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TRANSLATION

CATALYSIS OF REACTIONS IN SOLID PHASE

By

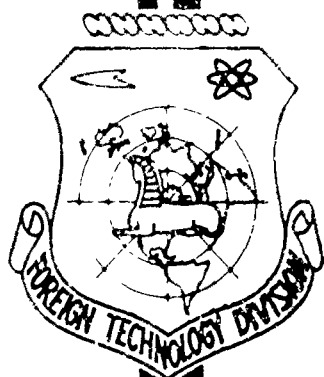
F. Shol'moshi and L. Reves

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CATALYSIS OF REACTIONS IN SOLID PHASE

BY: F. Shol'moshi and L. Reves

English Pages: 19

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CATALYSIS OF REACTIONS IN SOLID PHASE

Thermal Disintegration of Ammonium Perchlorate

In the Presence of Ferric Oxide

F. Shol'moshi, L. Reves

The catalytical action of ferric oxide on different stages of disintegration of ammonium perchlorate, and also disintegration of pure ammonium perchlorate in the same conditions, is studied. The addition of ferric oxide at 210-240°C hardly affected the course of the reaction, but at 245-270°C rendered significant catalytical action. Analysis of kinetic data leads to the conclusion that ferric oxide promotes acceleration of the process of transmission of electrons from anions to cations which is the controlling stage of the reaction. Ferric oxide also catalyzed the reaction of ammonium perchlorate at high temperature.

For the first time, the disintegration of ammonium perchlorate was investigated by Naoum and Aufschlager [1], and also Dodé [2]. These authors were occupied mainly with the determination of composition and quantity of products of the reaction. The characteristic features of the reaction and its kinetics were studied in detail by Bircumshaw and Newman [3], and also Galwey and Jacobs [4]. Thus, it was established that at 210-240°, decomposition of rhombohedral modification takes place, and at 240-300° - cubic

modification. In the shown temperature ranges, the degree of transformation constitutes 28-30%, above 350° practically full disintegration occurs.

The mechanism of disintegration is unequal in different temperature ranges. Below 300°, the reaction proceeds by an electronic mechanism with an activation energy of 32 kilocalorie/mole, at 350-440° — by a proton mechanism with activation energy of 40 kilocalorie/mole. According to the data of Galwey and Jacobs [5], an explosion of ammonium perchlorate takes place above 440°. From the fact of the equality of activation energy for the processes of explosion and reaction, taking place at high temperature (350-440°), the authors concluded that an explosion of ammonium perchlorate also proceeds by a proton mechanism.

Frequently, they investigated the influence of additions of different substances on the kinetics of disintegration of ammonium perchlorate. Of the oxides in this plan, only manganese dioxide [6] and magnesium oxide [6] were earlier studied in detail. Especially high catalytical activity was possessed by manganese dioxide.

The purpose of this work was the study of the influence of additions of ferric oxide on the kinetics of disintegration of ammonium perchlorate.

Methodology of Experiment and Experimental Data

Substance. In the experiments we used ammonium perchlorate from the firm "Merck" an analytically pure brand. A sample of perchlorate was ground into powder for the duration of 20 minutes. The average dimension of grains constituted 0.046 mm. Ferric oxide

was also an analytically pure brand.

To preliminary triturated ammonium perchlorate we added ferric oxide in the needed ratio. Homogeneity of the mixture was attained by mixing for the duration of several hours in ball mill (without balls). The powder obtained in this way was pressed into tablets at a pressure of 3700 kg/cm².

Measurements were conducted mainly in air, but for comparison, several experiments were conducted in a vacuum. For that, ammonium perchlorate was placed in a test-tube, united with a gas burette. The course of the reaction was registered by the measurement of the quantity of formed gases.

Disintegration of Pure Ammonium Perchlorate

Since the kinetic data of the reaction of disintegration — the period of induction, speed of reaction and so forth — depend on prehistory of preparation and conditions of carrying out the reaction, we preliminarily investigated the disintegration of pure ammonium perchlorate. Such an investigation presented interest also because till now, disintegration of ammonium perchlorate in air was not studied in detail.

