CONDENSATION OF A CHEMICALLY REACTING GAS ON A VERTICAL SURFACE

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It is shown that the rates of heat and mass transfer processes in this system are higher than in a "frozen" mixture.

Dissociative gases undergoing reversible chemical reactions have a potential application as heat carriers and as working media in power apparatus [1]. Of considerable interest is the gas – liquid cycle with $N_2O_4 \rightleftharpoons 2NO_2 \rightleftharpoons 2NO + O_2$ as the heat carrier. Condensation of this substance is complicated by the fact that the components NO and O_2 are gases which do not condense along the saturation line of the $N_2O_4 \rightleftharpoons 2NO_2$ system, while the recombination reaction $2NO + O_2 \rightleftharpoons 2NO_2$ proceeds at a low rate. Available test data [2, 3] and calculations based on a semiempirical model [4] show that the integral characteristics of heat transfer (the heat transfer coefficient, etc.) are much more affected by the kinetics of the chemical reaction than is the condensation of pure vapor or of a vapor and inert gas mixture. In this study the problem is first solved theoretically.

We consider the condensation of a stationary gas on a vertical surface during a laminar flow of the condensate film. In accordance with the conventional approach [5] and the usual assumptions concerning condensation [6, 7], the problem is formulated in terms of a system of differential equations describing the heat and the mass transfer in a gaseous boundary layer adjacent to the condensation surface and in the liquid condensate film.

For the gaseous phase

$$\begin{gathered}
\rho u \frac{\partial u}{\partial x} + \rho v \frac{\partial u}{\partial y} = \mu \frac{\partial^2 u}{\partial y^2} + g(\rho - \rho_\infty); \\
\frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} = 0; \\
\rho u c_p \frac{\partial T}{\partial x} + \rho v c_p \frac{\partial T}{\partial y} = \lambda \frac{\partial^2 T}{\partial y^2}; \\
\rho u \frac{\partial \rho_{k0}}{\partial x} + \rho v \frac{\partial \rho_{k0}}{\partial y} = \rho D_k \frac{\partial^2 \rho_{k0}}{\partial y^2} + I_k.
\end{gathered} \tag{1}$$

It has been established in several studies [7 et al.] that the convective terms may be omitted in the equations for the condensate film; furthermore, the system $N_2O_4 \rightleftharpoons 2NO_2$ may be treated as one substance when it is in the liquid state, and the equation of diffusion may thus be omitted from the analysis. In this way,

$$\begin{gathered}
\mu_L \frac{\partial^2 u_L}{\partial y^2} + g(\rho_L - \rho) = 0; \\
\frac{\partial u_L}{\partial x} + \frac{\partial v_L}{\partial y} = 0; \\
\frac{\partial^2 T_L}{\partial y^2} = 0.
\end{gathered} \tag{2}$$

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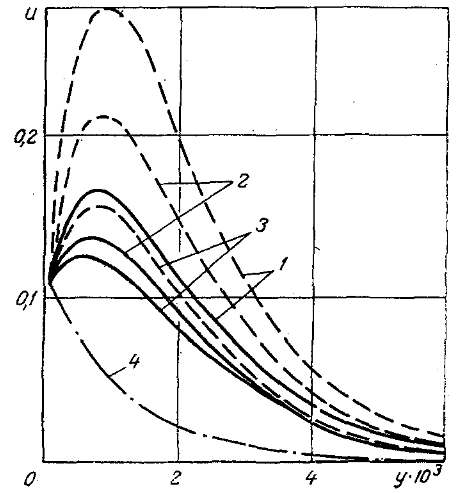

Fig. 1. Distribution of the longitudinal velocity in a gaseous boundary layer at T_∞ = 305°K and η_δ = 0.23: 1) $\rho_{k0\infty}$ = 0.02; 2) 0.01; 3) 0.005; 4) 0. Velocity u (m/sec), y (m).

