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MICRODYNAMICS OF SOLID-STATE REACTIONS *

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ABSTRACT

The fundamental laws of reaction kinetics that govern the processes in the solid-state are discussed. The transition state, the microscopic reversibility, the intermediates between the initial and final states, their particular reactivities, etc., furnish the possibility for elucidating many experimental findings that mostly have not hitherto been explicable.

INTRODUCTION

The classical reaction kinetic analysis of results obtained by laboratory measurements usually leads to the Arrhenius equation from which, although not always, we can gain some idea about the mechanism. If the rate equation shows a simple rational order, the pre-exponential factor and the activation energy can also be simple quantities. The reaction order, if not simple, points to a complex process and both $S^{\neq}$ and $E^{\neq}$ are composite, i.e., the algebraic sum of partial entropies and the activation energy, respectively. This treatment belongs to the category of macroscopic dynamics and is often satisfactory in gas- and liquid-phase reactions. We have many data on solid-state reactions but their treatment must be different, as we have to take into account that the concept of concentration has here no meaning and the activation energy is not a characteristic value. Nevertheless, it is possible to obtain some idea of the atomic events.

Transition state

With solids the reactant is also activated as a result of the resonance superposition lattice vibrations. The overall activation energy indicates that the process is hindered by some barriers and, to overcome these, an energy of activation is needed. Such barriers also appear when the particles are migrating.

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* Dedicated to Professor Viktor Gutmann on his 65th birthday.

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Microscopic reversibility

In any case, a transition state is built up somewhere between the initial and final stages through simultaneous bond loosening and bond formation. This can lead to a state of equilibrium or at least to a stationary state from which the reacting atoms or molecules may proceed towards the product, but may also return to the initial compound. This is expressed by the principle of microscopic reversibility and also furnishes the possibility of external interference. If the transition state is a relatively stable formation, there may be two kinds of intermediates: (1) loose molecules and (2) radicals. The rearrangement, with energy release without dissipation, leads to a "hot spot". The intermediates may also initiate a chain, although there are ample opportunities for breaking it. The reactivity of this nascent state is not the same as that of a block substance. The intermediates can also become catalysts.

Sources of enhanced reactivity also include lattice imperfections which may exist under certain conditions in the metastable state. Changes in the parameters, depending on the substance, can increase their number but can also reduce them, i.e., the disorders may be repaired. Their number, however, may increase above a certain temperature and this and the size of the oscillation amplitudes increase the reaction rate. All of these are manifested in migration.

Migration is a time process and a higher rate can be expected only if there is a shorter 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 rather than migration only a shift is necessary. This condition can hardly be accomplished macroscopically, but it can with

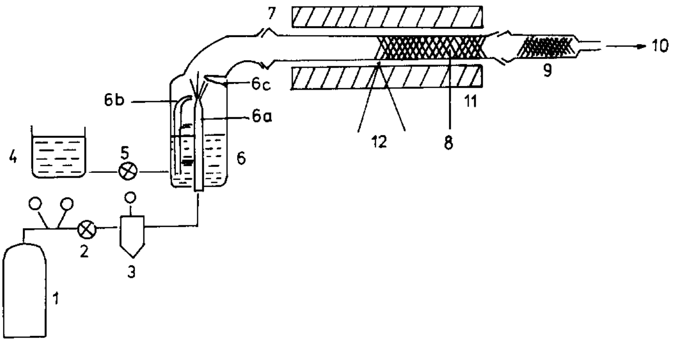

Fig. 1. Apparatus for spray-decomposition. 1 = Carrier gas; 2 = needle-valve; 3 = flow controller; 4 = solution supply; 5 = cut-off tap; 6 = spray generator (glass medical inhaler); 6a = gas jet; 6b = solution jet; 6c = glass rod to retain the coarse fraction of the aerosol; 7 = quartz-tube; 8 = quartz fragments as packing for better heat transfer; 9 = filter; 10 = gas outlet; 11 = electric furnace; 12 = thermocouple (temperature controller).

spray-decomposition (Fig. 1) [1]. 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 into a pre-heated furnace in the form of small droplets where evaporation and thermal decomposition take place so quickly that no segregation can take place. In a mixture of oxides the rearrangement into the final product is no longer a time- and energy-consuming migration but is 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.

Migration

In connection with migration, an essential step in solid-state reactions, an interesting phenomenon has been observed in the $Cr_2O_3 + H_2$ system by the measurement of electrical conductivity at about 300 °C with hydrogen being introduced in small pulses (Fig. 2). The conductivity of Cr_2O_3 decreased to a great extent but after a few minutes the initial conductivity was re-established. This effect was repeated several times with further pulses, but finally the resistance of Cr_2O_3 attained a steady, fairly high value. The explanation of the phenomenon is as follows [2].

