

# **SOLID-PHASE REACTION KINETICS**

## **Meaningful kinetic constants vs. formal parameters**

*A. Korobov*

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

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### **Abstract**

It is argued that, for the macroscopic parameters of conventional kinetic models to become meaningful, they may be and must be expressed in terms of elementary single-barrier processes. To accomplish this means to associate some (external) extensional measure with a single-barrier elementary act, remaining within the logic of the existing geometrical-probabilistic scheme. A manner of doing this involving the use of Dirichlet fragmentations is suggested.

**Keywords:** kinetics, solid-phase reaction kinetics

### **Introduction**

In a discussion of the meaning of conventional kinetic parameters, three aspects must be considered.

First of all, the meaning of the parameters is determined by the logic of model derivation. If the adopted assumptions are taken into account, this logic imposes definite restrictions and conditions on the model parameters. If they are ignored, a model is converted into a simple approximation function.

On the other hand, particular numerical values of model parameters are obtained (through the use of well-known statistical methods) from experimental data. These data reflect the "complicated reality": polydisperse or polycrystalline samples, possible change of mechanism or simultaneous realization of two mechanisms, etc. The substantiation of using this or that model practically always involves gaps, and this accordingly casts doubt on the meaning of the restored parameters.

A further aspect of the problem is that, in spite of the complex reality, we (consciously or subconsciously) keep in mind the well-defined rate constants of elementary single-barrier processes as the "reference point" when we talk about the meaning of macroscopic kinetic parameters.

The aim of the present paper is to discuss some essential interrelations between these three aspects of the problem.

### What parameters are we dealing with?

At present, more than twenty various (isothermal) mathematical models are used in heterogeneous chemical kinetics [1–3]. If it is agreed that the models of order type are borrowed from homogeneous kinetics without sufficient substantiation, we are dealing (from the viewpoint of meaning) with parameters of two main types:

- parameters of diffusive models;
- parameters of geometrical-probabilistic models.

It is clear that the criteria for estimating the meanings of these parameters are essentially different. If a process is believed to be limited by diffusion, the appropriate model is not expected to reflect any chemical features and, to be meaningful, the corresponding parameters must have the meaning of diffusion coefficients or be expressible through these coefficients. We shall be interested in the possibility of representing chemical regularities of heterogeneous reactions in mathematical models (without which we cannot talk about the interrelation between observed kinetic behaviour and reaction mechanism). Accordingly, we shall concentrate on the meaning of geometrical-probabilistic models.

Geometrical-probabilistic formalism, which originated in classical publications [4–6], is based on the concepts of nucleus formation, growth and impingement. This determines to some extent the nature and meaning of the model parameters. Any geometrical-probabilistic model contains two main parameters, depending in the general case on time  $t$ :

- the intensity of nuclei formation  $I(t)$ ;
- the linear rate of nucleus growth  $v(n,t)$ , which also depends on the direction  $n$ .

In addition, it includes the dimension of the problem,  $\nu$ .

In the most general case, the following restrictions are imposed on these parameters [4, 7]:

1. The nucleus formation process must be according to Poisson.
2. The linear growth rate must admit the representation  $v(n,t) = u(t)c(n)$  to separate the form factor  $c(n)$ . The ends of  $c(n)$  vectors starting from the origin must form a convex surface.
3. The corresponding dependence on  $n$  may be arbitrary, but one and the same for all points of the volume (surface) at given instant  $t$ . This means that all

nuclei must be either spherical or oriented in the same manner. It is worthy of note that the demand of a spherical form concerns not only the small nuclei of nearly critical size. This form has to be kept all the time. Naturally, nucleus impingement stops their growth in some directions, but in other directions they must grow as spheres till the very end of a process.

