Heterogeneous condensation of water vapor and carbon dioxide in rocket engine plumes, operated in the upper atmosphere

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Abstract

Models of combustion products temperature and pressure changes in rocket plumes of last stages of "Proton", "Molnija" and "Start" launcher engines, operated in the upper atmosphere at altitudes above 120 km are calculated. It is shown that condensation of water vapor can occur at distances 100 - 150 m from engine nozzles and condensation of carbon dioxide can take a place at distances 450 - 650 m.
The process of water vapor and carbon dioxide condensation in the plumes of these launchers are modeling. Effect of a heating of condensed particles by the latent heat of condensation and energy losses due to radiation and heat by an exchange with combustion products are taken into account. The dependences of temperature and a thickness of the condensate layer on time are obtained by means the solution of the equations of heat balance and mass balance of the condensed particles. Water vapor and carbon dioxide condensation in the exhaust stream of rocket "Start" practically does not occur. In plumes of "Proton" and "Molnija launchers a thickness of "water" layer on particles can reaches ~100 Å and a thickness of carbon dioxide may be ~ 60 Å.

1. Introduction

Impacts of rocket launches on the upper atmosphere have very diverse, complex character. Rocket engine exhausts may change the chemical composition of the environment, generate wave processes in the ionosphere and neutral atmosphere, develop unique, large-scale optical phenomena, etc. In particular, one of the most important processes developing under the interaction of combustion products of rocket engines with atmospheric components is the development of regions with low electron density ("electronic holes"). Such regions have typical sizes of several hundreds kilometers and are formed due to changes of velocities and directions of ion-molecule reactions in the upper atmosphere [1, 2]. It is obviously, the diffusion speed of a combustion products gas phase expansion can not provide a sufficiently rapid expansion of a gas at large (hundreds of kilometers) distances. In works [3,4] there were noted that a fast "transportation" of such components as water and carbon dioxide can occur as a result of their condensation in plumes of a rocket engine, following expansion of dispersed particles and their sublimate during this the process. Therefore it is highly relevant the study of the condensation of a gas phase combustion products in a rocket plume. In addition, the modeling of a dispersed particles formation and their expansion is necessary for identifications of optical phenomena in the upper atmosphere accompanied rocket launches.
In the papers [5, 6] the models of homogeneous condensation of water vapor in a plume of a hydrogen-oxygen engine are considered. However, modern rockets use fuels with different, rather complicated compositions. In this connection there is a need to investigate the process of condensation for various types of engines.
The aim of this article is to estimate the physical conditions and the possibility of water vapor and carbon dioxide condensation in the exhaust stream of rocket engines, operating on different fuels and calculate velocities of such condensations.

2. Model calculation of the physical conditions in a rocket plume

Changes of physical conditions in rocket engine plumes are described by the laws of gas dynamics for hypersonic flows. Problem of the flow of the under expanded gas jet in vacuum was considered at various approximations in fairly numerous works (see, for example, [7]). However, the findings results are very complex and are not applicable to simple modeling of temperature and pressure distribution in rocket plumes.
To determine the pressure and temperature dependence on the distance from the nozzle of the engine, we will use a relatively simple semi-empirical model proposed in 1966 [8]. According to this model, the pressure dependence on the distance *(x)* from the nozzle and the pressure on its exit section *(P_0)* is described by rather simple expression:

$$P(x) = P_0 \left(\frac{\gamma + 1}{\gamma - 1} \right)^{\gamma/(\gamma-1)} \left(\frac{\gamma + 1}{2\gamma} \right)^{1/(\gamma-1)} A^{-2/(\gamma-1)} \frac{D^2}{x^2} \qquad \textbf{(1)}$$

Here γ is the adiabatic index (ratio of specific heats), $A \sim 3.2 - 3.9$ - a parameter that depends on the adiabatic index, D - diameter of the nozzle exit section.
Obviously, the main parameter determining the change of pressure and temperature in a plume of a rocket engine is the adiabatic index of combustion products. Since the combustion products are a mixture of different components with different adiabatic indexes, it is necessary to determine the effective value of γ .
This can be done using such forms of total internal gas energy:

$$U= n\, RT/(\gamma\text{-}1) \quad and \quad U= n\, i\, RT/\, 2(\gamma\text{-}1) \qquad (2)$$