Cr_2O_3 is a p-conductor, and the defect electrons on the surface of the particles are destroyed under the influence of a small amount of H_2. As the electrical conductivity occurs merely on the surface of the particles, the destroyed defect electrons are supplied through diffusion from the bulk of the particle. After a certain number of H_2 pulses, the route to be passed by diffusion becomes so long that the defect electron supply is not able to restore the original conductivity and thus a stationary state is reached.

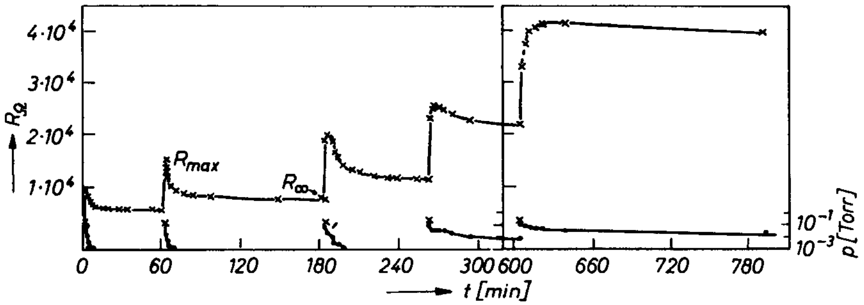

Fig. 2. Dependence of the resistance of a chromic oxide pellet (×) as a function of time after additions of hydrogen. (●) Measured hydrogen pressure.

This experiment explains convincingly the low diffusion rate in solid Cr_2O_3.

Principle of least motion

In addition to the short migration and shift already mentioned in the analysis of the elementary steps in solid-state reactions, it is advisable to take into consideration the Rice-Teller principle of least motions [3] and also the fact that during the reaction not only the atoms are trying to reach their final position from the initial structure by the shortest route, but that this requirement, maybe even more strictly, holds true for the rearrangement of bonds, i.e., of electrons also. In principle it can be imagined that with the transformation of a molecule (isomerization, decomposition) different final products may be obtained, in side reactions, via different reaction pathways. The main product will be the one in which the rearrangement of electrons can proceed with the least motion. It is also interesting that in most instances four or six centres are favoured in building up the transition-state complex [4], which seems to be a condition relating to the bond angles. A certain strain in the transition complex has to prevail. Thus the state with five centres in which the strain is the smallest, is extremely rare and with three or seven centres the strain is so great that the possibility of such a transition state is very small. There may be circumstances, however, e.g., neighbouring effect, solvation, where the transition complex has these rare centres.

Anyhow, the principle of least motion provides a strong selection rule for establishing the mechanism, as it automatically excludes certain side reactions or makes them at least improbable.

The reactions taking place in solid states can in many instances yield a number of by-products. These originate either in side reactions or, perhaps, in several subsequent steps. If the above-mentioned selection principles are valid this can only happen if there is not a great difference between the various reaction paths, atom and electron migration, such that one route would be exclusive.

Proximity effect

The sequence of such simultaneous reactions depends, however, on certain external parameters and on the neighbourhood of atomic environments. Their changes, however, may also influence the side reactions and may alter the product concentration considerably. The thermal degradation of NH_4NO_3 is a convincing example, leading, in addition to N_2O, to several toxic and inert products (NO, NO_2, N_2) when the solid is heated. The production of N_2O is, however, almost stoichiometric [5] if the decomposition takes place in a high temperature melt as a solvent. It is also known that certain reactions may take place in the solid phase only in the presence of a trace amount of water or in a molten state in micro-environments.

In the former instance the solvation layer exerts a neighbouring effect; this, however, may also be true in the latter instance when the molten substance either can reach the transition state more easily or the sample can be considered as solvated by its own melt.

Principle of least deformation

The energetics of solid-state reactions are naturally regulated by laws of thermodynamics. If, however, the required data are not available, we can obtain some information in this instance also, e.g., about the direction of the reaction $KCl + NaBr = KBr + NaCl$, based on the fact that the spherical electron shells of the ions prefer to become less deformed. This is the principle of least deformation [6]. As a consequence, the cations and anions will combine with each other such that the larger cation will form a compound of lower free energy with the larger anion, and vice versa. It is probable that the decrease in ΔG is not derived from ΔH but from ΔS. This principle is equivalent to the relationship of the bond distances:

$$(d_{AX} - d_{BY})^2 > (d_{AY} - d_{BX})^2$$

where the ds are the corresponding bond distances in the reaction $AX + BY = AY + BX$.

Surface energy

The fine grinding and dispersion of solid phases gives rise to a rapid increase in the surface free energy, which is why the system becomes unstable. On the other hand, the surface free energy depends on the state (cleanliness) of the surface to a considerable extent. Minimal contamination, e.g., even a monolayer of gas adsorbed on the surface, can decrease the energy substantially and hence also the instability. This explains the role of the carrier in heterogeneous catalysts in maintaining the activity of the catalyst.

It is probable that, e.g., in spinel formation the oxide particles ground separately to the limit $r < 1$ μm are unstable and agglomerate and thus the expected small particles will not react after mixing with the other oxide component. On grinding the mixture of the oxides there is the possibility of the mutual agglomeration of mixed particles, which will lead to a spinel.