System (1)-(2) is supplemented by the following boundary conditions:

$$u_L = v_L = 0; \quad T_L = T_W \ \text{at} \ y = 0;$$

at y = δ(x)

$$u_L = u; \quad \mu_L \frac{\partial u_L}{\partial y} = \mu \frac{\partial u}{\partial y};$$

$$\rho_L \left(u_L \frac{d\delta}{dx} - v_L \right) = \rho \left(u \frac{d\delta}{dx} - v \right);$$

$$\rho_{k0}\rho \left(u \frac{d\delta}{dx} - v \right) + \rho D_k \frac{\partial \rho_{k0}}{\partial y} = 0; \tag{3}$$

$$\lambda_L \frac{\partial T_L}{\partial y} = \rho r \left(u \frac{d\delta}{dx} - v \right) + \lambda \frac{\partial T}{\partial y};$$

$$T_L = T; \quad T = T_s(\rho_{k0}, P);$$

at y → ∞

$$T = T_\infty; \quad u(\infty) = 0; \quad \rho_{k0}(\infty) = \rho_{k0\infty}.$$

In Eqs. (1)-(2) the properties have been assumed constant except for the term $g(\rho - \rho_\infty)$, which is approximated by a linear function of the temperature. Calculations have shown that taking into account the variability of properties will make the expressions for the temperature, the concentration, and the velocity profiles not more accurate than within 1-3% when the temperature drop in the gaseous phase is 10°C. The equation of convective diffusion and the corresponding boundary conditions apply to any of the noncondensing components.

For our system here it is convenient to refer these equations to oxygen, and the kinetic relations will then yield [8]:

$$I_k = -\frac{\rho^3}{256} K_{\text{rec}} \rho_{k0}^3. \tag{4}$$

The temperature at the interphase boundary (saturation temperature) as a function of the composition and of the pressure has been tabulated on the basis of data in [8].

As has been shown in [7, 9], the system of partial differential equations (1)-(2) with the boundary conditions (3) is expediently solved by means of autonomous transformations in the dimensionless coordinate

$$\eta = \frac{y}{\sqrt[4]{x}} \sqrt[4]{\frac{g}{4\nu^2}}. \tag{5}$$

For liquid $0 \leq \eta \leq \eta_\delta$, for a gas $0 \leq \eta \leq \infty$.

If the flow function $\psi(x, y)$ is expressed as

$$\psi = 4\nu c x^{3/4} f(\eta), \tag{6}$$

where $c = \sqrt[4]{g/4\nu^2}$ and f denotes the dimensionless flow function, then the original system of equations transforms into a system of ordinary differential equations.

For a gas

$$F''' + 3FF'' - 2(F')^2 + \beta \frac{1}{T_\infty}(\Theta - 1) = 0; \tag{7}$$

$$\rho''_{k0} + 3\rho'_{k0} F \,\mathrm{Sc} + I_k' \mathrm{Sc} \sqrt{\frac{x}{g}} \frac{2}{\rho} = 0; \tag{8}$$

$$\Theta'' + 3 \Pr F\Theta' = 0; \tag{9}$$

for a liquid

$$f''' + 1 = 0; \tag{10}$$

$$\theta'' = 0. \tag{11}$$

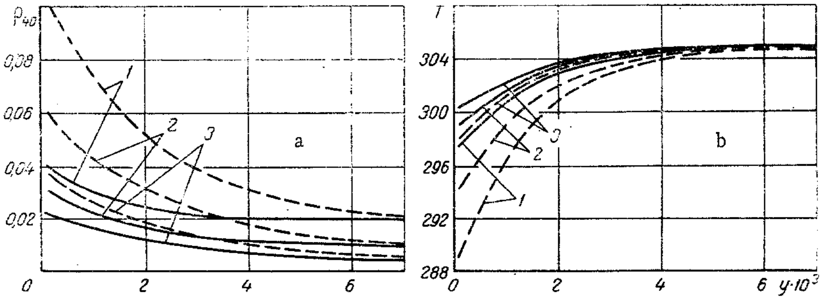

Fig. 2. Distribution of oxygen concentrations (a) and temperatures (b) in a gaseous boundary layer at η_δ = 0.23 and T_∞ = 305°K: 1) $\rho_{k0\infty}$ = 0.02; 2) 0.01; 3) 0.005. Temperature T (°K), y (m).

The boundary conditions transform into

$$f(0)=0;\quad f'(0)=0;\quad \theta(0)=\theta_0 \quad \text{for } \eta=0; \tag{12}$$

at $\eta \to \infty$

$$F'(\infty)=0;\quad \rho_{k0}(\infty)=\rho_{k0\infty};\quad \Theta(\infty)=1; \tag{13}$$

at $\eta = \eta_\delta$

$$F''(0)=Rf''(\eta_\delta); \tag{14}$$

$$F'(0)=f'(\eta_\delta); \tag{15}$$

$$F(0)=Rf(\eta_\delta)+4/3x\frac{d\eta_\delta}{dx}f'(\eta_\delta)(R-1); \tag{16}$$

$$\rho'_{k0}(0)+\rho_{k0}(0)\,3\,\mathrm{Sc}\left[F(0)+4/3x\frac{d\eta_\delta}{dx}F'(0)\right]=0; \tag{17}$$

$$\Theta'(0)=\left\{\lambda_L c_L\frac{T_s-T_W}{T_\infty}\frac{1}{\eta_\delta} -\frac{3rgc\mu}{T_\infty}\left[F(0)+4/3x\frac{d\eta_\delta}{dx}F'(0)\right]\right\}\frac{1}{\lambda c}, \tag{18}$$

where $R = \sqrt{\rho\mu/\rho_L\mu_L}$.

