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PHILOSOPHY OF THE MECHANISM OF DIFFUSION CONTROLED SOLID STATE PROCESSES

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Despite the significance of solid state reactions both in the industry of traditional ceramics and in the development of modern construction materials and despite the long history of ceramic industry - the processes leading to products formation could not be efficiently approached by theory till now [1, 2] . From the beginning of solid state chemistry in the twenties of this century solid state physics achieved a tremendous progress. Likewise the substance of transport processes in solids and the mechanism of qualitatively different isolated processes have been discovered and explained, like adsorbtion, nucleation, diffusion, grain growth, sintering, creep,crack formation, propagation and so on.

In the same period solid state chemistry accumulated a great amount of empirical material on solid state reactions, on qualitative effects and semiquantitative dependencies of reaction rate and products quality, on the conditions of preparation of starting materials and compact, and on the conditions of reaction as well. The explanations of these effects are not always convincing as it has been perceived recently by several authors.

A similar situation appears in the trials to describe the kinetics of solid state reactions, where the present achievements do not seem to fulfill the goals of kinetics in general, i. e. to disclose mechanisms and to provide a foundation for the use of the reaction studied on industrial scale. These objects have been fulfilled by kinetics of homogeneous systems to a great extent. Thus the questions arose

- what is the reason of this unsuccess, of solid state kinetics,
- is it reasonable to expect success - equivalent to the achievements of the kinetics of homogeneous systems ?

To answer the first question three principal reasons could be set: In contrast to homogeneous systems it is not possible till the present days :

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i. to define the "state" of a solid reactant,
i.i. to describe unambiguously the state of a reaction compact,
i.i.i. from the points mentioned above follows the impossibility to describe a solid state powder reaction in a deterministic way.

The state of a fluid system could be exactly defined by a few parameters i. e. temperature, pressure and composition. The state of a solid depends on a multitude of variables experimentally difficult to determine. The mechanism - even of a simple solid state reaction - is given by a set of simultaneous and consecutive competitive transport phenomena effected in complex gradient fields, in a system of intricate geometry. Transport processes are locally driven by gradients of temperature, chemical and electrochemical potentials and by gradients of local stresses.

Present deterministic theoretical means enable solution of similar problems only in simpler cases. Irreversible thermodynamics approaches complex transport phenomena in systems of simple geometry. Cybernetics allows the solving of simple mechanism processes even in very complex - but definable systems.

Another point to be considered is the requirement of practice on kinetics. Both homogeneous and solid state kinetics had to find conditions for getting the product in the most intensive way and in the required quality. The required quality means in homogeneous reactions simply a determined composition - given by the starting composition of the reaction mixture and the final extents /conversion degrees/ of the individual simultaneous reactions. This goal is only in smaller extent interesting for solid state reactions i. e. in preparation of pure phases. Required quality in producing materials by solid state reactions means prescribed physical properties, or standard properties of the product in service - irrespective - or only secondarily dependent on phase composition.

From the point of wiew of theory the reaction conditions of the solid state reaction in technique are different and two extreme situations might be distinguished :

i. in producing voluminous, great mass products the finding of optimal temperature - time dependence during firing is a problem of instationary heat transport from the surroundings /furnace/ of changing temperature into the product, the calculation of temperature gradients and local strains - which may not exceed the instantaneous strength of the material. This problem can not be considered as being solved till now and is complicated by continuous changing of physical parameters of the fired ware - depending on time, temperature and space coordinates and by springs and sinks of enthalpy coming from chemical reactions.

ii. the second extreme condition of technical practice limits to isothermal one - when in fast firing technologies or laboratory practice small pieces of samples are reacted. In this case heat transport is fast and the development of phase composition of the product is controlled exlusively by long range mass transport/diffusion/ processes.

This latter case is the object of traditional solid state kinetics and of following considerations as well.

Let us investigate the principles of the todays approach to solid state kinetics in powder compacts i. e. in the so called ceramic reactions. The base of all trials to describe kinetics of simple solid state reaction was given by the success of Tammans /1925/ parabolic low, excellently proven both by theory and experimental evidence as well.The transfer to powder reactions started with Janders low /1927/ - modelling an element of a reaction compact with a sphere of one substrate enbedded into the continuous surroundings of the second one.

