

AD/A-003 104

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

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Wright-Patterson Air Force Base, Ohio

25 November 1974

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U. S. DEPARTMENT OF COMMERCE

AD/A 003104

Security Classification

DOCUMENT CONTROL DATA - R & D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY (Corporate author) Foreign Technology Division Air Force Systems Command U. S. Air Force	2a. REPORT SECURITY CLASSIFICATION UNCLASSIFIED
	2b. GROUP

3. REPORT TITLE
SOLID-PHASE DECOMPOSITION OF POTASSIUM AND SODIUM CHLORATES AND PERCHLORATES IN THE PRESENCE OF MANGANESE DIOXIDE

4. DESCRIPTIVE NOTES (Type of report and inclusive dates)
Translation

5. AUTHOR(S) (First name, middle initial, last name)
B. I. Khorunzhiy, K. G. Il'in

6. REPORT DATE 1972	7a. TOTAL NO. OF PAGES 4	7b. NO. OF REFS 7
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8a. CONTRACT OR GRANT NO. b. PROJECT NO. c. d.	9a. ORIGINATOR'S REPORT NUMBER(S) FTD-HT-23-0211-75
	9b. OTHER REPORT NO'S (Any other numbers that may be assigned this report)

10. DISTRIBUTION STATEMENT
Approved for public release; distribution unlimited.

11. SUPPLEMENTARY NOTES	12. SPONSORING MILITARY ACTIVITY Foreign Technology Division Wright-Patterson AFB, Ohio
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13. ABSTRACT
07

Provided by
**NATIONAL TECHNICAL
 INFORMATION SERVICE**
 U. S. Department of Commerce
 Springfield VA 22151

EDITED TRANSLATION

FTD-HT-23-0211-75

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By: B. I. Khorunzhiy, K. G. Il'in

English pages: 4

Source. Izvestiya Vysshikh Uchebnykh Zavedeniy,
Khimiya i Khimicheskaya Tekhnologiya,
Vol. 15, Nr. 12, 1972, pp. 1886-1888

Country of Origin: USSR

Translated by: Dale A. Bostad

Requester: AFRPL/YPI

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TRANSLATION DIVISION
FOREIGN TECHNOLOGY DIVISION
WP-AFB, OHIO.

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U. S. BOARD ON GEOGRAPHIC NAMES TRANSLITERATION SYSTEM

Block	Italic	Transliteration	Block	Italic	Transliteration
А а	<i>А а</i>	A, a	Р р	<i>Р р</i>	R, r
Б б	<i>Б б</i>	B, b	С с	<i>С с</i>	S, s
В в	<i>В в</i>	V, v	Т т	<i>Т т</i>	T, t
Г г	<i>Г г</i>	G, g	У у	<i>У у</i>	U, u
Д д	<i>Д д</i>	D, d	Ф ф	<i>Ф ф</i>	F, f
Е е	<i>Е е</i>	Ye, ye; E, e*	Х х	<i>Х х</i>	Kh, kh
Ж ж	<i>Ж ж</i>	Zh, zh	Ц ц	<i>Ц ц</i>	Ts, ts
З з	<i>З з</i>	Z, z	Ч ч	<i>Ч ч</i>	Ch, ch
И и	<i>И и</i>	I, i	Ш ш	<i>Ш ш</i>	Sh, sh
Я я	<i>Я я</i>	Y, y	Щ щ	<i>Щ щ</i>	Shch, shch
К к	<i>К к</i>	K, k	Ъ ъ	<i>Ъ ъ</i>	"
Л л	<i>Л л</i>	L, l	Ы ы	<i>Ы ы</i>	Y, y
М м	<i>М м</i>	M, m	Ь ь	<i>Ь ь</i>	'
Н н	<i>Н н</i>	N, n	Э э	<i>Э э</i>	E, e
О о	<i>О о</i>	O, o	Ю ю	<i>Ю ю</i>	Yu, yu
П п	<i>П п</i>	P, p	Я я	<i>Я я</i>	Ya, ya

* ye initially, after vowels, and after ъ, ь; e elsewhere. When written as ѣ in Russian, transliterate as yě or ě. The use of diacritical marks is preferred, but such marks may be omitted when expediency dictates.

