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SOME NEW DATA CONCERNING THE INTERFACE CHEMISTRY OF DEHYDRATION REACTIONS

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ABSTRACT

Temperature dependence of the rate of reaction interface advance in reactions of thermal dehydration of single crystals was studied by means of quartz crystal microbalance along various crystallographic directions. Both kinetic and microscopic data show different interface chemistry for crystalline hydrates with equivalent and non-equivalent water molecules.

INTRODUCTION

The aim of kinetic analysis in homogeneous chemistry is to study the dependence of reaction rate upon concentration of reagents. In the reactions of thermal dehydration

$A \cdot m\ H_2O(solid) \longrightarrow A \cdot (m-n)H_2O(solid) + n\ H_2O(gas)$

the concentration of chemically bonded water molecules in initial hydrate is constant and consequently the study of the rate of a reaction interface advance under isothermal conditions gives an information concerning only the variation of the total area of reaction interface and gas-permeability of the solid product layer. More valuable are data on temperature dependence of the rate of a reaction interface advance $V(T)$. An experimental method developed by us [1] makes it possible to obtain reliable data $V(T)$. Together with microscopic investigations it gives new information on the mechanism of these reactions.

EXPERIMENTAL

The study of $V(T)$ was carried out in different crystallographic directions ($\perp$, Table I) under dynamic vacuum $\sim 7 \times 10^{-5}$ Pa by means of quartz crystal microbalance [1]. Geometry and structure of reaction interface was studied by SEM (JSM - T - 20).

RESULTS AND DISCUSSION

Crystalline hydrates with non-equivalent water molecules (type I) (Table I, N 1-4) and equivalent water molecules (type II) (Table I, N 5-7) were chosen for investigations. Experimental re-

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Table I

Kinetic parameters E and ν were calculated according to equation $V(T) = \delta\nu \exp(-E/RT)$, where δ -distance between neighbouring water molecules; n - the number of removed water molecules H_2O (see eq. (I))

N	Substance	E(kJ/mol)	ν, (s^{-1})	ΔT, k	$\perp$	n
I	$K_4Fe(CN)_6 \cdot 3H_2O$	54.0±1.3	$(0.9 \pm 0.4) \times 10^{11}$	246.9÷302.6	[010]	3
2	$CuSO_4 \cdot 5H_2O$	74.5±0.8	$(1.8 \pm 0.5) \times 10^{14}$	254.8÷305.7	[110]	4
3	$KNaC_4H_4O_6 \cdot 4H_2O$	87.5±1.7	$(2.5 \pm 1.8) \times 10^{16}$	275.6÷302.7	[100] [010] [001]	4
4	$Ba(NO_2)_2 \cdot H_2O$	91.7±0.8	$(4.5 \pm 1.2) \times 10^{16}$	292.4÷344.5	[001]	1
5	$K_2C_2O_4 \cdot H_2O$	74.5±0.8	$(7.6 \pm 2.0) \times 10^{13}$	274.6÷341.3	[100]	1
6	$CaSO_4 \cdot 2H_2O$	85.0±1.7	$(5.9 \pm 3.3) \times 10^{13}$	292.7÷357.4	[001]	2
7	$Li_2SO_4 \cdot H_2O$	87.1±0.8	$(1.3 \pm 0.4) \times 10^{14}$	300÷400	[101] [010]	1

sults are presented in Table I. It can be seen, that values of for crystalline hydrates (I) variate from "anomaly low" to "anomaly high", whereas those for crystalline hydrates (II) are "normal". More clearly this behaviour is shown graphically in coordinates ($\lg \nu$ - B) (Fig.1). The SEM investigation of single crystal cross sections after partial decomposition allows to resolve a distinct interface "reagent-product" for crystalline hydrates (II) and thin intermediate layer between undecomposed hydrate and porous product for crystalline hydrates (I). These data give some evidence for assumption that crystalline hydrates dehydration (II) is the most simple case of reversible decomposition of solids and mechanism of such reactions corresponds to that offered in the papers of [2, 3], whereas interface chemistry of hydrates (I) is more complex. An intermediate layer observed by SEM is possible to be a "lacunary" solid phase with some distribution of water molecules [4] and exists as a result of H_2O crystallographic non-equivalency.

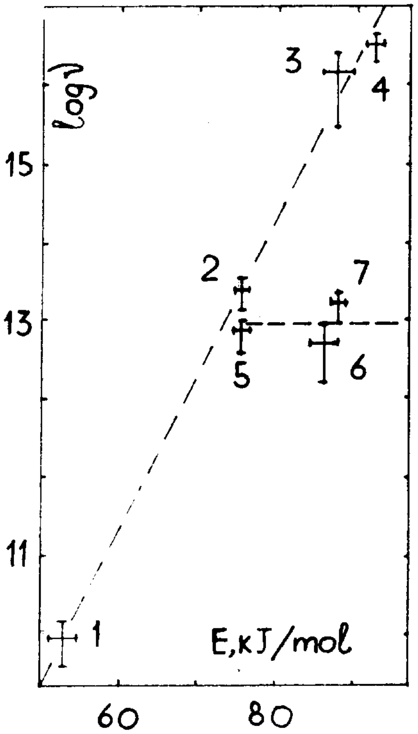

Fig. 1. The numbers correspond to the substances available in Table I.

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