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TRANSLATION

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ENGLISH TITLE: The Mechanism of Combustion of Ammonium Perchlorate

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ABSTRACT: A quantitive determination is made of the ionization zone in disequilibrium within the reaction layer of the flame jet used in studying the concentration of positive and negative ions present in a flame of ammonium perchlorate.

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In the study [1] concerning the measurement of the concentration of positive and negative ions in a flame of ammonium perchlorate (a. pc.), it was determined that in the reaction layer of the flame jet there is an ionization zone in disequilibrium. This zone is caused by physical-chemical processes of decomposition of the condensed phase. The concentration of charged particles in the zone of the chemical reaction at a relatively low temperature of 800-1300° K reaches 10^{17}-10^{18} cm^{-3}. The high degree of ionization, $\beta = 10^{-2}$-10^{-3}, shows that the gas in this zone is in a plasma state ($\frac{e^2}{r} \approx kT$, i.e. the Coulomb interaction between charged particles is comparable to thermal energy where r is the average distance between the ions).

A correlation was established between the speed of ionization and the speed of formation of Schottky effects on the surface of a. pc. crystals.

The present study is devoted to the explanation of the formation of the ionization zone during combustion of a. pc. and to the determination of quantitative relationships between the different kinetic regularities in the condensed and gas phases during decomposition (combustion) of inorganic oxidizers.

With this aim in mind, measurements were taken of the electric conductivity of a. pc. in the condensed phase during the process of combustion. The experiments were conducted with an atmosphere of nitrogen and a pressure range of from 200 mm of mercury column up to 100 atmospheres. The charges were prepared from two rectangular tablets with dimensions of 30 X 30 X 4 mm and a density $\rho = 1.94 - 1.96$ g/cm^3. Between the tablets probes of tungsten-rhenium wire were placed at a distance $l = 2$ mm. The difference in potentials applied to the probes varied, in relation to the conditions of the experiment, within the limits of 0-50 v. The temperature of the flame was measured simultaneously at a point on the location of the probes by a thermocouple. In separate experiments the probes themselves were used as thermocouples, and the speed of combustion was judged by the change of pressure in the bomb.

In crystals with Schottky defects, the number of vacant cation lattice points is equal to the number of vacant anion lattice points. In the case of Frenkel defects, the number of ions in the interstices equals the number of holes. As was shown by Mott and Gerni [2] , the conductivity is determined by the former defects at high temperatures and by the latter defects at low temperatures; however, in both cases the expression for electrical conductivity σ, with an accuracy up to the constant factor, can be expressed in the form

$$\sigma = \frac{A}{T} \exp(-E/kT). \qquad (1)$$

Only the defect activation energy E can vary to a significant degree (A = constant; T = temperature, °K; k = Boltzmann constant). From this it follows that the expression

$$d(\ln \sigma T)/d(1/kT) = -E \qquad (2)$$

determines the activation energy of the decomposition process. In fig. 1 the results of the measurement of electrical conductivity of a. pc. in the condensed phase (in the warmup and reaction zones) during combustion in an atmosphere of nitrogen at p = 200 mm merc. col. are plotted against inverse temperature. As can be seen from fig. 1, the change of activation energy in the temperature range of 200-300° C is approximately twice as small as in the range of 300-450° C and is on the order of 0.7 ev and 1.5 ev, respectively. In one study 3 measurements were taken of the relation between electrical conductivity and the temperature of monocrystals of a. pc. In this study four different regions were discovered in which the magnitude of the activation energy fluctuates between 45 kilocalories/mole at a temperature 255° C and 4 kilocalories/mole at temperatures less than 92° C. After taking the a. pc. crystal out of the electrical-conductivity measuring cell, it turned out that the crystal surface in the vicinity of the positive electrode turned opaque, while the rest of the crystal maintained its original transparency. If an a. pc. crystal is subjected to similar thermal action, but without the electric field, then it will become completely opaque. In the low-temperature region this effect can be related to the formation of the ammonium ion NH_4^+ (the size of NH_4^+ is small in comparison to ClO_4^-) and to the introduction of NH_4^+ into the lattice interstices (Frenkel defects). In the high-temperature range, $>300°$ C, Schottky defects will predominate. The reason for the loss of transparency at the positive electrode can possibly be related to the presence of the ClO_4^- ion.

