MUTUAL INFLUENCE OF REACTIONS DURING THERMAL DECOMPOSITION OF SOLIDS

Z.JERMAN

Research Institute of Inorganic Chemistry, 400 60 Ústi nad Labem

Effect of a side reaction upon rate of the reaction examined, or upon the Arrhenius parameters, has been investigated for the internal redox reaction of hydrated ferrous sulphate during last stages of its dehydration and during thermal decomposition of potassium disulphite to potassium sulphite and sulphur dioxide in the anion redox reaction proceeding simultaneously. Kinetics of thermal decomposition of potassium disulphite has been compared with the kinetics of thermal decomposition of sodium disulphite, where the internal redox reaction is not involved.

Recently[1], a relationship for an absolute rate of the decomposition reaction of a solid, controlled by one elementary chemical process has been derived by applying the Planck radiation law to internal crystal planes. This model characterized by neglecting geometric approach (nucleation, growth and branching of nuclei) of the decomposition reaction for small crystals gave a satisfying accordance with the experiment for some decomposition reactions. In the present paper, kinetics of the following reactions accompanied by a side reaction, has been studied:

1) Internal redox reaction between a cation and an anion of ferrous sulphate under conditions, when dehydration of its monohydrate is being put to an end.

2) Internal redox reaction of the disulphite anion in the thermal decomposition of potassium disulphite.

EXPERIMENTAL

Apparatus

The decomposition was carried out in an electric furnace consisting of an outside heated aluminium block having a hole for a glass tube 18 mm in diameter, or for a quartz tube, of diameter 17 mm, furnished with a sintered-glass disc in the middle part of the tube. An absorption cell containing starch solution was connected to the tube. The temperature was maintained within $\pm 0.5°C$.

Procedure

1) *Internal redox reaction of* $FeSO_4$. aq. Approximately 20 g $FeSO_4$. 7 H_2O (pure reagent, Lachema) in a quartz tube was put into the furnace and nitrogen was admitted to the tubing at

a rate of 0·2 l/min. The temperature of the sample was increasing with the proceeding dehydration to anhydrous $FeSO_4$ (according to X-ray structural analysis) which, after the temperature of 280—300°C had been attained, still contained 4—5 mass % of water. The kinetics of the SO_2 evolution was measured only at the temperatures above 280°C, when condensation of water vapour at the end of the tube protruding from the furnace no longer occurred. Sulphur dioxide was absorbed in a starch solution and determined iodometrically. Isothermic experiments were carried out with a smaller amount (0·8 to 8 g) of the sample partially dehydrated beforehand. The degree of decomposition is expressed as ratio of the amount of SO_2 liberated to the amount of SO_2 which can be liberated altogether according to equation (A):

$$2\,Fe^{+2} + SO_4^{2-} = 2\,Fe^{3+} + 2\,O^{2-} + SO_2\,. \qquad (A)$$
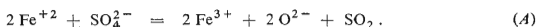
2) *Thermal decomposition of potassium and sodium disulphites.* 50 mg of $K_2S_2O_5$ (pure reagent, Lachema, crystals of prevailing size 0·4—0·8 mm, width 0·1—0·2 mm) or $Na_2S_2O_5$ (pure reagent, Lachema) was weighed into a small dish 11 mm in diameter, having a round shape and made of a micro-cover slip. For the decomposition measurements of $K_2S_2O_5$ under conditions of a slow diffusion of SO_2 from the layer, 50 mg of the sample was decomposed in a glass test tube 3 mm in diameter and 17 mm in length, this test tube being covered relatively tight by yet a smaller test tube dipping 5 mm into the first one; the remaining space of the test tube (the sample including) amounted to 0·057 cm^3. Diffusion of gas could proceed in a 5 mm long, narrow opening only. The SO_2 produced was carried away with nitrogen (0·16 l/min) into the absorption cell and determined iodometrically.

