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STRUCTURE AND REACTIVITY OF SOLIDS

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ABSTRACT

The structural characteristics which determine the behaviour of solids under various conditions, especially during the interactions with other substances, are summarized.

INTRODUCTION

The term "structure" in the title implies the quality of the reacting substance with all its properties. The term "reactivity", on the other hand, refers to the conversion rate of the chemical change.

If we start from gaseous and liquid systems towards solid state reactions, we encounter many, always more and more complicated systems, where the number of reaction parameters continuously increase. Another parameter, e.g., concentration here loses total signification. Due to the complexity of solid systems the reaction rate cannot be interpreted in the usual way; on the other hand, the morphology and, even more, the atomic state of solids determine the chemical changes, the velocity and so on.

The reactivity of solids can be understood when the macroscopic phenomena are discussed at atomic dimensions, in the microscopic way. These elementary happenings are governed through the structure. Thus, structure and reactivity are closely interdependent. A single elementary reaction step can hardly be determined.

While in homogeneous systems, if a reaction has reached equilibrium no further changes of state occur. In solid reactants pre-treatments (heat treatment, mechanical working) may lead to quite different behaviour. Lattice imperfections are important participants. They could even be termed as reactants in the chemical reactions of solids.

The crystallographic shear phases (C.S.) are directing the atomic movements during reactions. Nevertheless, formal kinetic data do not render hitherto any

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picture about the true mechanisms on an atomic scale. In this respect one must not neglect the possibility of the capillary condensation inside the shears turning a gas phase reaction into a fluid one. Further remarks on these reactions fall outside the scope of this paper.

The reaction initiates only at these specific sites in the lattice, usually on the surface but within the bulk as well.

The non-isothermal measurements TG, DTA and DSC have yielded a tremendous number of data. The evaluation of these techniques has mostly been treated without any limitation or reconsideration as parameters of isothermal processes. For example, the activation energy, frequency factor which are to be treated as apparent data even at complex homogeneous processes. Solid phase reactions are usually inhomogeneous, as conditions of migration continuously alter the permeability and the time for this transition almost incontrollably changes, not to speak of the reactive intermediates formed by chance and which contribute essentially to the conversion.

The driving force of solid state reactions

It is not necessary to emphasize that the decrease of free enthalpy is the driving force also for solid state reactions. Schmalzried[1] treated the problem from a thermodynamical point of view. The migration of atoms was discussed on the basis of defects. The spinel formation has been chosen as a model involving cation diffusion. Nevertheless, the thermodynamic potentials are not always known, at least not under the circumstances of the process to be investigated. There are, however, several auxiliary laws, statements, etc. in chemistry which can give conditions, ways or possibilities for the taking place of a process, or at least rendering it probable.

As to the starting temperature of solid state reactions, espcially those of double decomposition, Tammann and Hedvall suggested some correlations to other thermic behaviours, e.g. melting point. Except for a few systems, their formula does not give any orientation about the subject. The topic of solid state reactions still today needs some functional relation.

It is trivial that the heating and the increase of intramolecular vibration can lead to rupture or rearrangement of bonds during decomposition or phase transformation. The rigid structure does not allow the slowing down of the dissipation of energy. This can initiate, especially if connected with some change of reaction volume, which causes strain, further nucleation and so starts further conversion. It should be mentioned here that partial melting, if only at a microscopic scale, or as a consequence of transient formation of eutectics can alter considerably the course of a reaction.

If there is no affinity between two solids, or if the affinity between them is very small, no real compound is formed but only a solid solution. There are also limits of solubility and the activity of the solute may vary between very wide limits.

In many cases an acid-base reaction, or in its more general concept of donor-acceptor interaction including also redox processes (Gutmann[2]), represents the affinity between reacting solids even if the acidic or basic character of the reactants is not obvious, e.g., in the second step of the reaction between $BACO_3$ and SiO_2 which gives $BaSiO_3$ and CO_2, when the overall reaction $BaCO_3 + BaSiO_3 = Ba_2SiO_4 + CO_2$ takes place, not to speak of sometimes quite large nunbers of intermediate phases.