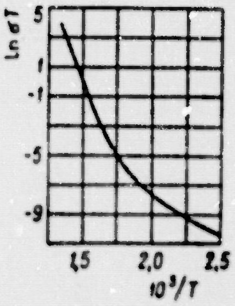

Fig. 1. Electric conductivity of a. pc. in condensed state as a function of temperature.

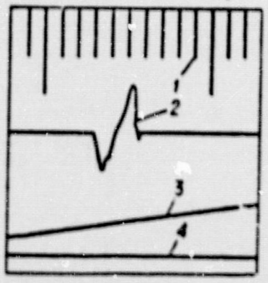

Fig. 2. Typical oscillogram recording of potential on a. pc. decomposition surface with potential difference between the probes equal to zero. 1-time marks; 2-recording of surface potential; 3-pressure in bomb; 4-base line.

Based on the results given above, it can be concluded as a first approximation, that in the temperature range of 20-300° C the electrical conductivity is determined by the formation of NH_4^+ ions, and in the range of 300-450° C electrical conductivity is determined by NH_4^+ and ClO_4^- ions. From the point of view of trying to understand the mechanism of combustion of a. pc., the following result obtained in our experiments is of considerable interest. If the probes are spread out a fraction of a millimeter on the vertical plane of the charge, and if a potential difference is not applied to them, then at the moment when the reaction layer of a. pc. passes through the plane of the probes, a potential difference develops which is on the order of 0.3 - 0.5 v (fig. 2). Thus, during combustion of a. pc. a relatively large difference in potentials develops on the surface.

Thus, we can note three significant results obtained in our experiments:

1) the decomposition-activation energy of a. pc. grows in relation to the increase of the temperature in the warmup zone (the Michelson layer) of the a. pc. charge;

2) a difference in potentials develops in the reaction layer;

3) the gas which is directly adjacent to the surface of burning a. pc. is in a state of plasma.

Discussion of the Results

The idea of the formation of dissociated atoms and holes within and on the surface of crystals was put forward and developed in the studies of Ioffe [4] and Frenkel [5] . If a positive ion leaves the surface and penetrates an interstice, then there is a surplus positive charge in the inner portion of the crystal, whereas the surface loses this charge. The presence of these intruding atoms creates strong electric fields in the crystal. However, the charge equilibrium in the crystal is maintained, if the positive ions do not leave the surface but rather move from the lattice points in the crystal. This defect is called the Frenkel defect.

The energy of Frenkel defect formation is the sum of the energy of cation vacancy formation and the energy of intrusion of the positive ion into the lattice. Generally speaking, the Frenkel defect can arise in any of the sublattices of the positive or negative ions. However, since the dimensions of the positive ion are smaller, and since the positive ion creates smaller internal stresses in the lattice, the energy of Frenkel pair formation is smaller in the positive than in the negative sublattice. For this reason there is a predominance of Frenkel defects which are caused by the intrusion of positive ions into the interstices. If the vacancies are formed by means of a transfer of positive ions from the inner lattice points to the points on the surface of the lattice (diffusion into the crystal of the surrounding vacancy [6]), then the surface is charged in relationship to the inner portion of the crystal. This transfer of charges obviously produces an increase of the energy necessary for further vacancy formation. Thus the number of surplus vacancies in one sublattice is small. One may expect that the formation of cation and anion vacancies (Schottky defects) will occur in such a manner so that the electrical neutrality of the crystal will be maintained to the extent possible.

In actuality, there exists a certain separation of charges which are on the surface and within an ion crystal like NH_4ClO_4. Since the NH_4^+ ions differ in size from the ClO_4^- ions, the energy of formation of a single vacancy in an NH_4 sublattice is smaller than the energy of vacancy formation in a ClO_4 sublattice. Accordingly, the probability of the formation of a cation vacancy, which can be determined by the Boltzmann constant and which contains the energy of vacancy formation $\exp(-E/kT)$, will be greater. On the surface of the crystal a surplus positive charge develops, while a surplus negative charge develops within. However, if the vacancies are mobile, then the total energy of the crystal reduces if surplus cation vacancies (they carry a negative charge) migrate to the surface and form a dipolar layer of Debye space charge with an excess of positive ions on the surface. At the same time cation vacancies which lie below this layer are neutralized. Thus the inner portion of the crystal again will have an equal quantity of anion and cation vacancies.

