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HEAT AND MASS TRANSFER AT A FRONTAL POINT OF BLUNT BODIES FOR GAS FLOW IN THE PRESENCE OF HETEROGENEOUS CHEMICAL REACTIONS

V. P. MOTULEVICH

Krzhizhanovsky Power Institute of the Academy of Sciences of the U.S.S.R., Moscow, U.S.S.R.

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Аннотация—В работе изложен теоретический анализ процессов тепло- и массообмена тел с потоком газа при наличии произвольных гетерогенных реакций, протекающих с конечной скоростью.

Проведен анализ устойчивости решения, а также предельных значений температур поверхности, интенсивности уноса вещества и концентрации исходных продуктов у стенки.

Приведен качественный анализ влияния на температуру поверхности, интенсивность уноса массы и концентрацию исходных продуктов у поверхности различных факторов, характеризующих теплообмен потока с телом при наличии гетерогенных реакций.

Особое внимание уделено процессам воспламенения и затухания.

NOMENCLATURE

A,	activation energy, initial gaseous chemical component;
B,	chemical component in the form of solid phase;
C,	gaseous reaction product;
c_p,	heat capacity at constant pressure;
D,	diffusion coefficient, characteristic dimension of a body;
f,	dimensionless function, equation (6);
i,	enthalpy;
K,	equilibrium constant;
k,	weight fraction of gas in mixture;
$\bar{k}$,	dimensionless concentration of a gas component in equation (9);
Le,	Lewis number;
l,	component of solid phase;
m,	molecular weight;
$\bar{m}$,	parameter of mass carrying over, equation (23);
n,	reaction order;
Pr,	Prandtl number;
R,	universal gas constant;
Re	$= \rho U_\infty D/\mu$, Reynolds number;
r,	reaction heat; $r_{av} = \sum_l \varphi_l \sum_{m_l} r_{m_l} (\rho v)^*_{m_l}$; $\bar{r} = r/(i_\infty - i_w)$;
r_0,	radius of an axisymmetric body;
T,	absolute temperature;
$\bar{T}$,	dimensionless temperature, equation (8);
U_∞,	flow velocity far from a body;
u,	tangential velocity component; $\bar{u} = u/U_\infty$;
u_∞,	velocity outside a boundary layer;
$(du_\infty/dx)_0$,	velocity gradient of a non-viscous flow in the vicinity of the front critical point;
v,	normal velocity component;
x,	longitudinal co-ordinate; $\bar{x} = x/D$;
y,	normal co-ordinate;
z,	kinetic constant;
γ^*,	parameter of a chemical reaction rate, equation (38);
η,	dimensionless co-ordinate, equation (2);
$\theta = (\rho v)_i/(\rho v)$;	
κ,	temperature coefficient of reaction rate;
λ,	thermal conductivity;
μ,	dynamic viscosity;
ν,	stoichiometric coefficient; $(\rho v)^*_{m_l} = (\rho v)_{m_l}/(\rho v)$;
ρ,	gas density;
φ_l,	surface fraction occupied by mass B_l.

Subscripts

i, γ, k,	initial, neutral components and reaction product, respectively;
l,	kind of substance in solid phase;

m, mode of reaction;
w, wall parameters;
∞, parameters outside a boundary layer.

INTRODUCTION

IN MODERN engineering there are many cases of heat and mass transfer complicated by chemical reactions proceeding both in a gas phase and at a surface. This includes a wide range of phenomena from various kinds of combustion to an interaction of high-velocity gas flows with solids. A number of investigations into such problems has been published recently [1–3].

The problem considered is very complex since it necessitates taking into account interconnected processes of heat conduction, diffusion and chemical reactions proceeding in the presence of large velocity, temperature and concentration gradients. This makes it necessary to introduce some simplifications bound up with the peculiarities of an incoming flow, properties of chemical processes, etc. In particular, there is a widespread assumption concerning the extremum value of the rate of reactions proceeding: systems are considered either "frozen" or equilibrium ones.

The aim of the present paper is to analyse theoretically heat- and mass-transfer processes in the vicinity of the frontal point of blunt bodies with regard to heterogeneous chemical reactions, the rates of which are not restricted.

1. FORMULATION OF THE PROBLEM

Consider some plane or axisymmetric body in a multicomponent gas flow A which can react with the body material B as a result of which the substance C is formed. Besides reacting components, there may also be neutral gases in the flow.

In a general case, the material of the body is a finely dispersed, mechanical l-component mixture the grains of which are sufficiently small compared with characteristic body dimensions.

Different velocities with which separate body components are carried over may roughen the initially smooth surface of the body, the flow near the wall acquires a complex turbulent character and the problem becomes extremely complicated.

The boundary layer round the body is a multicomponent mixture with concentration, temperature and pressure gradients, so that the processes of concentration thermo- and barodiffusion will arise in it and the gas density will change with temperature, pressure and composition.

Thus, the analysis of the problem in an exact formulation, even in the case of laminar fluid flow, necessitates solving the system of complex equations given in [4].

Since the development of the method by which the influence of heterogeneous reactions on the steady heat and mass transfer can be analysed is the main purpose of the present paper, a number of simplifications bound up with the gas properties and flow conditions is introduced.

(1) The flow develops in the vicinity of the front critical point. This problem is independently of great interest, since this very region is often characterized by maximum heat flows [5].

(2) The flow is laminar. This assumption is quite real in the case of a surface suffering no destruction [1]. If destruction of the surface takes place, it means that a limited time interval is considered during which the surface may be regarded as smooth.

(3) φ_l does not change with time; it is observed when the degree of heterogeneity of the material is constant.

(4) c_p, λ, ρ, μ are constant and the D's are equal for different mixture components.

(5) The concentration diffusion alone is taken into account.

(6) The wall is adiabatic, i.e. heat transmission inside the body and radiation are considered unessential.

(7) The influence of surface "contamination" by reaction products due to their adsorption, as well as the influence of partial progress of reaction inside a porous wall, is not taken into consideration or presumed to be known.

All these simplifying assumptions were made in order to reveal more efficiently the influence of various heterogeneous processes on heat transfer. Moreover, with the help of the method proposed, one may estimate the relative influence of these processes on heat transfer as compared with the cases when reactions do not take place;

these relative estimations will be of still more general meaning.

2. INITIAL SYSTEM OF EQUATIONS

The ordinary system of conservation equations for the boundary layer given in co-ordinates x–y (Fig. 1) can be transformed by introducing new independent variables:

$$\xi \equiv \rho\mu \left(\frac{\mathrm{d}u_\infty}{\mathrm{d}x}\right)_0 \frac{x^{2(\alpha+1)}}{2(\alpha+1)}, \qquad (1)$$

$$\eta \equiv \sqrt{\left[\frac{\rho}{\mu}\left(\frac{\mathrm{d}u_\infty}{\mathrm{d}x}\right)_0 (\alpha+1)\right]}\, y, \qquad (2)$$

where $\alpha = 0$ for plane bodies and $\alpha = 1$ for axisymmetric bodies.