Here, n - the number of moles, R - gas constant, T - temperature, i - number of degrees of freedom of gas molecules, γ – adiabatic index. It is not difficult to find that the effective value of the adiabatic index of a gas mixture can be expressed as $\gamma_{eff} = 1 + 2\, \Sigma n_k / \Sigma i_k n_k$, n_k - number of moles of *«k»*. type molecules. The number of degrees of freedom for monatomic molecules is 3, for rigid diatomic one it is 5 and for rigid polyatomic one it is 6. According to data presented in Table 1 [9], we can easy calculate that $\gamma_{eff} = 1.36$ for "Proton" and "Molnija" launchers and $\gamma_{eff} = 1.38$ for "Start" launcher.

Table 1. Compositions of combustion products of last stages engines “Proton”, “Molnija” and "Start launchers.

“Proton” launcher, unsymmetrical dimethyl hydrazine + nitrogen tetraksid				
matter	molar weight	mass*, kg	mass part, %	molar part N, %
H_2	2	510	0.69	255 / 8.53
H_2O	18	20200	27.22	1122 / 37.55
CO	28	4670	6.29	167 / 5.59
CO_2	44	23070	31.08	524 / 17.54
N_2	28	25740	34.68	919 / 30.76
NO	30	32	0.04	1 / 0.03
Total		74222	100	2988 / 100
“Molnija” launcher, kerosene + liquid oxygen				
H_2	2	230	1.06	115 / 12.86
H_2O	18	5900	27.11	327.8 / 36.66
CO	28	7400	34.01	264.3 / 29.56
CO_2	44	8230	37.82	187.1 / 20.92
Total		21760	100	894.2 / 100
“Start” launcher, solid fuel				
H_2	2	21	1.1	10.5 / 18.1

H_2O	18	84	4.4	4.7 / 8.1
CO	28	565	29.9	20.2 / 34.6
CO_2	44	34	1.8	0.8 / 1.4
N_2	28	243	12.8	8.7 / 15
NO	30	1	0	0.3 / 0.5
HCl	36	201	10.6	5.58 / 9.6
Cl_2	70	5	0.3	0.1 / 0.2
Al_2O_3	102	742	39.1	7.27 / 12.5
Total		1896	100	58.15 / 100

Note: m * mass component of combustion products emitted at altitudes of 100-150 km.

It should be noted that the adiabatic index, calculated by this way agrees well with its actual value for the monatomic molecules, but an agreement for diatomic and polyatomic molecules is bad. Besides, the real values of this parameter are depended on the temperature. For example, it changes for carbon dioxide from 1.31 at 0^0 C to 1.28 at 100^0 C. For the other components the data on the temperature dependence in the reference books available absent, what makes impossible a correct account of this parameter changes.
In fact, for the model calculations it is sufficient to use some average values of γ. It is easy to estimate the change in the calculated values of combustion products pressure, depending on the magnitude of the effective value of the adiabatic index. Figure 1 shows as an illustration of the combustion products pressure change at a distance of 200 m from the engine nozzle "Proton" launcher, depending on the value of the effective adiabatic index.

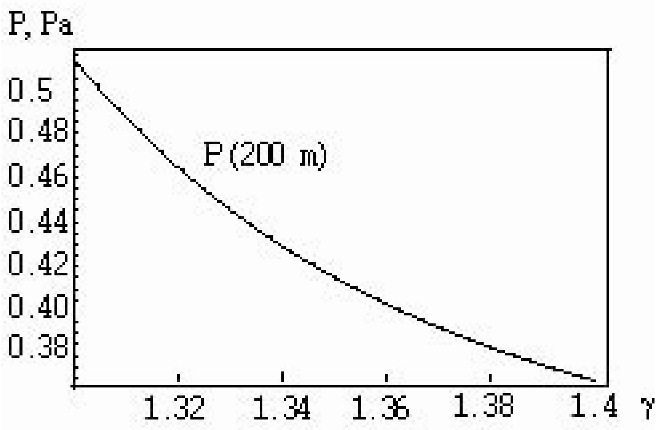


Fig. 1. Changing the combustion gas pressure at 200 m from the engine nozzle "Proton", depending on the effective value of the adiabatic index.

