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THE MECHANISM OF THE LOW-TEMPERATURE
THERMAL DECOMPOSITION OF AMMONIUM
PERCHLORATE

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Wright-Patterson Air Force Base, 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 yѣ or ѣ.
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
cos $\acute{e}$ c	csc
sh	sinh
ch	cosh
th	tanh
cth	coth
sch	sech
csch	csch
arc sin	sin ⁻¹
arc cos	cos ⁻¹
arc tg	tan ⁻¹
arc ctg	cot ⁻¹
arc sec	sec ⁻¹
arc cos $\acute{e}$ c	csc ⁻¹
arc sh	sinh ⁻¹
arc ch	cosh ⁻¹
arc th	tanh ⁻¹
arc cth	coth ⁻¹
arc sch	sech ⁻¹
arc csch	csch ⁻¹
rot	curl
lg	log

GREEK ALPHABET

Alpha	A	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	•	Rho	Ρ	ρ •
Zeta	Z	ζ		Sigma	Σ	σ ς
Eta	H	η		Tau	Τ	τ
Theta	Θ	θ	•	Upsilon	Υ	υ
Iota	I	ι		Phi	Φ	φ •
Kappa	K	κ	κ •	Chi	Χ	χ
Lambda	Λ	λ		Psi	Ψ	ψ
Mu	M	μ		Omega	Ω	ω

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The mechanism of the low-temperature thermal decomposition of ammonium

perchlorate.

Novosibirsk.

It is known that in the course of the thermal decomposition of the crystals of ammonium perchlorate at low temperatures occurs the formation and ^{growth} ~~increase~~ of ^{nuclei} ~~embryos~~ [1, 2]. For the understanding of the mechanism of decomposition NH_4ClO_4 , it is necessary to know, which stages of process are connected with nucleation, and which ~~a~~ with ^{the} ~~the~~ ^{growth} ~~increase~~.

It is possible to consider at present established that at low temperatures the thermal decomposition of ammonium perchlorate occurs ^{by} ~~flow/lasts over~~ proton mechanism, in primary stage occurs the process of the dissociation of salt ⁱⁿ to ammonia and ^{perchloric} ~~chloric~~ acid. The subsequent course of thermolysis is ^{coupled} ~~joined~~ with the oxidation of ammonia by the ^(decomposition) ~~decomposition~~ products of ^{perchloric acid} ~~chlorine~~ ~~acid~~ [3-6]. The majority of the authors ~~they~~ assume that the processes of formation and growth of ^{nuclei} ~~embryos~~ are caused by the course ^(of) ~~the same~~ of the stages of reaction. According to another point of view (Svetlov, Koroban; Rosser, ^{Inami, Wise} ~~Ayami, Vays~~) along with the course of the indicated reactions during thermal decomposition NH_4ClO_4 , occurs also the formation of substances, capable of entering ^{into} ~~the~~ interaction with

ammonia or solid ammonium perchlorate [7, 8]. In this case ~~the~~
~~growth of nuclei~~ (process)
~~increase in the embryos~~ can also, without the course of the stage
of dissociation.

We have made the ~~assumption~~ ^{proposition} that the nucleation occurs as a
result of the course of the primary stage of the dissociation of salt
and subsequent secondary reactions, ~~but an increase in the embryos~~ ^{and the growth of nuclei} is
caused by the oxidation-reduction reactions of the active oxidizers
(HClO, and the oxides of chlorine), ~~regenerated~~ ^{being regenerated} in the course
of process. For the check of the ~~assumed~~ ^(expressed propositions) was studied the effect of a
number of factors on the processes of formation and ~~increase in the~~ ^{growth of}
nuclei
embryos.

