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Phenomenology of phase transitions in describing the solid-phase reaction kinetics[☆]

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Abstract

Whereas phase transitions may occur without chemical transformations, any solid-phase chemical reaction involves the disappearance and formation of phases. At present, the phenomenological scheme, developed originally for phase transitions, is also used for describing solid-phase reaction kinetics. In discussing their distinctive features versus similar microscopic behavior, this geometric-probabilistic scheme is shown to necessitate modification, firstly with respect to the non-equilibrium and chemical essence of solid-phase reactions.

Keywords: Kinetics; Non-equilibrium; Phase transitions; Phenomenological description; Solid-phase reactions

Separate branches of the physical chemistry of surfaces generate, as a rule, peculiar phenomenology [1]. This is not the case for modern solid-phase reaction kinetics [2–4]: the geometric-probabilistic phenomenology of the *ensemble* of growing and impinging nuclei is borrowed from the field of first-order phase transitions. Note that this comparison is adequate not only because many solid-phase reactions start at a surface, but also with the view of the arguments in favor of a 2-D approach to heterogeneous kinetics [5].

Since the geometric-probabilistic approach was derived in well-known research [6–8] (1937–1940), the philosophy of phenomenological description has essentially changed, mainly due to the recent development of synergetics. It is clear that with increasing complexity the system acquires phenomenological features which are barely discerned in considering more simple subsystems or through direct extrapolation of

[☆] Dedicated to Hiroshi Suga on the Occasion of his 65th Birthday.

microscopic properties [9, 10]. For example the form of a crystal cannot be predicted from microscopic considerations alone, even if it is growing from a homogeneous, isotropic liquid [11]. This is the problem for localization forms of solid-phase chemical reactions.

In this context, the use of the same particular mathematical models for describing the kinetics of both phase transitions and solid-phase chemical reactions within the same geometric-probabilistic approach emphasizes the similarity of the observed macroscopic behavior in spite of the fairly different natures of the considered systems. The basis of this similarity is clear: both these processes take place through nuclei origin, growth and impingement. The universal geometrical regularities of nucleation and growth determine the (almost always) sigmoid form of experimentally registered curves, i.e. degree of conversion α –time t .

However, there is the set of problems succinctly characterized as “diagnostic limits” [12, 13], and also some issues concerning the intrinsic logic and formalism of the geometric probabilistic scheme [5, 14] that lead one to discuss the essential distinctions which are obscured by the above similarity. Enabling one “to see the forest for the trees”, the macroscopic phenomenological description not only admits such discussion, but even indicates the correct approach in the logic of eliminating the “extra variables”, i.e. factors that do not influence or influence insignificantly the observed macroscopic behavior [15].

As noted earlier [5, 16], the essence of the geometric-probabilistic approach is embodied not only in the final relationship

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

between the degree of conversion $\alpha(t)$, the nucleation law $L_n(t)$ and the growth law $L_g(\tau, t)$ (where t is the current time and τ is the instant of nucleus appearance), but also in the corresponding applicability conditions, the misinterpretation of which reduces a meaningful simulation to a formal approximation. These four conditions, forming a kind of (incomplete) bridge between macro and micro, provide the context for discussing the phenomenological description with respect to the peculiarities of solid-phase chemical reactions. In contrast to the fundamental physics encountered with such an “esthetic ideal” as the laser, for which the elimination of extra variables may be made explicitly, step by step, proceeding from first principles [15], the situation in chemistry is more involved: the distance between the elementary processes and the observed macroscopic behavior is considerably greater. This is especially true for solid-phase reactions since the separate elementary acts are interconnected in both time and space due to localization phenomena. The result is the less efficient use of phenomenological relationships and the need for a peculiar way of deriving and substantiating them based on chemical knowledge and experience.

In discussing this problem with respect to the phenomenology of solid-phase reaction kinetics, the following points are worth emphasizing.

(i) In some way or other, we deal with a transformation of one phase into some new phase. Where phase transitions are concerned, the symmetry of a phase becomes

relevant as one of its distinctive features; this is not explicit in the conventional definition [17]. Keeping in mind the “order–disorder” concept [9], one may expect the symmetry considerations to be useful in developing the phenomenology of solid-phase reaction kinetics. These considerations are applicable to the original solid reagent in the form of a single crystal alone. Dealing with a single crystal one may, in particular, represent its chemical individuality by mathematical models [14, 16].

(ii) A solid-phase chemical reaction is the essentially non-equilibrium phase transition, that may be caused not obligatorily by temperature but, for example, by a chemically active medium. (We will restrict our discussion to isothermal reactions.)

(iii) A specific role in creating and keeping this non-equilibrium is played by crystal defects, the probability of finding them at small distances being considerable in the reaction zone. This role is determined to a degree by the cooperative phenomena, the phenomenology of which belongs to the most complicated problems [9]. In particular, one may expect a second-order structural phase transition in the nearest vicinity of the reaction zone preceding a solid-phase chemical transformation.

(iv) On a microscopic scale, the essence of the processes discussed is the formation and breaking of chemical bonds. From this viewpoint, different phase transitions may, at first glance, appear to be fairly similar, e.g. the sublimation of sulfur and iodine. The latter necessitates the breaking of Van der Waals bonds, whereas the former proceeds through the breaking of the covalent S–S bonds. In this respect, sulfur sublimation is closer to such decomposition reactions as $\text{HgO} \rightarrow \text{Hg} + \text{O}_2$ (breaking ionic bonds) than to the “purely physical” sublimation of iodine. In this connection we must consider the electronic factor in one way or the other.