We will make an estimate of the space charge, of the lattice defects, and of the potential on the surface of the burning a. pc. charge. We will assume that the following defects are possible in an a. pc. crystal: 1) positive ions n_1 move from the inner mass of the crystal to the surface (the diffusion of a negative hole); 2) negative ions n_2 move from the inner mass to the surface of the crystal (the diffusion of a positive hole); 3) positive ions n_3 move from the surface to the interstice; 4) negative ions n_4 move from the surface to the interstice. At first, as an approximation, we will not take into account the decrease of the energy of NH_4^+ and ClO_4^- ion formation. This decrease is caused by the interaction between the forming ions and the lattice points (Debye-Hückel shadowing potential). We will also disregard the influence of ion concentration on the formation of ion pairs (associates). When there is no interaction between the defects, then their concentrations can be determined separately by the minimum condition of that portion of free energy (or thermodynamic potential) of the crystal which is caused by the presence of the defects [2] .

It can be concluded that, as a result of symmetry the mass of the macrocrystal has a constant potential when it is in a state of thermal equilibrium. Accordingly, the space charge of the crystal mass is equal to zero. For this reason the difference in potentials, φ_0 , between the surface and the volume of the crystal can be calculated from the neutrality condition of the crystal as a whole

$$\rho = e(n_3 - n_4 - n_1 + n_2), \tag{3}$$

where ρ is the density of the volume charge. From Poisson's equation

$$\frac{d^2\varphi}{dx^2} = -\frac{\rho}{\varepsilon\varepsilon_0} \tag{4}$$

with the limit conditions $\frac{d\varphi}{dx} = 0,\ x \to \infty$ and $\varphi = 0$ at $x = 0$, and from equation (3), one can calculate the magnitude of the volume charge (ε - the dielectric constant of a. pc. ≈ 5; $E_o = 8.84 \times 10^{-14}$ $\frac{а \cdot сек}{в \cdot см}$; $\rho - \frac{а \cdot сек}{см^3}$; $x - см$; $\varphi - в$).

φ denotes the field potential at point x, which is near the surface. In order to obtain the energy of occurence of a defect at a corresponding (inner) point of the a. pc. crystal, we subtract the derivate of $e\varphi$ from the defect formation energies E_1 and E_4, and we add the derivative to E_2 and E_3. Under such conditions the volume concentrations of these defects can be written in the form

$$n_1 = n_0 \exp\left(-\frac{E_1 - e\varphi}{kT}\right); \quad n_3 = n_0 \exp\left(-\frac{E_3 + e\varphi}{kT}\right); \tag{5}$$
$$n_2 = n_0 \exp\left(-\frac{E_2 + e\varphi}{kT}\right); \quad n_4 = n_0 \exp\left(-\frac{E_4 - e\varphi}{kT}\right),$$

where n_0 is the number of nodes (of ions) in a unit of volume (cm^3). In accordance with Schottky and Frenkel, we will consider that the interstices of the a. pc. crystal are too small to allow the intrusion of positive or negative ions (i.e., E_3 and E_4 are infinitely large magnitudes). As we will show below, this assumption does not in any way change the generality of the solution, but it does simplify the solution of the problem.

Now, (3)-(5) reduce to the following:

$$\Delta\varphi = -\frac{en_0}{\varepsilon\varepsilon_0}\left(e^{-\frac{E_2 + e\varphi}{kT}} - e^{-\frac{E_1 - e\varphi}{kT}}\right) \tag{6}$$

with limit conditions

$$\varphi = 0 \ \text{при} \ x = 0 \ \text{и} \ \frac{d\varphi}{dx} = 0; \quad \varphi^0 = \frac{E_1 - E_2}{2e} \ \text{при} \ x \to \infty.$$