Electrical interactions

The catalytic activity of a thin nickel layer, reduced on the surface of pure and/or doped NiO, has already indicated the electrical interaction between the carrier and active substance. This interaction, however, is effective only at very short distances [2]. It the reduced Ni layer is thick ($> 1\ \mu m$), the effect induced by the carrier no longer occurs. This could be observed in the activation energy of reactions catalysed by Ni, which could be reduced to a surprisingly low value by suitable doping. A thicker Ni layer has shown the same activation energy as that measured on bulk Ni.

Microstabilization of phases

We have observed a similar and surprising reducing power of newly precipitated $Fe(OH)_2$ when it was deposited on MgO [7]. Fresh $Fe(OH)_2$ itself ages quickly and it is not able to reduce, e.g., the NO_3^- ion to ammonia; we must use silver ion catalysis in the analytical application for the determination of NO_3^- ion by its reduction to NH_3 in an equivalent ratio of 1 : 8 [8]. The reduction was completed, however, with $Fe(OH)_2$ precipitated on MgO.

These phenomena strengthen the old comment that a substrate to be catalysed makes its own catalyst.

Intermediates

The nascent state may lead to a fine, unstabilized, agglomerated product that does not show the property of the bulk substance, e.g., reducibility. By bringing two substances to a nascent state simultaneously, e.g., by simultaneous decomposition, the transformation into a new substance—the product—can be made favourable.

Influencing solid-state reactions

The thermal decomposition of silver oxalate offers an example of the properties of the transition state [9]. The excellently reproducible kinetic curves were shifted towards slower rates when the decomposition took place in a CO_2 atmosphere (Fig. 3). The decomposition almost ceased (137 °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. Hauffe related this phenomenon to the ionization potential of the gases concerned. However, this does not hold, nor does the dependence on thermal conductivity (Fig. 4).

On the other hand, we experienced running down in the same direction when the influence was plotted as a function of the reciprocal of the square root of molecular weight of the gases (Fig. 5). 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 sub-

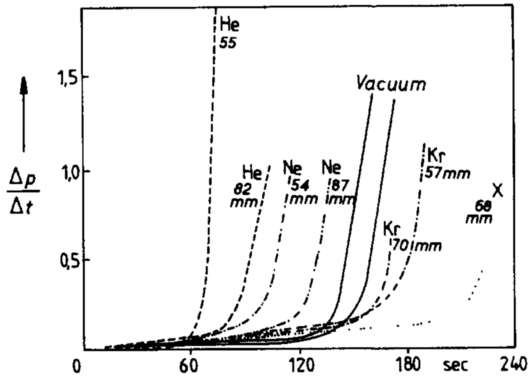

Fig. 3. Reaction rate versus time in the presence of various gases.

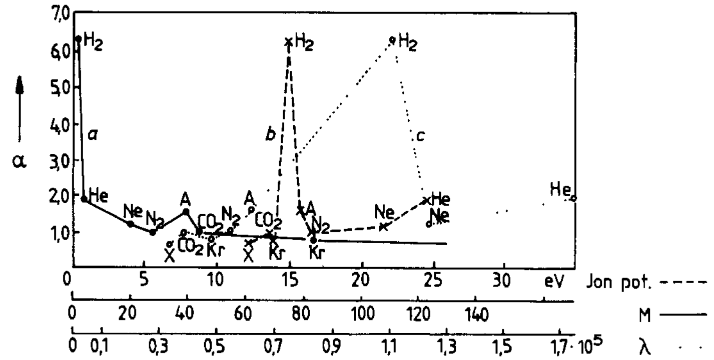

Fig. 4. Acceleration coefficient, α, as a function of (a) molecular weight, (b) ionization potential (eV) and (c) thermal conductivity.

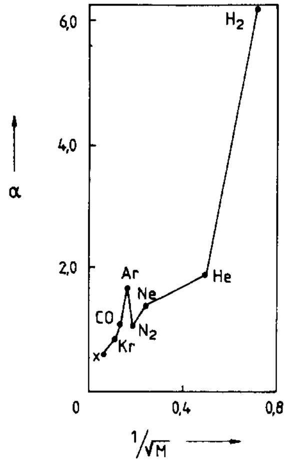

Fig. 5. Acceleration coefficient, α, as a function of $1/\sqrt{M}$.

stance and thus enhance the conversion [10]. It has been found experimentally that in reactions with evolving gas the substances must be laid on a flat. plate-like sample holder.

The transient species formed in the transition state may, under certain circumstances, be stabilized. The decomposition of silver oxalate is an example. This reaction always began with an induction period, then the kinetic curve declined after reaching a maximum. 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. This behaviour is analogous to the phenomena experienced in homogeneous gas phase reactions, where the chain carriers can be frozen in.

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—probably the chain carrier—reacts with oxygen, thus losing a substantial part of its reactivity.

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