The Concept of the Individual Chemical for Reacting Berthollide Compounds: The Loss of Certainty[†]

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In describing the solid-phase reaction kinetics, we face the need to clarify the concept of the chemical individual in both conceptual and formal respects. For Berthollide compounds it cannot be defined as unambiguously as for Daltonide compounds. The mathematical description of this concept is suggested for reacting Berthollide compounds in terms of Dirichlet domains. The way in which the loss of certainty is represented provides insight into the interplay between chemical and mathematical concepts.

The question "What is the individual chemical?" has been raised now and again in different connections throughout the history of chemistry. For the present these are attempts to get more deep insight into the regularities of solid-phase chemical reactions[1,2] that revert us for the nth time to this old but not obsolete problem. Among other points, a more deep insight implies the necessity to approach a solid-phase chemical reaction in terms of elementary single-barrier processes.[3] A stumbling block to this is the generalization of microscopic regularities on the macroscopic scale with the view that reaction products form the new phases through the origination and growth of nuclei. The nature of a solid-phase reaction is such that the chemical individuality of a solid reagent determines the observed kinetic behavior indirectly, breaking through the universal geometrical laws of new phase formation. These geometrical laws appear to be so powerful that eventually geometry has eclipsed chemistry within the theory of solid-phase reactions, upsetting the balance between chemical and geometrical outlooks inherent to the basic work of Langmuir.[4] The adopted geometric-probabilistic formalism (see, for example, ref 5) provides the rigorous and elegant solution to the problem of the impingement of growing nuclei and enables one to follow the origination and evolution of the (multiply connected) reaction zone. But it is nearly free from chemistry, and there is no room for discussing the issues concerning the chemical individuality within its logic. To overcome this gap, chemical and geometrical aspects of the organization of kinetic systems including solids must be considered from one and the same viewpoint and in one and the same terms.

In what way and to what extent does this touch the problem of the chemical individual?

The concept of the chemical individual is conceived in the well-known controversy between Berthollet and Proust (~1800) that virtually originated two fairly different views on the chemical organization of matter. The history of chemistry shows that the ways of solving many theoretical problems were influenced considerably by the predominance of one of these views at the given period of time. First it was Proust's views that got the upper hand, and this promoted the appearance of Dalton theory and the strengthening of the notion of molecule with which classical

chemistry associates traditionally the chemical individuality. In the triad "atom < molecule ≪ macrobody" it was the molecule that played for a long time the central role, all chemical phenomena being attributed exclusively to its formation and rearrangement.[6] In retrospect this may partly elucidate the relatively greater progress in understanding the nature of gaseous reactions as well as the material distinctions in the logic and formalism of homogeneous and heterogeneous kinetics.

The organization of a kinetic system is determined by both chemical nature and the state of aggregation of reagents. And whereas the gaseous kinetics is the kinetics of Daltonide compounds alone, condensed reagents may be Berthollide compounds as well as Daltonide compounds. In this respect the following contradiction is associated with the idea of the molecule as being a chemical individual. The mutual perturbation of molecules accompanying their transition into a condensed state vary in quite broad limits. A molecule of a Daltonide compound passes into condensed phase as a closed quantum mechanical system, preserving in the main its individuality. But the properties of thus formed macrobody differ materially from the properties of a separate molecule resulting in the two-level description of a kinetic system. This is not the case for Berthollide compounds due to the complete loss of the individuality by a molecule in passing into a condensed phase.

Consequently the questions arise what may serve as the individual chemical for Berthollide compounds and what considerations determine this. Conventional discussions of these points are mainly verbal. In contrast to this, we will approach them using the mathematical notion of Dirichlet domains in the form of planigons and random mosaics, the nontrivial interplay of which were recently employed to progress in understanding the nature of solid-phase reactions.[1−3]