The rate of conversion

So far the treatment of the reaction kinetics of solid phase processes can be regarded as the quasi-classical analysis. The only difference is that instead of concentrations, the mass of substances which have already reacted is accounted for. The correlation between rates of initial reaction and those of the following steps determines the overall progress of conversion. This is usually expressed in the form of fractional reaction-time ($\alpha \rightarrow t$) curves. Even a quick survey of kinetic treatments of solid phase processes makes it clear that quite a large number of further parameters must be taken into consideration. To mention a few only, e.g., the dispersion of particles, the number and size of contacting surfaces, the nature of various interfaces, including also the crystal imperfections, the different intermediates which may be formed and play the role of chain carriers, etc.

These parameters do not necessarily always and simultaneously control the velocity of conversion. It may even occur that the experimental conditions are such that only a few of them influence the rate when other factors are kept constant. However, it is very difficult to select the parameters which are to be regraded decisive and those which can be disregarded.

Reconsidering the complexity of the general rate equation of solids it is extremely difficult, in most cases even impossible, to find out the steps of the real mechanism. Some results have been achieved where the reactants have a rather simple composition with few components and with which there is no secondary reaction. Classical examples are the decompositions of azides investigated and analysed by Tompkins.

Solymosi assumed that with ammonium salts of halogen oxyacids the slowest step in the decomposition is most likely the proton transfer. Due to the instability of the chlorine-oxygen bond, oxygen stoms and one special radical ClO occur in these reactions which are fairly complex as a result of criss-crossing secondary steps. Thus the variety of products is unpredictable.

From a microscopical point of view the solids are never isotropic, in atomic dimensions lattice sites are not homogeneous, i.e., have not the same energy. Such sites are the edges, the peaks, in larger dimensions the dislocations etc. All these sites have an energy surplus, greater mobility, are able to start a local reaction, hot spot, nucleation, followed by increasing disorder, especially vacancies which then facilitate the progress of a reaction front. During decomposition processes, the increasing number of molecules represents an intensive mechanical stress disrupting the lattice framework, preparing further nucleation possibilities. Thus the progress of such a reaction is mainly controlled by this mechanical process and less by migration of particles. It is interesting to mention that this mechanical phenomenon can be described by the kinetic treatment of the gas phase chain reaction.

Thus it is better to speak of the velocity of the running process, or the rate of conversion by fractional transformation, i.e. the actual amount related to the initial mass of substance or substances which is designated by α. Of course, the classical rate equation alters its shape. The most important expressions for the conversion rate are:

$1-(1-\alpha)^{1/3} = kt$	(contracting volume)
$\alpha = (kt)^{n}$	(the power law $n = 2-4$)
$-\ln(1-\alpha) = k(k_G t)^{3}$	Erofe'ev's equation
$\ln\alpha = kt$	exponential rate law
$-\ln(1-\alpha)^{1/n} = k(t-t_o)$	Avrami Erofe'ev equation
$\ln\alpha(1-\alpha) = kt + c$	Prout-Tompkins equation

An expression suggested by Jander takes the number of contact points between particles into account.

These curves are sigmoid in shape: the first stage, the initiation state, which of course has the greatest activation energy - this secures that stability of the system - and generates dislocations of further sites of high energy more favourable to reaction due to the evolved stress, when the very reactive intermediates - showing smaller activation - interacting with the reactant. The third stage, the deceleratory period, when the adjacent product reduces the interactions between the reactive intermediate, and the initial substance is present already in small amounts. The cascade-like stages takes the more place the more instable the substance or the intermediates are, i.e., the weaker bonds between the atoms lead more easily to stable products with strong bonds.

Considering these circumstances, it is quite understandable that the velocity of such interchanging processes may vary between extremely wide limits.

As the reactivity manifests itself in the reaction rate, the experience shows that the degree of conversion is influenced by numerous parameters, thus an equation for reaction rate takes approximately the shape.

$$w = F(T,\ m, n,\ i, g,\ x_I \ldots x_n)$$

where T = temperature, m = mass of reacting substance or substances usually denoted by α in rate expressions, n = number of contact points between particles, thus i controls the interfaces through which the migrating species must pass. If the process is running down by such intermediates which are sensitive to ambient gas then g represents this effect, x_I ... x_n are parameters of further possible rate influencing effects.

