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THE SOLID-PHASE DECOMPOSITION OF
POTASSIUM AND SOLIUM CHLORATES AND
PERCHLORATES IN THE PRESENCE OF
MANGANESE DIOXIDE

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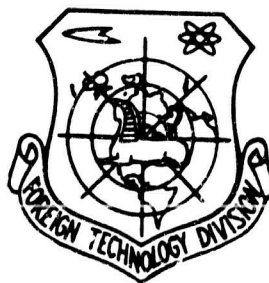
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THE SOLID-PHASE DECOMPOSITION OF POTASSIUM AND SODIUM CHLORATES AND PERCHLORATES IN THE PRESENCE OF MANGANESE DIOXIDE

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The solid-phase decomposition of $KClO_3$ and $KClO_4$ in the presence of oxide catalysts has been studied in [1-3]; however, the tests were run at comparatively high temperatures, as a result of which the picture was complicated by the phenomenon of noncatalytic dissociation or the presence of the liquid phase. Both of these hindered ubsequent kinetic analysis of the experimental data and their unambiguous interpretation.

In this report we give the results of a study of the catalytic decomposition of potassium and sodium chlorates and perchlorates at low temperatures, when there is practically no dissociation in the absence of a catalyst. In the tests we used the fraction of salt crystals 0.14-0.20 mm in diameter mixed with MnO_2 (~1%). The degree of decomposition of the weighed sample (~300 mg) was recorded using an ADV-200 balance.

The experimental data are satisfactorily described by the topokinetic equation $\alpha = 1 - \exp(-kt^n)$, where α is the precentage of decomposed substance; t is the time; n and k are constants [4-6]. In the majority of cases this equation encompasses the entire kinetic

curve (no break in the anamorphosis), and only in one experiment
with $KClO_3$ did parameter n have the value of 1 (in the initial
stage) and then 0.5 (in the remaining stage). In the case of $NaClO_3$,
variation of n as a function of temperature is characteristic (see
the table).

Calculated values of kinetic parameter n

Substance	Temperature, °C	α	n
$KClO_4$	425, 435 445, 465	0.68-0.85	0.66
$NaClO_4$	350, 370 380	0.7 -0.81	0.63
$NaClO_3$	240 245 255	0.74 0.85 0.90	0.66 0.72 1.05
$KClO_3$	315, 320 325, 330 335 335	0.68-0.85 0.20 from 0.30 to 0.90	0.50 1.00 0.50

Judging from the value of n ($0.5 < n < 1$), predominant decom-
position of the salts occurs in the diffusion region, and the dif-
ference ($1 - n$) characterizes the measure of immersion of the pro-
cess into this region [5]. The initial stage of decomposition of
$KClO_3$ at 335°C is an exception; here the general rate of the pro-
cess is determined by the strictly chemical kinetics at the phase
interface. As measurements of the electrical conductivity of a
mixture of $KClO_3$-MnO_2 showed, this was caused by the temporary
appearance of the liquid phase — the eutectic. An analogous phe-
nomeron was detected in experiments with $NaClO_3$, where the percen-
tage of the liquid phase decreases with a drop in temperature.

Comparing the volumes of reacting substance and the product,
we can estimate the nature of the diffusion resistance of the latter
[7]. As follows from such calculations, with decomposition of both
chlorates and perchlorates the volume of the forming chlorides is
less than that of the initial substances, which predetermines the
presence of macropores in the product layer, thus facilitating the
feeding and removal of the corresponding components. However, when

$KClO_3$ decomposes this layer is denser than in the case of $KClO_4$ and, consequently, here we should expect greater immersion of the process into the diffusion region. The values of n completely agree with this:

$$(1 - n_{KClO_3}) > (1 - n_{KClO_4}).$$

The diffusion resistance can be variable (for $NaClO_3$ as well), and then the kinetic parameter also changes.

CONCLUSION

Comparing the reaction capability of solid substances under conditions of volumetric diffusion [7] and with decomposition of the investigated salts $KClO_3$ and $KClO_4$ (two orders higher), in the second case we should assume that an essential role is played by surface diffusion and diffusion along the boundaries of the crystallites.

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