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EXCHANGE CHEMICAL REACTIONS IN SOLID PHASES AND CONTACT BETWEEN REACTING PARTICLES OF SOLIDS

One of the necessary conditions for chemical reactions between solid substances to proceed is the formation of close contact between the particles of the reacting substances. The presence of such contact is also a necessary condition for the solid reaction product to exert a catalytic effect on the reaction taking place. The absence of such an effect when solid reaction products are mixed and ground with the initial solid substances is explained by the weak contact of the externally introduced catalyst with the particles of the substance entering into the reaction (*1*). Experimental data confirming this assumption are lacking in the literature. Meanwhile, these questions are of primary importance for understanding the mechanism of heterogeneous chemical reactions and for clarifying the nature of the self-acceleration observed in these reactions. Reliable methods that would make it possible to judge the contacts ensuring the course of solid-phase reactions under the corresponding conditions have not yet been proposed. The use of radioactive isotopes for these purposes (*2*) has not given positive results. Chemical analysis of a powder mixture with the use of a solvent will lead to incorrect notions about the contacts.

In the present work, on the basis of a study, by the method described below, of a series of heterogeneous chemical reactions, it is experimentally shown that, when powdered solids are ground or pressed, a contact is formed that is sufficient for chemical reactions to proceed and, consequently, also for the catalytic action of a solid product, if the self-acceleration of the reaction is due to it. The results obtained by us with the aid of this method make it possible to draw a number of important conclusions bearing on an understanding of the mechanism of solid-phase reactions. The proposed method is based on reactions that lead to the formation of products less stable than the initial substances and decomposing with the evolution of gaseous products at lower temperatures than the starting substances.

We have studied in detail the reaction in solid phases between silver sulfate and sodium sulfite. Both salts were heated for 6 hours in vacuum at 200° in

Figure 1 and Figure 2

Figure 1: Figure 1 and Figure 2

order to remove adsorbed gases and moisture. The first salt melts without decomposition at 652°, while the second decomposes at a higher temperature. Under suitable conditions the indicated salts react, as a result of which sodium sulfate and silver sulfite are formed; the latter, as we have shown (*3*), decomposes in the temperature range 160-200° with the formation of silver, silver sulfate, and SO_2. The course of the reaction between Ag_2SO_4 and Na_2SO_3 and the formation of contact between the solid particles of the indicated salts can be judged from the change in pressure in a vacuum apparatus. A mixture of salts prepared without grinding or pressing was heated in a vacuum apparatus for 4 hours at 190°. No gas evolution was observed in this case. Apparently, in this case contact sufficient for the reaction to proceed was not ensured between the crystals. However, a mixture previously ground in a porcelain mortar for 2 min., decom-

is released in vacuum at 190° by 17.5%, calculated from the amount of silver sulfate that has entered into the reaction. A pressed tablet of an unground mixture of silver sulfate with sodium sulfite decomposes at 190° by 88% with the evolution of sulfur dioxide. This indicates that, when the mixture is ground or pressed at room temperature, good contact is ensured between its components, leading to the exchange reaction

$$Ag_2SO_4 + Na_2SO_3 = Ag_2SO_3 + Na_2SO_4. \quad (1)$$

On subsequent heating, silver sulfite decomposes into metallic silver, silver sulfate, and sulfur dioxide

$$2Ag_2SO_3 = 2Ag + Ag_2SO_4 + SO_2. \quad (2)$$

As can be seen from Fig. 1, with increasing grinding time the amount of substance entering into reaction (1) increases considerably. In works ([4–7])

Fig. 1. Dependence of the fraction α of silver sulfate entering into the reaction on the duration of heating at 190° and grinding: 1–2 min., 2–5 min., 3–10 min., 4–sample pressed without grinding