The Arrhenius equation for the temperature dependences usually holds. However, E, activation energy, as well as A, preexponential factor, are never simple parameters but rather complicated summations of energy and/or entropy components of different partial steps.

A clear approximation is:

$$\frac{dx}{dt} = \left(\frac{Z\mu E}{RT}\right) x_o \exp(-E/RT)$$

by Polanyi and Wigner, where μ is the vibration frequency, which is expected to be $\sim 10^{13}$ sec^{-1}. As the preexponential factor may be regarded as a picture of the transition state, its low value indicates a highly ordered complex: a tighter arrangement means the reaction is affected by the neighbouring attached molecules. A high value of the preexponential factor points to a looser or mobile complex.

Between homogeneous and heterogeneous processes there is quite a great difference. However, they have also a few features in common. The fundamental definition is: bonds bread down and new ones form. The process from the initial to final state goes via a transition state, building up from the components of the original atoms or groups, and may revise or advance in both directions. In atomic dimensions this involves the principle of microscopic reversibility and giving the possibility for influencing the conversion course.

The lattice at clean crystal surface is constructed with a smaller coordination number than in the bulk. This implies shortening of bonds between the surface atoms (Lennard-Jones, 1928; a bond length variation rule Gutmann[2], 1976) and thus the increased surface energies increase the reactivity. At these sites there is an ample, though extremely sensitive, possibility for nucleation.

The initiation steps may be either transfer of one electron if the bond is of rather ionic nature or breaking of the weakest covalent bond connected with switching over one atom. Both ways result in groups of atoms. These uncharged groups of various stability have different life times and can thus be considered as intermediates possessing enhanced reactivity. Owing to this they propagate the solid phase process interacting with the initial reactant which may lead to chain-like, even branching chain-like processs, especially with strongly exothermic decompositions, which may even lead to an explosion.

It is formally possible to describe it mathematically without much chemistry. A convincing explanation has been experimentally shown where the process was interrupted by cooling for some time. Then the reheated reaction substance proceeded at a rate measured at the former temperature without any induction period. This behaviour is analogous to the phenomena experienced in homogeneous gas phase reactions where the chain carriers can be frozen in. That here, in solid state processes, the "chain carriers" are not energized particles, has also been proved in the presence of different gases. During the reaction some gases can alter the velocity of conversion in positive as well as in negative direction. This can happen due to an interaction between the ambient atmosphere and one or more intermediates. Due to the enhanced reactivity of the latter a reaction takes place with the gas, mostly exerting an inhibiting effect through blocking the reactivity. Such an effect is a strong proof for existence of intermediates.

One can also observe that neutral gases, especially noble gases may interfere with the decomposition of some solids. Careful measurements have shown that their effect is a function of $1/\tau M$, M being the molecular weight[3]. In this case the rinsing out of product gases may accelerate or inhibit the conversion according to the microscopic reversibility. The thermal decomposition of silver oxalate made convincingly clear the nature of chain carriers. The excellently reproducible kinetic curves shifted towards different directions depending on gases applied (cf. later).

These intermediates, being much more reactive than the starting substance, can sometimes accelerate the conversion towards explosion. This is the case with solid explosives. With such a chain-like conversion it occurs frequently that some foreign substances, often as impurities in very small amounts, can alter the velocity of reaction by annihilating these active intermediates, i.e., breaking down the chain. It is sufficient here to mention Nobel's invention on production of dynamite where infusorial earth had decreased the brisance of the nitroglycerine.

Another point is, that also the bulk substance may considerably alter the physical and chemical properties, e.g., the ionization potential, whereby such oxidation states arise, which commonly do not exist.* Such stages are usually very reactive. The change reactivity at microcrystalline solids and very thin layers has beeen demonstrated by X-ray measurements, and also by Mossbauer isomer shifts.

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* e.g. the dielectric constant in interstitial position is $\epsilon_{Ge} = 16.1$, thus the ionization energy of Ge-atom is $1/259.8,13 = 0.0314$ eV only. Thus an interstitial Ge loses its electron already under the thermic effect.