The mechanism of the reaction was supposed to be a solid state diffusion - with a constant value of the diffusion coefficient. Further improvements were made by extending the model to cylinders and other regular bodies /Valensi, 1935-36/ and considering volume changes joined with reaction /Ginstling - Brounstein, 1950/. Suggestions have been made to describe powder reactions by instationary diffusion models, without a moving phase boundary /Dünwald-Wagner 1934, Serin and Ellickson 1941/. Surprisingly came different authors - starting from quite different prepositions-to the same results as did Johnson and Mehl /1939/, Avrami /1940/ and Jerofejev /1946/ - though for different assumed mechanisms. Refinements followed by taking polydispersity of one reactant into account /Myagi 1951/, /Sasaki 1964/, /Gallagher 1965/ - the approach of each author differing in the combinations of the distribution function of grain radii with different features of the conversion-time functions - mentioned above.

An outstanding position in this branch has the Jerofejevs statistical approach. His "universal kinetic relation" - as stated by the author itself achieved just after expansion by Avrami popularity in nucleation kinetics but not in powder reactions, for his "reaction probabilities" could not be correlated with any physical quantity.

Surprisingly many authors of kinetic investigations till to the present days - try to find an agreement between traditional kinetics and experimental results. However the consent of experiment with theory is a necessery but not sufficient proof of the theory. As a matter of fact discrepancies between traditional kinetics and experimental evidence have been found as well, mainly in the following points :

- describing the course of the process up to high conversion degrees,
- often an expressive slowing down or halt of the process is observed long before reaching equilibrium,
- the temperature dependence of the rate constant does not agree with Arrhennius'low, /irrespective of Hedvalls effect/,
- the dispersity of the reactant - derived from rate constants does not agree with those experimetally estimated.

These problems gave rise to further improvements of traditional kinetics, as to the introduction of corrections for pseudo-equilibria /Gordejev, Syčov/ [3], to the presumption of surface layers with enhanced reactivity /Komatsu/ [4], to models of porous grains /Szekely, Ewans/ [5]. But it has been percieved, that not additional corrections of deterministic kinetic models are the proper way to further progress in this field [6] [7].

Moreover serious theoretical reservations might be set up against both the modelling principles of traditional kinetics and its method of deriving conclusions :

i. the physical models do not correspond with the referent object i. e. with a real green compact,

ii. the model object can not be described by deterministic models,

iii. the supposed mechanism of the process is in contradiction with todays knowledge on diffusion in real structures of solids.

iv. the supposed behaviour of an element of the system has been transfered to the whole - violating the principles of systems analysis.

A real solid might be considered as a set of mass points - the Gibbs'energy of which is not constant but a distributed quantity. Similarly the local values of transport coefficients are distributed as well, according to different possible diffusion paths in the solid. A real reaction mixture /compact/ is moreover characterized by local changes of density and of the molar ratio of reactants both caused by porosity, dispersity and necessary imperfection of homogenity of mixing. These effects together with residual strains cause a dispersity of local values of driving forces, of transport coefficients and of the local values of transport cross sections as well [8].

The "structure" of such systems can not be described unambiguously, so we have to resort to statistics. The probability density of each of these quantities might be defined by distribution functions. However each value of driving force might be combined with each transport coefficient and each local cross section value. Local "chemical flows" depend according to irreversible thermodynamics on local transport coefficients and the local intensive state [9]. Exact dependencies of local flow rates on the internal state of the elements are unknown. Thus but a phenomenological approach is possible. Consider the local reaction simply as relaxation of thermodynamic strains proceeding each with a definite rate constant. From the reasoning above follows that these rate constants will be distributed as well. Thus the reaction system might be sketched according to our crude phenomenological model as made up of groups of mass elements /homoreactive fractions/ each characterized by a definite value of the rate constant and occuring in the whole system in a certain mass fraction.