In the case of a particular equation, some additional conditions are imposed. Consider, for example, one of the most frequently used equations:

$$\alpha(t) = 1 - e^{-\rho t^m} \quad (1)$$

Like any other geometrical-probabilistic model, this one must contain two above-mentioned parameters. In this case, both are included in  $\rho$  [4]:

$$\rho = (4\pi/3)c^\nu I u^\nu \quad (2)$$

where  $c^\nu = (1/4\pi) \int c^\nu(n) d\sigma$  and integration is carried out over the surface of the unit sphere. This combination of parameters results from two additional assumptions:  $I(t) = \text{const.} = I$  and  $u(t) = \text{const.} = u$ . At first sight, these assumptions seem to be quite natural: the "veritable" kinetic constants must not depend on time. But on the other hand they agree poorly with simulated reality (for instance, with the considerable possible variation in the activity of potential centres).

The parameter  $\rho$  includes the dimension of a problem  $\nu$ , involving the parameter  $m$ :  $m = \nu + 1$ . In the framework of geometrical-probabilistic formalism, all results are independent of  $\nu$  [7]. However, its value must be an integer: either 2 or 3. When parameters are restored from experimental data, it may well appear that some fractional value of  $m$  provides a better fit. This may be due to the violation of one or more of the above-mentioned conditions. It should be taken into account that the choice of a fractional  $m$  deprives parameters  $I$  and  $u$  of their meaning, Eq. (1) being transformed into a formal approximation function with a rather weak approximation ability. It is also worthy of note that the value of  $\nu$  must be set up before the inverse kinetic problem is solved.

Such is the meaning of the parameters determined by the logic of the geometrical-probabilistic scheme. And what meaning would one like to attach to them as concerns a discussion of the chemical features of heterogeneous reactions?

### What meaning is implied?

When talking about the meanings of kinetic parameters, we (consciously or subconsciously) draw an analogy with homogeneous chemical kinetics. In this

framework, the question "What is the meaning of the parameter of the kinetic model?" is equivalent to the question "In what way is this macroscopic parameter expressed through the microscopic rate constants of elementary single-barrier processes?"

Naturally, the questions arise of whether it is sensible and whether it is possible to keep the same criterion of meaningfulness for parameters of geometrical-probabilistic models.

As concerns the first question, we shall touch (apart from general aesthetic attractiveness) on only one of the numerous arguments in favour of the positive answer, i.e. the well-known problem of temperature dependence. It is common practice to check the model parameters for the *formal* fulfilment of the Arrhenius law. The misinterpretations here are due not so much to the disputable character of the approach [8, 9] as to the essential ambiguity of the possible conclusions.

Suppose that there is no formal fulfilment. It does not necessarily follow that the regime of a process is different from the kinetic one. It may well be, for example, that some constant involves macroscopic parameter of the elementary processes in the form of an algebraic sum, i.e.

$$\kappa = \kappa_1 \pm \kappa_2 \quad (3)$$

This is enough for a mismatch, even provided that the separate elementary acts satisfy the Arrhenius law and the process as a whole proceeds in the purely kinetic regime. To provide the fulfilment, the rate constants of elementary processes must be contained in the expression for the macroscopic parameter in the form of a product or quotient (possibly to certain powers):

$$\kappa = \kappa_1^{n_1} \cdot \kappa_2^{n_2} \cdot \kappa_3^{n_3} \dots \quad (4)$$

However, even in this case the obtained value of the "observed" (or "effective") activation energy  $E'$  may be provided with a meaningful interpretation only if the exact form of relationship (4) is known and  $E'$  may be presented in the form

$$E' = n_1 E_1 + n_2 E_2 + n_3 E_3 + \dots \quad (5)$$

Otherwise, the value of  $E'$  has no explicit relation to any particular activated state. In this case, the broad range of observed values of  $E'$  may even cast doubt on whether the discrete activated states actually exist for reactions with solids [8].

A similar ambiguity of argumentation is reproduced almost word for word in practically all respects as concerns the interpretation of the restored values of the parameters. It must be recognized that the whole range of related problems

may be solved finally only in terms of single-barrier processes. In this connection, we are faced with two questions: (i) Are the geometrical-probabilistic concepts and the concept of single-barrier processes compatible in principle? If so, (ii) in what particular way may the appropriate meaning be attached to the geometrical-probabilistic parameters?