Further intrinsic influence is exerted by electronic orbitals. The new techniques have made possible the application of high and even very high pressures (several 100 Kbar) leading to shifts in physical as well as chemical behavior. As the valence band is primarily determined by the anions and the conduction band by the cations, e.g. reduction of Fe^{3+} to Fe^{2+} with all the consequences of its electrodynamical behavior.

The compensation effect ($\log A = B + eE$) has often been observed. This points to the fact that the apparent activation energy and the activation entropy in many cases may be correlative. This correlation would merit more attention. In any case, the correlation of A^+ and E^+ points to the same reaction step.

For a solid state reaction it is extremely important that the stable cloud of electrons becomes loose, i.e., the original, especially spherical symmetry at higher temperatures deforms. One consequence of this is the change of reactivity due to the more or less decreasing bond strengths of certain components: in other words the affinity changes. Perhaps, the best known case is the change of affinity of proton towards some or other parts of the molecule during the thermal decomposition of ammonium chloride. At room temperature the proton affinity of NH_3 is greater. Therefore H_4N^+ and Cl^- ions are formed. At heating the proton affinity of the Cl^- ion enhances, the proton slides over onto the Cl^- ion, resulting in $H_3N + HCl$ products.

The polarization thus plays a distinguished role in reactivity with dependence on temperature. In ionic salts, cations of greater polarizing power, due to their smaller dimension, deform the more easily polarizable anions. The cation disturbs the amphibious components of the anion: thus metal oxide and acidic residue forms. The tendency of differently deformed electron clouds which controlled the stability of salts is working also in double decomposition, as in the following examples:

1) $NaBr + KCl = NaCl + KBr$	H.L. Link & L.J. Wood (1938)
2) $AgCl + NaI = AgI + NaCl$	C. Wagner (1938)
3) $CsCl + NaI = CsI + NaCl$	Massarotti & al. (1977)
4) $CdTe + HgSe = CdSe + HgTe$	Leute & al. (1977)
5) $Cu + AgCl = CuCl + Ag$	C. Wagner (1938)

where also the redox relations are operating. There is here also a striking common feature: the larger the size of the anion, the easier it combines with a larger cation. The ratio of r_{anion}/r_{cation} is a fairly right measure for polarization and can be termed as "<u>principle of least deformation</u>" of electron shells: <u>PLD</u>". Thus the condition for the reaction $AX + BY = AY + BX$ is

$$\frac{r_x}{r_A} + \frac{r_y}{r_B} > \frac{r_y}{r_A} + \frac{r_x}{r_B}$$

being of a rather general validity in structural chemistry elucidating several properties of solid phases as melting point, colour solubility, etc.

By transforming this inequality we get

$$r_A r_X + r_B r_Y < r_A r_Y + r_B r_X.$$

This more advantageous transformation expresses the "principle of maximal shrinking of bond distances". This formulation is more general as it is not confined to ionic crystals. The solid state processes seem also to obey Pearson's rule as to hard cations combined with hard anions and vice versa, because the hard and soft quality of reactants can be substantiated by the geometrical parameters.

After discussing the general features and laws of solid state processes I should like to speak about two groups of reactions where the processes reveal some typical representations.

1. Dehydration together with dehydroxylation

If the dehydration does not initiate at the surface only but from bulk nuclation, too, the rate can be described through the contracting cube equation by Jacobs and Tompkins. In many cases the internal migration of water leads to an incomplete and reversible process. The removal of water from layer structures happens frequently from hydroxyl radicals but of course at considerably higher temperatures. This requires minimum displacement of lattice structure, i.e., the Rice-Teller principle materializes.

The oxyhydroxides of metals of changing valency states involve, apart from proton transfer, also an electron transfer, releasing oxygen. The hydroxyhalides decompose at increasing polarizability of anions with greater velocity.

Another charateristic of dehydrations, being endothermic reactions, is that they decrease at lower temperatures without recrystallization. Infrared measurements proved this. The recrystallization under such conditions being slow, the system can take up the water molecules very easily: this is the "memory effect".