Disintegration below 240°C. Disintegration of ammonium perchlorate below 240°C was incomplete. On the average, the degree of decomposition constituted 31-34%* which by 2-3% exceeds the magnitudes, received by other authors [4] in carrying out the reaction in a

* Degree of decomposition was calculated by the change of weight.

vacuum. The cause of the increased degree of decomposition was, apparently, the adsorptive film of water vapor, the presence of which, according to the data of Galwey and Jacobs, leads to a certain continuation of the reaction.

In Fig. 1 are represented kinetic curves in coordinates: volume of formed gas (v) — time (t). The curves have an S-form character.

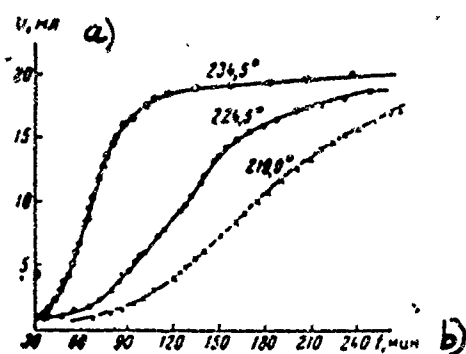


Fig. 1. Kinetic curves of thermal disintegration of pure ammonium perchlorate below 240° . a) ml; b) minutes.

Mathematical approximation of curves $v-t$ was accomplished in the following way. The constant of speed of the period of acceleration was calculated by the Prout — Thomkins equation

$$\log \frac{\alpha}{1-\alpha} = k_1 t + C_1, \text{ where } \alpha = \frac{v}{v_f} \quad (1)$$

(v — volume of gas, formed at a moment of time t ; v_f — volume of gas upon completion of disintegration) and by the equation of exponential law

$$P = k_2 t^n \quad (2)$$

(P — pressure).

For the period of drop in speed, besides the Prout — Thomkins equation

$$\log \frac{\alpha}{1-\alpha} = k_3 t + C_3, \quad (3)$$

this equation was applied

$$\log \frac{\alpha}{1-\alpha} = k_2 t + C_2. \quad (4)$$

Calculations were also made by the Avrama — Yerofeyev equation:

$$-\log (1-\alpha) = (k_3 t)^n \quad (n = 2, 3, 4) \quad (5)$$

and the Roginskiy — Todes equation:

$$1 - (1 - \alpha)^{1/2} = k_4 t. \quad (6)$$

The last equation earlier turned out to be convenient for description of disintegration of ammonium perchlorate at high temperature.

The temperature dependence of the period of induction was calculated by the equation

$$\tau e^{-E/RT} = \text{const.} \quad (7)$$

Because of the determination of the period of induction in literature there are contradictory opinions. Certain authors, studying disintegration of ammonium perchlorate, determined τ as the time of the beginning of the reaction.

In such a case, τ to a considerable extent depends on the sensitivity of the method of measurement. Other authors determine τ as the time, for the duration of which the tenth part or half of the final pressure of the products is formed. Finally, they mention the period of induction as the time of achievement of maximum speed. In such a meaning, the period of induction also contains the period of acceleration. In our work, the induction period was determined as the time of achievement of maximum speed ($\tau_{\max}$) and as the time of beginning of the reaction (τ).

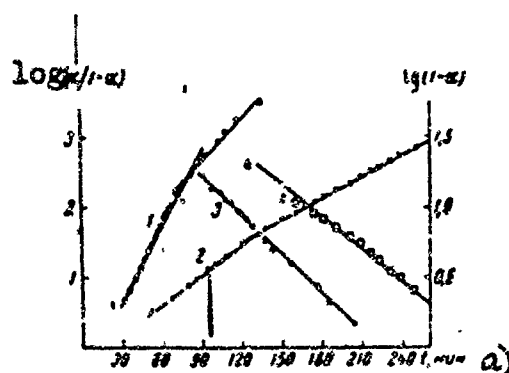


Fig. 2.