RESULTS AND DISCUSSION

Internal Redox Reaction of $FeSO_4$. aq

According to the derivatogram of $FeSO_4$. 7 H_2O last[2] portion of water escapes at 250—300°C. In the experiment, in which liberation of water vapour from the specimen was followed by condensation of water, it was found that the main portion escaped at a temperature below 131°C; from 184 to 245°C no liberation was observed, from 268°C water again condensed; at 304°C only, no condensation was apparent. By a direct determination of water in $FeSO_4$, which according to the structural analysis corresponded to anhydrous $FeSO_4$, water was in addition found (by a 42 min heating up to 112—260°C anhydrous $FeSO_4$ was produced according to X-ray structural analysis, which, however, still contained 4·1% of water; by a 60 min heating to 94—308°C followed by a 420 min heating to 327—353°C, anhydrous $FeSO_4$ with 1·7% H_2O was produced, as was proved by X-ray structural analysis). For that reason, even during the measurements above 300°C effect of the simultaneously proceeding dehydration must be taken into account.

In Fig. 1 showing dependence upon time, beginning of the internal redox reaction during heating of $FeSO_4$. 7 H_2O is illustrated. Fig. 2 shows kinetics of the internal redox reaction of sample A which was prepared by heating $FeSO_4$. 7 H_2O for 60 min to a temperature of 120—310°C; according to X-ray structural analysis the sample corresponded to anhydrous $FeSO_4$, whereas chemical analysis proved

existence of 94·0% $FeSO_4$ and 4·7% H_2O. It can be seen from Fig. 1−2 that the initial rate of the redox reaction (the heating period up to a given temperature being not considered) is by one or two orders of magnitude higher than that calculated from the relationship established[1] on the basis of the activation energy measurements of this reaction at 477−610°C. In Figs. 1 and 2, these dependences for temperatures close to the temperature of the experiment are also graphically presented. A rapid course of the internal redox reaction was observed up to the degree of decomposition $\eta = 0.02$ only, this part of the kinetic curve reminding thus of the so-called period of initial rapid decomposition[3], appearing sometimes with the kinetic curves.

In the thermal decomposition of $FeSO_4$. aq, a partial disproportionation redox reaction proceeds then, during bringing dehydration to an end, by another mechanism than the internal redox reaction under a higher temperature[1] and in absence of water in the crystal lattice. Water which can be removed with difficulties only is probably bound through hydrogen bonds to oxygen atoms of the anions; a couple anion–H_2O may produce couple hydroanion–OH^-; hydroanion then oxidizes the Fe^{2+} ion:

$$2\,Fe^{2+} + SO_4H^- = 2\,Fe^{3+} + OH^- + O^{2-} + SO_2 . \qquad (B)$$
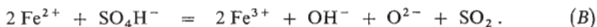
This reaction competes with the dehydration reaction.

An overlapping of the end of dehydration with the beginning of a deeper de-

FIG. 1

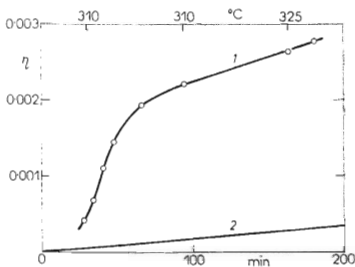Kinetics of Internal Redox Reaction during Heating of $FeSO_4$. 7 H_2O

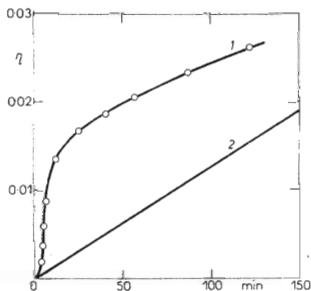 1 $FeSO_4$. aq, 2 theory for 337°C.