Mixed hydroxides decompose into mixed oxides at lower temperatures than the formation of mechanical mixed oxides. Here the metal oxides are reacting in the "nascent" state. Coprecipitation often does not lead to a homogeneous product.

The addition of nickel formate to magnesium formate significantly reduced the temperature of decomposition. The same is also true for mixed oxalates.

The thermal decomposition of oxides show general features to find some regularity for them. Special difficulty arises with more noble metal oxides due to secondary processes, the recrystallization of reduced metal particles into bulk, where considerable surface energy may evolve - without any dissipation of heat.

Another phenomenon of dehydration is the appearance of pseudomorphism. The dehydrate substance maintains its external morphology, though X-ray shows the total transformation into another phase. This has been proved, e.g., by the unchanged catalytic activity.

2. Decomposition

Generally, the conversion temperature is lower with greater polarization of the anion, i.e., the smaller the cation radius. Kinetic parameters are consistent with the Polanyi-Wigner equation. Comparing the decomposition temperatures of $CaCO_3$ and $MgCO_3$, 934-1043K and 813-873K, resp. with that of dolomite (900-950K) one can see that in dolomite the formation of the electron cloud of CO_3 anions is equalized. In other words the MgO is stabilized and CaO is destabilized in dolomite.

A large number of decompositions of coordination compounds have also been investigated. These may be interesting from one or another point of view. Nevertheless, due to the thermal behaviour of ligands the many various routes are more characteristic of the ligands than the general mechanism of the solid state processes. Therefore, I have abandoned the discussion of this topic.

The thermal decomposition of silver oxalate offers an example of the properties of the transition state. The kinetic curves were shifted towards slower rates when the decomposition took place in a CO_2 atmosphere. The decomposition almost ceased (130°C) when we admit O_2 into the reaction vessel. The rate hardly differed when the decomposition was carried out in vacuo or in an inert gas. The fastest decomposition occurred in the presence of hydrogen and helium. We obtained a monotonous function when the influence was plotted as a function of the reciprocal of the square root of molecular weight of the gases. This time the gases play a "rinsing" role proportional to their molecular velocity, i.e., they remove the gaseous product formed from the environment of the decomposing substance and thus enhance the conversion.

The transient species formed in the transition state may, under certain circumstances, be stabalized. The decomposition of silver oxalate is an example. This reaction always began after an induction period. On interrupting the process during the rising period, by withdrawing the silver oxalate into the colder part of the reaction tube, the decomposition stopped completely. Subsequently, on pushing the sample back into the previous hot zone, the kinetic curve did not show any induction period and the reaction proceeded at the rate measured at the former temperature.

The thermal behaviour of silver oxalate has shown not only that the decomposition takes place through a transient product or products, but also that these products can be frozen in, in spite of their great reactivity. Further, they are very sensitive to the environment because, e.g., atomic silver - probable chain carrier - reacts with oxygen, thus losing a substantial part of its reactivity. Here two entirely different effects are working. The CO_2 and O_2 react with the chain carriers and paralyse them. The extremely fine, nearly atomic silver, the presumed chain carrier is not as noble a metal as in its bulk state.

Silver oxide decomposition, especially during reduction at $T < 100°$ by hydrogen, yields silver of different morphology. We get mercury-like drops at 120°, which is due to the extremely fine dispersion. However, this never occurs if the oxide is distributed on the surface of the alumina. On the surface of the alumina no movement is possible and thus no coalescence can take place. This extremely fine silver can be oxidized and again reduced by hydrogen several times before reaching the bulk state. Even this finely dispersed silver on alumina exhibits the "spill over" process.

Migration and interfaces

Displacements in solids are only possible when the geometrical conditions, i.e. the size of ions and the interstitial volumes, promote the defect structure of the phases, e.g. vacancies, dislocations facilitate them. In any case the energy of the migrating ion must be sufficient to surmount the attractive force of ions of opposite charge and the repulsive effect of ions of identical charge.

The top most ambition of thermal analysis should be to establish any well founded relation for the onset of the reaction in solids as a function of temperature. The function cannot be unequivocal and simple, because the past treatments of solid systems play determining conditions on reactivity. Only standardized conditions may be correlated.

