CHEMICALLY NONEQUILIBRIUM MULTICOMPONENT BOUNDARY LAYER

FOR A PLASMA OF MOLECULAR GASES WITH ADDITION OF ALKALI

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In connection with analyzing the operation of technical installations, the problem arises of working out chemically nonequilibrium characteristics for the flow of combustion products of hydrocarbon fuel with alkali additions in a boundary layer at a cooled surface. Satisfactory solution of this problem requires in the general case construction of models taking account of detailed chemical kinetics. This work is devoted to constructing such a model.

1. Statement of the Problem

We consider steady-state subsonic laminar planar or axisymmetric flow around a cooled body of a chemically reactive single-temperature stoichiometric mixture of combustion products of hydrocarbon fuel in air, possibly enriched by oxygen with addition of an easily ionized metal (potassium). We shall assume that the Reynolds number of the approach stream is sufficiently large and flow around the body proceeds in a viscous boundary-layer regime. The Mach number of the approach stream is considered to be small, and changes in temperature and pressure in the nonviscous region are ignored; it is assumed that the body is sufficiently distant from the combustion zone so that in the approach stream chemical (in particular ionization) equilibrium is established between all of the mixture components. Thus, the question involves calculation of distributions for average mass velocity, temperature, and component concentration in the boundary layer.

<u>Set of Characteristic Equations</u>. In order to find the distributions indicated above, we take as a starting point a set of equations for a multicomponent chemically reactive boundary layer.

We shall assume that the temperature in the mixture varies from ~400 at the body surface to ~2500°K in the approach stream, pressure is of the order of atmospheric, and the weight fraction of the potassium element does not exceed 1%. Under these conditions it is possible to isolate components whose content in the mixture is of the order of tens of percent (N₂, H₂O, CO₂), and we shall call them the basic components; the content of the rest of the components is quite low, and we shall call them impurities. The problem of determining velocity, mixture temperature, and the concentration of the basic components to a first approximation is separated from the problem of determining the concentration of impurity components. Since the basic components do not react with each other, the first of these problems disregarding the effect of thermal diffusion, which for this mixture is insignificant, for distribution of the basic components gives a trivial solution (molar fractions are constant across the boundary layer), and in order to determine the fields for velocities and temperature of the mixture, equations are obtained for a single-component compressible boundary layer with effective heat capacity c_p , viscosity coefficients μ , and thermal conductivities λ , depending on temperature and molar fractions of the basic components.

We consider equations governing the distribution of impurity component concentration. Taking account of constancy, to a first approximation within the limits of the model being considered for the average molecular weight of the mixture, the equation for mass conservation of the i-th component is written as

$$nu \frac{\partial}{\partial x} (x_i) + nv \frac{\partial}{\partial y} (x_i) + \frac{\partial}{\partial y} (J_i) = n_i, \quad x_i = \frac{n_i}{n}.$$
(1.1)

Here x and y are coordinates reckoned, respectively, along the body surface and along the normal to it; u and v are projections of the vector for average mass velocity at their axes;

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xi and ni, molar fraction and numerical concentration of the i-th component; n, total numerical concentration; Ji, projection of the vector for diffusion flow particle density of the i-th component at the y axis; ni, rate of change in concentration of the i-th component in a unit volume as a result of chemical reactions. Equations for transfer of impurity components (Stefan-Maxwell relationships [1]) take the form of Fick's laws

$$J_{i} = nD_{i}\left(-\frac{\partial x_{i}}{\partial y} + z_{i}x_{i}\frac{eE}{kT}\right), \quad D_{i} = \left(\sum_{k}\frac{x_{k}}{D_{ik}}\right)^{-1}, \quad (1.2)$$

where summation is carried out for the basic components; E is projection of the vector for electrical field voltage on the y axis; T, mixture temperature; z_i , charge number of the i-th component; e, electron charge; k, Boltzmann constant; D_{ik} , binary diffusion coefficients.

We shall assume that conditions of quasineutrality and absence of an electrical current are fulfilled. Then from systems (1.1) and (1.2) we shall exclude equations for electrons, substituting them by expressions x_e and J_e in terms of the rest of the unknowns; a similar expression is obtained for E.