In work used ~~single~~ ^{many} crystals ^{all} NH_4ClO_4 , obtained by the
evaporation ^{quality}
~~vaporization~~ of the aqueous solution of salt of ~~high~~ "chemically
pure" at ~~constant~~ ^{room} temperature. The investigated crystal was placed
under microscope in ^(a) special furnace and in the course of reaction
was taken photograph. Temperature was not more than 235° C.
According to the obtained negatives ~~related to the future~~ ^(was determined) ^{time} of the
appearance of the first ~~embryo~~ ^{nucleus} (induction period), ~~calculated~~ ^(were) the

rates of formation and ^{growth of nuclei} ~~increase in the embryos.~~

For the solution to the assigned task was used the method of

^{doping} ~~dopiraniya~~. During introduction to crystal NH_4ClO_4 ^{of} the additions of bivalent cations occurs the formation of ^{additional} ~~supplementary~~ cation vacancies.

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In this case because of the presence in the crystals of proton conductivity [9] and of the possibility of the transmission of proton to significant distances [5] will be increased the rate of the process of dissociation. The additions of bivalent anions must increase the number of anionic vacancies, ^{leading} ~~conduct~~ to diminution in the quantity of being present in crystal cation vacancies and to the slow down of the rate of dissociation ^(of) NH_4ClO_4 .

If the stage of dissociation is responsible for formation and ^{growth of nuclei} ~~increase in the embryos~~, then bivalent additions must affect the rate of both processes. But if dissociation does not play the significant

growth of nuclei
role in the course of ~~an increase in the embryos~~, then the indicated
additions will affect only the rate of their growth. In this case
nucleation
cation additions will increase rate of ~~nuclei forming~~, and anionic -
decrease.

doping
It was established that the ~~dissociative~~ by ions Cu^{++} and Sr^{++}
nucleation and
increases rate of ~~nuclei forming~~, but by ions $\text{Cr}_2\text{O}_7^{--}$ it decreases.

In this case additions Cu^{++} and Sr^{++} do not affect the rate of growth of
nuclei
embryos. Addition $\text{Cr}_2\text{O}_7^{--}$ increases the rate of growth, which can be
caused by the catalytic influence of the generation during reaction

doping
oxides of chromium. Thus, by the method of ~~dissociative~~ it is shown
that the dissociation does not play the significant role in the course
the growth of nuclei during
of ~~an increase in the embryos with~~ thermolysis [10, 11]. If the made

is correct
conclusion ~~probably~~ then the ammonia, introduced into reaction vessel,

growth nuclei
must differently affect formation and ~~increase in the embryos~~. At

(decomposition)
atmospheric pressure the ~~decomposition~~ rate of ammonium perchlorate, which

takes place by proton mechanism, is proportional to the equilibrium

pressure of the vapors of perchloric acid [12]. Therefore one should

nucleation
expect the linear dependence of the rate of ~~formation of embryos~~ on

the partial equilibrium pressure of perchloric acid in system. If the developed point of view about ~~a~~^{the} difference in the mechanisms of formation and growth is accurate, then this dependence must not be observed for the rate of growth of ~~embryos~~^{nuclei}. The obtained results confirmed ~~assumption~~^{proposition} about the fact that the dissociation of salt was important only for nucleation, and was not essential for their ~~growth~~^(nuclei). Actually, the rate of ~~formation of embryos~~^{nucleation} decreases in proportion to an increase in the partial pressure of ammonia ~~in~~^(according to the) hyperbolic law, and the rate of growth ~~is~~^(according to the) linear. The rate of ~~formation of embryos~~^{nucleation} linearly ~~grows up~~^{increases} in proportion to the increase in the partial pressure of perchloric acid in system [10], ~~the~~^(by the) calculated ~~is~~^{known} equilibrium constant of the process of the dissociation of salt [13].

Thus, it is established that the mechanisms of formation and growth of ~~embryos~~^{nuclei} are different. ~~On~~^{To} this testify ~~the~~ also the discovered by us differences in the activation energy of these processes (activation energy of formation is equal to 50 kcal/mole, the activation energy of growth 30 kcal/mole). Consequently, the process of nucleation is caused by the course of the reaction of

dissociation and subsequent secondary reactions, ^{and} ~~but~~ the process of growth is connected in essence with the secondary reactions, in the course of which occurs the regeneration of the products, which facilitate the oxidation of solid salt.