The answer to the first question is connected with the mathematical structure of the discussed geometrical-probabilistic scheme. According to Erofeev [10], the same probabilistic scheme may be used to obtain the well-known equations of mono- and bimolecular reactions (without integrating equations of the law of mass action). In our context, this important result leads to the following picture. We have the formal probabilistic scheme, in the framework of which some "complicated" probability may be calculated through certain "simple" probabilities. This scheme may be provided with the "homogeneous interpretation", and the logic of derivation of mono- and bimolecular equations helps towards an understanding of the place of single-barrier constants in its structure. The same scheme may be provided with the "heterogeneous interpretation" in terms of nucleus formation, growth and impingement. This leads to the results obtained in [4-6], and in particular to Eq. (1).

From a formal aspect, the discussed probabilistic scheme is based on the following considerations. The degree of conversion  $\alpha$  is identified with some probability  $P$ . In the homogeneous case, this is the probability that an arbitrary molecule in a gaseous mixture will have reacted up to the given instant of time  $t$ . In the heterogeneous case, it is the probability that an arbitrary point of the original phase will have appeared inside the new phase up to the instant  $t$ . The logic of probability theory is the calculation of "more complicated" probabilities through "more simple" probabilities, which are treated as elementary ones within the problem and are specified on the basis of considerations exceeding the limits of probability theory (and often the limits of formal mathematical considerations too). The elementary probability  $p_i^j$  is determined as the probability that the given molecule  $i$  will have reacted in the  $j$ -th subdivision of the time interval  $0 = t_0 \leq t_1 \leq t_2 \leq t_3 \leq \dots \leq t_n = t$  (in the homogeneous case), or that the given point will be consumed by the new phase within the  $j$ -th subdivision of the time interval (in the heterogeneous case).

From a mathematical aspect, the discussed scheme is based on the theorem of the multiplication of probabilities of mutually independent events. The events mentioned above are not mutually independent, but the opposite events characterized by probabilities  $q_i^j = 1 - p_i^j$  (e.g. the probability that the given molecule  $i$  will not have reacted within the  $j$ -th subdivision of the time interval). For these probabilities, we may write

$$Q_i = \prod_{j=1}^n q_i^j \quad (6)$$

where  $Q_i = 1 - P_i$ . The further calculations make it possible to pass from  $q_i^j$  to  $p_i^j$  and include no other meaning. By taking logarithms, we may transform the product into a sum:

$$\ln Q_i = \ln \prod_{j=1}^n q_i^j = \sum_{j=1}^n \ln q_i^j \quad (7)$$

and then pass naturally to the limit of  $\Delta t \rightarrow 0$ :

$$\ln Q_i = \ln (1 - P_i) = \lim_{n \rightarrow \infty} \sum_{j=1}^n \ln (1 - p_i^j) \quad (8)$$

After expanding  $\ln$  in a series up to the first term, we get

$$\ln (1 - P_i) = \lim_{n \rightarrow \infty} \sum_{j=1}^n \ln (-p_i^j) = - \int_0^t p dt \quad (9)$$

As a result, the final equation takes the form

$$\alpha = P = 1 - \exp \left( - \int_0^t p dt \right) \quad (10)$$

It is worth emphasizing once more that Eq. (10) has the same meaning as Eq. (6): it expresses some probability  $P$  of a "complicated" event through some probability  $p$  of a "simple" event. This is where the boundary between the meaningful and the formal lies: formal considerations determine the form of relationship (10), but the meaning of "elementary" probabilities must be assigned, various possibilities being admitted by the formal scheme itself.

Setting (according to [10])  $p = \text{const.} = \kappa$  in Eq. (10), we immediately arrive at the equation of a monomolecular reaction:

$$\alpha = 1 - \exp (-\kappa t) \quad (11)$$

In this interpretation, Eq. (11) includes the only parameter  $\kappa$ , and this parameter has the meaning of the rate constant of a single-barrier process (in contrast with the parameter  $\rho$  in the externally similar Eq. (1)).