Set of Components and a Model of Chemical Kinetics. In the first stage the set of components includes those whose concentrations in the approach stream are not too small: N_2 , NO, H_2O , H_2 , O_2 , OH, H, O, CO_2 , CO, K, KOH, K⁺, e, HCO_3^- , OH⁻. Of all the known chemical reactions between these components in the model of chemical kinetics, those reactions are excluded whose typical times do not exceed hydrodynamic time and which are known to be unimportant compared with other reactions involving these components (as a rough estimate for hydrodynamic time, 0.1 sec was adopted). However, the calculation model constructed appears to be unclosed, since part of the components formed in these reactions $(NO_2, HO_2,$ HCO, KO₂, H⁻, O₂⁻, OH⁻·H₂O) do not enter into the system. Therefore, in the second stage the calculation model is expanded: the set is supplemented with these new components, and the model of chemical kinetics is supplemented by reactions with participation of new components (these reactions are selected from all the known reactions for new components between themselves and with the old components, as is done in the first stage). The calculation model constructed in this way appears to be closed, and further expansion is not necessary. Analysis shows that it involves some components (HCO, H⁻) for which there is a single chemical reaction (the typical time for which is markedly less than that for all the rest of the reactions involving this component, and also hydrodynamic time), and the equilibrium constant in the reaction is such that the concentration of the given component is small. Estimates indicate that reactions involving these components have a weak effect on the rest of the components and, therefore, reactions corresponding to them were excluded from the model. The final model involves the components N_2 , NO, NO_2 , H_2O , H_2 , O_2 , OH, H, O, HO_2 , CO_2 , CO, K, KOH, KO₂, K⁺, e, HCO₃⁻, OH⁻, OH⁻·H₂O, O_2^- and reactions between them presented in Table 1. It is noted that, in the first stage of constructing the calculation model, it is necessary to make a priori estimates of component concentration within the boundary layer; after obtaining the actual solution, the validity of these estimates is confirmed.

Rate constants for forward reactions Kf are given in Table 1 (Kf = $AT^n \exp(-B/T)$, [A] = cm, molecule, sec), [B] = K, [T] = K), and also given are the works from which these constants were taken. Rate constants for reverse reactions were calculated as the ratio of the rate constants for forward reactions to equilibrium constants Keg, which are also given in Table 1($K_{eq} = CT^m \exp(D/T)$, [C] = (cm, molecule), [D] = K). In calculating equilibrium constants for all the reaction other than C7, C17-C19, coefficients in the indices of exponents were calculated from values of enthalpy for formation of components with T = 0, and pre-exponential functions were calculated from the prescribed Gibbs energy for components and approximated by stepped functions. In the temperature range T = $1.5 \cdot 10^3 - 3 \cdot 10^3$ K the error of approximation for all of the pre-exponential functions did not exceed 5%. For all the reactions whose activation energies for the reverse stages were not very large (B + $D \leq 8000$ °K), with the exception of reactions B6 and C13, in the range 500 ... $1.5 \cdot 10^3$ °K, the error of approximation also did not exceed 5%. For reactions B6 and C13, the error is, respectively, 17 and 4% with T = 10^3 ... $1.5 \cdot 10^3 \circ K$, and 54 and 17% with T = 500 ... 1.5. 10^{3} °K. Enthalpies for formation of KO₂ and KCO₃ were calculated from the dissociation energies [11, 19], and for the rest of the components they were taken from [21]. The prescribed Gibbs energy for KO2 molecules was taken from [22], for the HCO3 ion it was calculated in an approximation of a rigid rotator-harmonic oscillator for molecular parameters [23], and for the rest of the components it was taken from [21]. The equilibrium constant