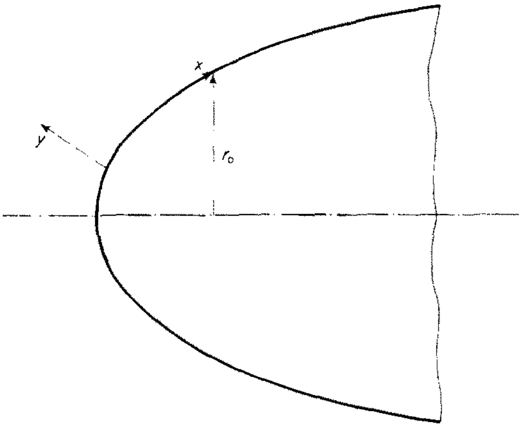

FIG. 1. Scheme of the body in a flow.

In the considered case for which $(\mathrm{d}u_\infty/\mathrm{d}x)_0 \simeq$ const. and $r_0 \simeq x$, it may be shown that the boundary-layer equations are reduced to the relations:

$$f''' + ff'' + \frac{1}{\alpha+1}[1-(f')^2] = 0, \qquad (3)$$

$$\bar{T}'' + f\bar{T}' = 0, \qquad (4)$$

$$\bar{k}''_i + f\bar{k}'_i = 0, \qquad (5)$$

all the functions of which depend on η alone. Their physical meaning becomes clear when analysing the following relations:

$$f = -\frac{\rho v}{\sqrt{[\mu\rho\,(\mathrm{d}u_\infty/\mathrm{d}x)_0\,(\alpha+1)]}}, \qquad (6)$$

$$f' = \frac{u}{u_\infty}, \qquad (7)$$

$$\bar{T} \equiv \frac{T - T_w}{T_\infty - T_w}, \qquad (8)$$

$$\bar{k}_i \equiv \frac{k_i - k_{iw}}{k_{i\infty} - k_{iw}}. \qquad (9)$$

Equations (3–5) are valid only in the case when all the parameters near the surface characterizing the phenomenon are constant. Only the boundary condition may be predicted *a priori* for the velocity component u_w equal to zero for not too rarefied flows. As to other values, they are unknown beforehand and are to be determined while solving the problem. Nevertheless, on the basis of the following obvious assumptions:

(a) mass carrying over is proportional to heat flow from the gas to the wall, equal to heat release due to reaction;
(b) reaction rate depends only on a concentration of reactants near the surface and the temperature of the latter;

it may be shown even before solving the problem that all the flow parameters are constant in the vicinity of the frontal point. Thus, boundary conditions may be given in the form:

$$\text{at } \eta = \infty, \quad f' = \bar{T} = \bar{k}_i = 1; \qquad (10)$$

$$\text{at } \eta = 0, \quad f = f_w; \quad f' = \bar{T} = \bar{k}_i = 0. \qquad (11)$$

From the analysis of the initial system of equations and boundary conditions it follows that:

(1) Temperature and concentration profiles of all the components are similar, and determined by the relation:

$$\bar{T} = \bar{k}_i = \frac{\int_0^\eta \exp\left(-\int_0^\eta f\,\mathrm{d}\eta\right)\mathrm{d}\eta}{\int_0^\infty \exp\left(-\int_\eta^0 f\,\mathrm{d}\eta\right)\mathrm{d}\eta} \qquad (12)$$

hence:

$$(\bar{T}_w)' = \left[\int_0^\infty \exp\left(-\int_0 f\,\mathrm{d}\eta\right)\mathrm{d}\eta\right]^{-1} = \varphi(f_w) \qquad (12a)$$

(2) The momentum equation is solved independent of energy, concentration equations

being bound with the latter ones only through the boundary condition f_w.

At $f_w = 0$, equation (3) was solved numerically and tabulated by Howarth for a plane case and by Frössling for an axisymmetric one [8]; an analogous problem was solved by Schlichting [6] at $\alpha = 0$ and various f_w.

3. BOUNDARY CONDITIONS AT THE BODY SURFACE

Since, in a general case, a body may represent a mechanical mixture of various substances, then to characterize it we shall introduce

$$\varphi_l \equiv \frac{s_l}{s} \tag{13}$$

which is a surface fraction occupied by the substance B_l, the specific rate of which will be designated by $(\rho v)_l$.†

It is evident that the average rate of the substance from the unit surface of the body is equal to

$$\rho v = \sum_l (\rho v)_l \varphi_l. \tag{14}$$

each of l components of the surface may take part in m_l reactions of the type

$$\sum_i \nu_{im_l} A_i + \nu_{lm_l} B_l \rightleftarrows \sum_k \nu_{km_l} C_k. \tag{15}$$

Designate a fraction of the substance A or C separated out when reacting with the unit mass of the substance B_l through θ:

$$\theta_{im_l} \equiv \frac{(\rho v)_{im_l}}{(\rho v)_{m_l}} = -\frac{\nu_{im_l} m_i}{\nu_{lm_l} m_l}, \tag{16}$$

$$\theta_{km_l} \equiv \frac{(\rho v)_{km_l}}{(\rho v)_{m_l}} = \frac{\nu_{km_l} m_k}{\nu_{lm_l} m_l} \tag{17}$$

where $(\rho v)_{m_l}$ is the rate of the substance B_l from the unit surface due to the reaction m_l.

It follows, from the law of mass conservation, in the reaction m_l:

$$\sum_i \theta_{im_l} + \sum_k \theta_{km_l} = 1 \tag{18}$$

A. *Energy-conservation equation*

With regard to condition (6), the energy-conservation equation at the wall has the form

$$\left(\lambda \frac{\partial T}{\partial y}\right)_w = r_{\text{av}} (\rho v), \tag{19}$$

where r_{av} is determined by the expression

$$r_{\text{av}} = \sum_l \varphi_l \sum_{m_l} r_{m_l} (\rho v)^*_{m_l}, \tag{20}$$

and

$$(\rho v)^*_{m_l} \equiv \frac{(\rho v)_{m_l}}{(\rho v)} \tag{21}$$

is a fraction of the substance B destroyed in the reaction m_l, and r_{m_l} is the reaction heat; $r > 0$ when the reaction is endothermal and $r < 0$ in the reverse case.

There is an apparent relation between various $(\rho v)^*_{m_l}$:

$$\sum_l \varphi_l \sum_{m_l} (\rho v)^*_{m_l} = 1. \tag{22}$$

Note that the average reaction heat r_{av} remains unknown till the complete solution of the problem.