For us, the case of bimolecular reaction is more interesting. To obtain the corresponding equation from Eq. (10), we have to set [10]

$$p = \eta(b - \alpha a) \quad (12)$$

where  $\eta$  is a parameter, and  $a$  and  $b$  are the original concentrations of reagents  $A$  and  $B$  participating in the reaction  $A + B \rightarrow$  products. From our viewpoint, two aspects are essential here: (i) the probability  $p$ , treated within the probabilistic scheme as the "elementary" one, attains the complex structure outside this scheme; (ii) since the co-factor  $(b - \alpha a)$  is simply the number of particles  $n_B$  of the reagent  $B$ , probability  $p$  includes not only the single-barrier constant  $\kappa$ , but also some other (different in nature) quantities:  $p = \kappa \cdot z_0 \cdot n_B$  where  $z_0$  is the collision factor.

In terms of nucleus formation, growth and impingement, the probability  $p$  acquires a more complex structure [4, 7]:

$$p = L_n(t) \cdot L_g(\tau, t) \quad (13)$$

where the nucleation law  $L_n(t)$  is the intensity of nucleus formation, and the growth law

$$L_g(\tau, t) = (4\pi/3)c^v \left( \int_{\tau}^t u(\xi) d\xi \right)^v$$

includes the linear growth rate  $u(t)$ , form factor  $c$  and dimension  $v$ . The restrictions for these parameters, determined by the probabilistic scheme itself, were discussed in Section 1. It is clear that these parameters can have no relation to single-barrier processes: publications [4-6] were devoted to phase transitions, and no chemical transformations were assumed. At the same time, the examples of mono- and bimolecular reactions demonstrate the possibility of talking about single-barrier processes within the framework of the discussed scheme.

### Model parameters in terms of single-barrier constants

One of the material features of the parameters determined by the geometrical-probabilistic scheme is that they have to represent extensional relations. This is a direct consequence of the concepts of nucleus formation and growth: it is necessary to characterize nuclear dimensions, mutual situation and impingements. Homogeneous kinetics provides no appropriate analogy.

In this respect, the peculiarity of heterogeneous kinetics is that, in aiming to operate with single-barrier constants, one must at the same time keep this extensional character of macroscopic kinetic parameters. The single-barrier processes themselves possess no external extensional measure. (The internal characteristic of a single-barrier process is its cross-section [11]. *This means*

*that some extensional measure has to be associated with an elementary single-barrier act (characterized by its meaningful constant).*

A heterogeneous reaction is localized in a number of (singly connected) reaction zones situated around growing nuclei. From this viewpoint, to associate an extensional measure with a single-barrier elementary act means to answer the following questions:

- Does this act result in the appearance of a new, singly connected zone (nucleus formation) or in the evolution of one of the existing zones?
- What is the distance of zone propagation (in the given direction) due to a single elementary act, and how many similar acts proceed (practically) simultaneously?
- In what way are the "domains of influence" and the mutual situation of growing nuclei changed due to a new zone formation?

One may answer these questions in terms of the suggested model representation based on the use of Dirichlet fragmentations [12, 13]. As concerns the discussed problem, the main advantage of this approach is that, in terms of Dirichlet fragmentations, a definite domain of the crystal space may be associated with any lattice point, both the symmetry and the values of lattice parameters being taken into account.

At this stage, we are faced with the non-equivalence of dimension values  $\nu=2$  and  $\nu=3$  determined by mathematical considerations. The complete theory of Dirichlet fragmentations exists only for 2-dimensional crystal lattices (theory of planigons [14]). In the case  $\nu=3$ , there is no corresponding complete theory. However, at the same time, an argument of quite a different nature in favour of the 2-dimensional consideration may be pointed out. Heterogeneous reactions not infrequently start at the surface, their development along the surface and into the bulk differing materially. By setting  $\nu=3$ , we deprive ourselves of the possibilities of representing this in the geometrical-probabilistic models.