a) minutes

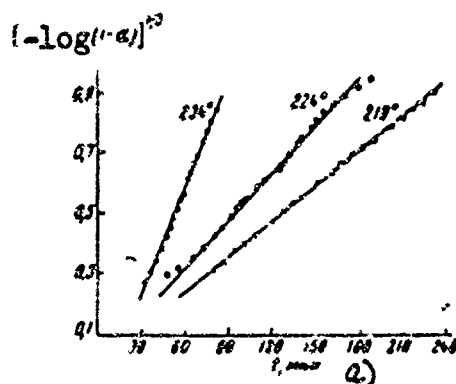


Fig. 3.

a) minutes

Fig. 2. Kinetic analysis of disintegration of pure ammonium perchlorate with the help of the Prout - Thomkins equation and equation (4):

1, 2 - curves in coordinates $\log(a/(1-a)) - t$ (234 and 219°, correspondingly); 3, 4 - curves in coordinates $\log(1-a) - t$ (225 and 219°, correspondingly)

Fig. 3. Kinetic analysis of disintegration of pure ammonium perchlorate with the help of the Avrami - Yerofeyev equation.

Table 1

a) Индукционный период (τ) и константы скорости (k)	b) Температура, град										c) Энергия активации, ккал/моль
	216	219	223	224.5	225.5	229	230	231	234	234.5	
τ, max, мин d)	218	151	116	90	106	79	76	90	59	61	32,1
τ, мин d)	119	—	90	64	73,5	65	43	59	39	39,5	32,8
k ₁ · 10 ³	—	—	—	—	—	—	—	—	—	—	—
(α=0,34+0,5)	1,04	1,46	2,15	1,53	2,01	3,43	2,3	3,35	3,87	3,62	33,5
k ₂ · 10 ³	—	—	—	—	—	—	—	—	—	—	—
(α=0,54+0,91)	0,60	0,74	1,49	1,0	1,08	1,43	1,18	—	—	1,83	32,7
k ₃ · 10 ³	—	—	—	—	—	—	—	—	—	—	—
(α=0,3+0,9)	0,47	0,60	0,847	0,834	0,95	0,95	1,18	—	—	1,86	29,6
k ₄ · 10 ³	—	—	—	—	—	—	—	—	—	—	—
(α=0,05+0,81)	0,25	0,38	—	0,53	—	0,77	0,76	—	1,16	1,10	34,9

a) Induction period (τ) and velocity constants (k); b) Temperature, degrees; c) Activation energy, kilocalories/mole; d) minutes.

In Fig. 2, the kinetic data is represented in coordinates $\log (\alpha/1-\alpha) -t$, corresponding to the Prout - Thomson equation, and in coordinates $\log (1/1-\alpha) -t$, corresponding to equation (4) (period of drop in speed). According to the theory of Prout and Thomkins, the experimental points in coordinates $\log (\alpha/1-\alpha) -t$ must be fit into one straight line both for the period of acceleration, and also for the period of slump of speed. Temperature dependence k_1 is well described by Arrhenius equation. The significantly worst agreement with Arrhenius equation is observed in the case of temperature dependence k_2 and k_3 .

In Fig. 3, the kinetic data are represented in coordinates $[-\log (1-\alpha)]^{1/3}-t$, corresponding to equation (5) at $n = 3$. As follows from Fig. 3, this equation in the very best way describes the kinetics of disintegration.

The values of speed constants, periods of induction and activation energy, calculated by the temperature dependence of speed constants and induction periods, are represented in Table 1.

Disintegration above 240°. The period of acceleration in the temperature range 245-270° is shorter than the period of slump of speed. Decomposition proceeded to 31-33%. The most suitable for calculation of speed constants turned out to be equation (5).