It is worth noting that the conception of the individual itself does not belong to the well-defined and steady in meaning conceptions. In the ancient times M. Tullius Cicero used the latin term "individuus" practically for the same meaning in which Auctores Ecclesiastici used the term "indivisibilis", i.e., as a synonym for Greek ατομοσ (atom).[7] With time the meanings of these terms diverge. And nowadays, following Seneca, the term "individual" is used to emphasize that something cannot be further subdivided without loss of its peculiarity.
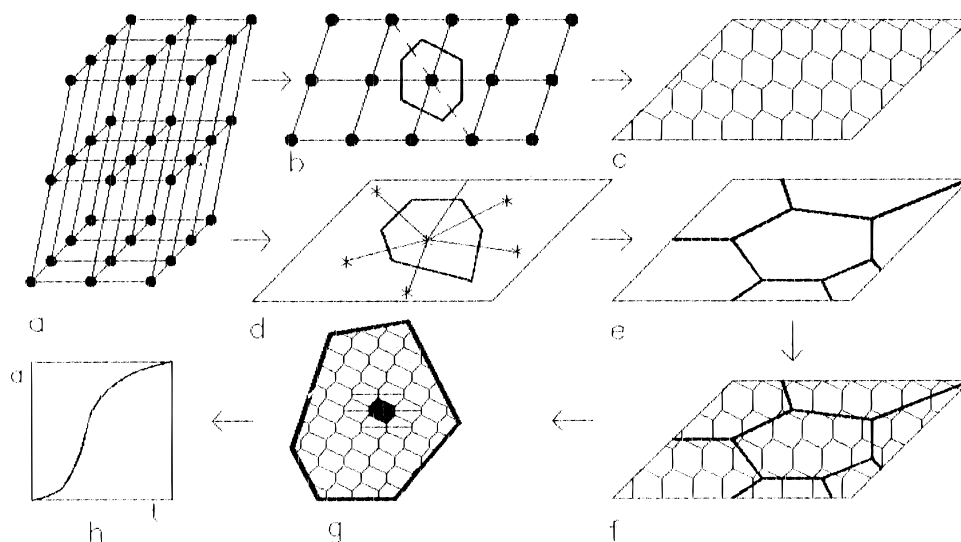
Figure 1. Two different aspects of the individuality of a solid Berthollide compound (a), crystal structure and reaction centers, may be characterized in one and the same terms of Dirichlet tessellations as follows. A single crystal face plays the central role for symmetry considerations. Bisecting the distance between the given lattice point and its nearest neighbors by perpendiculars, one gets a planigon (b). The symmetry and combinatorial-topological structure of a crystal face is represented uniquely in terms of planigons (c). In so doing for randomly distributed reaction centers, one gets a domain shown in (d) and thus represents the number and mutual situation of these centers in terms of random mosaics (e). Two particular cases of Dirichlet tessellations, (c) and (e), are superimposed (f). An averaged hexagon cell of the random mosaic restricts the part of a crystal face (g) which is sufficient for representing the chemical individuality of a Berthollide compound. Animating this model representation, one gets a sigmoid kinetic curve "degree of conversion α − time t" (h).

Among numerous considerations determining peculiarities of a solid Berthollide compound that must not be missed in representing its chemical individuality, the following three seem to be most material.

(i) The inherent factor of the individuality of a solid reagent is its crystal chemical structure. According to the Curie principle the symmetry of a solid reagent must be inherited by the organization of a kinetic system. This inspires the hope to agree chemical and geometrical aspects of this organization using the fundamental symmetry considerations. These considerations determine the choice of a single crystal face for representing the chemical individuality of a solid Berthollide compounds: various two-dimensional Fedorov groups corresponding to the same spatial group may result in fairly different kinetic behavior. Note that this choice determines an essentially two-dimensional approach to describing the chemical organization of a kinetic system,[8] a single crystal being treated as a set of parallel crystallographic planes (Figure 1a).

(ii) Further, to interrelate the chemical and geometrical factors, an elementary single-barrier event has to be associated with some extensional measure.[3] For this reason a single crystal face has to be represented in terms of planigons (Figure 1c) rather than in more habitual terms of crystal lattices (Figure 1b). The complete mathematical theory of planigons is developed in ref 9. A single planigon contains all the necessary information concerning the symmetry and combinatorial-topological structure of a two-dimensional lattice, enabling one to talk about the reaction front advance in terms of single-barrier events. Note also that planigons provide more fractional, more detailed description of the surface structure: 46 types of planigons correspond to only 17 two-dimensional Fedorov groups.[9]

But still a single crystal face in terms of planigons does not represent to the full extent the chemical individuality of a solid Berthollide reagent. There is one more essential peculiarity that must be taken into consideration.

(iii) A single crystal face as the individual chemical differs essentially from a molecule in many respects. Thus, the break of a single bond in a molecule is sufficient for the loss of its individuality. In the case of a crystal face this break results in the appearance of a surface reaction center. It may be argued whether this alters the chemical individuality and, if so, to what extent. But there is no doubt that in characterizing a Berthollide compound the surface centers, both equilibrium and nonequilibrium, cannot be dispensed with. Moreover, we face here the need to make an important conceptual choice. The surface centers may be treated, of course, in the old way as the annoying distortion of the ideal crystal structure. But when the reaction dynamics is concerned, these two factors of reactivity may hardly be subdivided into more and less important. We put forward here the alternative viewpoint: in contrast to traditional reductionism, reaction centers must be included "on terms of equality" into description of considered compounds. First of all, these are various point defects (dangling bonds, vacancies, interstitial and substituting atoms, etc.) and their small complexes. This agrees with the idea that in the case of solid Berthollide compounds (in comparison with gaseous Daltonide compounds) it is much more difficult to draw a sharp boundary between the individual chemical out of a reaction and the individual chemical as a subsystem of a more involved kinetic system.[6] And it is not casually that main arguments in this paper are of kinetic origin. As a result, the probabilistic aspect appears in the description of a Berthollide compound, being determined by the randomness of the number, mutual situation, and activity of reaction centers, and so, the concept of an individual chemical losing to a degree its habitual certainty.