FOLLOWING ARE THE CORRESPONDING RUSSIAN AND ENGLISH
DESIGNATIONS OF THE TRIGONOMETRIC FUNCTIONS

Russian	English
sin	sin
cos	cos
tg	tan
ctg	cot
sec	sec
cosec	csc
sh	sinh
ch	cosh
th	tanh
cth	coth
sch	sech
cach	cach
arc sin	sin ⁻¹
arc cos	cos ⁻¹
arc tg	tan ⁻¹
arc ctg	cot ⁻¹
arc sec	sec ⁻¹
arc cosec	csc ⁻¹
arc sh	sinh ⁻¹
arc ch	cosh ⁻¹
arc th	tanh ⁻¹
arc cth	coth ⁻¹
arc sch	sech ⁻¹
arc cach	cach ⁻¹

rot	curl
lg	log

GREEK ALPHABET

Alpha	A	α	α	Nu	N	ν
Beta	B	β		Xi	Ξ	ξ
Gamma	Γ	γ		Omicron	Ο	ο
Delta	Δ	δ		Pi	Π	π
Epsilon	E	ε	ε	Rho	Ρ	ρ ϱ
Zeta	Z	ζ		Sigma	Σ	σ ς
Eta	H	η		Tau	Τ	τ
Theta	Θ	θ	θ	Upsilon	Υ	υ
Iota	I	ι		Phi	Φ	φ ϕ
Kappa	K	κ	κ	Chi	Χ	χ
Lambda	Λ	λ		Psi	Ψ	ψ
Mu	M	μ		Omega	Ω	ω

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 experiments were conducted at relatively high temperatures with the result that the picture was complicated by the appearance of noncatalytic dissociation or the presence of the liquid phase. Both of these factors have increased the difficulty of subsequent kinetic analyses of the experimental data and their unambiguous interpretation.

This report gives the results of research on the catalytic decomposition of sodium and potassium chlorates and perchlorates at low temperatures, and at these temperatures dissociation, when there is practically no dissociation, in the absence of a catalyst. In the experiments a fraction of salt crystals with a diameter of 0.14-0.20 mm mixed with MnO_2 ($\sim 1\%$) was used. The degree of decomposition of the specimen (~ 300 mg) was recorded using a type ADB-200 balance.

The experimental data are satisfactorily described by the topokinetic equation $\alpha=1-\exp(-kt^n)$, where α - the portion of the decomposed substance; t - time; and n and k - constants [4-6]. In the majority of cases the stated equation encompasses the whole kinetic curve (there is no anamorphosis break), and only in one experiment with KClO_3 did parameter n assume the value 1 (in the initial stage) and then 0.5 (in the rest of the stage). In the case of NaClO_3 it is characteristic that n varies according to the temperature (see table).

Table. Calculated values of the kinetic parameter n .

Substance	Temperature °C	α , in fractional units	n
KClO_3	425, 435, } 445, 465 }	0.69-0.85	0.66
	NaClO_3	350, 370, } 380 }	0.7-0.81
NaClO_3		240	0.74
	245	0.85	0.72
	255	0.90	1.05
KClO_3	315, 320, } 325, 330 }	0.68-0.85	0.50
	335	0.20	1.00
	335	or 0.30 to	0.50
	335	0.90	

Judging by the magnitude of n ($0.5 < n < 1$), the primary decomposition of salts takes place in the diffusion region, and the difference $(1-n)$ characterizes the extent to which this process extends into this region [5]. An exception is the initial stage of decomposition of KClO_3 at 335°C ; here the total rate of the process is determined by strictly chemical kinetics at the phase interface. As measurements of the electroconductivity of the mixture $\text{KClO}_3\text{-MnO}_2$ demonstrated, this is caused by the brief appearance of the liquid phase - the eutetic. A similar phenomenon is also observed in experiments with NaClO_3 where the percentage of the liquid phase decreases with a drop in temperature.

By comparing the volumes of the reacted substance and the produce we can assess the nature of the latter's diffusion resistance [7]. It follows from such calculations that when chlorates and perchlorates are decomposed, the volume of the chlorides formed is less than the volume of the initial substances, which predetermines the presence of macropores in a layer of the product and this facilitates the input and removal of the corresponding components. However, when KClO_3 is decomposed, this layer is much more compact than in the case of KClO_4 , and it follows that one can expect here a greater extension of the process into the diffusion region. The values of n are in complete accord with such evaluations:

$$(1 - \alpha_{\text{KClO}_3}) > (1 - \alpha_{\text{KClO}_4}).$$

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

Conclusion

When comparing the reaction capability of solid substances under volume diffusion conditions [7] and when the investigated salts KClO_3 and KClO_4 are decomposed (two orders higher), in the latter case it is necessary to acknowledge the fundamental role played by surface diffusion and diffusion along the boundaries of the crystallites.

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of Inorganic Substances

Received
9 July 1971