In the equation of diffusion, after transformation, coordinate x is retained as a parameter and the conditions at the variable interphase boundary contain the derivative $d\eta_\delta/dx$. Consequently, the solution

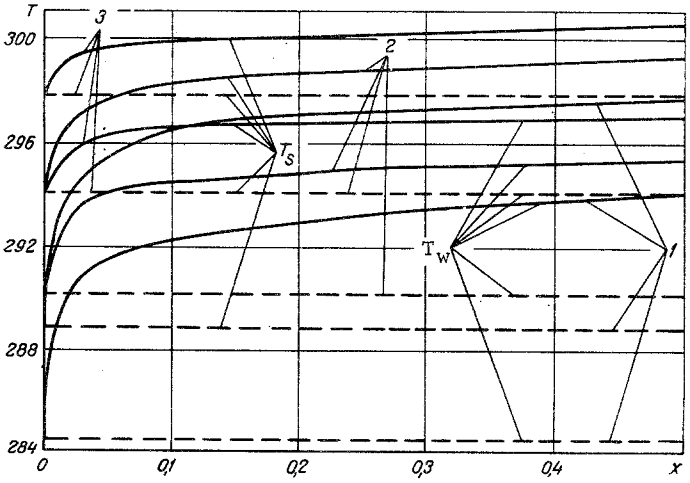

Fig. 3. Heightwise variation of the temperature of the condensation surface and of the wall temperature, at η_δ = 0.23 and T_∞ = 305°K: 1) $\rho_{k0\infty}$ = 0.02; 2) 0.01; 3) 0.005. Temperature T (°K), x (m).

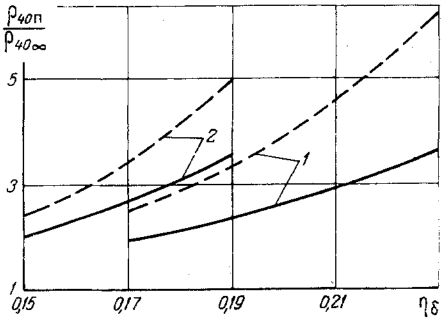

Fig. 4. Effect of the condensation rate on the relative concentration of oxygen at the interphase boundary, at $\rho_{k0\infty} = 0.01$ and x = 0.13 m: 1) P = 1.6 bar; 2) 1.0 bar.

TABLE 1. Variation of Heat and Mass Transfer Parameters at Various Concentrations of Oxygen in the Volume

Oxygen concentration in the volume, $\rho_{k0\infty}$	Derivative $\partial u/\partial y\|_\delta$, sec^{-1}	Ratio of condensed N_2O_4 quantity per 0.5 m length to that calculated in accordance with the Nusselt theory	
		"frozen" mode	with kinetics taken into account
0	—81,0	—	—
0,005	85,5	0,712	0,797
0,01	312	0,690	0,755
0,02	488	0,585	0,725

to system (7)-(18) will not be a similarity (autonomous) solution. Considerable simplifications are possible by assuming that $d\eta_\delta/dx = 0$ or, which is equivalent, that

$$\eta_\delta = \frac{\delta}{\sqrt[4]{x}} \sqrt[4]{\frac{g}{4\nu^2}} = \mathrm{const.} \tag{19}$$

This condition corresponds to a Nusselt profile for a condensate film flowing down a vertical surface. The surface will not be isothermal then, however, with the temperature T_W varying along coordinate x. The problem was solved numerically on a Minsk-22 computer by the following scheme.

1. At definite values of x and η_δ one assumes initially a parabolic temperature profile $\Theta(\eta)$ and T_W. Equations (10) and (7) are solved as differential equations with the initial conditions (12) and with an initially assumed approximate value for f"(0). If, beginning at some k, the condition

$$|F'(\eta_k)| \leqslant \varepsilon_f; \quad |F'(\eta_{k+1})| \leqslant \varepsilon_f; \quad k = 2, 3, \ldots,$$

holds true within a specified accuracy, then one passes on to the next equation; otherwise, a correction is made for f"(0), whereupon f and F are recalculated.