The reactions between solid-solid phase occur at interfaces and the reacting species must migrate to and through the active reaction zone. The conversion rate is controlled by diffusion, which takes place preferably on paths of imperfection. From empirical data it seems, that the A.E. of diffusion is the smallest although it may also depend on the shape of particles. As the interface layer increases the overall rate diminishes and the process shows deceleratory shape. Some sorts of catalysis, however, may accelerate the interaction, or if one of the products is volatile, the geometrical condition can enhance the conversion. In most inorganic systems the cations are - by chance - mutually migrating while the larger anions, generally the oxygen framework, do not considerably alter their position.

Until now the concept of interface has been used for the transition zone between the reactant and product or between two reactants. Through this zone it is assumed that the chemical step is slow and controls the rate. In numerous cases it is experimentally proved to be true.

But we must differentiate between the main and the bulk interface in which the migration can be measured (cf. Wagner experiments) and the surely thin layer which contacts directly the reactant. In my nomenclature this zone is where the chemical reaction takes place.

We have every reason to assume that at interfaces, especially at the very first formation, when there is a great disorder, also uncommon valency states occur and contribute to enhanced reactivity.

The uncommon oxidation states in interfaces is supported by the Wagner-mechanism of cation defects. We are not very much informed about the reactivity of these states. In any case, the nitridation temperature of Mg is substantially lowered if Mg is covered with MgO or even with Al_2O_3. It was assumed that, in the interface Mg/MgO, a Mg^+ ion formed and this already reacts with N_2 at 600°C instead of the usual 700°C temperature. An ion in an unstable oxidation state is much more reactive than in the normal state.

In numerous investigations we have found that the electric conductivity and catalytic activity of solid oxides or their mixtures, to a quite mysterious state show surprisingly extreme values between 600-799°C. Until now this phenomenon has not been elucidated. Today we only hope that in some way this phenomenon will be cleared.

Technique

Migration is a time process and a higher conversion rate can be expected only if there is a short distance of migration. Thus, in solid-state reactions we have to aim for a situation where the reaction components are originally close to adjacent positions, so that only a shift is necessary rather than a migration. This condition can hardly be accomplished macroscopically, but it can be by spray-decomposition. In this procedure a solution of two or more (in principle an unlimited number) compounds in arbitrary proportions is sprayed through a medical inhaler with a high-speed carrier gas in the form of small droplets (3-4 µm) into a pre-heated furnace where evaporation and thermal decomposition take place so quickly that no segregation can at all take place. In a mixture of oxides the rearangement to the final product is no longer a time and energy consuming migration but only a shift. In this instance the otherwise high-temperature treatment is not needed and the product will not be oversintered or overtreated, e.g. in spinel formation. At the same time, the extra activation energy necessary for passing the product-interphase can be saved. The surface area is several hundred times larger than in the traditional process.

I am of the opinion that this way of production of composite solid phases in future occurs often, and has hitherto not been regarded sufficiently as a possibility to offer a solid compound of high surface area and, if necessary, catalytic activity. Of course, the catalytic effect of proper impurity added, e.g. excess cation, should be considered.

In order to follow a solid state process, the position of the initial reactant-reactant contact surface can be fixed through insertion of inert marker which does not move with the advancing reactant-product interface. The electron probe microanalysis offers a quick and convenient tool to obtain information about the change of the reaction zones.

The conditions for the position of the sample within the reaction vessel influences intensely the whole conversion, its velocity, product formation, etc.

I have made an attempt to summarize the fundamental laws of reaction kinetics in solid phases and the structural correlations which govern them. Due to the tremendous literature this was not an easy task.

REFERENCES

1. H. Schmalzried, Reactivity of Solids, Fifth Symp. Elsevier, 1964, p. 204; Eighth Symp. 1986, p. 237.
2. V. Gutmann, The Donor-Acceptor Approach to Molecular interactions, Plenum Press, 1978, p. 14., 71., 79.
3. Z.G. Szabo and I.K. Thege, Thermal Analysis, I.C.T.A. 80, Bayreuth V.2. Birkhauser, p. 229.
4. Z.G. Szabo, Thermal Analysis, Budapest, 1 (1974) 19.