TABLE 1

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Reac-	o Reaction	A	n	B	Source	c	m	D
		7 5.40-10	05	3	0 [2]	4 14.10-2	0.23	8 410
A1	$0H+0=0_2+H$	84.40-21	28	1950	[2]	4 36.40-2	0,20	1 000
AZ	$0H+H=H_2+0$	0.1.10	2.0	1,00	191	2 50 10-1	0,0	7 460
A3	$OH+H_2=H_2O+H$	1.00.10 -	2.0	1490	141	2.30.10 -	0.0	8 460
A4	$0H+0H=H_{2}0+0$	$3.3 \cdot 10^{-35}$	1.4	-20	0 [4]	7 47 40-25	0.0	50 400
A5	$^{1}H+OH+M=H_{2}O+M$	3,9.10 -9	-2,0		0 [0,4] 0 [9]	2 96 40-24	-0.22	54 060
A 6	$^{2}H+H+M=H_{2}+M$	3.2.10 20	-1.0		0 121	2.00.10	0.22	50 060
A7		1,0.10	-1.0	00		7 40 40-26	0.22	59 370
A8	$^{\circ}0+0+M=0_{2}+M$	3.0.10 **	0	50	0 [3]	2 23 40-24	0.01	25 380
A9	$H_{+}U_{2}+M=HU_{2}+M$	2 5 40-10	0.0	50		2.55.10	0.04	17 170
A10	$HO_2 + H = OH + OH$	4.2.40-11		35		4.93	-0.48	26 580
A11	$\Pi O_2 + \Pi = \Pi_2 + O_2$	3 3.40-11				3 08.10-2	-0.18	34 040
A12	$HO_2 + OH - H_2O + O_2$	3 3.40-11			n [3]	2.82	_0.18	25 580
A15	$HO_2 + O = OH + O_2$	$1.0.10^{-12}$		9 40		6 18.101	_0.10	24 630
A14	$10_2 + 11_2 - 11_2 0 + 01_1$	2 5.40-17	1 1 3	38	5 161	7 95.10-6	0.84	12 320
AID	$3CO \pm O \pm M = CO \pm M$	7 0.10-33		2200	151	5 23.40-29	0.62	63 280
A10	CO + HO - CO + OH	2 5.40-10		11 900	161	1 96.10-3	0.43	29 490
A17 A49	$C0 + 10^{2} - C0^{2} + 01$	42.40^{-12}	Ň	24 000	161	6.98.10-4	0.61	3 910
A10	4NO + O + M = NO + M	1.9.10-32	l õ	-940	161	1.09.10-27	0.40	36 150
A13	$NO_{+}H=NO+OH$	5.8.10-10	l ů	750	16]	6.05.103	-0.62	14 810
A 94	$N_{0} + 0 = N_{0} + 0$	1.7.10-11		300	161	6.89.10 ¹	-0.39	23 220
A 22	$NO_{+}HO_{-}=NO_{+}OH$	3.5.10-12	lõ	-240	0 [7]	$4.08 \cdot 10^{-2}$	0.21	2 360
A22	$NO_2 + CO = NO + CO_2$	1.5.10-10	l õ	17 010	[8]	$4.81 \cdot 10^{-2}$	0.22	27 130
A 24	$NO+NO=N_{0}+O_{0}$	2.2.10-10	0	38 060	61	1.06-10-1	-0.094	21 830
B 4	$KOH+H=K+H_{2}O$	1.8.10-11	0.	1 000	[9]	$1.10.10^{3}$	-1.22	16 960
B2	$^{3}K+OH+M=KOH+M$	$1.5 \cdot 10^{-27}$	-1.0		191	6.53.10-28	1.0	42 460
B3	${}^{5}K+O_{a}+M=KO_{a}+M$	$1.7 \cdot 10^{-27}$	-1.0		[10]	3.45.10-27	0.83	20 450
B4	$KO_{2}+OH=KOH+O_{2}$	1.0.10-11	0	2 000	[11]	1.89.10-1	0.17	22 010
B5	KO ₂ +H ₂ =KOH+OH	3.0.10-12	0	10 000	[5]	3.80.101	-0.06	12 600
B6	KO ₂ +H=K+HO ₂	4.6.10-11	0	350	6	$6.76 \cdot 10^2$	-0.87	4 930
C1	$^{3}K^{+}+e^{+}M=K^{+}M$	$4.0 \cdot 10^{-24}$	1.0	0	[12]	4.14.10-16	-1,5	50 370
C2	$K^++e^+e^-=K^+e$	$1.0.10^{-8}$	-4.5	0	[13]	4.14.10-16	-1.5	50 370
C3	$K^{+} + O_{-} = K + O_{2}$	2,5.10-6	-0.5	0	7	5.26	-0.22	45 260
G4	$K^{+}+O_{2}^{-}+M=KO_{2}+M$				8	1,81.10-26	0,61	65 710
	$M = H_2O$	1.1.10-16	-3.38	0				
	$M = N_2$	3.6.10-18	-3.0	0				
	M=CO ₂	$4.5 \cdot 10^{-18}$	-3.0	0				90 400
C5	K++OH-=K+OH	1,0.10-8	-0.5	0	[5]	5.47	0.05	49 190 74 650
C6	$K^++OH^-+M=KOH+M$	·	1		8	3.57.10-27	1.05	11 000
	$M = H_2O$	$1.3 \cdot 10^{-16}$		0				
	$M = N_2$	4.1.10-18	-3.0	0				
	M=CO ₂	4.9.10-18	-3.0	0		1		
C7	$ \mathbf{K}^+ + \mathbf{OH}^- \cdot \mathbf{H}_2 \mathbf{O} = \mathbf{K} + \mathbf{OH} +$	1.0.10-8	-0.5	0	9	6.00.1026	-0,95	17 820
	/ +H₂O		· · ·			4 25 101	0.077	27 550
C8	$K^++HCO_3^-=KOH+CO_2$	$1.0.10^{-8}$	-0.5	0	9	4,20.10-	0.077	21 000
C 9	$^{10}e + O_2 + M = O_2^- + M$				11	7,87.10-17	-1.28	5 110
	$M = H_2O$	$1.2 \cdot 10^{-23} \phi$	-1.88	882			ł	
	$M = N_2$	9.7·10 ⁻²⁷ φ		882		1		
	M=CO ₂	3.0·10 ⁻²⁵ φ	-1.5	882			1	
C 10	$e + OH + M = OH^- + M$	$3.0.10^{-31}$	0	0	[5]	7.57.10-17	-1,55	21 180
C11	$0_{2}^{-}+0H=0H^{-}+0_{2}$	1.0.10-9	0	0	[16]	9.62.10-1	-0.27 1	6 070
C12	$O_2^-+H=e+HO_2$	1.4·10 ⁻⁹	0	0	[17]	2.96.10-8	1,24	20 270
C13	$O_2^-+H_2=OH^-+OH$	4.0.10-11	0	0	[18]	$1.94 \cdot 10^2$ -	-0,50	6 660
C14	$OH^-+H=e^+H_{0}O$	$6.3 \cdot 10^{-12}$	0	-1060	[5]	9.46.10-9	1.33	8 240
C15	$OH^-+O=e+HO_2$	2.0.10-10	0	0	[17]	3.51.10-1	1.74 1	2 610
C16	$^{12}OH^-+CO_0+M=HCO^-+M$				11	8.41.10-29	0.973	4 100
	$M = H_0$	8 6.40-17/m	_4.98	~				
	$M = N_0$	$2.4.10^{-18/m_{3}}$	3 0	0			ł	
	$M = CO_{2}$	$2.6 \cdot 10^{-18}/m_{\odot}$	3.9	0				
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TABLE 1 (continued)									
C17	$ ^{13}\text{OH}^++\text{H}_2\text{O}^+M=\text{OH}^-\times$ $\times \text{H}_2\text{O}^+M$				11	9.11.10-27	1.0	11 370	
	$M = H_2O$	$1.4 \cdot 10^{-18}/\varphi_4$	-3.68	0					
	$M = N_2$	$3.9 \cdot 10^{-20}/\varphi_4$	-3.3	0					
	M=CO ₂	$4.3 \cdot 10^{-20}/\phi_4$	-3,3	0		•			
C18	$OH^{-}H_2O+CO_2=HCO_3^{-}+H_2O$	1.0.10-9	0.	0	[19]	9.22·10 ⁻³	-0.027	32 730	
C19	$OH^{-} \cdot H_2O + H = e + 2H_2O$	8.5.10-10	0	0	14	1.03.1018	0.33	26 870	