2. Equation (8) is solved with the initial conditions (13) and (17). One assumes a value for $\rho_{k0}(0)$ and determines $\rho'_{k0}(0)$ from Eq. (7) so as to satisfy, within a specified accuracy, the condition at infinity

$$|\rho_{k0}(\eta_m) - \rho_{k0\infty}| \leqslant \varepsilon_\rho; \quad |\rho_{k0}(\eta_{m+1}) - \rho_{k0\infty}| \leqslant \varepsilon_\rho, \quad m = 2, 3, \ldots \tag{20}$$

3. Equation (9) is solved with the boundary conditions (12), (13), and (18). The solution to Eq. (11) is

$$\theta(\eta) = \frac{T_s - T_W}{\eta_\delta}. \tag{21}$$

The temperature T_s is calculated after the composition at the condensation surface has been determined from tables. For the solution of (9) the wall temperature is selected so as to satisfy a condition like (20) at infinity and is then compared with T_W specified in step 1. If the difference between the two is within specified accuracy limits, then one passes on to the next section; otherwise, the calculation is repeated beginning with step 1 with a new assumed temperature profile.

The differential equations with the given initial conditions were solved by the method proposed in [10].

Some results of these calculations are shown in Figs. 1-4. The calculations were made essentially with the pressure of the condensing gas equal to 1.6 bar, the thermophysical properties as well as the recombination constant and other necessary data taken from [8].

In Fig. 1 is shown the distribution of the longitudinal velocity at one section (x = 0.37 m) along the gaseous boundary layer. The dashed-dotted curve represents condensation of pure vapor, the dashed curves represent the "frozen" mode without chemical reactions ($J_k = 0$), and the solid curves account also for the kinetics of the chemical reaction. The presence of noncondensing components is favorable to free convection developing in the gaseous boundary layer as a result of nonuniform gas density. The chemical

TABLE 2. Values of the Heat Transfer Coefficients According to Formulas (22): (1) for the "Frozen" Mode, (2) with the Kinetics of the Chemical Reaction Taken into Account

$\rho_{k0\infty}$	α_1		α_2 [2]		α_3[11]	
	1	2	1	2	1	2
0,005	1,39	1,08	0,675	0,525	0,565	0,435
0,01	1,56	1,18	0,55	0,415	0,435	0,328
0,02	1,75	1,28	0,380	0,370	0,258	0,254

reaction tends to suppress convection, which is indirectly confirmed by the curves of temperature and concentration distribution in Fig. 2.

The effect of the chemical reaction is to make the temperature profile smoother than under "frozen" conditions. At the same time, the saturation temperature at the interphase boundary rises and this leads to a higher rate of heat transfer during condensation. Thorough calculations have shown that the mass flow rate of condensing vapor through the interphase boundary

$$j = \frac{\rho D_k}{\rho_{k0\delta}} \left(\frac{\partial \rho_{k0}}{\partial y} \right)_\delta$$

is always higher in a chemically reacting gas mixture than when the reaction rate is zero. Thus, in terms of heat and mass transfer during condensation, the given system $N_2O_4 \rightleftharpoons 2NO_2 \rightleftharpoons 2NO + O_2$ ranks somewhere between a pure vapor and a vapor–gas mixture.

In Table 1 are listed values of the ratio of condensed N_2O_4 quantity per 0.5 m length to that of pure vapor calculated in accordance with the Nusselt theory, at a mean wall temperature $T_W = 297$°K and $T_\infty = 305$°K.

In [7] and in the classical Nusselt solution no consideration was given to friction at the interphase boundary, i.e., it was assumed that $\mu (\partial u/\partial y)|_\delta = 0$. In Table 1 are shown the values of derivative $\partial u/\partial y|_\delta$ for various concentrations of the noncondensing gas (O_2) in the volume. It can be seen here that the derivative $\partial u/\partial y|_\delta$ differs from zero appreciably. In the final analysis, this affects also the heat transfer parameters. Thus, at $x = 0.37$ m, $T_\infty = 305$°K, and $\delta = 0.784 \cdot 10^{-4}$ m the local thermal flux density calculated for the condition $\partial u/\partial y|_\delta = 0$ is equal to 4338 W/m^2, while with friction at the interphase boundary taken into account it is only 4178 W/m^2.