Introduce dimensionless parameters, characterizing the velocity of the substance carrying over:

$$\bar{m} \equiv -f_w = \frac{(\rho v)}{\sqrt{[\rho\mu (\mathrm{d}u_\infty/\mathrm{d}x)_0 (\alpha + 1)]}} = \frac{(\rho v)}{(\rho U)_\infty} \sqrt{\left(\frac{Re}{(\mathrm{d}\bar{u}/\mathrm{d}x)_0 (\alpha + 1)}\right)}, \tag{23}$$

and the average reaction heat:

$$\bar{r}_{\text{av}} \equiv \frac{r_{\text{av}}}{i_\infty - i_w}. \tag{24}$$

Substituting relations (23) and (24) into equation (19), we obtain, after some transformations,

$$(\bar{T}')_w = \bar{r}_{\text{av}} \bar{m}. \tag{25}$$

B. *Component-conservation equation*

A mixture component separated out on the surface during the progress of a chemical reaction is removed from the latter owing to convective and diffusion flows:

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† Henceforth, the value v alone will be used on the body surface, the subscript w being omitted for the sake of abbreviation.

$$k_w\,(\rho v) - \rho D \left(\frac{\partial k}{\partial y}\right)_w = (\rho v) \sum_l \varphi_l \sum_{m_l} (\rho v)^*_{m_l}\, \theta_{m_l}. \tag{26}$$

The similarity of concentration and temperature profiles, as well as the assumption that $Le = 1$, makes it possible to write this relation in the form

$$\frac{k_w - \sum\limits_l \varphi_l \sum\limits_{ml} \theta_{m_l}\,(\rho v)^*_{mi}}{k_\infty - k_w} = \bar{r}_{\text{av}} \tag{27}$$

which is valid for any mixture component.

C. *Equation of chemical kinetics*

Generally speaking, the rate of the substance separation on the surface is determined by the difference of direct and inverse reactions in which this substance may precipitate. Therefore, for each of the m_l reactions we may write

$$(\rho v)_{m_l} = \kappa_{m_l} \prod_i \left(\frac{\rho}{m_i}\, k_{iw}\right)^{n_{im_l}} \times \left[1 - K_{m_l} \frac{\prod\limits_k \left[(\rho/m_k)\, k_{kw}\right]^{n_{km_l}}}{\prod\limits_i \left[(\rho/m_i)\, k_{iw}\right]^{n_{im_l}}}\right], \tag{28}$$

where the order of reaction n, and the dependence of the equilibrium constant K and the temperature coefficient of the direct reaction κ on temperature are supposed to be known. In particular, the Arrhenius law can be used for the latter:

$$\kappa_{m_l} = z_{m_l} \exp\left(-\frac{A_{m_l}}{RT_w}\right). \tag{29}$$

It should be noted that equation (28) is strictly valid only in the case when the substance B_l, separated out at the inverse reaction, settles entirely on the surface. In reality, this process may either take place partially or not occur at all, i.e. the substance B_l separated out will be carried away by the flow. In this case, the carrying over of the substance is determined by relation (28), where one should assume that $K_{m_l} = 0$, though the reaction is reversible. The process stops being purely heterogeneous, as a reaction will proceed not only on the surface of the body.

Further, two limited cases will be considered: the complete settling of the substance B_l upon the surface evolved at the inverse reaction, and the irreversible process equivalent to the complete substance carrying over by the flow.

Introduce a dimensionless value characterizing the kinetic peculiarities of the reaction m_l:

$$\gamma^*_{m_l} \equiv \frac{\kappa_{m_l} \prod \left[(\rho/m_i)\, k_{iw}\right]^{n_{im_l}}}{\sqrt{\left[\rho\mu\,(\mathrm{d}u_\infty/\mathrm{d}x)_0\,(\alpha + 1)\right]}} \times \left[1 - K_{m_l} \frac{\prod\limits_k \left[(\rho/m_k)\, k_{kw}\right]^{n_{km_l}}}{\prod\limits_i \left[(\rho/m_i)\, k_{iw}\right]^{n_{im_l}}}\right]. \tag{30}$$

Then, applying the conservation law to the destroyed substance of the surface, we may write

$$\gamma^*_{ml} = (\rho v)^*_{ml}\, \bar{m}. \tag{31}$$

Thus, we obtain the system of equations (12a), (20), (23–25), (27) and (29–31), the addition to which of both the obvious equality

$$\sum_{i,j,k} k_w = 1 \tag{32}$$

and the known dependence of the constant of chemical equilibrium on temperature makes this system closed. The analysis shows that it is necessary to solve the differential equation only to obtain relation (12a). Eliminating $(\bar{T}'_w)$ from equations (12a) and (25), we may obtain the approximating dependence $\bar{m} = \bar{m}(\bar{r}_{\text{av}})$ which should be used henceforth. It should be noted that this dependence, given qualitatively in Fig. 2, has a universal character and does not depend on the specific characteristics of the flow, body, reactions proceeding, etc.

Consequently, to determine all the parameters in question, including the rate of the substance carrying over the surface temperature, it is essential to solve the system of non-linear algebraic equations, which can be, generally speaking, achieved by numerical methods alone.

This is more convenient to perform by prescribing the wall temperature and solving the whole system except one equation, for example (20), which should then be used to check the correctness of the chosen T_w.

4. HOMOGENEOUS BODY IN THE PRESENCE OF ONE IRREVERSIBLE REACTION

In a general form, the analysis of the system obtained is difficult; it is easier to carry it out by application to a more simple case; hence a number of qualitative conclusions will have a general meaning.

Consider the thermal interaction of the flow with a homogeneous object, on the surface of which one irreversible reaction of the following type is proceeding:

$$\gamma^* = \frac{z\left(\frac{\rho}{m_i}\frac{k_{i\infty}\bar{r}+\theta_i}{1+\bar{r}}\right)^n}{\left\{\sqrt{\left[\rho\mu\left(\frac{du_\infty}{dx}\right)_0(\alpha-1)\right]}\exp\left[\frac{A}{R(T_\infty-r/\bar{r}\,c_p)}\right]\right\}}. \tag{38}$$

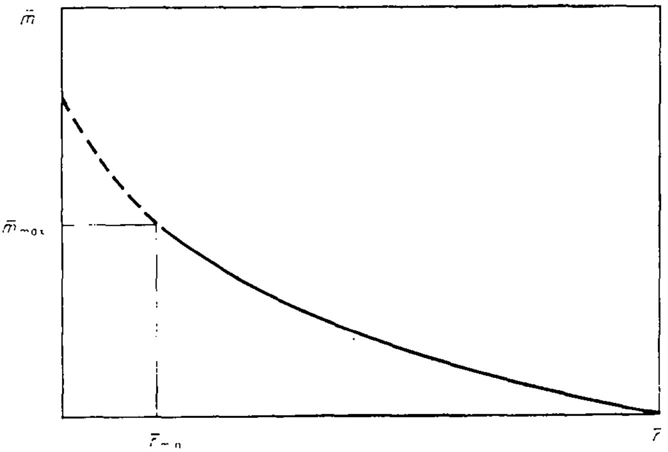

FIG. 2. Universal dependence of the parameter of the substance carrying over on dimensionless reaction heat.

$$\nu_i A + \nu B \rightarrow \nu_k C \tag{33}$$

and the number of neutral components is not restricted.