In coordinates $[-\log (1-\alpha)]^{1/3}-t$, the experimental points in the range $\alpha = 0.05 - 6.0$ lie on a straight line. The activation energy, calculated by the temperature dependence k_5 , constitutes 31.6 kilocalories/mole. Inasmuch as equation (6) in the very best way describes the experimental results on the kinetics of disintegration of ammonium perchlorate with the addition of ferric oxide, it was used also for calculation of constants of the disintegration

rate of pure ammonium perchlorate. Magnitudes k_5 and k_6 are represented in Table 2.

Table 2

a)	Температура, град	k_5	k_6
		($\alpha=0.05-0.50$)	($\alpha=0.5-0.51$)
	249,0	1,28	0,540
	255,0	1,66	0,700
	258,0	—	0,836
	258,0	2,01	0,872
	259,0	2,28	0,943
	262,0	2,87	0,968
	263,0	2,55	1,24
	265,5	3,57	1,14
	267,0	3,22	—
b)	Энергия активации, ккал/моль		
		31,6	32,7

a- Temperature, degrees; b- Activation energy, kilocalories/mole.

Disintegration of Ammonium Perchlorate in the Presence of Ferric Oxide

Kinetics of reaction below 240°. The addition of ferric oxide changes the form of curve $v - t$; however the reaction of disintegration of ammonium perchlorate remains autocatalytic. In the presence of ferric oxide, the period of induction (τ) decreases, while the disintegration rate (i.e. the value of k_1 , calculated by the Prout - Thomkins equation) in the period of acceleration is somewhat increased. With the addition of ferric oxide in a large quantity, we observed a certain increase of $\tau_{\max}$. A relatively large action is rendered by ferric oxide after achievement of maximum speed. Besides the increase of speed, in this case we observed also a large degree of decomposition (40-45%).

Table 3

a) Температура, град	NH ₄ ClO ₄ :Fe ₂ O ₃ =1:1					NH ₄ ClO ₄ :Fe ₂ O ₃ =1:5				
	$\tau_{\max}$, мин с)	$k_1 \cdot 10^3$ ($\alpha=0.017$) с)	$k_2 \cdot 10^3$ ($\alpha=0.37$) с)	$k_3 \cdot 10^3$ ($\alpha=0.09$) с)	$k_4 \cdot 10^3$ ($\alpha=0.34$) с)	$\tau_{\max}$, мин с)	$k_1 \cdot 10^3$ ($\alpha=0.013$) с)	$k_2 \cdot 10^3$ ($\alpha=0.41$) с)	$k_3 \cdot 10^3$ ($\alpha=0.16$) с)	$k_4 \cdot 10^3$ ($\alpha=0.07$) с)
268	12	(17,5)	1,7	10,9	5,60	9	21,0	5,0	34,0	20,2
265,5	13	13,0	1,2	9,82	5,30	10	14,0	3,6	25,4	14,0
262	16	9,1	1,38	8,42	4,50	11	13,1	4,3	25,0	14,5
259	18	7,8	1,14	8,25	4,28	14	10,0	3,6	21,9	12,0
255	23	5,7	0,95	5,28	3,05	15	—	2,6	15,6	9,1
249	—	5,3	0,69	4,36	2,3	—	6,3	1,9	11,1	6,7
b) Энергии активации, ккал/моль	29,8	35,6	30,9	28,2	30,6	27,6	28,5	29	31,9	30,9

(a) Temperature, degrees; (b) Activation energy, kilocalories/mole;
(c) Minutes.