The figure shows that the change of the adiabatic index at ~ 5% leads to a change in the design pressure of the combustion products of ~ 10%. So, for model calculations, we may use the approximate values of this parameter, $\gamma_{eff} = 1.37$ for all three engines.

To determine the changes in the physical conditions in the plume downstream from the engine nozzle one need the data on the output engine parameters. For the considered motors these are shown in Table 2.

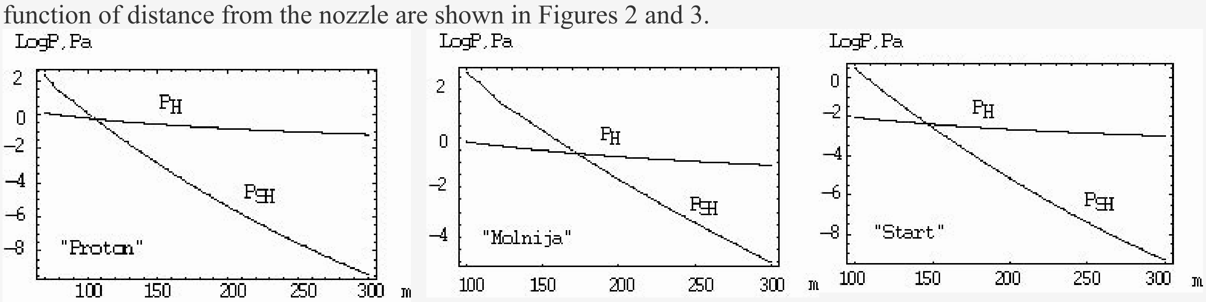
Table 2. Last stages engines of "Proton", "Molnija" and "Start" launcgers specifications.

Launcher/ engine	Nozzle diameter, m	Temperature at nozzle exit section, K	Preasure at nozzle exit section, MPa	adiabatic index	"A" - parameter
"Proton"/ -RD 0212	1.470	~ 1700	0.014	1.36	3.75
"Molnija"/ -RD 0110	2.240	~ 1700	0.0074	1.36	3.75
"Start"/-RC-12M2	1.860	~ 1700	0.0006	1.38	3.69

Changes of pressure and temperature under the adiabatic process are described by expression - $P(x)\ T(x)^{\gamma/(\gamma-1)} = const$, and it is easy to find that the change of pressure and temperature of combustion products in the exhaust stream for the various engines is described by simple expressions:

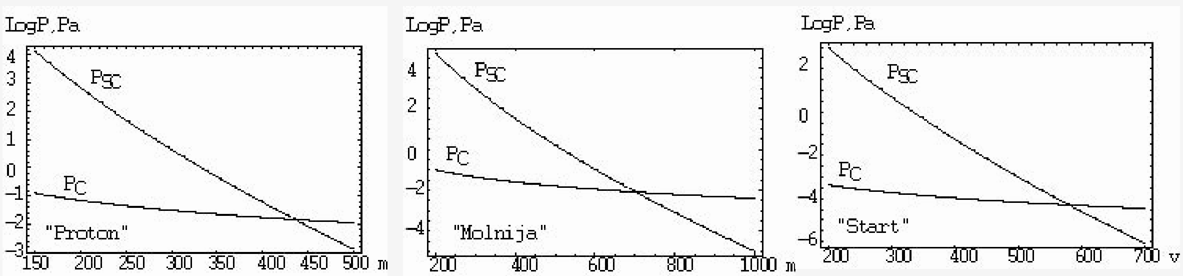
Launcher "Proton»: $P(x) \approx P_0\ 1.6\ 10^4\ x^{-2}$, $T(x) \approx 2500\ x^{-0.53}\ K$
Launcher "Molnija»: $P(x) \approx P_0\ 2\ 10^4\ x^{-2}$, $T(x) \approx 3080\ x^{-0.53}\ K$
Launcher "Start»: $P(x) \approx P_0\ 1.1\ 10^3\ x^{-2}$, $T(x) \approx 2800\ x^{-0.53}\ K$