Notes. 1) $[M] = [H_2O] + 0.16[N_2] + 0.23[CO_2];$ the rate constant for $M = H_2O$ and relative effectiveness of CO_2 molecules were taken from [3], and the effectiveness for N_2 was taken from [4]. 2) $[M] = H_2 0$ + 0.06 $[N_2]$ + 0.23 $[CO_2]$. 3) The effective value for rate constants is provided; in calculating recombination rate, by concentration of third bodies we understand the total concentration of particles. 4) $[M] = [H_20] +$ $0.23[N_2] + 0.34[CO_2]$. 5) [M] = [N₂] + 2.4[CO₂] + 10[H₂O]; the ratio of efficiencies for H_2O and CO_2 molecules was taken as equal to the similar ratio in reaction A9. 6) Estimate from comparison of this reaction with reaction All similar to the estimate in [5]. 7) Estimate by an equation in [14, p. 140]. 8) Estimate by an equation in [15]. 9) Rate constants taken as equal to that for reaction C5. 10) $\varphi = \varphi_1/\varphi_2$, $\varphi_1 = 1 - \exp(-2270/T)$, $\varphi_2 = i + 3.8 \cdot 10^{-18} T^{-0.38} n_{H_2O} + 9.7 \cdot 10^{-20} n_{CO_2};$ 11) See text. 12) $\varphi_3 = 1 + 10^{-10} r_{CO_2};$ $8.0 \cdot 10^{-8} T^{-4,28} n_{\rm H_2O} + 2.3 \cdot 10^{-9} T^{-3,9} n_{\rm N_2} + 2.4 \cdot 10^{-9} \times T^{-3,9} n_{\rm CO_2}; \quad 13) \ \varphi_4 = 1 + 4.2 \cdot 10^{-9} \times T^{-3,9} n_{\rm CO_2};$ $10^{-11}T^{-3,3}n_{H_{2}O} + 1.2 \cdot 10^{-12}T^{-2,92}n_{N_{2}} + 1.3 \cdot 10^{-12}T^{-2,92}n_{CO_{2}}$. 14) Estimate using experimental data in [20].

for reaction C17 was calculated assuming that the change in enthalpy and entropy in this reaction depends weakly on temperature and it equals the value at T = 300 K given in [24], after which equilibrium constants were calculated for the rest of the reactions involving the ion $OH^- H_2O$ (C7, C18, C19).