To specify, assume first a simple reaction system, where only a single product might be formed :

$A + B = AB$ (1)

/but similarly also $A + BC = AB + C$ (2)

$AB + CD = AC + BD$/ (3)

/Further indications according to (1) !/

The rate of consumption of a homoreactive fraction /i/ of the substrates /A,B/ defined by the rate constant /r_i/ might be described by an arbitrary simple growth low

$$\frac{dn_i}{dt} = f/n_i,r_i/ \qquad /1/$$

where n_i - the instantaneous amount of the substrate concerned, t - time and r_i the rate constant,that further will be called the "reactivity". Integrating /1/ with suitable initial conditions we get the "relaxation function" :

$$n_i = n_{io}\, F/r_i,t/ \qquad /2/$$

For the whole system - as the sum of all homoreactive fractions - holds

$$n = \sum_{i=1}^{m} n_i = \sum_{i=1}^{m} n_{io}\, F/r_i,t/ \qquad /3/$$

where n_{io} the initial amount of the reactant considered in the system, m - the number of reactivity fractions and n - the total amount of reactant, present in the system as an independent mineralogic phase. The conversion degree will then be

$$U = \sum_{i=1}^{m} X_i \left[1 - F/r_i,t/\right] \qquad /4/$$

Assuming a continuous distribution of reactivities :

$X = X/r/$

and derivating we get

$$dX = X'/r/\, dr = E/r/\, dr \qquad /5/$$

where $E/r/ = E/r,a,b, \ldots/$ the probability density of the occurence of the reactivity r, and a,b, ... the parameters of that "distribution function". Introducing /5/ into /4/ we get the relaxation function as

$$U = \int_0^{\infty} E/r,a,b, \ldots/ \left[1 - F_{r,t}/\right] dr = U/t/ \qquad /6/$$

As we have pointed out the function $F/r,t/$ might be different and its shape does not matter, when satisfying /1/ and suitable initial conditions. The apparent state of the reactants - in their actual situation in the reacting system under given reaction conditions are thus characterized by the distribution function $E/r/$ -

which is in relation to the "statistical structure" of the system but in no deterministic relation with any physical parameter.

Relation /6/ might be considered as a universal "grey box" kinetic model for diffusion controlled solid state reactions, as no complete information on the inward of system exists.

The $E_{/r,a,b,\ldots/}$ function - if once established its mathematical form - might be specified from experiment, i. e. from couples of U-t data by computer evaluation with the aid of some gradient methods using the least sum of deviations squares as a stop criterium.

Let us take into consideration our grey box kinetic model in general. Suppose, we had the structure of the system unamiguously defined by the set $S/s_1, s_2 ../$of structure parameters. Then - in principle - all physical properties of the system, done by the set $P/p_1, p_2 \ldots/$ are related to, and derivable from this set, i.e.

$$p_k = p_k\ /s_1, s_2 \ldots/ \qquad /7/$$

That means that the set of physical properties is equivalent to the set of structure parameters. However these relations are not exactly know and particularly for solids - till now - not recognizable. What we could define - say - more exactly for a starting powder system are two sets of input parameters : K_1 being the set of preparation conditions and K_2 the set of parameters defining reaction conditions. From these variables a definite but not completely known structure results, characterized, say by the set S_o of output parameters. To every couple of input $/K_1$, K_2, U/ and output $/S_o/$ parameters a definite inner state of the system has to be ascribed [11], relating to its microstructure and of course, to its physical properties $/P_o/$ as well. So kinetics provide additional information on the structure of the system - however in our case only in a phenomenological and complex feature i. e. by the $E_{/r/}$ distribution function. This function - or when more convenient its statistic moments - is dependent on all input parameters and represents an aid to study relations between K_{1i}, K_{2i}, S_i, P_i and S_o P_o /indexes : i-input, o - output/.

Let us now advance to a little more complicated case, to reactions where a single intermediate might be formed during reaction i. e. to reactions of the type /and similars as well - like above/ :

$$A + B \xrightarrow{A_2B} AB \qquad (4)$$

starting with a stoichiometric composition of the reaction mixture $/n_{oA} = n_{oB} = 1/$. Here the consumption of both reactants /A,B/ does not equal, so that the $U_{/r,t/}$ function /6/ has to be specified particularly for both A and B, resulting in different $E_{A/r/}$ and $E_{B/r/}$ functions. As the system consists during the reaction of four phases $/A,B,AB,A_2B/$ it is possible to evaluate the complete phase composition of the system from materials balance in dependence of time when $U_{A/t/}$ and $U_{B/t/}$ are known :

$$n_A = 1 - U_{A/t/} \qquad /8/ \qquad n_{AB} = 2\,U_{B/t/} - U_{A/t/} \qquad /10/$$

$$n_B = 1 - U_{B/t/} \qquad /9/ \qquad n_{A_2B} = U_{A/t/} - U_{B/t/} \qquad /11/$$