Obviously, in this case, the initial system of equations can be obtained from the general one if we assume that

$$\varphi_i = (\rho v^*)_{m_i} = 1; \quad K_{m_i} = 0.$$

As a result we shall have

$$\bar{m} = \bar{m}(\bar{r}), \tag{34}$$

$$\bar{r} = \frac{r}{c_p(T_\infty - T_w)} = \frac{-r}{c_p(T_w - T_\infty)}, \tag{35}$$

$$k_{iw} = \frac{k_{i\infty}\bar{r} + \theta_i}{1 + \bar{r}}, \tag{36}$$

$$\gamma^* = \bar{m}, \tag{37}$$

A. *On limiting values of some parameters*

The analysis of the system obtained allows some preliminary conclusions to be made before the system is completely solved. In particular, from equation (36) it follows that:

(1) The concentration of primary products near the wall does not depend explicitly on the reaction kinetics, flow velocity, form and size of the body, etc., and for the given reaction it is determined only by the temperature difference (Fig. 3).

(2) Since $k_{iw} \geq 0$, there exists a minimum possible positive value of $\bar{r}$:

$$\bar{r}_{\min} = -\frac{\theta_i}{k_{i\infty}} \tag{39}$$

and the maximum value of the parameter of mass carrying over $\bar{m}_{\max}$ bound with it (Fig. 2).

(3) It follows from equations (35) and (39) that there exist extreme values of temperature of the reacting surfaces. They may change from the temperature of the surrounding medium to the

maximum one for exothermal reactions, and from the temperature of the surrounding medium to the minimum one for endothermal reactions, and are determined by the general formula

$$T_w = T_\infty + \frac{k_{i\infty} r}{c_p \theta_i}. \tag{40}$$

(4) Since the minimum temperature for endothermal reactions, $T_{w\,\min} > 0$, one may conclude from expressions (35) and (36) that there is a minimum concentration of primary products near the wall

$$k_{iw\,\min} = \frac{k_{i\infty} r + \theta_i c_p T_\infty}{r + c_p T_\infty}. \tag{41}$$

As can be seen, $k_{w\,\min} > 0$ at $k_{i\infty} r > -\theta_i c_p T_\infty$, which, correspondingly, will give rise to $r_{\min}$ and decrease to $\bar{m}_{\max}$. Such a limit does not exist in the case of exothermal reaction.

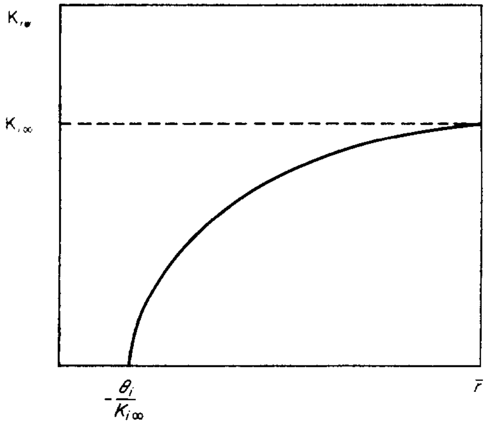

FIG. 3. Dependence of the initial component concentration near the wall on dimensionless reaction heat.

B. *On stability of solutions*

From the analysis of the system of equations (34–38) it follows that the solution may be found at the point of intersection (or contact) of curves of the dependences $\bar{m} = \bar{m}(\bar{r})$ (Fig. 2) and $\gamma^* = \gamma^*(\bar{r})$ plotted by equation (38).

Stable solutions, at small deviations from which the system returns spontaneously to the initial state, are particularly interesting.

In Fig. 4, all possible cases of mutual disposition of curves $\bar{m} = \bar{m}(\bar{r})$ and $\gamma^* = \gamma^*(\bar{r})$ in the region of solution are given.

For the analysis of the stability one should keep in mind the physical meaning of the values $\bar{m}$ and γ^*. The first of these characterizes the intensity of heat transfer between the flow and the body; the second, the intensity of energy release due to chemical reactions. Moreover, it is necessary to take into account that, according to equation (35), $\bar{r}$ and T_w change in the same way

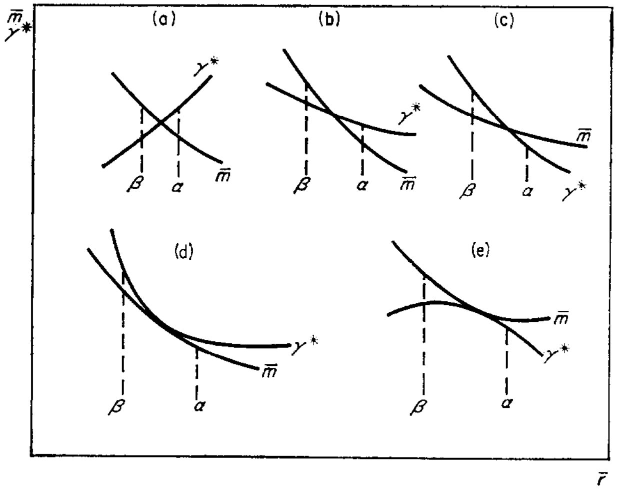

FIG. 4. Possible cases of mutual position of curves $\bar{m} = \bar{m}(\bar{r})$ and $\gamma^* = \gamma^*(\bar{r})$.

in the case of endothermal reactions, and, in that of exothermal reactions, in a contrary way.

We may show that the solution will always be of the type (a) with endothermal reactions (Fig. 4), while for an exothermal process any variety of it is possible.

Consider in detail the case of endothermal reaction as an example of the analysis of stability. Let us assume that, for some reason or other, the system is converted from the equilibrium state (Fig. 4) into the state (α) characterized by a higher value of T_w. As can be seen, the heat supply to the wall decreases, while the absorption of it increases, which will lead to a decrease in T_w until the initial equilibrium state is reached. We shall observe a contrary but stable picture for the deviation of the system into state (β).

Similarly, considering exothermal reactions, we may show that the cases (a) and (b) will be quite stable, the case (c) quite unstable, and the cases (d) and (e) unilaterally stable: the system is stable with respect to deviations from the equilibrium position on one side and unstable with respect to deviations of the contrary sign.

Analysing Fig. 4, we may conclude that there is a stable domain when

$$\frac{\mathrm{d}\bar{m}}{\mathrm{d}\bar{r}} \leqslant \left(\frac{\mathrm{d}\gamma^*}{\mathrm{d}\bar{r}}\right). \tag{42}$$

Moreover, in the case of equality, the solution will be stable from that side where the inequality (42) is fulfilled.