Considering the growing nucleus as a figure consisting of planigons [12, 13], we may easily associate the extensional measure with the single-barrier act responsible for the evolution of the reaction zone and characterized by microscopic rate constant  $\kappa$ . It is assumed that one of the species participating in this act is situated at the centre of action of the planigon. The accomplishment of one elementary act means that one planigon, characterized by some extensional measure  $\mu$ , is added to the growing nucleus. The complete table of planigons, with their forms, dimensions, and one-to-one correspondence with two-dimensional Fedorov groups, is given in [14]. Since the elementary acts are equiprobable for all planigons forming the reaction zone at the given instant of time, all of them may be considered as joining the growing figure practically simultaneously. This makes it possible to write



$$L_g(\tau, t) = \kappa \cdot \mu \cdot N(\tau, t) \quad (14)$$

where  $N(\tau, t)$  is the number of planigons that at instant  $t$  form the nucleus that appeared at instant  $\tau$ .

Following this logic, we also have to associate some extensional measure with  $L_n$ . The way to do this is not so obvious: nucleus formation is usually treated as a purely temporal process. The aim may be achieved by using the second variety of Dirichlet fragmentations, random mosaics [15]. In these terms, we may represent the correspondence between the elementary act leading to the formation of a new nucleus and the cell of the random mosaic characterized by a definite extensional measure  $\mu'$ , depending among other factors on the number and "age" of the existing nuclei [13]. Each appearance of a new nucleus leads to a rearrangement of the random mosaic.

As a result, we arrive at the following interconnection of temporal and extensional measures of a process: temporal measures are the rate constants of single-barrier elementary acts responsible for the origin and evolution of the reaction zone, and extensional measures are the corresponding measures  $\mu$  and  $\mu'$  determined by planigons and random mosaics, respectively. This enables us to attach the meaning required to discuss the chemical features of heterogeneous reactions to the parameters of geometrical-probabilistic models. The forms and dimensions of the planigons, and also the characteristics of the random mosaics, are determined by the particular reaction.

However, with the appropriate interpretation this provides only the geometrical-probabilistic scheme itself, making nothing clearer in respect to its relation with real complicated reactions. The term "heterogeneous reaction" is practically always accompanied by the epithet "complicated". This epithet is of little value until the "complicated reaction" is compared with a "simple reaction". Here we are faced with one more peculiarity of heterogeneous kinetics. In homogeneous kinetics, the simple reaction is the totality of independent similar elementary acts. This is the notion used to construct the models of complicated multistage reactions. In heterogeneous kinetics, the interrelation between the notion of a simple reaction and the notion of an elementary act is much more involved, due to the simultaneous spatial and temporal interconnection of the separate elementary acts. It seems that the earlier-suggested [12, 13] 2-dimensional model representation of a heterogeneous reaction as the ever-decreasing averaged cell of the random mosaic with the ever-growing nucleus (consisting of planigons) inside it is suitable in our context for playing the role of a simple reaction. The manner of its further formalization is determined to a considerable extent by the logic of expressing model parameters in terms of single-barrier rate constants.

To conclude, it follows from the given considerations that the meaningful kinetic parameters must be expressed in terms of single-barrier processes. Only in this case may they be considered as meaningful in a discussion of the chemical features of heterogeneous reactions. At the same time we have to remain within the limits of the existing geometrical-probabilistic scheme in order not to miss the important concepts of nucleus formation, growth and impingement. This scheme is shown to be adaptable for associating an extensional measure with a single-barrier process in terms of Dirichlet fragmentations. This transforms the problem into two dimensions and requires the proper mathematical formalization.

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**Zusammenfassung** — Es ist umstritten, ob makroskopische Parameter herkömmlicher kinetischer Modelle sinnvoll sind und ob sie in Ausdrücken von Elementarprozessen dargestellt werden können bzw. müssen. Dies zu erreichen bedeutet, einige erweiterte Messungen mit Elementarereignissen zu verbinden und dabei innerhalb der Logistik von existierenden Schemen geometrischer Wahrscheinlichkeit zu bleiben. Hierzu wird eine Methode unter Einbeziehung von Dirichlet-Fragmentationen vorgeschlagen.