If a dimensionless magnitude is introduced

$$\psi = -\frac{e\varphi}{kT} + \frac{E_1 - E_2}{2kT}, \tag{6'}$$

then

$$\Delta\psi = \frac{2e^2 n_0}{\varepsilon\varepsilon_0 kT} e^{-\frac{E_1 + E_2}{2kT}} \operatorname{sh}\psi. \tag{7}$$

we introduce a new variable $\xi = ax$ and designate $a^2 = \frac{2en_0}{\varepsilon\varepsilon_0 kT} e^{-\frac{E_1 + E_2}{2kT}}$. Then (7) can be represented as

$$\frac{d^2\psi}{d\xi^2} = \operatorname{sh}\psi \tag{8}$$

with limit conditions $\psi = 0; \ \frac{d\psi}{d\xi} = 0 \ \text{при} \ \xi \to \infty \ \text{и} \ \psi = \psi_0 = -\frac{E_2 - E_1}{2kT}$ at $\xi = 0$.

The first integral of equation (8) with limit conditions taken into account is

$$\left(\frac{d\psi}{d\xi}\right)^2 = 2(\operatorname{ch}\psi - 1). \tag{9}$$

With allowances made for the properties of the hyberbolic cosine, we can write

$$\frac{d\psi}{d\xi} = -2\operatorname{sh}\frac{\psi}{2}. \tag{10}$$

Further integration gives the following expression for potential distribution

$$\ln\frac{\exp(-\psi/2)+1}{\exp(-\psi/2)-1}=2\xi+\ln\frac{\exp(-\psi_0/2)+1}{\exp(-\psi_0/2)-1}\,. \qquad (11)$$

If the formation of defects n_3 and n_4 is taken into account, a coefficient of $\sqrt{2}$ is placed in front of ξ in (11). A consistent solution for (5) and (11) determines the concentration of the defects as a function of the distance from the surface.

Now let us make a numeral estimate of the magnitude of the surface charge δ , of the potential difference φ_0, and of the width of the surface layer of charge on an a. pc. crystal ds = 1/a, in which the condition of equality of the defects is not met.

If the assumption is made (cf. fig. 1) that the energy required to transfer the positive ions n_1 from the mass of the crystal to the surface is $E_1 \approx 0.6$ ev, and that this same energy for the negative ions is $E_2 \approx 1.5$ ev, then the difference in potentials between the surface and the mass of a. pc. will be

$$\varphi_0=\frac{E_1-E_2}{2e}\approx 0{,}5\ \text{v}, \qquad (12)$$

i.e., there is agreement in magnitude with the results obtained. Accordingly, in the region directly adjacent to the surface there will be a surplus of positive ion vacancies. This vacancy surplus has a negative charge, while the positive ions form a positive charge on the surface of the a. pc. crystal.

The quantity d_s = 1/a, which characterizes the extent of the penetration of charge into the crystal,

$$d_s=\left(\frac{\varepsilon\varepsilon_0 kT}{2e^2 n_0}\right)^{0,5} e^{\frac{E_1+E_2}{4kT}}=2{,}2\cdot 10^{-10}\sqrt{T}\,\exp\frac{6100}{T}\,, \qquad (13)$$

is presented in fig. 3.

Thus, the neutrality condition $n_1 = n_2$ is met only at distances from the surface of the a. pc. crystal which are large in comparison to 1/a (when the concentration is small, 1/a can be of the same order of magnitude as the linear dimensions of a. pc. crystals which make up the fuel charge; in this case the neutrality condition is not met at all).

The magnitude of the charge δ per unit of area can be obtained from equations (10) and (6'), since these formulas determine the field potential on the very surface and, thus, the charge magnitude.

$$\delta=\left(\frac{d\varphi}{dx}\right)_{x=0}=(2\varepsilon\varepsilon_0 kTa/e)\,\mathrm{sh}\,\frac{e\varphi_0}{2kT}\,. \qquad (14)$$

For an a. pc. crystal at T = 700° K, we obtain the value $\delta = 1.1 \times 10^{12}$ charges per cm^2 (fig. 4). Since there are $\sim 5 \times 10^{14}$ ions in 1 cm^3 of surface volume, the absence of 0.2 - 0.3% of the negative ions is sufficient to create the necessary space charge.