One more important aspect of the above choice is connected with the mathematical description of the concept under discussion. The surface centers may be adequately described in our context in terms of random mosaics[10] (Figure 1d,e). The main reason for this is that random mosaics and

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planigons are particular cases of the same more general mathematical notion of Dirichlet tessellations. Superimposing these two types of tessellations (Figure 1f), one gets thereby the means for characterizing in one and the same terms two essentially different sides of individuality of a Berthollide compound: the regular crystal structure and the random reaction centers. The former is represented by planigons, their form and dimensions being determined uniquely by the symmetry and cell parameters of a crystal face (corresponding tables are given in ref 9). The latter is represented by the random mosaic characterized by its averaged random cell, which is always a hexagon.[10] It is the essentially probabilistic character of this second description that determines the nature and inherence of the uncertainty in characterizing the individuality of a solid Berthollide compound. Within approach suggested it is represented by the part of a single crystal face in terms of planigons restricted by the averaged hexagon cell (Figure 1g). Note the difference between hexagons in Figure 1f,g: the former is one of many cells of the random mosaic, whereas the latter is the averaged cell characterizing this mosaic as a whole. They differ in both form and numbers of planigons inside them. Their scales are also a bit different. In contrast to the form and dimensions of planigons, the form and dimensions of the averaged random cell cannot be associated with a solid reagent alone, being also dependent on a considered kinetic system.

Accordingly, the above considerations are justified primarily through animating the suggested model. This animation was suggested in ref 2 and is also discussed in more details in the accompanying paper. A surface atom participating in an elementary event is the center of action of a planigon. This enables one to characterize the result of this elementary event in geometrical terms as the "entering of a planigon into reaction" (solid hatching in Figure 1g). The formation of the reaction zone is represented as the simultaneous propagation of chemical interactions from the given planigon to all nearest planigons (marked in Figure 1g by crossing lines). In this way the origination and growth of a nucleus are simulated. The successive activation of the potential surface centers leads to the rearrangement of the random mosaic and is described as the decrease of its averaged hexagon cell resulting from the appearance of new random cells in the course of a process. This makes it possible to pass from adopted now purely temporal representation of this process to more adequate spatial representation.[1] The ever growing nucleus impinges with the ever decreasing hexagonal cell thus simulating the nuclei impingements in terms of Dirichlet tessellations. The result is the "degree of conversion-time" curve (Figure 1h), the constant sigmoid form of which emphasizes the prevalence of universal geometrical regularities over basic chemical concepts. This model representation provides not only a more detailed insight into the way in which chemical features of a kinetic system are masked by the geometrical regularities but also the means for constructing the bridge between the observed kinetic behavior and the chemical individuality through these geometrical regularities.

Summing up, the partial loss of the accustomed certainty is inevitable when the chemical individuality of a Berthollide compound is concerned. The existing essential contradiction between chemical and geometrical outlooks on the complex organization of a kinetic system including solids may be reconciled on the fundamental level of the chemical individual alone. In the case of a solid Berthollide compound it may be represented as part of a single crystal face in terms of planigons restricted by an averaged random hexagon (Figure 1g). The suggested representation provides a basis for more deep understanding the nature of solid-phase chemical reactions through more adequate description of their dynamics in terms of discrete mathematics. It seems also that the above considerations may promote the desirable convergence of the kinetics of heterogeneous, surface, and catalytic reactions, each of them being developed historically in its particular way and now differing essentially from the other two in both logic and mathematical formalism.

REFERENCES AND NOTES

(1) Korobov, A. A. Geometric-Probabilistic Approach to Heterogeneous Chemical Kinetics with respect to the IKP Ambiguity. *Thermochim. Acta* **1994**, *243*, 79−93.
(2) Korobov, A. The Rate of a Heterogeneous Chemical Reaction as a Measure of the Random Marked-Point Process. *Thermochim. Acta* **1993**, *224*, 281−289.
(3) Korobov, A. Solid-Phase Reaction Kinetics: Meaningful Kinetic Constants vs. Formal Parameters. *J. Thermal Anal.* **1995**, *44*, 187−196.
(4) Langmuir, I. The Constitution and Fundamental Properties of Solids and Liquids. *J. Am. Chem. Soc.* **1916**, *38*, 2221−2295.
(5) Brown, M. E.; Dollimore, D.; Galwey, A. K. *Reactions in the Solid State*; Elsevier: Amsterdam, 1980.
(6) Kuznetsov, V. I. *General Chemistry, Trends of Development*; Higher School: Moscow, 1989 (in Russian).
(7) Dvoretskiy, I. H. *Latin-Russian Dictionary*; Russian Language: Moscow, 1976.
(8) Korobov, A. Localization Phenomena in Heterogeneous Chemical Kinetics with respect to a Geometric-Probabilistic Description. *Thermochim. Acta* **1995**, *254*, 1−10.
(9) Delaunay, B. N.; Dolbilin, N. P.; Shtogrin, M. P. Combinatorial and Metrical Theory of Planigons. *Proc. Math. Inst. Acad. Sci. USSR* **1978**, *149*, 109−140 (in Russian).
(10) Stoyan, D.; Kendall, W. S.; Mecke, J. *Stochastic Geometry and its Applications*; Wiley: Chichester, 1987.

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