As the driving force of solid state reactions depend according to Mčedlov-Petrosjans thermodynamic concept [12] on the mixing ratio of reactants - the local reactions will depend on local compositions. In this case it is evident - as has been shown recently [10] that the reaction path is expressively dependent on the local inhomogeneity distribution and accordingly on $E_{A/r/}$ and $E_{B/r/}$ as well. Thus the systems phase composition development might be unambiguously described by /8/ - /11/. But this development proceeds not monotonously - but through local oscillations of phase composition - likewise manifesting themselves macroscopically by their superposition. The mechanism of the course of phase composition development is done by three phases

$$\text{phase 1.} \quad A + B = AB \quad (5) \qquad \text{phase 2.} \quad A + AB = A_2B \quad (7)$$

$$2\,A + B = A_2B \quad (6) \qquad \text{phase 3.} \quad A_2B + B = 2\,AB \quad (8)$$

The three phases of the total reaction might be considered as consecutive, but at the same time simultaneous as well - as the rates of the reactions in each phase differ by order. The specific course of the total process might be - in accordance with our "grey box" considerations - influenced by all input parameters of the sets K_1 and K_2 /e.g. milling time, mixing mode, pressing force, lubrication, reaction temperature, atmosphere composition a.s.o./. It has to be pointed out, that above considerations are valid likewise for reactions of more complex type /e.g. for reactions between binary and ternary compounds/, when preposition of one single intermediate has been fulfilled.

The oscillations experimentally observed might be reproduced by the proposed kinetic approach - moreover - they were recognized and theoretically explained by the aid of it [8], [10]. Observing structures development in space e.g. by microscopic or microprobe investigation - patterns are shown resembling dissipation or so called self-organizing structures [13], occuring in homogeneous or biological systems. Oscillations in homogeneous systeme are being explained either by deterministic kinetic modelling - firstly performed by Lottka /1920/ and Volterra /1931/ - presuming in the simplest case the coupling of two autocatalytic steps with irreversible reaction. The other /stochastic/ approach explains the effect starting with stationary fluctuations in systems out of equilibrium. However "the study of fluctuations in unstable systems is far from being complete" [13] p.243/. The existence of dissipative structures is being explained by coupling chemical reactions with autocatalytic steps and mass transport. This feature is similar to those we have in powder reactions.

The reaction scheme given in (5) - (8) presumes the transport of the substrate/A/ after phases 1. and 2. beyond the regions, where the partial reactions occur. However, the analogy is not quite unanimous, and remains open for further discussion. The oscillation of the products portion in the system and of its formation rate is strongly damped. Poor possibilities of quantitative phase analysis do not enable till now to get more exact foundation for deeper reasoning.

At last let us consider the problem in a fairly general way. The question would be : what are the preconditions for getting a system into oscillation ? We may set the folloving points : 1./the system must be intertial, 2./it must be elastic, 3./a possibility may exist to pass over equilibrium state.

Intertia - as the general property of mass might be a property of chemical and solid systems as well /it is - of course - not meant the inertia coming from the mass of the system as a whole/. So might be elasticity too - as the driving force of a chemical process is proportional to the distance from equilibrium. Third, the possibility to pass over equilibrium state - is given in systems where according to phase equilibrium at least one intermediate exists - either stoichiometric, or as a broader region of solid solutions. Concluding we may state that the oscillating effect has been observed just in systems, where the third condition was fulfilled - the first and second being general ones.

Thermal analysis has made an enormous progress in the last decades in its technique and possibilities. Simultaneously a bunch of skilled methods has been developed to evaluate kinetics from thermoanalytical investigations. The bottleneck seems to be solid state kinetics itself. A topic has been suggested for a new approach to diffusion controlled solid state kinetics. Outlooks and limits of the method have been discussed. From the approach suggested expectations of solid state oscillating reactions arose. Conditions and causes of this effect have been analysed. The approach seems to be hopeful in stimulating further progress and extension to more complex solid state reactions.

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