Fig. 2. Dependence of the fraction α of decomposed substance on the duration of heating of mixtures: 1, 2–silver sulfate with potassium oxalate at 190°; 3, 4 –nickel sulfate with potassium oxalate at 305°; 5, 6–silver sulfate with sodium carbonate at 190°; 7, 8–calcium oxide with silver sulfate at 320°; 1, 3, 5, 7 –previously ground; 2, 4, 6, 8–pressed without grinding (curves 5-8 shifted upward by 0.3)

it was shown that, under plastic deformation of NaCl and AgJ single crystals, their electrical conductivity sharply increases, which is associated with the formation of additional defects in the lattice at block boundaries or near dislocations ([7–9]). Apparently, such deformations must lead to an increase in the diffusion coefficients of the crystal ions, an increase in the reactivity of solid salts, and an intensive course of the exchange reaction between substances in the solid state at low temperatures. Removal, by decomposition, of one of the products of the exchange reaction considerably increases its rate.

From experiments in which preliminary grinding was carried out for 10 min., it is seen that such a mixture decomposes by 78%, whereas one pressed without grinding decomposes by 88%. From equation (2) it follows that, in the thermal decomposition of silver sulfite, theoretically only half of the sulfur is released into the gas phase. The other half remains in the solid phase in the form of silver sulfate. Hence it follows that, even with the complete conversion of silver sulfate into silver sulfite during preliminary grinding, the amount of sulfur in the evolved gas should not have exceeded 50% of its content in the initial silver sulfate. In the experiment, however, considerably more is obtained. Consequently, at the decomposition temperature there occurs not only thermal decomposition of the silver sulfite formed during grinding, but also an exchange reaction in the solid state between silver sulfate and sodium sulfite proceeds. The decomposition proceeds with self-acceleration and is described by the equation $\alpha = 1 - e^{-kt^n}$. When α changes from 0 to 0.4, the reaction proceeds

in the kinetic region with an exponent $n \simeq 4$, and this period probably corresponds to the decomposition of silver sulfite formed during the preliminary treatment of the mixture. At $\alpha > 0.7$ and up to the end of decomposition at the given temperature, the process proceeds in the diffusion region with an exponent n of about 0.4, and the rate is determined by the diffusion rate. The activation energy of the reaction proceeding in the diffusion region, calculated from the temperature dependence of the reaction-rate constant, is 25.4 kcal/mole, which is considerably lower than the activation energy of the thermal decomposition of pure silver sulfite ([3]). It is possible that in this case the silver sulfite formed as a result of ion diffusion does not have time to form a new stable phase and decomposes much more readily than crystalline silver sulfite.

To verify the results obtained, we additionally investigated reactions in mixtures of silver sulfate with sodium carbonate, silver sulfate with potassium oxalate, nickel sulfate with potassium oxalate, and calcium oxide with silver sulfate. In all these systems, grinding or pressing without preliminary grinding ensured sufficient contact for an exchange chemical reaction to proceed at room temperature. A decomposition reaction and exchange by ion diffusion were observed in those temperature ranges in which one of the components formed as a result of the exchange reaction proves unstable and decomposes. Such products in our experiments were Ag_2SO_3, Ag_2CO_3, $Ag_2C_2O_4$, NiC_2O_4, and Ag_2O, which decompose at a noticeable rate at temperatures of 160 ([3]), 110 ([10]), 105 ([11]), 270 ([12]), and 300° ([13]), respectively, and thereby significantly accelerate the

exchange reaction proceeding by ion diffusion in solid phases.

The acceleration of a chemical reaction observed in some cases upon preliminary grinding or pressing of the initial substance with foreign substances may be explained, in light of the foregoing, not by their catalytic action, but by the occurrence of an exchange reaction with the formation of thermally less stable substances, which decompose at a higher rate. Conversely, the absence of acceleration of the thermal decomposition of solid substances ground or pressed with an introduced solid product is not, as some believe, the result of poor contact between these substances.

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Note: Figure translations are in progress. See original paper for figures.