Up until now, although there are a large number of studies devoted to the combustion of a. pc. (references in the reviews [7, 8]), there is not one that presents a concept of the mechanism of the a. pc. decomposition reaction. A number of investigators assume that the limiting stage during thermal decomposition of a. pc. is the transfer of an electron from a ClO_4^- ion to an NH_4^+ ion. Others conclude that the stage which determines the speed of the reaction is the transfer of a proton from the NH_4^+ ion to the ClO_4^- ion. The authors of studies [9] consider that both mechanisms occur.

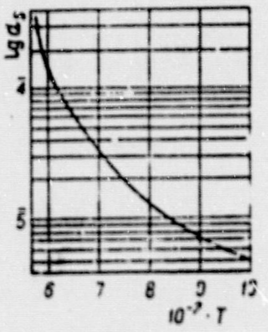

Fig. 3. Width of the layer of space charge as a function of temperature.

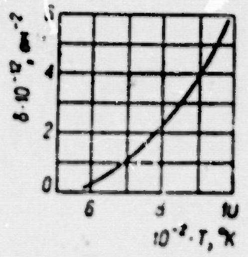

Fig. 4. Magnitude of surface charge as a function of temperature.

At relatively low temperatures there is an electron transfer. In the high temperature range there is a proton transfer. It is proposed that these reactions occur in the solid phase.

As is seen in the results presented above, the most probable limiting stage is the stage of defect formation (the role which dislocations play in thermal decomposition of NH_4ClO_4 crystals is treated in studies [3, 7]) and defect association, since the reactions described ~~are~~ related to the transfers, these reactions must occur on the surface where the probability of an inverse process is reduced to a minimum.

Accordingly, the anion and cation vacancies forming within the a. pc. crystal will most probably associate with the formation of ion pairs (neutral dipolar molecules), if we disregard the possibility of migration of the vacancies to the surface. This association is advantageous from the energetic point of view since the total energy of the crystal is reduced. In study [10] it was shown that in solutions with high concentrations of ions (in our case, defects) a state is realized in which the Debye sphere contains only one ion, which is of the opposite sign of the central ion. In this case the formation of a pair (an associate) is more likely than the formation of a central ion with the atmosphere.

We will estimate the quantity of ion pairs forming as a result of the association of oppositely charged ions.

Assume that there are N lattice points per unit volume. n_s is the quantity of unassociated ion pairs (an estimate of the speed of formation of Schottky defects is made in study [1]). n_a is the quantity of associated ion pairs. W_a is the association energy for one pair. Z is the number of possible orientations of the group. The free energy F (or Gibb potential) can be represented as

$$F = -n_a W_a + kT \ln P_1 P_2, \tag{15}$$

where $\ln P_1 P_2$ is the configuration enthropy, P_1 is the number of different ways of distributing the associated ion pairs in the lattice

$$P_1 = Z^{n_a} \frac{N!}{n_a!\,(N-n_a)!}, \tag{16}$$

and P_2 is the number of ways of transfering the remaining unassociated ions into the $(N-n_a)$ lattice points.

$$P_2 = \frac{(N-n_a)!}{2(n_s-n_a)!\,(N-2n_s+n_a)!}\,. \tag{17}$$

Substituting (16) and (17) in (15) and taking Stirling's formula into account, we obtain

$$F = -n_a W_a - kT\,[n_a \ln Z + N \ln N - n_a \ln n_a + n_a - 2(n_s - n_a) \times \\ \times \ln(n_s - n_a) + 2(n_s - n_a) - (N - 2n_s + n_a) \cdot \ln(N - 2n_s \mp n_a). \tag{18}$$

The concentration of associated vacancy pairs can be obtained from the minimum energy condition: $\left(\frac{\partial F}{\partial n_a}\right)_{T,\,n_s,\,V} = 0.$

$$-\frac{W_a}{kT} - \ln Z + \ln n_a - \ln(n \quad - n_a)^2 + \ln N = 0. \tag{19}$$

Assuming that $N \gg n_a; n_s$.

$$\frac{n_a N}{(n \quad - n_a)^2} = z \cdot e^{\frac{W_a}{kT}}.$$

Designating the extent of defect formation as $\mu = \frac{n_s}{N}$, and the extent of association as $\alpha = \frac{n_a}{n_s}$, equation (19) can be represented in the form

$$\frac{\alpha}{(1-\alpha)^2} = \mu Z e^{\frac{W_a}{kT}} . \qquad (20)$$

When deriving equation (20), interaction of the defects among themselves and with the lattice points was disregarded. One can discount this interaction on the basis of the Debye-Hückel theory, which means that the energy of association W_a decreases. In accordance with these factors, one can expect that the extent of association obtained above will be somewhat less. As a result of the interaction, the effective enthalpy of defect formation will decrease, and accordingly, more defects will form.