Condensation of combustion products, of course, can take a place when the partial pressure of water vapor or carbon dioxide in the exhaust stream exceeds its saturation pressure. Comparison of the partial pressures of water vapor and carbon dioxide in the combustion products for different engines and saturated vapor pressures of these gases as a function of distance from the nozzle are shown in Figures 2 and 3.



a) b) c)

Fig.2. The dependence of water vapor partial (P_H) and saturation (P_{SH}) pressures corresponding to the local value of the combustion products temperature on a distance from a nozzle to a central stream tube (P_H): a) - "Proton", b) - "Molnija", c) - "Start" launchers.



a) b) c)

Fig.3. The dependence of carbon dioxide partial (P_C) and saturation (P_{SC}) pressures corresponding to the local value of the combustion products temperature on a distance from a nozzle to a central stream tube: a) - "Proton", b) - "Molnija", c) - "Start" launchers.

It follows from these figures that the conditions necessary for the condensation of water vapor in exhaust jets of last stages of "Proton", "Molnija" and "Start" launchers are started at the distances from the nozzle of ~ 100, ~ 150 and ~ 120 m, respectively.
The condensation of carbon dioxide in plumes of these engines can occur at distances greater than ~ 450, ~ 650 and ~ 600 m. It is obvious that a large distance from the nozzle for carbon dioxide condensation area in comparison with the zone of water vapor condensation is determined mainly by the fact that the temperature of carbon dioxide condensation (-78.5^0 C) is much less than the temperature of condensation of water vapor (0^0 C).

3. Heterogeneous condensation of combustion products in rocket plume

Condensation of water vapor in the exhaust stream of hydrogen-oxygen rocket engine, i.e., in the case where the combustion products contain only one component (water vapor - homogeneous condensation) was considered in [5, 6, 10]. In the latter paper it is shown that in the heat balance of condensed particles a dominant process of cooling is the energy losses due to thermal radiation of particles.
In the case of the heterogeneous combustion products the condensation of carbon dioxide can occur also, since the temperature of the combustion products at a sufficient distance from the nozzle of the engine can drop well below the sublimation temperature of CO_2.
In modern engines operated on fuels with a complex composition, the molar fraction of water in the combustion products is 8 - 40%, and carbon dioxide is 1 - 20%. It is obviously, at condensation of water vapor and carbon dioxide in some cases the heat exchange with the other components of combustion products may be important in thermal balance of condensed particles. Below the processes of water vapor and carbon dioxide condensation in combustion products of rocket engines, operating on three different fuels (asymmetrical dimethylhydrazine and nitrogen tetraksid ("Proton"), kerosene and liquid oxygen ("Molnija") and solid composite propellant ("Start") are considered.
The following notations are used below:
$l\ (t)$ - the distance from the nozzle to the field of condensation;
t - the time of combustion products motion from the engine nozzle to a distance $l(\ t)$;
$T_V\ (t)$ - the local combustion products temperature in rocket plume;
T_P - the temperature of condensed particles;
$r(t)$ - characteristic size (radius) of condensed particles;
ρ - density of particles;
$q\ (T_P)$ - the specific heat of particles;
Q_{con} - the specific heat condensation;
α - the coefficient of adaptation of water molecules (carbon dioxide) to the surface of the condensate;
β - the emissivity of the condensed particles;
$P_{SW}(T_P)$ - saturation vapor pressure of water, and $P_{SS}(T_P)$ - carbon dioxide over the surface of the particles;
$P_{W(t)}$ - the partial pressure of water vapor, and $P_{C(t)}$ - carbon dioxide in the exhaust stream;
$P_{V(t)}$ - the pressure of combustion products in the exhaust stream;
k - Boltzmann constant;
σ - Stefan-Boltzmann constant;
Q_{col} - heat transfer coefficient;
η - coefficient of removal efficiency of energy by heat exchange with combustion products,
$m_W\ (m_C)$ the mass, μ- molar weight of water molecules (carbon dioxide),
m_o - the atomic mass unit,
$\chi_{i.}$ - the pressure of i^{th} - components of the combustion products (partial pressure),
V - velocity of the combustion gases flow from the engine nozzle.
As in the case of homogeneous condensation [6], changes of temperature and particle sizes of condensed particles are described by the equations of its heat balance and mass balance:

$$\frac{dT}{dt} = \frac{3}{r(t)\rho q(T_p)}\{\alpha Q_{con}[\frac{P_V(t)}{T_V^{1/2}} - \frac{P_S(T_P)}{T(t)^{1/2}}]\left(\frac{m_{W(C)}}{2k\pi}\right)^{1/2} - \beta\sigma T^4 - Q_{col}(\Delta T)]\}$$

$$\frac{dr}{dt} = \frac{1}{\rho} \frac{\alpha[P_V(t) - P_S(T_p)]}{T_V^{1/2}} \left(\frac{m_{W(C)}}{2k\pi} \right)^{1/2} \qquad (3)$$

The difference between homogeneous and heterogeneous approximation is that the last energy balance equation includes the equation term – $Q_{col}(\Delta T)$, which takes into account the energy loss of condensed particles by heat exchange with the surrounding gas (combustion products).

$$Q_{col}(\Delta T) = \eta \sum_i \frac{P_{Vi}}{(2k\pi m_i T_V)^{1/2}} \frac{3}{2} k(T_V - T_P) = \eta \frac{3k(T_V - T_P)P_V}{2(2k\pi m_0 T_V)^{1/2}} \sum_i \frac{\chi_i}{\mu_i^{1/2}} \qquad (4)$$

The summation is over all gas components of combustion products, i.e. energy lost by the condensate due to interaction with the surrounding gas. It is determined by the frequency of collisions of molecules with the surface of the particles and the temperature difference between gas and condensate. The factor $\eta \le 1$determines the efficiency of energy exchange by this way. It is obvious that $\eta = 1$ corresponds to the maximum value of this type of energy loss. Since the particles energy loss due to heat exchange with the surrounding gas depends on the temperature of the condensate, the efficiency of this process in comparison with radiative energy loss can be determined only by solving of the above equations.
In calculations it was assumed that the velocities of the combustion products in plumes of these launchers are ~ 4000 m/s, ~ 3500 m/s and ~3000 m/s, respectively.
The initial conditions for solving the equations of balance, calculated for H_2O (CO_2) are shown in Table 3 as well as the parameters $\Sigma_{H_2O(CO_q)}$ and $\chi_{H_2O(CO_q)}$
Since the solution of balance equations is not determined by the absolute value of the particle size, but thickness of the condensate layer only, the choice of initial values of particle size r_0 rather arbitrary and is taken to be 5Å.

Table3. The initial conditions for solving the balance equations and Σ and χ parameters for different launchers.