The temperature of the wall and the temperature of the interphase boundary have been plotted in Fig. 3 as functions of the x-coordinate at a constant η_δ. The "kinetic" mode, unlike the "frozen" mode, is characterized by a variable temperature at the boundary of the condensate film.

The ratio of oxygen concentration at the condensation surface to its overall concentration in the volume has been plotted in Fig. 4 as a function of the condensation rate.

As the parameter characterizing the condensation process we have chosen the dimensionless quantity η_δ, which can be expressed accurately enough in terms of known similarity numbers:

$$\eta_\delta = (K\,\mathrm{Pr})^{-1/4}.$$

An increase of the condensation rate raises appreciably the concentration of noncondensing gas at the condensation surface and this, in turn, lowers the saturation temperature.

It has been proposed by several authors [2, 11, et al.] that the heat transfer during condensation of a mixture which contains noncondensing and chemically reacting gases be calculated with the aid of the respective heat coefficients. The values of these coefficients, calculated according to the formulas [2, 11]

$$\alpha_1 = \frac{q_c}{T_s - T_W}; \quad \alpha_2 = \frac{q_c}{T_{s,\infty} - T_W}; \quad \alpha_3 = \frac{q_c}{T_\infty - T_W} \tag{22}$$

are shown in Table 2.

As can be seen here, the heat transfer coefficient is a rather tentative parameter, inasmuch as its magnitude depends very much on the method of its determination and, furthermore, the method of its determination may involve a change in the character of its dependence on the concentration (which, according to [2, 11], should be defined uniquely).

NOTATION

x, y	are the longitudinal and transverse coordinates on the vertical wall;
u, v	are the longitudinal and transverse velocity components;
T	is the temperature;
T_s	is the saturation temperature;
D_k	is the diffusivity of the k-th component;
λ	is the thermal conductivity;
c_p	is the specific heat;
μ	is the dynamic viscosity;
ρ	is the density;
ρ_{k0}	is the relative mass concentration of the k-th component;
g	is the acceleration of gravity;
I_k	is the source (sink) mass intensity of the k-th component, as a result of the chemical reaction;
δ	is the thickness of condensate film;
r	is the heat of evaporation;
P	is the pressure;
k_{rec}	is the rate constant of system $2NO + O_2 \rightleftharpoons 2NO_2$ recombination;
$\Theta = T/T_\infty$	is the relative temperature;
Pr	is the Prandtl number;
Sc	is the Schmidt number;
$K = r/(c_{pL}(T_s - T_w))$;	
α	is the heat transfer coefficient;
q	is the thermal flux density.

Subscripts

L	refers to liquid;
w	refers to wall;
0	refers to condensate film;
∞	refers to infinity.

LITERATURE CITED

1. A. K. Krasin and V. P. Nesterenko, in: Dissociative Gases as Heat Carriers and Working Media in Power Apparatus [in Russian], Izd. Nauka i Tekhnika, Minsk (1970).
2. S. A. Kovalev, L. S. Komendantov, and B. S. Petukhov, Teplofiz. Vys. Temp., No. 6, 1151 (1969); No. 1, 207 (1971).
3. V. T. Derov, L. I. Kolykhan, and V. F. Pulyaev, Izv. Akad. Nauk SSSR Ser. Fiz.-Énerg. Nauk, No. 2 (1971).
4. A. A. Mikhalevich, V. B. Nesterenko, and G. G. Novikov, in: Dissociative Gases as Heat Carriers and Working Media in Power Apparatus [in Russian], Izd. Nauka i Tekhnika, Minsk (1970).
5. A. V. Lykov, Theory of Heat Conduction [in Russian], Izd. Vysshaya Shkola, Moscow (1967).
6. G. G. Chernyi, Izv. Akad. Nauk SSSR OTN, No. 12 (1954).
7. W. J. Minkowycz and E. M. Sparrow, Internatl. J. Heat and Mass Transfer, 9, 1125 (1966).
8. A. A. Krasin and V. B. Nesterenko (editors), in: Thermodynamic and Transfer Properties of Chemically Reacting Gas Systems [in Russian], Izd. Nauka i Tekhnika, Minsk (1967), Vol. 1; (1971), Vol. 2.
9. G. Schlichting, Boundary-Layer Theory [Russian translation], Izd. Nauka, Moscow (1969).
10. I. I. Eterman, Izv. VUZov Matematika, No. 3 (1962).
11. V. P. Isachenko and A. S. Bogorodskii, Teploénergetika, No. 2 (1969).