FIG. 2

Kinetics of Internal Redox Reaction of Sample A at 425°C

  1 Sample A, 2 theory for 425°C, weighed portion 0·8 g.

composition of the salt hydrates has been also observed for $MgCO_3 . 3 H_2O$ (ref.[4]), $3 K_2S_2O_5 . 2 H_2O$ (ref.[5]), perchlorates of metals in the odd series of the second group[6], and for magnesium nitrate[7].

Thermal Decomposition of Potassium and Sodium Disulphites

The Arrhenius relations for the rate constants of the $Na_2S_2O_5$ decomposition, measured by various methods, are presented in Fig. 3; the constants of the Arrhenius equation are given in Table I. The disintegration of $Na_2S_2O_5$ crystals had a similar effect as the partial decomposition of crystals, when also reduction of size of the crystals had to set in. The Arrhenius straight lines determined after the partial decomposition or after grinding the crystals are shifted towards higher rates. The reason for it is not in a change of the reaction mechanism (only reaction (C) always
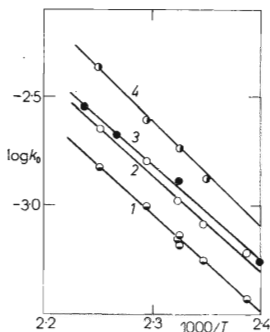

FIG. 3

Arrhenius Relations for Decomposition of $Na_2S_2O_5$

Rate constants of the zero-order reaction are determined: *1* using point of inflexion of total kinetic curve, *2* from point of inflexion of the kinetic curve after a preliminary 50% decomposition, *3* as for *1*, but with pulverized $Na_2S_2O_5$, *4* from the initial rate after a preceding 75% decomposition without a preliminary cooling.
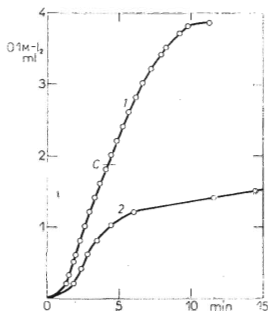
FIG. 4

Time Dependence of SO_2 Evolution during Decomposition of $K_2S_2O_5$ at 236°C

1 Decomposition in the open cell (starting from point C, reaction (D) stops taking place beside reaction (C)), *2* reaction in the covered cell (reaction (D) only proceeds over the whole range presented).

took place), but changes in the heat transfer and in diffusion. The accordance with the theory as well as with the measurement made previously[1] is good.

The kinetic curves which describe decomposition of $K_2S_2O_5$ according to the SO_2 evolution in an open and covered cells are illustrated in Fig. 4. In the covered cell, the second part of the decomposition is considerably retarded. In order to elucidate the reaction mechanism we used analytical methods according to Kurtenacker[8], similarly as Foerster and Hamprecht[5] did. In the two arrangements given, no other reactions than (C) and (D) were found:

$$S_2O_5^{2-} = SO_3^{2-} + SO_2, \qquad (C)$$

$$3\,S_2O_5^{2-} = S_2O_3^{2-} + 2\,SO_4^{2-} + 2\,SO_2. \qquad (D)$$

It holds that $\eta = \alpha + \beta$, where η denotes the degree of decomposition, resulting from reactions (C) and (D), α is the degree of decomposition due to reaction (C), and β is the degree of decomposition, due to reaction (D), $\eta = \alpha + \beta$ being equal to unity at the end of the reaction.

FIG. 5

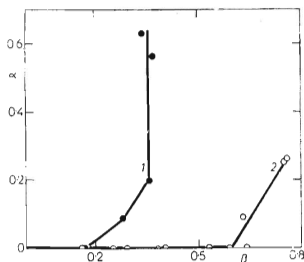Relation between Taking Place of Reactions (C) and (D) in Decomposition of $K_2S_2O_5$

1 Open cell, *2* covered cell; α degree of decomposition due to reaction C, β degree of decomposition due to reaction D.
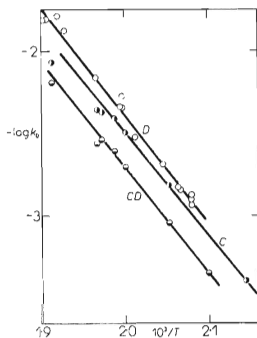

FIG. 6

Arrhenius Relations for Decomposition of $K_2S_2O_5$

D Reaction (D), C reaction (C), CD reaction $(C) + (D)$; k_0 are the rate constants of the zero-order reactions.