Unfortunately, the energy of a. pc. lattice formation is not known. However, if we proceed from the data for salts such as NH_4Cl, then the energy for a. pc. lattice formation should be on the order of 100-150 kcal/mole. It is known that the energy of ion pair formation W_a accounts for ~0.7 of the lattice energy. Therefore, with $\mu = 10^{-2} - 10^{-3}$ [1] and $Z = 6 \div 10$, the right half of equation (20)

$$\mu Z e^{\frac{W_a}{kT}} \gg 1 .$$

Accordingly, the degree of association of the defects forming in the a. pc. crystal will be close to one.

As was shown above, the a. pc. decomposition process proceeds through defect formation. Some of these defects form a space charge as a result of transfer to the surface. Other defects form associates (ion pairs) which pass into the gas phase or dissociate near the surface and form radicals or products such as $HClO_4$ and NH_3. These ion pairs can also form a space charge near the surface (a low-temperature chemical plasma).

We will make an estimate of the concentration of ion pairs occuring in the gas state. We will assume that the quantity of associates in the solid phase n_a and in the gas phase n_g remains constant:

$$n_a + n_g = n. \qquad (21)$$

The free energy of the condensed phase of a. pc. F_a can be written in the form

$$F_a = -kT\left[\ln\frac{(N+n_a)!}{n_a!N!} + \left(2\,\mathrm{sh}\frac{\hbar\omega}{2kT}\right)^{-3n_a}\right]. \qquad (22)$$

Here it is assumed that the ions are in a quasi-crystal state and have three degrees of vibrational freedom. We will disregard the degree of rotational freedom. The free energy of the gas phase

$$F_g = n_g W_g - n_g kT\left[\ln\left(\frac{2\pi m kT}{h^2}\right)^{3/2} - \ln n_g + 1\right] - kT\left[2\,\mathrm{sh}\frac{\hbar\omega}{kT}\right]^{-n_g}, \qquad (23)$$

where W_g is the vaporization heat of one ion pair; from the condition of the minimum of free energy

$$\left(\frac{\partial F_g}{\partial n_g}\right)_{T,V,n} + \left(\frac{\partial F_a}{\partial n_g}\right)_{T,V,n} = 0 \qquad (24)$$

we obtain

$$n_g = \left(\frac{2\pi mkT}{\hbar^2}\right)^{3/2}\left(2\,\mathrm{sh}\,\frac{\hbar\omega}{2kT}\right)^2 e^{-\frac{W_g}{kT}}\frac{n_a}{N}, \qquad (25)$$

where m is the mass of the ion pair, $W_g = U_0 - W_a$ is on the order of 30 Kcal/mole, $T \simeq 700^\circ$ K, $\frac{h\omega}{2kT} \simeq$ 3-4, and according to the estimate made in [1] , the ratio $\frac{n_a}{N} \approx \frac{n_i}{N}$ is on the order of 10^{-1}-10^{-2}. Consequently, as can be seen from equation (25), n_g will have an order of magnitude of 10^{16}-10^{17} cm^{-3}. From this information it becomes clear, from the point of view of energetics, how a chemical plasma in the gas phase can form at such a low temperature of 1000° K. The fact is that the dissociation energy of ion pairs (associates) of a. pc. is on the order of 2-2.5 ev; i.e., this energy is much lower than the potential of ionization of combustion products such as NO, CO, HCl, etc. If one also takes into account the decrease of dissociation energy caused by the interaction of dipole molecules and ions $\sim \frac{e^2}{r}\mu \approx 0.6$-$0.8$ ev (μ is the dipole moment, e is the charge, r is the approach distance of the molecules and an ion) in the plasma, then the dissociation energy can turn out to be equal to 1.0-1.5 ev. Now we will give an estimate of the width of the ionized layer in the flame jet of a. pc.