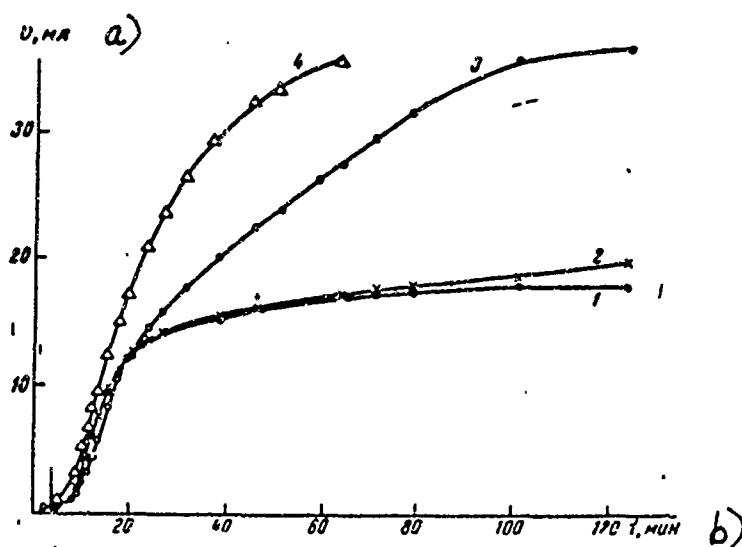


Fig. 4. Kinetics of thermal disintegration of ammonium perchlorate in the presence of ferric oxide (265.5°):

1 — pure ammonium perchlorate; 2 — NH₄ClO₄:

Fe₂O₃ = 8: 1; 3 — NH₄ClO₄: Fe₂O₃ = 1 : 1;

4 — NH₄ClO₄: Fe₂O₃ = 1:5.

a) ml; b) minutes.

The kinetics of disintegration above 240°. Above 240°, under the influence of ferric oxide, the degree of decomposition of ammonium perchlorate reaches 60-95%. A period of induction (τ) was not detected. In the presence of small additions of ferric oxide ($\text{NH}_4\text{ClO}_4 : \text{Fe}_2\text{O}_3 = 50 : 1-8:1$) to the achievement of a degree decomposition, equal to 25-28%, the reaction proceeds practically with the same speed as in the case of pure ammonium perchlorate.

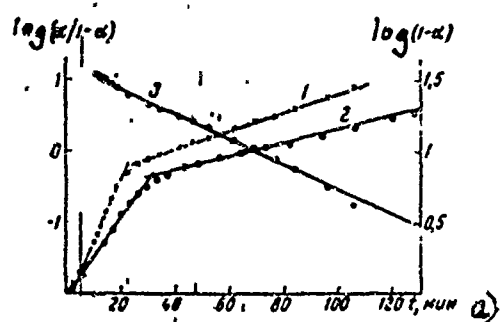


Fig. 5. Kinetic analysis of disintegration of ammonium perchlorate in the presence of ferric oxide.
1, 2 - Prout - Thomkins equation (262 and 255° correspondingly): 3 - equation (4) (262°).
a) minutes

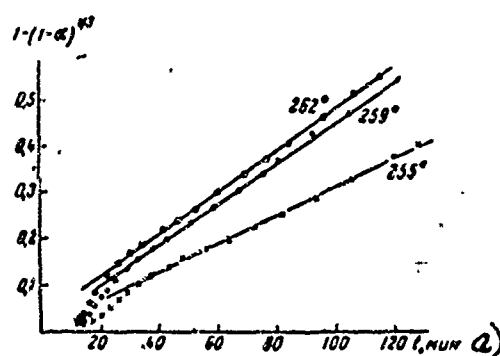


Fig. 6. Kinetic analysis of disintegration of ammonium perchlorate in the presence of ferric oxide with help of equation (6).
a) minutes

With a large content of ferric oxide ($\text{NH}_4\text{ClO}_4 : \text{Fe}_2\text{O}_3 = 1:5$) the speed of the reaction increases almost twice. Curves $v - t$ confirm the autocatalytic flow of the reaction, the values of τ_{max} are practically identical in different compositions. With an increase of temperature, τ_{max} decreases, and the maximum speed of the

reaction is increased.

Mathematical processing kinetic curves was conducted with the help of equations (1), (3), (4), and (6).