In constructing the model, apart from positive ion K⁺ consideration was given to lowtemperature composite ion $K^+ \cdot H_2 O$. Analysis using rate constants and equilibrium constants for the hydration reaction of K⁺ ions [24], and also estimates for rate constants of paired recombination for $K^+ \cdot H_2O$ ions and HCO_3^- ions (main carriers of the negative charge with $T \leq 10^3$ K) indicate that the reaction of K⁺ ions hydration is fundamental for K⁺·H₂O ions and it is close to equilibrium, and the concentration of these ions becomes comparable with the concentration of K^+ ions only at T \leq 800°K. Since at all low temperatures the main channel for loss of $K^+\cdot H_2O$ and K^+ ions is paired recombination with HCO_3^- ions and estimates indicate that rate constants of the process for K^+ , $K^+ \cdot H_2 O$ and diffusion coefficients for these ions are similar, then consideration in the calculation model of $K^+ \cdot H_2 O$ ions does not markedly change the distribution of HCO3⁻ ion concentration and the overall concentration of positive ions, and there is only redistribution of the positive charge between K⁺ and $K^+ \cdot H_2 O$ ions. In this situation it is not desirable to introduce $K^+ \cdot H_2 O$ ions. In the case when the distribution of concentration for each of these ions is of independent interest, it may be found easily, after solving the problem in an arrangement for the known distribution of concentration of the effective ion and the equilibrium constant for the hydration reaction of K⁺ ions. Such an approach is also used in this work; the conversion indicated was not made, and in the calculated results given below by K+ we understand the effective ion.

In order to estimate rate constants for the reactions C4 and C6 with $M = H_20$ consideration was given to effective polarizability [15] of water molecules depending on temperature. Calculation of this value from experimental values of ion mobility in water vapor [25] gave for its value $2.4 \cdot 10^{-18} \times T^{-0.75} \text{ mm}^3$, and calculation from the values of the capture constant [26] gave $1.6 \cdot 10^{-18} \times T^{-0.76} \text{ mm}^3$. Use in calculating for reactions C4 and C6 of these two values leads to a relatively small difference (of the order of 20%) since the rate constants are proportional to the square root of polarizability [15]. In calculating these rate constants use was made of a value for effective polarizability obtained by the second method.

TABLE 2

	Components j										
Components	Nz			H ₂ O			CO_2				
i	A	n	method	A	n	method	A	n	method		
NO	1.27.10-5	1.76	1	2.01.10-5	1.67	2	1.21.10-5	1,67	2		
NO ₂	$1.26 \cdot 10^{-5}$	1.67		1.67.10-5	1.67	4	9.95.10-6	1.67	2		
H ₂	$4.51 \cdot 10^{-5}$	1.72	3	3.06.10-5	1,80	3	4.82.10-5	1.67	4		
0 ₂	1.19.10-5	1.72	3	1.48.10-5	1,73	3	9.87.10-6	1.67	2:		
OH	$2.10 \cdot 10^{-5}$	1.67		2,64.10-5	1,67	2	1.67.10-5	1.67	2		
Н	$8.40 \cdot 10^{-5}$	1,67	2	8.07.10-5	1,67	4	$7.01 \cdot 10^{-5}$	1,67	4		
0	1.39.10-5	1,77	3	$2,71 \cdot 10^{-5}$	1.67	2	$1.72 \cdot 10^{-5}$	1.67	2		
HO ₂	$1.66 \cdot 10^{-5}$	1.67	4	2.21.10-5	1.67	2	1.30.10~5	1,67	4		
CO	$2.51 \cdot 10^{-5}$	1.58	3	1.99.10-5	1,67	2	1.20.10~5	1.67	2		
K	$1.52 \cdot 10^{-5}$	1.67	5	2,09.10-5	1.67	5	1,16.10-5	1.67	5		
KOH	1,42.10-5	1,67	6	1.99.10-5	1.67	6	1.06.10-5	1.67	6		
KO ₂	$1.20 \cdot 10^{-5}$	1.67	7	$1.67 \cdot 10^{-5}$	1.67	7	9.00.10-6	1.67	7		
K+	4.78.10-7	2.09	8	$2.56 \cdot 10^{-8}$	2.38	12	4.73.10-7	1,99	8		
e	0,405	1.18	9	8.97.10-7	2.61	9	$1.48 \cdot 10^{-4}$	2,09	11		
HCO ₃	7,64.10-7	2.0	10	$2.42 \cdot 10^{-8}$	2.38	13	5.43.10-7	2.0	10-		
OH-	1,03-10-6	2.0	10	3.05.10-8	2.38	13	7.83.10-7	2.0	10		
OH-·H ₂ O	8.49.10-7	2,0	10	$2.61 \cdot 10^{-8}$	2.38	13	6.21 • 10-7	2.0	10.		
0_2	$8.66 \cdot 10^{-7}$	2.0	10	$2.65 \cdot 10^{-8}$	2.38	13	6.37 · 10-7	2,0	10		