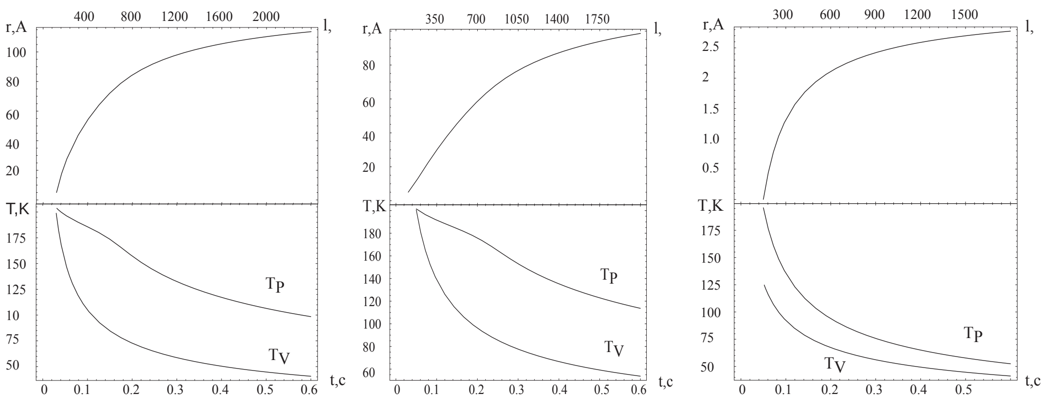
Launcher	«Proton»	«Molnija»	«Start»
$t_{o,H_2O(CO_2)}$	*0.03 s (0.13s)*	*0.05 s (0.2 s)*	*0.05sc (0.2)*c
$T_{o,H_2O(CO_2)}$	*215 K (100 K)*	*195 K (95 K)*	*190 K (95 K)*
$\chi_{H_2O(CO_2)}$	*0.375 (0.175)*	*0.37 (0.24)*	*0.08 (0.015)*
$\Sigma_{H_2O(CO_2)}$	*0.156 (0.22)*	*0.18 (0.21);*	*0.23 (0.24)*

The results of the numerical solution of the equations shown on Fig. 4 and Fig 5.
These graphics show that in the exhaust stream of the last stages of "Proton" and "Molnija" launchers the sufficiently intense condensation of water vapor and carbon dioxide are take place. The thickness of the condensate layers can be up to ~ 100 Å. The actual size of condensed particles depends on the size of condensation centre and may significantly exceed the obtained values. In the exhaust stream of a solid-fuel rocket "Start" virtually no condensation occurs. It is determined obviously by the relatively low partial pressure of water vapor and carbon dioxide in the combustion products.
As in the case of homogeneous condensation, heat equilibrium between the condensed particles and gas phase of combustion products is absent. Moreover, for water the difference in their temperatures is significant, while for the

carbon dioxide does not exceed 10˚. For water vapor condensate layer thickness in the homogeneous and heterogeneous cases may differ by factor ~ 2 (Fig. 6).
Formally, in the case of thermal equilibrium, changing the size of condensed particles should be described only by the equation

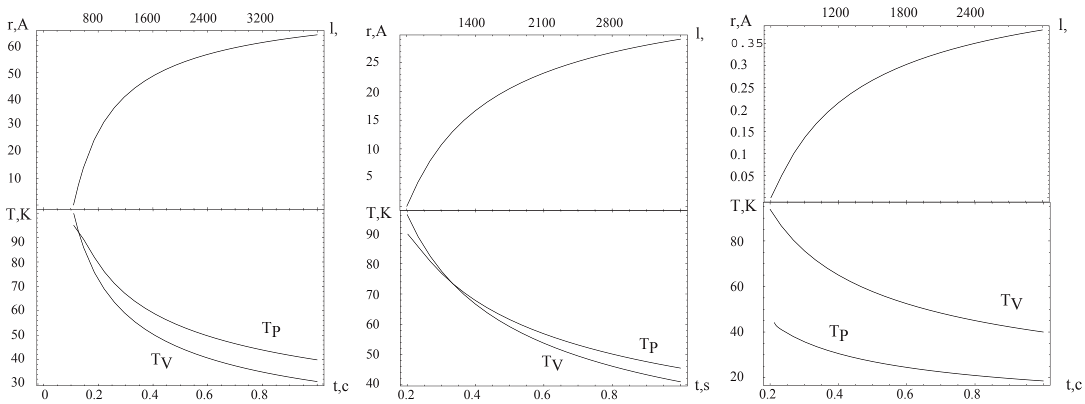
$$\frac{dr}{dt} = \frac{1}{\rho} \frac{\alpha P_V(t)}{T_V^{1/2}} \left(\frac{m_{W(C)}}{2k\pi} \right)^{1/2} \qquad (5)$$

instead of the system of equations (1).



a) b) c)

Figure 4. Changing the thickness of the condensed layer *(r, Å)* and a temperature of condensed particles *(T_P)* for water vapor in the exhaust jet engines: a) "Proton", b) "Molnija", c) "Start", on the time (the distance from a nozzle). For comparison, the figures show also the change in temperature of the combustion products *(T_V)*.



a) b) c)

Figure 5. Changing the thickness of the condensed layer *(r, Å)* and a temperature of condensed particles *(T_P)* for carbon dioxide in the exhaust jet engines: a) "Proton, b) "Molnija", c) "Start", depending on the time (the distance from a nozzle .) T_V - the temperature of combustion products.