Upon differentiation of equation (38) with respect to $\bar{r}$ and substitution of the result into equation (42), the stability condition may be presented in the following form:

$$\frac{\mathrm{d}}{\mathrm{d}\bar{r}}(\ln \bar{m}) \leqslant \frac{n}{1+\bar{r}}\,\frac{k_{i\infty}-\theta_i}{k_{i\infty}\bar{r}+\theta_i} + \frac{A}{R}\,\frac{r}{c_p\bar{r}^2T_w^2}. \tag{43}$$

C. *Possible types of solutions*

It has already been mentioned that, to solve the problem, the solution of the system of equations (34–38) is necessary, in particular, the point of intersection of curves $\bar{m} = \bar{m}(\bar{r})$ (34) and $\gamma^* = \gamma^*(\bar{r})$ (38) is to be found. If the first of the curves is universal and does not depend on the type of reaction, then the form of the second is essentially different at the endothermal and exothermal reactions.

For endothermal reactions ($r > 0$), it follows from equation (38) that γ^* increases with increasing $\bar{r}$, approaching some limit (Fig. 5). This is explained by a simultaneous increase in the concentration of primary products k_{iw} (36) and in the surface temperature T_w (35), which gives rise to the reaction rate.

As can be seen, there is a single solution for endothermal reactions and it is stable (Fig. 4a).

With exothermal reactions ($r < 0$), it follows from equation (38) that the curve $\gamma^* = \gamma^*(\bar{r})$

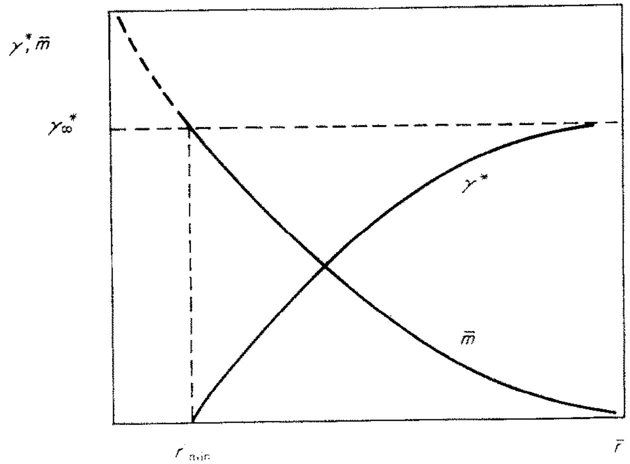

FIG. 5. Solution for endothermal reaction.

may have a maximum. This is explained by the fact that, as always, k_{iw} increases with $\bar{r}$ (36) while T_w decreases (35), which brings first an increase and then a decrease in the reaction rate.

Five different versions of mutual disposition of the curves $\bar{m} = \bar{m}(\bar{r})$ and $\gamma^* = \gamma^*(\bar{r})$ in the region of the solution are given in Fig. 6.

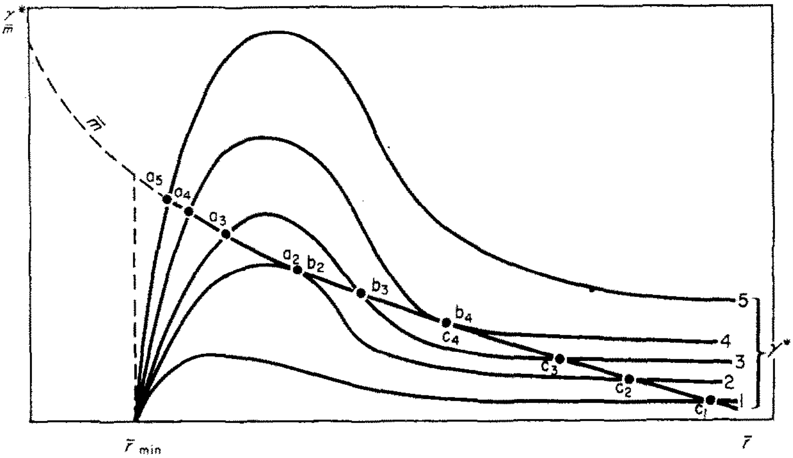

FIG. 6. Solution for exothermal reaction.

The first curve bears a relation to the domain of "cold" reaction. In this case there is a single stable solution (Fig. 4b) characterized by the point c_1.

The curve of the second type may have two solutions: "cold", characterized by the point c_2, and "hot", characterized by the points a_2 and b_2 merged.

The cold domain is stable (Fig. 4b) and the hot one is stable from the side of higher temperature and unstable from the side of lower temperature (Fig. 4e). It will be shown below that this case corresponds to the domain of "extinction".

The third curve is the most general. Three solutions are possible in this case: "hot" (point a_3), "intermediate" (point b_3) and "cold" (point c_3). The "hot" and "cold" domains are stable (Fig. 4a and b, respectively), while the "intermediate" domain is unstable (Fig. 4c). Thus the existence of the "hot" and "cold" stable domains of the course of the process is a characteristic feature of the third curve.

Two solutions are possible for the curve of the fourth type: "hot" (point a_4) and "cold" (coinciding points b_4 and c_4). However, in this case, in contrast to the second curve, the "hot" domain is stable (Fig. 4a), while the cold domain is stable from the side of low temperature and unstable from the side of high temperature (Fig. 4d). It will be shown below that this case corresponds to the "ignition" domain.

Finally, the fifth curve corresponds to the case at which there is only "hot" solution (the point a_5) which is stable (Fig. 4a).

It can be seen from the analysis of the family of curves that all purely "hot" and "cold" domains are stable, while a purely "intermediate" domain is absolutely non-stable, and mixed ones, where the "intermediate" domain fuses with a "hot" or "cold" one, are one-sidedly stable, i.e. stable only with respect to deviations of temperature in the direction of the domain which coincided with the intermediate one.

D. *Ignition and extinction regimes*

It is known from experiments on carbon combustion [8] that if the temperature of the incoming flow increases gradually, then, at some value of this temperature called the temperature of ignition, the reaction proceeds with small intensity at a low value of the surface temperature and passes with a sudden jump to another domain, at which the rate of burn-up and temperature of the burning surface increase sharply and subsequently continues to remain at this new higher level.

Apparently, an analogous picture may also be observed in other cases of heterogeneous exothermal reactions.

It is easy to investigate ignition phenomena and dependence of the ignition temperature on different factors, with the help of curves analogous to those in Fig. 6.

Let the initial gas temperature of the incoming flow (T_∞) be so low that the dependence $\gamma^* = \gamma^*(\bar{r})$ is characterized by the curve of type (1). There will be one stable domain with low surface temperature and intensity of mass carrying over (point c_1).

The analysis of equation (38) show that, with increase in T_∞, other conditions being constant, the process may be illustrated by the curves of Fig. 6, the ordinates being higher. Moreover, the wall temperature and the intensity of mass carrying over will rise gradually, though still remaining relatively small. The domains will be stable until we achieve the temperature of the incoming flow, to which the curve of the type (4) will correspond.

In this case, a negligible occasional increase in the wall temperature (or non-vortex flow) is sufficient for heat release due to reaction to become higher than heat removal due to convection; the wall will grow intensely warm, and the system will pass rapidly on to a new stable state (a_4) characterized by considerably higher values, both of the reacting surface temperature and the intensity of mass carrying over. The further increase in temperature of the incoming flow will give a small increase of these parameters.