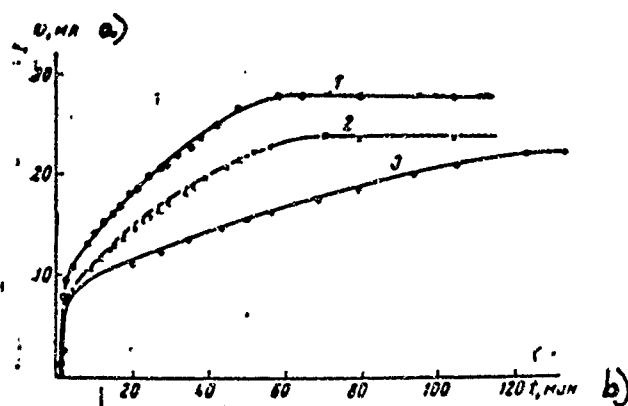


Fig. 7. Curves $v - t$ of thermal disintegration of ammonium perchlorate in the presence of ferric oxide above 320° :
 1 - $\text{NH}_4\text{ClO}_4:\text{Fe}_2\text{O}_3 = 50:1$ (359.5°);
 2 - $\text{NH}_4\text{ClO}_4:\text{Fe}_2\text{O}_3 = 20:1$ (341°);
 3 - $\text{NH}_4\text{ClO}_4:\text{Fe}_2\text{O}_3 = 20:1$ (325°)
 a) ml; b) minutes

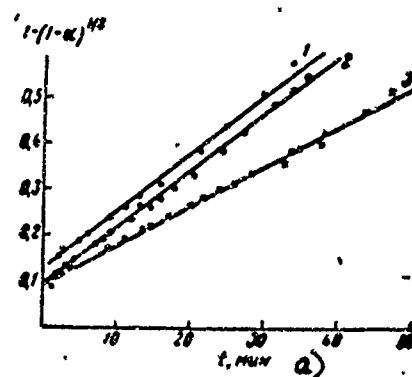


Fig. 8. Kinetic analysis of disintegration of ammonium perchlorate in the presence of ferric oxide with the help of equation (6)
 1 - $\text{NH}_4\text{ClO}_4:\text{Fe}_2\text{O}_3 = 8:1$ (325°);
 2 - $\text{NH}_4\text{ClO}_4:\text{Fe}_2\text{O}_3 = 50:1$ (366°);
 3 - $\text{NH}_4\text{ClO}_4:\text{Fe}_2\text{O}_3 = 20:1$ (341°)
 a) minutes

The magnitudes of speed constants are given in Table 3. The temperature dependence of speed constants is well described by Arrhenius equation.

Kinetics of reactions above 300° . Inasmuch as above 380° , ammonium perchlorate explodes even with a small addition of ferric oxide, the experiments were conducted in the range of $320-380^\circ$. We investigated mixtures of the composition $\text{NH}_4\text{ClO}_4:\text{Fe}_2\text{O}_3 = 20:1; 50:1$ and $8:1$. The reaction proceeded in two stages: for the duration

of the first 2-3 minutes independent of the quantity of ferric oxide and temperature, we observed very fast decomposition, after which followed a slow reaction.

The quantity of gas formed in the course of the initial stage depended only on the initial quantity of perchlorate and did not depend on the temperature and content of ferric oxide in the samples. The kinetics of the slow stage in the best way is described by equation (6). To establish a kinetic law of initial stage of the reaction was not possible due to the high speed. The values of k_0 and activation energies are given in Table 4.

Table 4

a) Температура, град	NH_4ClO_4 $k_0 \cdot 10^3$ ($\alpha = 0.33 \div$ $\div 0.72$)	$\text{NH}_4\text{ClO}_4:\text{Fe}_2\text{O}_3$		
		50:1	20:1	3:1
		$k_0 \cdot 10^3$ ($\alpha = 0.32 \div$ $\div 0.81$)	$k_0 \cdot 10^3$ ($\alpha = 0.32 \div$ $\div 0.88$)	$k_0 \cdot 10^3$ ($\alpha = 0.33 \div$ $\div 0.85$)
377	—	17,4	18,8	—
366	7,42	11,9	14,0	—
359	5,14	8,83	—	Взрыв
350	—	4,85	8,51	Взрыв
341	1,08	3,81	8,43	16,6
335	1,05	3,03	6,44	14,5
330	1,14	3,16	—	10,8
325	0,746	—	3,72	12,3
320	—	—	—	8,8
b) Энергия активации, ккал/моль	40,9	30,9	25,7	22,0

- a) Temperature, degrees; b) Activation energy, kilocalories/mole;
c) Explosion.