^A The fact, which confirms the expressed point of view, is also the predominance ^{the growth of nuclei over} ~~preponderance of an increase in the embryos above~~ ^{during} emergence ~~with the~~

thermolysis of the ammonium salts, formed by acid-oxidizers (NH_4ClO_3 ,

NH_4BrO_3 , NH_4IO_3), and the absence of ^{the growth of nucleus during} ~~an increase in the embryo with~~

the thermolysis of the salts, formed by the acids, not capable of

oxidizing ammonia (NH_4Cl , NH_4HCO_3) [10, 11]. Assumption about the

fact that in process ^{of} ~~the development~~ of reaction zone ^a ~~the~~ significant

role play the generat^{ed}~~ing~~ in reaction oxides of chlorine is confirmed

by the fact of the acceleration of nucleation in the crystals of

ammonium perchlorate, ^(preliminarily) ~~exposed/persistent~~ ^{an} in the atmosphere of

dioxide ~~amount~~ of chlorine - one of reaction gases. Actually, of the

crystals, exposed ~~/persistent~~ 20 min in the atmosphere with the partial

pressure of the dioxide of chlorine equal to 3 torr, time of the

formation of the ^(nucleus) ~~growing~~ at linear speed ~~embryo~~ is reduced to 12 min

^{at}
~~with~~ 230° C (for the untreated crystals this time is equal to 30 min).

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Thus, it is established that the process of nucleation during thermal

decomposition ^{of} NH_4ClO_4 is connected with the course of the reaction of

the dissociation of salt and subsequent secondary reactions. In the

process of ^{growth of} ~~an increase in~~ the ^{nuclei} ~~embryos~~ occur the secondary reactions of

the interaction of solid salt with those which are being regenerating

in the course of process by oxidizers. Dissociation ^{of} NH_4ClO_4 does not

⁽ⁱⁿ⁾ ~~play~~ this case ^a ~~of~~ significant role.

The process of nucleation can be presented in the following form.

Thermal dissociation during the decomposition of salt occurs both on

external and on internal surface. The latter can be formed by the

pores, which are hollow dislocation cores, which emerge on surface.

During the diffusion ^{of the forming} ~~directions~~ in the pores ~~of~~ ammonia and

perchloric acid to external crystal ^{surface} ~~boundary~~ occurs the accumulation

of the excess of perchloric acid as a result of its ^{lower} ~~less~~ diffusion

rate, which leads to the initiation of the process of decomposition.

Nucleation ^{during} ~~with~~ thermolysis ^{of} ~~of~~ NH_4ClO_4 , begins under surface [2], since

there are more favorable ~~than the stacking~~ ^(for accumulation) conditions of perchloric

acid. The separation efficiency of the components of gaseous mixture

depends, other conditions being equal, on the diameter of pore.

Consequently, the important role in the course of nucleation ~~they~~ must

play dislocations with the determined value and the orientation of

Burgers's vector. ~~the~~ To investigation of the role of dislocations ^{during} ~~with~~

thermolysis ^(of) NH_4ClO_4 , ^(we dedicated a number of articles) ~~we have dedicated a number of articles~~ [14, 15]. However, until

now, ^(the question) ~~remains that which was~~ not solved ^{of} ~~question~~, why in the process of

nucleation is active only one thousandth of the dislocations, which are

present in the initial crystal. Probably this is caused by the

favorable stereochemical arrangement of dislocations, analogous with

that ^{which} ~~as this~~ was revealed by Thomas for the carbonate of calcium [16].

For the explanation of the role of dislocations together with

Thomas and Williams we studied the dislocation structure of ammonium

perchlorate. Investigations were conducted by the method of optical

microscopy ^{using} ~~and by the utilization of an~~ interferential contrast. It

was established that in the process of the sublimation of salt most active are ^{screw} ~~surface~~ dislocations, which can serve as indication of their important role in the process of nucleation.

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