Values α and β are presented in Table II, relations between α and β in the measurements with the open as well as covered cells can be seen in Fig. 5. In the $K_2S_2O_5$

TABLE I

Parameters $A(s^{-1})$ of the Arrhenius Equation for Decomposition of Sodium Disulphite

Temperature °C	Number of isothermal measurements	Method of determining the rate constants	$\log A \pm \sigma \log A$	$E \pm \sigma_E$ kcal/mol
146—171	7	a	$7\cdot31 \pm 0\cdot06$	$20\cdot6 \pm 0\cdot8$
146—171	5	b	$7\cdot31 \pm 0\cdot10$	$20\cdot2 \pm 1\cdot4$
144—174	4	a^d	$7\cdot16 \pm 0\cdot07$	$19\cdot8 \pm 1\cdot0$
146—171	5	c	$8\cdot41 \pm 0\cdot06$	$21\cdot9 \pm 0\cdot9$

[a] In the point of inflexion of the kinetic curve, [b] as for a, but after a preceding 50% decomposition [c] as the initial rate of the fourth quarter of the reaction without breaking decomposition from the curve presented for b. [d] Sample of $Na_2S_2O_5$ was pulverized beforehand.

TABLE II

Results of Measurements of the Thermal Decomposition of $K_2S_2O_5$

°C	min	Cell	Degree of decomposition	
			α	β
208	7·6	covered	0	0·16
208	12·3	covered	0	0·25
208	16·5	covered	0	0·29
208	24·6	covered	0	0·38
208	43·8	covered	0	0·59
216	86	covered	0	0·64
224	135	covered	0·09	0·63
228	7·2	covered	0	0·40
228	17·7	covered	0	0·53
236	195	covered	0·24	0·83
246	103	covered	0·26	0·76
252	81	covered	0·25	0·75
230	1·9	open	0	0·16
230	3·8	open	0·09	0·28
230	4·8	open	0·20	0·36
230	9·6	open	0·56	0·37
230	27	open	0·63	0·34

TABLE III
Parameters of the Arrhenius Equation of Decomposition of $K_2S_2O_5$

Kind of reaction	°C	Number of isothermic measurements	Constants of the Arrhenius equation	
			log A	E, kcal/mol
(C)	193—230	4	10·0	28·5
(D)	208—253	16	10·55	30·0
$(C) + (D)$	193—230	4	10·2	29·4

lattice as many as 75% of the $S_2O_5^{2-}$ anions (covered cell) may be reacted according to equation (D), which represents a mere sum of equations (C) and (D). In the open cell, approximately 64% of anions was the maximum amount that reacted according to equation (C) so that about one half of all the anions capable of being reacted in reaction (D) (let us suppose that by the reaction in the covered cell, the amount of anions capable of being reacted according to this equation, was determined), reacted also in the experimental arrangement suitable for reaction (C). At the beginning also in the open cell only reaction (D) takes place. From time dependences of values 0·1M-I_2 ml (Fig. 4) the rate constants of reactions (C) and (D) were determined for those parts of the curves, in which according to the relation of α to β (Fig. 5) either only reaction (C) or only reaction (D) takes place; the rate constants for the region in which reactions (C) and (D) in the open cell simultaneously took place were also determined from the time dependences quoted. The Arrhenius straight lines constructed for the three alternatives given are graphically presented in Fig. 6, whereas constants of the Arrhenius equation are given in Table III. The shift of the straight lines is not distinct; the rate constants were calculated using different procedures (further presented), and drawing a conclusion about the sequence of the reaction rates employing sequence of the straight lines is therefore not possible.