For a comparison in that same temperature range, we investigated the decomposition of pure ammonium perchlorate. Kinetic curves of decomposition are represented in Fig. 9 and 10. The activation energy calculated by the temperature dependence k_s , consists of 40.9 kilocalories/mole, which well coincides with the value of 40 kilocalories/mole obtained by Galwey and Jacobs [4] for the range 30-33%.

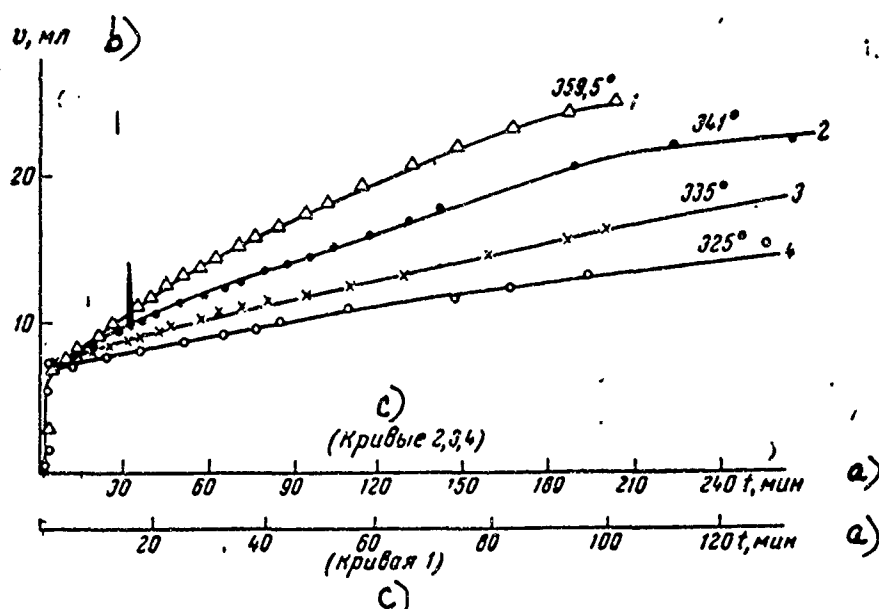


Fig. 9. Curves $v - t$ of thermal disintegration of pure ammonium perchlorate above 320°
a) minutes; b) ml; c) Curves

Below 240° comparatively weak catalytical action of ferric oxide took place; however, even in this case the reaction proceeded to a degree of decomposition greater than 30-33%.

A more significant catalytical action was detected in the range $245-270^\circ$. Decomposition proceeded by 60-100% without a period of induction. Such a disintegration rate was observed for pure

ammonium perchlorate only at a temperature considerably exceeding 300° . The magnitudes of activation energy, calculated from the temperature dependence of speed constants, computed with the help of different kinetic equations, constitute 29-33 kilocalories/mole, which coincides with the magnitude of activation energy, received for disintegration of ammonium perchlorate at low temperatures.

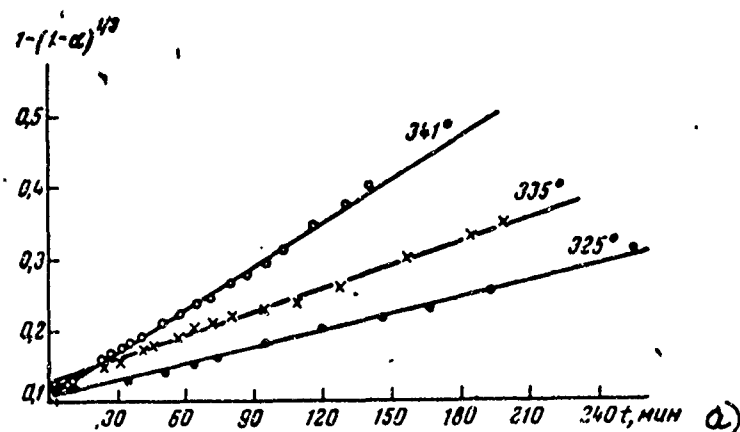


Fig. 10. Kinetic analysis of thermal disintegration of pure ammonium perchlorate with the help of equation (6)
a) minutes