Notes. 1) Calculation for cross sections from [34]. 2) For Lennard-Jones (L-J) potential; potential parameters were obtained from rules for combination $\varepsilon_{ij} = \sqrt{\varepsilon_{ii}\varepsilon_{jj}}$, $\sigma_{ij} = (\sigma_{ii} +$ σ_{jj})/2 from original data in [35]. 3) From [36]]. 4) For L-J potential; potential parameters were obtained by the rules of combination from original data in [37]. 5) for L-J potential; potential parameters were obtained by the rules for combination from original data in [35, 36]. 6) for L-J potential; potential parameters were obtained by the rules for combination; σ and ε for KOH were taken the same as for K by analogy with similar relationships for other alkali metals [35, 38]. 7) For L-J potential; parameters were obtained as an approximation of additive reactions from original data in [35, 38]. 8) Experimental values of mobility from [39]. 9) For cross sections from [40]. 10) In a polarization approximation. 11) For cross sections from [41]. 12) For experimental values of mobility from [25]. 13) For an equation of polarization approximation using effective polarizability for water molecules; since the diffusion coefficient is inversely proportional to the square root of polarizability, then use of two values of effective polarizability in calculations (see Sec. 1.2) leads to a relatively small difference; in this case, a value obtained by the first method was used.

In calculating rate constants for three-body attachment of electrons to O_2 molecules of C9, it was assumed that attachment proceeds through the first autoionization level for O_2^- (for M = N₂ see [27]; for M = H₂O, CO₂ this follows from treatment of experimental data carried out by the authors [28]). Absolute values of extinction constants were determined on the basis of rate constants for attachment with T = 300°K [27]. In analyzing dependences for extinction constant on temperature it was assumed that this constant is proportional to the capture rate constant for ion O_2^- with molecule M. A multiple φ_1 is introduced into the rate constant equal to the function of O_2 molecules found in the basic vibrational state, since with attachment of electrons two vibrationally excited O_2^- ions form with energies corresponding to the second and higher autoionization levels for O_2^- . Also introduced is a correction multiple φ_2 , taking account of the effect on the rate constant of the concentration of third bodies, calculated as in [27], but for the case of a mixture of third bodies.

Rate constants for reactions C16 and C17 were calculated by an equation in [29]. Extinction constants were taken as equal to the constant for capture rate of a cluster ion by a molecule (third body). Absolute values of equilibrium constants for the first stages of the reactions were calculated from experimental data for rate constants for reactions C16 and C17 with T \approx 300°K [17, 18, 30], treated on this assumption, temperature dependences for equilibrium constants were determined by Eq. (12) from [29], and then approximated by stepped functions. Correlation multiples φ_3 and φ_4 were introduced into rate constants of these reactions taking account of the effect on rate constant of third-body concentration obtained as in [29], but for the case of a mixture of third bodies.

Chemical kinetics models for detailed calculation of chemical nonequilibrium flows of the combustion products of hydrocarbon fuel with addition of alkali metal (potassium) were suggested in [5, 31]. The model for the present work may be considered as a develop-



ment of these models; in particular, taking account of new experimental results, the suggested model involves components HCO_3^- , $OH^- \cdot H_2O$, which are important, as will be seen subsequently for calculating electron concentration.

<u>Transfer Coefficients and Thermodynamic Properties</u>. Thermal conductivity coefficients λ and viscosity μ for the mixture were calculated in terms of thermal conductivity coefficients and viscosity for the basic mixture components, which in turn were taken from [32, 33].

Approximations for binary diffusion coefficients D_{ij} of impurity components in a gas of basic component are given in Table 2 ($D_{ij} = AT^n/p$, $[A] = cm^2/sec$, [T] = K, [p] = 0.1 MPa), and it also contains information about the methods of obtaining these coefficients. Heat capacity of the mixture c_p was calculated from tables [21].

As was apparent above, the gas mixture is assumed to be single-temperature, which suggests, in particular, equilibrium excitation of vibrational degrees of freedom for molecules (under the conditions being considered, the time for vibrational relaxation of molecules of the basic components does not exceed 10^{-5} sec, and this assumption is fulfilled), and also equality for the temperatures of electrons and heavy particles, which is correct as a result of high values of inelastic loss coefficient in the mixture being considered (of the order of 10^3).

<u>Boundary Conditions</u>. For projections of average mass velocity and mixture temperature, we have normal boundary conditions which for brevity are not written out. In view of formulation of boundary conditions for the concentration of impurity components, analysis of surface processes was carried out; for definiteness it was assumed that the surface of the body was made of platinum and its temperature $T_W = 400$ °K. It might be expected that the highest concentrations in the adsorbed layer of the surface applied to stable compounds of K, CO, and H, having sufficiently high bonding energy with surface centers, and the concentration of free centers is low. Condensation at the surface of potassium compounds is disregarded (this is valid, in particular, in the case when the concentration of the additive in the approach stream is quite low). Radicals OH, H, O, HO₂ arriving from the plasma will rapidly recombine at the surface; for components NO, NO₂, H₂, O₂, CO, K, KOH, KO₂ chemi-

