosaic superimposes on the planigon structure (Fig. 1a).

(3) The reaction front evolves through the edges of the planigons (not through their vertexes) because it is the edge alone that, by definition,

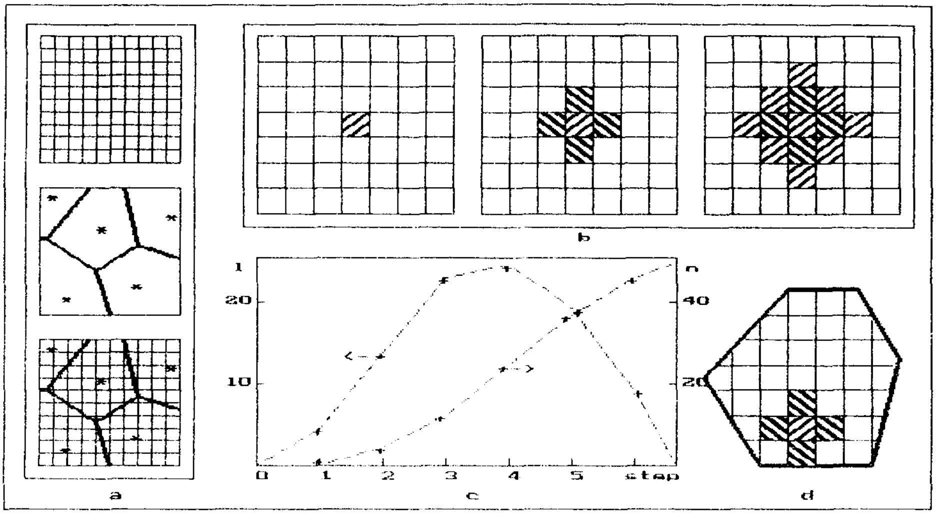

Fig. 1. a. The superposition of two different types of Dirichlet fragmentation. b. Planigons enter into the reaction. c. Dependencies of rate (l) and completeness (n) on time (step). d. The averaged cell of the random mosaic with the growing nuclei inside it.

bisects the nearest centers of action. This determines the "first surrounding" of a nucleus, which is included in the interaction at the first "step", i.e. the discrete time. Then this interaction is transmitted to the "second surrounding" and so on, as shown in Fig. 1b. In the zero approximation, one may characterize (at each step) the completeness of the process (α) by the number of "converted" planigons (n), and the rate ($\dot{\alpha}$) by the number of edges (l) of the obtained figure, i.e. by the length of the interface.

It is essential to emphasize here that within the approach suggested, the dependence of rate on time (for the stage preceding impingement of the nuclei) is linear, with a deviation from linearity at the very beginning of the process; this is independent of the type of planigon. This is in agreement with the empirical linearity mentioned in practically all the literature on the subject.

(4) The growing nuclei impingements occur along the edges of random cells. In the general case the position of the nucleus inside the random cell may be quite asymmetric, and thus the first impingement with the nearest edge may occur within a small time interval. The existance of a maximum on the $\dot{\alpha}(t)$ curves (and consequently the existance of a point of inflection on the $\alpha(t)$ curves) is due to the nuclei impingements alone, their positions being determined by the particular geometry of these successive impingements. Thus, continuing to hatch the squares in Fig. 1b, one will get the curves shown in Fig. 1c, which assume the habitual form in the limit of the large number of planigons (squares).

(5) New nuclei appear in the course of the process, along with the growth of the old nuclei, causing a continuous rearrangement of the initial random mosaic. As a result, the corresponding averaged random cell (hexagon) decreases all the time.

One of the important aspects of the suggested approach is connected with this rearrangement of the random mosaic. In the case of the simultaneous appearance of all nuclei, the edges of an averaged cell are the lines along which the growing nuclei impinge. To keep this role of the edges in the general case, one does not have to halve the distance between "old" and "new" nuclei but to divide it, taking into account the size of the "old" nucleus. Thus the random Voronoi mosaic is determined by the random marked-point process.

Thus, we arrive at the model representation of the chemical reaction on a particular crystal face in the form of the continuously decreasing hexagon of the averaged cell with the continuously growing nucleus inside it (Fig. 1d). And taking into account the possibility of introducing some measure for any point process [14], this permits one to represent the rate of a heterogeneous chemical reaction as the measure of the intensity of the random marked-point process.

This definition makes it possible to take into consideration different types of chemical interactions as well as different types of surface structures. And this seems to be the main physico-chemical argument in favor of using it, in spite of some abstractness.

The developed formal scheme may acquire physical-chemical contents in terms of measure assignment using various chemical considerations. There is a wide choice of various hypotheses in these terms, that may later be subjected to discrimination. Because the model parameters acquire a more precise meaning when the basic chemical notions are considered, the discrimination procedure itself is enriched, for now it assesses the models for physic.-chemical adequacy. In the zero approximation, we characterized the completeness and rate of the process by the number of planigons and by the number of edges forming the growing figure, respectively. But in the next stage, it must be considered that the form and metric of the particlar planigon are determined uniquely by the symmetry and metric of the two-dimensional surface lattice and, in this way, are connected with the composition and structure of the solid reagent. The formation of the nuclei may be connected, for example, with corrosive chemisorption (chemidesorption), and the corresponding model parameter acquires a meaning associated with the activation energy of chemisorption. As a rule, the reaction front evolution is somehow connected with the activated diffusion.

This is a very brief description of the manner of measure assignment using chemical considerations; a more detailed discussion is beyond the scope of this paper and will be given elsewhere.

ACKNOWLEDGMENTS

This work was undertaken in the Laboratory of Molecular Dynamics and Structure, Low Temperature Physics, Department of Physics, Kharkov University. I express my gratitude to Professor I.V. Krivoshey for much stimulating discussion and to Professor M.A. Obolenskiy for encouragement and organizational support.

REFERENCES

1 K.R. Popper, The Logic of Scientific Discovery, Hutchinson, London, 1965
2 V.V. Nalimov, Zavod. Lab., 3 (1978) 325 (in Russian).
3 S.V. Vyazovkin and A.I. Lesnikovich, J. Therm. Anal., 32 (1978) 249.
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 W.A. Johnson and R.F. Mehl, Trans. Am. Inst. Min. Metall. Eng. 135 (1939) 416.
7 B.V. Erofeev, Dolk. Akad. Nauk SSSR, LII (1946) 515 (in Russian).
8 B. Delmon, Introduction a la Cinėtique Hétérogène, Éditions Technip, Paris, 1969.
9 P. Barret, Cinétique Hétérogène, Gauthier-Villars, Paris, 1973.
10 M.E. Brown, D. Dollimore and A.K. Galwey, Reactions in the Solid State, Elsevier, Amsterdam, 1980.

11 V.Z. Belen'kiy, Geometric-Probability Models of Crystallization, Moscow, Nauka, 1980 (in Russian).
12 K.R. Parthasarathy, Introduction to Probability and Measure, New Delhi, 1980.
13 J. Mecke and D. Stoyan, Introduction to Stochastic Geometry, Academie Verlag, Berlin, 1984.
14 O. Kallenberg, Random Measures, Akademie Verlag, Berlin, 1983.
15 H.S.M. Coxeter, Introduction to Geometry, Wiley, New York, 1961.
16 B.N. Delaunay, N.P. Dolbilin and M.P. Shtogrin, Proc. Math. Inst. Acad. Sci. SSSR, 148 (1978) 109 (in Russian).