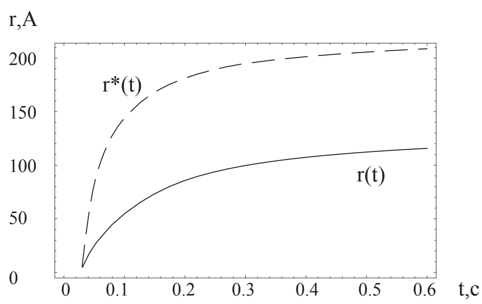


Figure 6. Changing of the layer thickness of the condensate water in the exhaust of "Proton", calculated for real conditions - r (t) and in the case of thermal equilibrium between the condensate and the products of combustion - r * (t).

4. Discussion of results

Let us compare the effectiveness of process of cooling of the condensate due to collisions with a gas phase of combustion products and loss of energy by means a thermal radiation. Assuming, in accordance with the results of the calculation, that a temperature of condensed particles at distance from the nozzle of ~ 1000 m (for "Proton" launcher) is ~ 150^0 K, the difference between the temperature of particle and the temperature of the combustion products is ~ 75^0 , we can easy find that the ratio of energy transmitted at the surrounding gas to the radiative losses is: ~ 0.25. This value is close to the maximum possible value. Thus, as in the case of homogeneous condensation, the dominant mechanism of energy losses of condensed particles is losing energy by radiation. In the calculations we have allow, the factor determining the efficiency of heat transfer through collisions is maximum - $\eta = 1$. In reality, of course, $\eta <1$, what, however, can not lead to the essential change in the results of the calculations, since the process of energy loss by thermal radiation is the dominant one.

As for the model of homogeneous condensation in the calculations it was assumed that the particles formed by condensation of combustion products have a spherical shape. The calculations also assumed that the temperature is the same throughout the volume of the particle and does not take into account the increase in saturation vapor pressure over a curved surface, i.e. above the surface of the condensate. The validity of these assumptions is justified in [6].

The condensation process was considered for three different engines, so the calculations with a certain degree of conditionality was accepted that the velocity of combustion products in the plumes of "Proton", "Lightning" and "Start" launchers, are respectively, ~4000, ~3500 and ~3000 m/s. The real velocities, of course, differ from the accepted values. Moreover, in the process of expanding of combustion products physical and chemical processes can be develop, what lead to a change of the of gas flow velocities. In particular, the processes of after-burning of the fuel component in the exhaust stream, accompanied by heat release should lead to an increase in flow velocity. The exact calculation of the physical conditions in the exhaust stream of rocket engine is a separate problem and it is out of the scopes of this paper. However, the use in the calculation of more accurate values of the velocities of the combustion products should not change the whole picture of the condensation process, and will only lead to some changes in the estimates of the extent of condensation.

5. Conclusion

The solution of the equations of heat balance and mass balance of particles of condensed water vapor and carbon dioxide in the upper atmosphere in the exhaust of rocket engines operated on different fuels, to determine the dynamics of change in their size and temperature is obtained. As in the case of homogeneous condensation, the condensed particles are not in thermal equilibrium with the gaseous products of combustion. The dominant process in the losses of the released latent energy at the particles condensation is their thermal radiation.

The thickness of the water vapor condensate (carbon dioxide) formed in the plumes of the last stage of "Proton" launcher can be up to ~ 100 (60) Å. For "Molnija launcher these values may consists ~ 100 (40) Å. For solid-fuel launcher "Start" condensation of water vapor and carbon dioxide is not occurring practically.

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