cal reactions at the surface are unimportant compared with typical values of their diffusion fluxes in the plasma. For recombination of charged particles the surface is assumed to be catalytic. Thus, we have at the surface

$$\begin{aligned} x_i &= 0 \quad (i = \text{OH}, \text{ H}, \text{ O}, \text{HO}_2, \text{ K}^+, e, \text{HCO}_3^-, \text{OH}^-, \text{OH}^- \cdot \text{H}_2\text{O}, \text{O}_2^-), \\ J_i &= 0 \quad (i = \text{NO}, \text{ NO}_2, \text{ H}_2, \text{ O}_2, \text{ CO}, \text{ K}, \text{ KOH}, \text{ KO}_2). \end{aligned}$$

TABLE 3

ⁿ K∞', cm ⁻³	NO	NO2	H ₂	O_2	OH,	н
1013	1.81.10-3	3,56.10-7	2.47·10 ⁻³	4.71 · 10 ⁻³	2.35.10-3	2.79·10-4
1016	1.91.10-3	3.96.10-7	2,33.10-3	5,25·10 ⁻³	2.41 · 10 ⁻³	2.71.10-4
	0	HO ₂	co	к	кон	KO2
1013	1.82.10-4	7.68.10-7	9.97.10-3	3.00.10-6	8.14.10-6	1.05.10-9
1016	1.93.10-4	8.31.10-7	9,85.10-3	3.00.10-3	8.34·10 ⁻³	1.17.10-6
	к+	e	нсо3	он-	OH−∙H₂O	0 2
1013	2,68.10-7	· 9.53·10 ⁻⁸	1.67.10-7	5.66·10-9	1.03.10-11	6.33·10 ⁻¹¹
1016	8.67.10-6	2.95.10-6	5.54.10-6	1.80.10-7	3.25.10-10	2,18·10 ⁻⁹

In formulating these conditions it was considered that, as a result of the smallness of radicals and charged particle concentration, their diffusion fluxes toward the surface are quite small compared with the typical diffusion fluxes for components NO, NO₂, H₂, O₂, CO, K, KOH, KO₂. At the outer limit of the boundary layer $x_i = x_{i\infty}$, where $x_{i\infty}$ is equilibrium value of molar fractions for impurity components in the approach stream. Here and subsequently, index ∞ relates to values corresponding to functions in the approach stream.

2. Algorithm for Numerical Solution

The problem formulated is transformed to a Doroditsyn-Liz variable. Equations for distribution of average mass velocity and plasma temperature were resolved as in [42]. In order to solve the problem for distribution of impurity component concentrations in each cross section of the boundary layer, use was made of an iteration algorithm which consists of the following. The whole system of impurity components was divided into three subsystems: 1) CO, H₂, O₂, OH, H, O, KOH, K, KO₂; 2) NO, NO₂, HO₂; 3) K⁺, HCO₃⁻, OH⁻, O₂⁻, OH⁻·H₂O. The second and third subsystems have a relatively weak effect on each other and on the first subsystem, whereas within each subsystem the components affect each other quite strongly. Taking account of this situation, a step in the iteration process is organized as a combination of three subsystems. These equations, linearized by means of the Newton method, are solved together with matrix runs (a generalized scale of runs [42] was used in the case of a set of equations) using a difference scheme [42]. This approach provides considerable saving in machine time and operating memory compared with indirect application of matrix runs for combined solution of linearized equations for the whole system of impurity components.

The difference scheme used [42] has four orders of accuracy over the transverse coordinate and three over the longitudinal coordinate. The difference step for the network over the transverse coordinate is variable; in particular, it was selected as quite close to the surface where temperature gradients are greatest and the reaction rate constant, for which activation energy is markedly greater than the thermal energy of particles, changes very rapidly.

3. Calculated Results

We consider the results obtained in applying the mathematical model given above to conditions typical for experiments with a gas flame [43]: a sphere or thin cylinder of radius R = 0.25 cm made of platinum has flowing around it a plasma stream of combustion products from a stoichiometric mixture of propane with air at atmospheric pressure with addition of potash (K_2CO_3) with a velocity of 5 m/sec. The temperature of the mixture in

the approach stream is 2200 K, and the temperature of the surface is 400 K. The amount of alkali added to the approach stream is conveniently characterized by prescribing the concentration of potassium atoms $n_{K\infty}$, since in experiments the concentration of alkali metal atoms is mainly measured [43]; in calculation it was assumed that $n_{K\infty} = 10^{13}$ and 10^{16} cm⁻³.