The temperature of the incoming flow to which curve (4) of Fig. 6 corresponds will be called the ignition temperature T_{ign}. Similarly the "extinction" phenomenon may be predicted and the corresponding temperature of extinction introduced T_{ext}, to which the curve (2) corresponds.

It should be noted that, generally speaking, ignition may take place at $T_\infty < T_{\text{ign}}$ also, with extinction at $T_\infty > T_{\text{ext}}$. In effect, the analysis of Fig. 6 shows that for a sharp transition from "cold" to "hot" domains it is necessary that the fluctuation of the wall temperature should be such that:

$$|\,\Delta\bar{r}\,| > \bar{r}_c - \bar{r}_b.$$

An analogous value leading to a sharp transition from a "hot" to a "cold" domain should be

$$\Delta\bar{r} > \bar{r}_b - \bar{r}_a.$$

When determining the concept of ignition and extinction temperatures we assumed that these differences are equal to zero. Thus the more irregularly the process proceeds (due to irregularities of the flow, body, etc.), the more considerably the actual ignition and extinction temperatures may differ from the theoretical ones.

As can be seen from Fig. 6, the temperature of ignition is always higher than that of extinction. An analogous relation exists also between the surface temperatures (between both "hot" and "cold" ones) at the times of ignition and extinction. This is proved by the hysteresis loop formed by plotting the dependence of the wall temperature on the temperature of the incoming flow when the latter increases and decreases successively (Fig. 7).

Let us analyse the dependence of ignition and extinction temperatures on various factors characterizing the process. The analysis of curves (2) and (4) on Fig. 6 shows that the following system of equations should be solved to find T_{ign} and T_{ext}:

$$\bar{m} = \gamma^*, \tag{44}$$

$$\frac{\mathrm{d}\bar{m}}{\mathrm{d}\bar{r}} = \frac{\mathrm{d}\gamma^*}{\mathrm{d}\bar{r}}. \tag{45}$$

Two solutions have to be obtained, the lesser of them corresponds to T_{ext}, the greater to T_{ign}.

Transforming equations (44) and (45) by means of relations (38) and (43), we get:

$$\bar{m} = \frac{z\left[\dfrac{\rho\,(k_{i\infty}\,\bar{r} + \theta_i)}{m_i\,(1+\bar{r})}\right]^n}{\sqrt{\left[\rho\mu\left(\dfrac{\mathrm{d}u_\infty}{\mathrm{d}x}\right)(\alpha+1)\right]\exp\left[\dfrac{A}{R\,[T_\infty - (r/\bar{r}\,c_p)]}\right]}} \tag{46}$$

$$\frac{\mathrm{d}}{\mathrm{d}r}(\ln m) = \frac{n}{1+\bar{r}}\,\frac{k_{i\infty} - \theta_i}{k_{i\infty}\,\bar{r} + \theta_i} + \frac{A}{R}\,\frac{r}{c_p\,\bar{r}^2[T_\infty - (r/\bar{r}c_p)]^2} \tag{47}$$

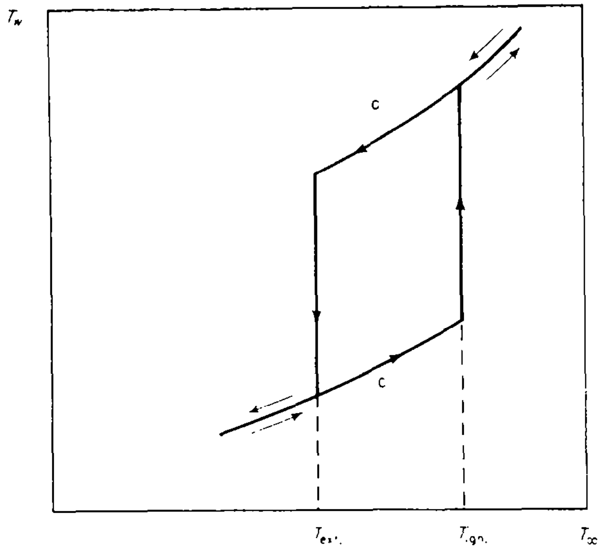

FIG. 7. Dependence of the surface temperature on the flow temperature with exothermal reactions.

If we assume that the dependence $\bar{m} = \bar{m}(\bar{r})$ is known, then equations (46) and (47) may be considered as a system with two unknowns, $\bar{r}$ and T_∞, the latter being the ignition and extinction temperature.

However, it is more convenient to make use of the grapho-analytical method given below for a qualitative analysis of the dependence of T_{ign} and T_{ext} on different parameters characterizing the process.

In Fig. 8, sections of the curves (4) and (2) on Fig. 7 corresponding to ignition and extinction domains are given as solid lines, while dotted lines stand for the sections of the neighbour curves of the same family obtained when any parameters determining the value γ^* (38) change at the same values of T_∞. It is evident that, at the deviation in the direction of α, T_∞ should be lowered in order to return to one of the transitional domains which means that in this case

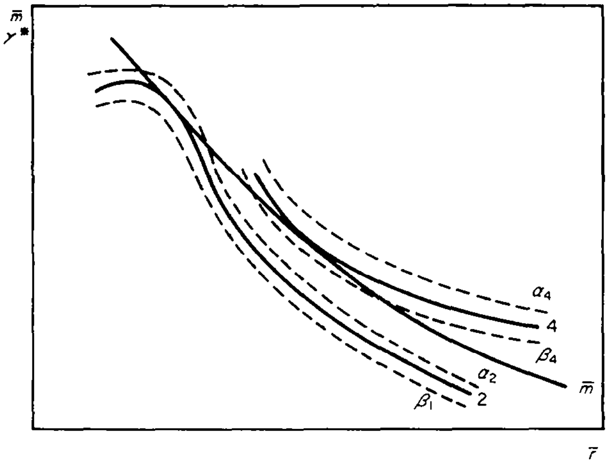

FIG. 8. Dependence of ignition and extinction temperatures on various factors.

both the ignition and extinction temperatures will fall. A reverse picture is observed at changes of the domain deviating the curves γ^* into the position β.

Thus the following conclusions may be drawn from Fig. 8: all the changes of parameters characterizing the process which favour the increase in γ^* (38) bring the decrease in temperatures of the incoming flow corresponding to the transitional domains. Utilizing these circumstances, we shall investigate the influence of various factors on T_{ign} and T_{ext}.

It should be noted at once that, as seen from equation (38), the ignition and extinction temperatures do not depend only on the chemical characteristics of the reacting substances; such hydrodynamic parameters as velocity and density of the incoming flow, as well as the sizes and the form of the body in the flow, are also of essential importance.

With increase in $(\mathrm{d}u_\infty/\mathrm{d}x)_0$, the value γ^* (38) decreases, which gives rise to the temperature of the transitional processes.

Thus the increase in velocity of the incoming flow, the decrease in size of the body and the choice of a more streamlined form favour the rise of ignition and extinction temperatures.