(v) Even in refined experiments on phase transitions, “practically all the chemical thermodynamical equilibria are pseudo-equilibria in the sense that it is not the absolute minima of Gibbs energy with respect to all possible processes but only with respect to the processes which could take place within a reasonable time” [18]. Therefore, this is the case for solid-phase chemical reactions, the products of which (especially berthollide compounds) may be rather sensitive to reaction conditions and may be formed through a number of intermediate transformations.

Earlier, the inherent ambiguity of the geometric-probabilistic scheme with respect to the IKP solution was shown [5]. In addition, the above considerations lead to the conclusion that the numerous problems of experimental data interpretation are not connected with this ambiguity alone: the phenomenological scheme is not adequate to consider these items. At least three aspects of this may be pointed out:

(i) A single phase transition and, therefore, the complete coherence of all processes are implied by conventional equations now in use, whereas in the general case the initial phase disappearance and new phase formation are not coherent processes.

(ii) A phase transition is considered as the equilibrium one, since there is no room for discussing the dependence on geometry within the existing formalism. (One of the applicability conditions requires an unrestricted initial volume which means the thermodynamic limit [11].)

(iii) The way in which the geometric-probabilistic scheme is used means that L_n and L_g are derived directly from microscopical considerations. Among other things, this results in the following contradiction. The geometric-probabilistic scheme itself admits

arbitrary localization forms. The only requirement is that they must be convex. But, however, these localization forms cannot be predicted directly from microscopical considerations, as mentioned above.

The last item suggests that a more adequate representation may be reached by including in the formal description one more level, i.e. the phenomenology of a separate nucleus. In this connection, we face two interrelated problems. Keeping in mind the issues of experimental data interpretation and the trend accounting for the electronic factor, it would be desirable to represent the corresponding order parameter in a proper way, e.g. in terms of the system ρ_G of Fourier components of electronic density $\rho(r)$ [19]

$$\rho(r) = \sum_G \rho_G e^{iGr} \quad (2)$$

where G is the vector of the reciprocal lattice. But the number of components in this case is infinite. The obvious problem here is the solution of nonlinear equations, now the subject of intensive research. A discussion of this, in the case of scalar order parameters and homogeneous isotropic original phases can be found, for example, in Ref. [20]. But there is also a more subtle and involved problem of interpretation, which does not disappear but only transforms with the progress in nonlinear equation solution, remaining always significant, especially in the context of IKP.

It is at this point that we must bring chemical considerations and chemical intuition into play. In this context the use of planigons and Wigner–Seitz cells, suggested earlier [14, 16, 21], may be treated as one of the possible ways of excluding “extra variables” using symmetry considerations. Planigons represent the symmetry not only of nuclei atomic positions but also of the (averaged) electron density distribution [22]. At the same time a single planigon, characterized by a definite form and dimensions, holds all the necessary information for representing a 2-D crystal structure [23]. Simulating nucleus growth in terms of planigons, one passes from a continuous to a more “roughly grained” discrete description, which seems to be more constructive at the present stage. At the same time, it becomes explicit that in order to describe adequately solid-phase reaction kinetics, the discussed geometric-probabilistic scheme requires modifications, at least in the following respects.

It was mentioned above that the similarity of solid-phase chemical reactions and phase transitions with respect to the observed macroscopic kinetic behavior is due mainly to universal geometrical regularities of nucleation and growth processes. But if the scheme is adapted for taking into account new phase nuclei alone, there is no room for representing the original solid reagent. This gap becomes explicit when only gaseous products are formed, e.g. $\text{HgO} \rightarrow \text{Hg} + \text{O}_2$. The origin and growth of which nuclei are described in this case in terms of conventional geometric-probabilistic scheme? Obviously, these may be only the nuclei of negative crystals of the original solid phase. The reaction front may be treated in this context as the boundary between the crystal order and some disorder. It follows that the general phenomenological scheme must be more involved than it is now, admitting, in particular, a separate description of the negative crystal growth. In addition, it was shown in Ref. [21] that

for symmetry considerations such a description has to be essentially two-dimensional. In this case the transition mentioned above to the discrete approach is possible with the account of the chemical individuality of a solid reagent.

The origin and growth of new phase nuclei thus become a separate stage of the description. Now one has to consider that these processes occur inside the negative crystals, the dimensions of which may be fairly limited, especially at the very beginning of a process. Accordingly, the requirement of unrestricted initial volume is no longer satisfied. As a result, various structures are admitted depending on the geometry of the problem [11]. This is in line with the fact that the new phase may appear to be not the most stable, undergoing further transformations (perhaps through different phase transitions). Among other related issues, note the problem of combining a continuous three-dimensional description at this stage with a discrete two-dimensional description at the previous stage.

The above somewhat fragmentary considerations argue that the conventional phenomenological geometric-probabilistic formalism, developed for first-order phase transitions, is not adequate for taking into account some essential features of solid-phase reactions. They also suggest some ideas about the required modifications concerning mainly non-equilibrium and the chemical essence of the considered processes. The first step in developing a more involved hierarchical scheme is the discrete description of a separate negative crystal growth. This deserves a more detailed discussion and will be presented elsewhere.

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