In this case, Poisson's equation is written in the form

$$\Delta\varphi = -\frac{en_g}{\varepsilon\varepsilon_0}\left(e^{-\frac{W_a+e\varphi}{kT}} + e^{-\frac{W_a-e\varphi}{kT}}\right) \qquad (26)$$

with the limit condition $\varphi = 0$ at $x = 0$ & $\varphi_0 = \frac{E_1 - E_2}{2e}$ at $x \to \infty$. The solution will be analagous to that of (6). The magnitude d_g, which characterizes the width of the ionized zone in the gas phase of the a. pc. jet, is equal to

$$d_g = \left(\frac{\varepsilon\varepsilon_0 kT}{2e^2 n_g}\right)^{0.5} e^{\frac{W_a}{2kT}}. \qquad (27)$$

At T = 1000° K we have d_g = 0.5 mm. This order of magnitude (if we account for the fact that accurate values of U_0, W_a, and W_g are not known) agree with the width of the ionized zone found during combustion of a. pc. in a vacuum (P = 200 mm of mercury column). In fig. 5, a narrow, luminous strip, which is about 1 mm wide, can be seen above the combustion surface of the a. pc. charge.

From the results presented above, one can conceive of a possible mechanism of combustion of ammonium perchlorate (fig. 6):

1. In the warmup zone of condensed phase there is a formation of negative and positive ion defects. The ions form a space charge of high conductivity in the reaction layer of the a. pc.

2. Since exchange reactions are hindered in the layer near the surface, the association of ions occurs with a formation of ion pairs since this formation is more advantageous from an energetics point of view.

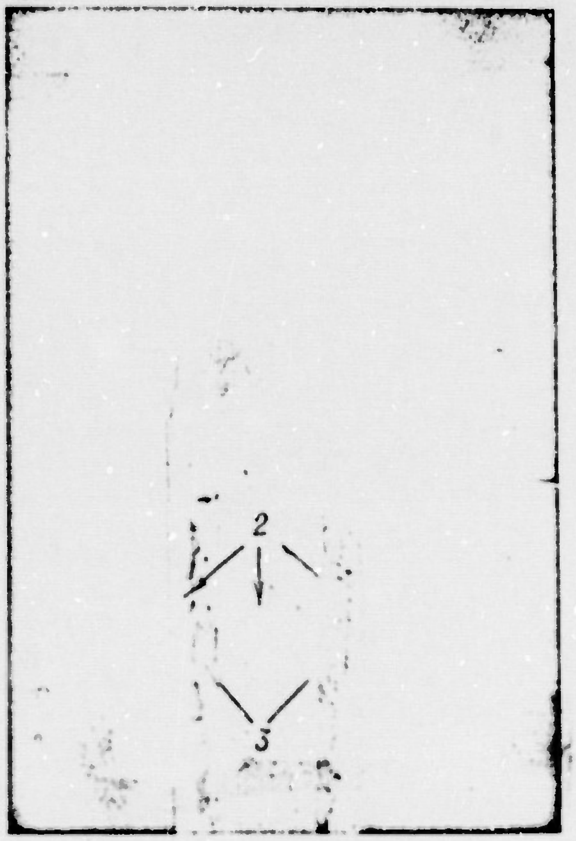

Fig. 5. Combustion of a. pc. at p = 200 mm of mercury column 1 - zone of chemical plasma; 2 ammonium perchlorate; 3 - fuel layer.

3. When the associates come out onto the surface of the a. pc. crystal, they dissociate and form radicals of the type like $ClO_4^{\cdot}$ and $NH_4^{\cdot}$ or HCl_4 and NH_3. Zones of ionization in the gas phase (chemical plasma where $e^2/r = kT$) are formed from these surfacing associates.

Now let us examine how the speed of combustion of a. pc. can be effected by the physical-chemical processes which occur in the condensed phase of the a. pc. crystal.