The theory elaborated[1] results in the conclusion that a condition for the side reactions (C) and (D) to take place are close values of activation energies of appropriate elementary processes; the reaction of lower activation energy proceeds more rapidly than that of higher activation energy. This may, of course, be valid for irreversible reactions only, or for those carried out under conditions which suppress taking place of the reversible reaction. If both reactions are reversible and if the equilibrium pressure of gaseous product common for both reactions is not the same for both reactions, the change in the partial pressure of the gaseous product provokes a change in the reaction mechanism in the sense that application of both reactions during decomposition of the substance is changed. In case that one of the side reactions is

irreversible, this reaction may proceed more easily and at a lower temperature than the other one, even if the former will possess somewhat higher activation energy. From reactions (C) and (D) reaction (D) has the kinetic presumptions for irreversibility, since the reversible reaction assumes interaction of two solid phases with gas. Reactions (C) and (D) differ little in activation energies (Table III), but considerably in reaction enthalpies. For $K_2S_2O_5$, reactions (C) and (D) have $\Delta H = 26\cdot8$ (ref.[5]) and $11\cdot3$ kcal (calculated according to ref.[9]), respectively. Hence, assumptions for reaction (D) to be reversible are on one side thermodynamically supported, on the other side the fact may be thus explained that, contrary to reaction (C), no deviation of values of the rate constant logarithm from the straight line of the Arrhenius equation occurs in reaction (D), the deviation being caused by cooling the specimen, due to endothermic reaction at a high rate of decomposition (Fig. 6). It is true that reaction (D) affects taking place of reaction (C), the simultaneous course of both reactions, however, has no substantial effect on the activation energy measured (Table III). The fact cannot be excluded that under conditions suitable for a simultaneous course of reactions (C) and (D), both reactions are controlled by the same process. The rate constants of reaction (C) were determined from the upper half of the kinetic curves measured using the open cell. As for reaction (D), one half to two thirds of the $S_2O_3^{2-}$ anions capable of taking part in this reaction (total representation of these anions amounts to 75% according to Fig. 5) react considerably more readily than the rest of these anions, which means that reaction (D) has two controlling processes. The rate constants of reaction (D) could be established only for the more rapid part of this reaction; when calculating them, value $0\cdot1\text{M-}I_2$ ml which corresponds to a half decomposition by total reaction (D) (according to the measurements in the covered cell) was taken for the total conversion by the rapid part of reaction
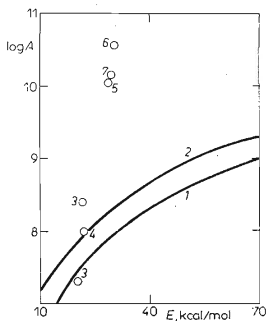

Fig. 7

Relation between the Arrhenius Parameters
1, 2 Theoretical relations[1], 3 $Na_2S_2O_5$ (Table I), 4 previous[1] measurement for $Na_2S_2O_5$, 5 $K_2S_2O_5$ reaction (C), 6 $K_2S_2O_5$ reaction (D), 7 $K_2S_2O_5$ reaction $(C) + (D)$ under conditions proper for reaction (C).

(D). The reason for the differences in the reactivity of anions in the $K_2S_2O_5$ crystal is obviously great complexity of the crystal lattice of this substance[10]. These differences were proved for reaction (D) only, similar differences, however, may occur also in reaction (C).

All frequency factors of the Arrhenius relation for the decomposition of $K_2S_2O_5$ are higher than it would be expected according to theory[1] with respect to appropriate values of the activation energy (Fig. 7). Certain increase of the frequency factor may be for reaction (D), in comparison with (C), expected as a result of the fact that one energy quantum can activate a triple of the $S_2O_5^{2-}$ anions for reaction (D).

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