This magnitude corresponds to the activation energy of the transfer of an electron from an anion to a cation; in other words, it is identical to the energy, necessary for transference of an electron from the valence band into the conduction band.

From the coincidence of magnitudes of activation energy we can make the conclusion that in the presence of ferric oxide at $245-270^{\circ}$, a decisive role is played by the electron mechanism. In all probability, the catalytical action of ferric oxide is reduced to acceleration of the transition of electrons from anion

to cation, i.e. the process of formation of radicals NH_4 and ClO_4 . This process, apparently, proceeds in two stages. In the first stage transition of an electron from an anion of perchlorate to an ion of Fe^{3+} takes place with the formation of an ion of Fe^{2+} and radical ClO_4 . In the following stage, ion Fe^{2+} transmits the electron to an ion of ammonium, as a result of which the latter is turned into a radical and again Fe^{3+} will be formed. On the basis of this mechanism it is possible to expect that oxides of other transitional metals also will render a catalyzing action on the disintegration of ammonium perchlorate, which must depend on the electron structure of oxidized metal. The results of our investigations with nickel oxide completely confirm this hypothesis.

Investigation of disintegration of ammonium perchlorate in the absence of ferric oxide and in mixtures with the latter at 330-380° showed that in these conditions decomposition proceeds practically by 100%. In both cases disintegration proceeded in two stages. The speed of first, very fast stage practically did not depend on the content of ferric oxide. The content of ferric oxide led to a significant increase of speed and lowering of activation energy. That fact that in the initial, fast stage only 31-33% perchlorate reacts, indicates flow of the reaction in the pre-surface layer, occurring in a general case in the range 200-300°. The main mass of perchlorate is disintegrated in the second stage. Activation energy of the second stage is equal to the activation energy of the high-temperature reaction, proceeding, according to Galwey and Jacobs, by the proton mechanism. In this case of a limiting stage of reaction is the transmission of proton from an ion of ammonium to a perchlorate-

ion $\text{NH}_4\text{ClO}_4 \rightleftharpoons \text{NH}_3 + \text{HClO}_4$, after which follows oxidation of ammonia by the products of disintegration of chloric acid. In spite of the fact that the value of activation energy of disintegration of pure ammonium perchlorate coincides with the value of activation energy of the reaction, proceeding by the proton mechanism, in our opinion, is so incredible that this mechanism takes place in the presence of ferric oxide, inasmuch as the addition of ferric oxide significantly lowers the activation energy. It is more probable that the action of ferric oxide consists in catalysis of the reaction of decomposition of a perchlorate anion and oxidation of ammonia by the products of disintegration.

The experiments of Bircumshaw and Newman [9] indicate that in the disintegration of ammonium perchlorate decomposition of the perchlorate-ion can be the limiting stage. According to the data of these authors, the activation energy of disintegration of perchlorate at high temperature is practically equal to the activation energy of disintegration of pure potassium perchlorate. The data of Otto and Fry [10], and also our results indicate that ferric oxide, similar to nickel and copper oxide, significantly lowers the activation energy of disintegration of potassium perchlorate, and this can be explained only in the assumption on breaking the bond $\text{Cl} - \text{O}$.

Lowering the activation energy of disintegration of ammonium perchlorate with an increase of the content of ferric oxide is explained by the fact that the growth of quantity of ferric oxide in mixtures leads to an increase of the surface of contact of perchlorate with the catalyst, in consequence of which the

catalytical reaction, energetically more profitable, appears on the first plan as compared with the reaction of disintegration of pure perchlorate.

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