From the first portion of this study, it can be concluded that the limiting stage of the combustion of a. pc. is most probably the defect formation in the condensed phase. In accordance with the studies of Zel'dovich and Frank-Kamenetskiy [11] , we will assume that the formation of defects and the ensuing chemical reactions which liberate heat occur in a narrow zone near and on the surface of the burning a. pc. at a temperature T_a. Using the substance-balance method [12] and assuming that the reaction is accompanied by the formation of only one interstitial product (Schottky defects), we can write:

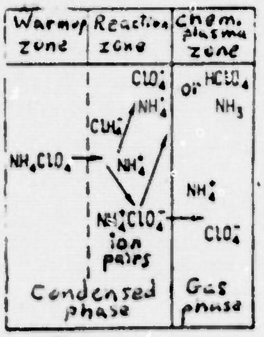

Fig. 6. The proposed scheme of a. pc. decomposition.

$$un_1 = \int_0^{\infty} n_0 Z_1 e^{-E_1/RT} dx, \tag{28}$$

where u is the speed of combustion; n_0 and n_1 are the numbers of a. pc. molecules and defects in a unit volume, and Z_1 is the pre-exponential factor of a monomolecular reaction. It is necessary to decide on one important circumstance: the dependence of energy E_1 upon the volume of the crystal v and, consequently, upon the pressure, temperature, and concentrations of the solvents which are formed as end products of combustion (for example, at a certain pressure and temperature, water can condense on the combustion surface of a. pc. [13]). Then with a change within limits which are not too wide, the dependence of E_1 upon v can be represented by the linear relationship

$$E_1 = E_0 - v_0\beta\alpha T + \frac{v_0\beta p}{K} - \gamma\sqrt{c}\,T. \qquad (29)$$

Here v_0 is the volume necessary for one molecule (atom) at P = 0;   is the coefficient of thermal expansion; K is the modulus of compressibility of the crystal; β, γ , are the proportionality constants; and c is the concentration of the solvent.

Using Frank-Kamenetskiy's exponent expansion method and substituting (29) in (28), we obtain

$$n_1 = n_0 Z_1 e^{-\frac{E_0 + v_0\beta p/K}{RT_{\text{п}}}} e^{\frac{v_0\beta\alpha + \gamma\sqrt{c}}{R}} \frac{\varkappa}{u^2}\cdot\frac{1}{\theta_1},$$

where $\varkappa$ is the thermoconductivity coefficient, and $\theta_1 = \frac{E_0 + v_0\beta p/K}{RT_{\text{п}}^2}(T_{\text{п}} - T_0)$.

Using a simple approximation of the calculation of the energetic conditions in the crystal lattice, Jost [14] estimated the order of magnitude of the additional factor $e^{\frac{v_0\beta\alpha}{R}} > 10^2$.

As we see, the factor $e^{\frac{v_0\beta\alpha + \gamma\sqrt{c}}{R}}$ can make a significant contribution to the concentration of defects n_1. Since the given estimates show that the reaction zone measures hundredths of a millimeter at high temperatures and that the reaction itself occurs near or on the combustion surface of the a. pc. crystal, it is possible to assume that the diffusion coefficient D = 0. Then the speed of combustion can be found from the equation of the balance of the original material n_0, assuming that the concentration of the interstitial product is equal to its maximum value n_1.

In the case of a bimolecular reaction

$$un_0 = \int_0^\infty n_0^2 Z_1^2 Z_2 e^{-\frac{2(E_0 + v_0\beta p/K)}{RT_{\text{п}}}} e^{\frac{2(v_0\beta\alpha + \gamma\sqrt{c})}{R}} \frac{\varkappa^2}{u^4}\cdot\frac{1}{\theta_1^2} e^{-E_2/RT}dx,$$

where E_2 and Z_2 are the activation energy and the preexponential factor of a bimolecular reaction. Carrying out the expansion of the exponent and calculating the integral, we get as a final result

$$u = \left(\frac{n_0 Z_1^2 Z_2}{\theta_1^2\theta_2}\right)^{1/3} \varkappa^{0.5} e^{-\frac{E_0 + v_0\beta p/K + E_2/2}{3RT_{\text{п}}}} e^{\frac{v_0\beta\alpha + \gamma\sqrt{c}}{3R}},$$

$$\theta_2 = \frac{E_2}{RT_{\text{п}}^2}(T_{\text{п}} - T_0).$$

The speed of combustion of a. pc. will be determined by the physical-chemical processes occurring in the condensed phase of the crystal.

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