The dependence of γ^* on ρ is essentially determined by the order of the reaction proceeding:

$$\gamma^* \sim \rho^{n-1/2}. \tag{48}$$

It should be noted that in our problem the influence of the change of ρ corresponds to some extent to the influence of pressure change when a body is in a compressible liquid.

It follows from relation (48) that, if the order of reaction $n > \frac{1}{2}$, the ignition and extinction temperatures decrease with increase in density. A contrary picture is observed at $n < \frac{1}{2}$. Finally, at $n = \frac{1}{2}$, since $\gamma^* \neq f(\rho)$, the ignition and extinction temperatures are independent of density.

The growth of the kinetic constant and decrease in the activation energy giving rise to the chemical reaction rate simultaneously increase γ^* (38) also. Consequently, in this case, ignition and extinction temperatures decrease.

An analogous picture is observed when the content of the initial component in an incoming flow increases. The same effect may occur for an increase in the reaction heat as well: an increase of the latter brings a decrease in ignition and extinction temperatures.

E. *The analysis of the influence of various factors on the main characteristics of the process*

Usually, the rate with which the surface undergoes destruction, the surface temperature and, to some extent, the concentration of the initial components near it are of the most practical interest.

In most cases the diagrams plotted make it possible to solve qualitatively (and quantitatively at exact plotting) the problem of the influence of various parameters of a flow and of a body in it on these characteristics of the process. All the values in the right-hand side of equation (38) except $\bar{r}$ can be considered parameters of the family of curves $\gamma^* = \gamma^*(\bar{r})$.

The analysis of Figs. 5 and 6 shows that with endothermal and stable exothermal reactions (both "hot" and "cold" ones) the description of the process by the curves corresponding to greater values of γ^* brings a decrease in $\bar{r}$ and an increase in $\bar{m}$. (Parameters of the non-stable domain behave in contrary fashion, but they will not be considered.) In most cases, this causes an increase in the mass carrying over, a decrease in concentration of the primary components near the wall and in the surface temperature for endothermal reactions, and an increase in it for exothermal reactions. Henceforth such changes will be called "conventional". However, there may be exceptions to this rule.

The physical explanation of all these effects can easily be given by the analysis of the relative influence of the changes made on heat and mass transfer with surrounding medium and on energy release at the wall. Therefore, in each particular case, as a rule, the physical interpretation of the phenomenon will not be given.

With exothermal reactions, the influence of the temperature of the incoming flow is conventional: its growth gives increase in the surface temperature and mass carrying over and brings a decrease in the content of primary products near the wall.

An analogous dependence with respect to the mass carrying over and concentration is observed with endothermal reactions. An abnormal behaviour of the surface temperature is accounted for by the fact that, in this case, T_w should not be judged by equation (35), since an increase in T_w brings a decrease in $\bar{r}$. However, simultaneous increase in the reaction rate (38) and decrease in concentration of the primary products may occur only at the increase in the surface temperature.

On account of relation (48), the influence of the density depends on the order of the reaction proceeding; moreover, it is conventional in every respect with the exception that, even at $n \leq 0{\cdot}5$ when $\bar{m}$ decreases or does not change, the substance rate increases in the power less than the order of the reaction (23).

Thus, with an increase in density at $n < 0{\cdot}5$, the concentration k_{iw} increases; T_w rises with an endothermal reaction, while it decreases with an exothermal one; at $n = 0{\cdot}5$ these parameters do not change, while at $n > 0{\cdot}5$ they behave in a contrary fashion.

The rates of the incoming flow, size and form of the body exhibit themselves through one general parameter: the velocity gradient in the vicinity of the front stagnation point $(\mathrm{d}u_\infty/\mathrm{d}x)_0$. The latter behaves conventionally with respect to the surface temperatures and concentration: k_{iw} increases with $(\mathrm{d}u_\infty/\mathrm{d}x)_0$ and T_w increases for endothermal reactions and decreases for exothermal reactions.

As to the mass carrying over, then apparently, despite a decrease in $\bar{m}$, the intensity of it increases (23) in the power $k < \frac{1}{2}$.

It should be recalled that according to the assumptions made we do not take into account the radiant-heat transfer, which in some cases is of essential importance and can even give results qualitatively different from those given above. Thus, radiation from the wall will effect a decrease in the wall temperature, a fact which is proved by the equation:

$$\alpha(T_w - T_\infty) + \epsilon\sigma T_w^4 = mr. \tag{49}$$

The term characterizing the radiative heat transfer does not depend on the intensity of convective heat transfer, so that with the increase of the latter its role decreases, and this may lead not to a decrease but to an increase in the surface temperature at the intensification of the convective heat transfer. This is illustrated in Fig. 9 where the values:

$$q_{\mathrm{rad}} = \epsilon\sigma T_w^4, \tag{50}$$

$$q = -\alpha T_w + (\alpha T_\infty + mr) \tag{51}$$

are plotted depending on T_w, and should be equal, according to (49). In the diagram, the straight line q_2 corresponds to a greater intensity of the convective heat transfer in comparison with the straight line q_1.

As can be seen, the temperature of the surface,

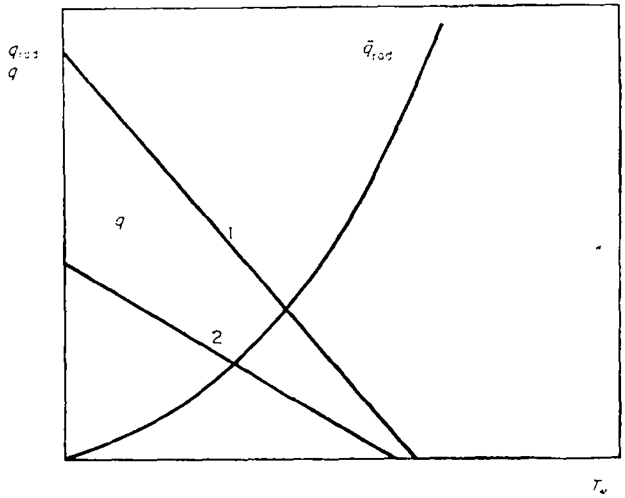

FIG. 9. Influence of the flow of radiative energy on the surface temperature.

on which the exothermal reaction proceeds, increases with convective heat transfer. An analogous influence of radiation is mentioned in [9].

The increase in the reaction heat modulus relative to mass carrying over and concentration k_{iw} reveals itself conventionally: the mass carrying over decreases with endothermal reactions, k_{iw} rises, and, with exothermal reactions, vice versa. As to the temperature of the surface, then it can be judged not by equation (35) but by relations (36) and (38).

The increase in concentration of the primary products near the wall with simultaneous decrease in the intensity of carrying over can occur, with endothermal reactions, only at decrease in the wall temperature. The reverse change of the surface temperature at heat release on it is explained in similar fashion.

The change of chemico-kinetic parameters leads to conventional results. The increase in the kinetic constant z and the decrease in the energy of activation A always cause an increase in the mass carrying over, a decrease in concentration of the primary products on the wall, and a decrease of the wall temperature for endothermal, and an increase for exothermal reactions.

The increase in the concentration of initial components in a non-disturbed flow leads to the conventional increase in the mass carrying over, decrease in the wall temperature with endothermal reactions and increase of it with exothermal processes.

As to the concentration of these products on the wall, we ought to judge its changes not from equation (36), but from the analysis of changes undergone by T_w (35) and γ_w (38). For endothermal reactions we come to a definite conclusion about the rise of k_{iw} with $k_{i\infty}$; for exothermal reactions an analogous conclusion can be strictly drawn only on the basis of quantitative errors.

5. ON THE INFLUENCE OF REVERSIBILITY OF CHEMICAL REACTIONS

For the case of reversible reactions, with regard to the remarks made above on the possible influence of reversibility on heterogeneous processes, the initial system of equations will be completely preserved. The difference will lie only in the fact that, instead of γ^*_{irrev}, which was determined by equation (38), it is necessary to make use of γ^*_{rev} determined by the corresponding relation of the type (30), as well as to apply the question characterizing the dependence of the reaction equilibrium constant on temperature. The methods of analysis of such a system remain the same. Apparently, the main qualitative conclusions do not change either.

It is of interest to discover, at other equivalent conditions, whether the tendency to reversibility influences the parameters of the process. It follows from the analysis of equation (30) that

$$\gamma^*_{\text{irrev}} > \gamma^*_{\text{rev}}.$$

Physically this means that the velocity of the disappearance of any component taking part in the chemical reaction will be smaller if the presence of the reverse reaction is taken into account.

Figures 5 and 6 show that the tendency to reversibility both of endothermal and exothermal reactions (stable cases of solution) leads to an increase in $\bar{r}$, a decrease in $\bar{m}$ and to the growth of k_{iw}, lowering γ^*.

Thus the tendency to reversibility in reactions of any type will lead to some decrease in the intensity of the mass carrying over and to an increase in concentration of the initial components near the wall. From the physical point of view this effect is obvious.

As to the temperatures of the steady-state processes, here then the tendency to reversibility for endothermal and exothermal reactions will result in contrary consequences: the surface temperature increases with endothermal reactions while it decreases with exothermal ones.

Physically this is explained by the fact that the reversible reaction has a thermal effect, the sign of which is contrary to the sign of the straight line. As a result, some compensating process arises which increases the wall temperature with endothermal and decreases it with exothermal reactions.

As to the temperatures of the transitional processes (ignition and extinction), then, proceeding as in the previous sections, it is easy to show that accounting for the reversibility leads to some increase in their values which is again explained by the "compensation" influence of the reversible endothermal reaction.

CONCLUSION

The analysis of heat- and mass-transfer processes in the frontal part of bodies in a gas flow is given for heterogeneous chemical reactions, with highly general assumptions about their character.

The problem is practically reduced to the solution of a system of algebraic equations, and a possible method of solution for this system is given. The limit values of the surface temperature and of the parameter of the mass carrying over are shown for a particular case of a uniform body on the surface of which a simple non-reversible endothermal or exothermal reaction proceeds.

The question of the stability of the possible solutions is analysed.

The influence of various parameters characterizing the process on the intensity of the substance carrying over, concentration of the primary products near the surface and the temperature of the latter is qualitatively investigated.

The paper presents the analysis of ignition and extinction of bodies in a flow of a gas and the dependence of the corresponding temperatures on the factors determining it.

The case of the simplest reaction is investigated; however, qualitative conclusions will be changed little if more complicated processes are analysed.

It should be noted that the method developed is easily generalized for reactions of the catalyst type, as well as for the processes of sublimation or vaporization.

REFERENCES

1. J. Fay and F. Riddell, *J. Aero. Sci.* **35**, 73–85 (1958).
2. L. Lees, *Jet Propulsion*, **26**, 4, 259–269, 274 (1956).
3. V. P. Motulevich and G. P. Malyshev, Sbornik, Fizicheskaya gazodinamika i teploobmen, *Izd. Akad. Nauk. SSSR* (1961).
4. V. P. Motulevich, *J. Eng. Phys.* No. 10, 44–52 (1961).
5. H. Allen and A. Eggers, *N.A.C.A.* N 1381 (1958) (translated into Russian).
6. H. Schlichting, *Grenzschicht-Theorie* (Russian edition). Izd. inostrannoi literatury (1956).
7. M. Jakob, *Heat Transfer* (Russian edition). Izd. inostrannoi literatury (1960).
8. L. N. Khitrin, Fizika goreniya i vzryva, *Izd. MGU* (1957).
9. D. B. Spalding, *Some Fundamentals of Combustion* (Russian edition). Gosenergoizdat (1959).

Abstract—The paper contains a theoretical analysis of the heat- and mass-transfer processes between bodies and the gas flow in the presence of arbitrary heterogeneous reactions proceeding with finite rate.

The stability of the solution, the limiting values of the surface temperatures, the intensity of the substance carrying over and the concentration of the primary products near the wall are all analysed.

A qualitative analysis is given of the influence of various factors, characterizing heat transfer of the flow with the body, on the surface temperature, intensity of the mass carrying over and the concentration of primary products near the surface in the presence of heterogeneous reactions.

Special attention is given to the processes of ignition and extinction.

Résumé—Cet article fait une étude théorique des processus des transports de masse et de chaleur entre des corps et un écoulement de gaz, en présence de réactions hétérogènes quelconques s'effectuant à une vitesse finie.

La stabilité de la solution, les valeurs limites des températures de surface, l'intensité du transport de masse et la concentration des produits initiaux au voisinage de la paroi sont étudiées.

L'auteur a fait également une analyse qualitative de l'influence de différents facteurs caractérisant la transmission de chaleur entre l'écoulement et le corps, la température de surface, l'intensité du transport de masse et la concentration des produits initiaux au voisinage de la surface en présence de réactions hétérogènes.

Les phénomènes d'inflammation et d'extinction sont étudiés en particulier.

Zusammenfassung—Die Vorgänge beim Wärme- und Stoffübergang zwischen einem festen Körper einem strömenden Gas, in dem willkürlich heterogene Reaktionen endlicher Geschwindigkeit auftreten können, werden einer theoretischen Analyse unterzogen.

Dabei werden der Gültigkeitsbereich, die Grenzwerte der Oberflächentemperatur, die Intensität der übergehenden Substanz und die Konzentration der Primärprodukte in Wandnähe untersucht.

Eine qualitative Analyse erfasst den Einfluss verschiedener, für den Wärmeübergang charakteristischer Faktoren, wie der Oberflächentemperatur, der Intensität der übergehenden Menge und der Konzentration der Primärprodukte in Oberflächennähe, bei Berücksichtigung der heterogenen Reaktionen.

Besondere Aufmerksamkeit wurde der Zündung und Löschung gewidmet.