Calculated normalized distributions for molar fractions of impurity components in the critical line of the boundary layer on a sphere are presented in Figs. 1, 2 and 3, 4 for $n_{K_{\infty}} = 10^{13}$ and 10^{16} cm⁻³, respectively. Molar fractions of components were normalized in the following way: $x_i/x_{i\infty}$ for i = CO, H_2 , O_2 , OH, H, O, NO, OH⁻, OH⁻·H₂O; $x_{HO_2}/(x_{HO_2^{\infty}}.10)$, $x_{NO_2}/(x_{NO_2^{\infty}}.10)$ (Fig. 1); $x_{NO_2}/(x_{NO_2^{\infty}}.10^2)$ (Fig. 3); $x_i/x_{KOH^{\infty}}$ for i = KOH, K, KO_2 ; x_i/x_K+_{∞} for $i = K^+$, HCO_3^- , e; $x_{O_2^-}/(x_{O_2^{\infty}}.10)$ (Fig. 2); $x_{O_2^-}/x_{O_2^{\infty}}$ (Fig. 4). Given in Table 3 are values of molar fractions for impurity components in the approach stream (i.e., their equilibrium values with $p = 10^5$ Pa and T = 22 K) for $n_{K^{\infty}} = 10^{13}$ and 10^{16} cm⁻³. Also given in Fig. 1 is the normalized distribution of plasma temperature T/T_{∞} .

It can be seen above all from Figs. 1-4 that the distribution of concentrations for impurities in the boundary layer is markedly nonuniform. With an increase in alkali additive concentration the degree of nonuniformity in the hot region (T \ge 1600 K) decreases.

For neutral components this effect is mainly connected with development at high values of additive concentration of a new markedly more rapid channel for the occurrence of recombination reaction A5 (this reaction is the slowest among the independent reactions governing the concentration of predominantly neutral impurity components in the hot region), which forms a combination of reactions B1 and B2. A reduction in the degree of nonuniformity leads to a marked drop in the concentration of chemically active radicals, in particular H atoms and OH hydroxyl groups. It is noted that reaction B2, in which radical OH recombines, at relatively low temperatures also proceeds through another channel, which forms a combination of reactions B3 and B4. On the other hand, this change in distributions of H and OH radical concentrations, caused by an increase in the amount of additive, leads, for example in the temperature region $T \ge 1500$ °K, to a change in distribution of concentration of the basic potassium-containing neutral components K and KOH. This is connected with the fact that, in this region, the concentration temperature for K and KOH is governed mainly by reactions B1 and B2.

For ionized components this effect is also caused by an increase in the ionization rate for additive atoms and electron-ionic recombination in reaction Cl. It can be seen from Figs. 2 and 4 and Table 3 that in the mixture being considered the main carriers of a negative charge are HCO_3^- ions and electrons, whereas ions O_2^- , OH^- , $OH^- \cdot H_2O$ are intermediate compounds during conversion of electrons into the most stable negative ions HCO_3^- . Calculations have shown that the main channel for conversion of electrons into HCO_3^- ions forms the following reaction sequence: attachment of electrons to O_2 in reaction C9, conversion of unstable O_2^- into stable OH^- ions in reactions Cll and Cl3, subsequent formation of OH^- ions either by entrapment of CO_2 molecules in reaction Cl6, or through ions $OH^- \cdot H_2O$ in reactions C17 and Cl8. Formation of OH^- ions proceeds more effectively through a sequence of reactions C9 and Cl1, and not through direct channel Cl0, since attachment of electrons to O_2 molecules proceeds at a greater rate than attachment to hydroxyl OH; a similar conclusion was made in [16].

With $N_{K\infty} = 10^{13}$ cm⁻³, the molar fraction of free potassium atoms in the outer part of the boundary layer in a direction toward the surface not only does not decrease (as it would in the case of equilibrium occurrence of chemical reactions), but, conversely, it increases. Experimental confirmation and detailed discussion of this interesting effect were given in [44].

Presented in Figs. 5 and 6 are normalized distributions of molar fractions for potassium-containing neutral components and the basic ionized components, and also the plasma temperature in the middle line of the boundary layer on a sphere (with $x = \pi R/2$) for $n_{K\infty} = 10^{13}$ and 10^{16} cm⁻³. From comparison of the corresponding curves in Figs. 2 and 5, 4 and 6, it can be seen that taking account of an increase by a factor of ~1.5 in the thickness of the boundary layer, the distribution is close to the corresponding distribution in the critical line. An increase in boundary layer thickness, and consequently hydrodynamic time, might lead to some reduction in the level of nonuniformity for component distribution. In the case of $n_{K\infty} = 10^{16}$ cm⁻³, for example, this effect for ionized components actually exists, although it is weak; for strongly nonequilibrium flow with $n_{K\infty} = 10^{13}$ cm⁻³, it is practically unnoticeable.

Calculations were also carried out for the boundary layer of a cylinder. It appeared that distributions of parameters are similar to the corresponding distributions in the case of a sphere and for brevity they are not given here.

Thus, application of the model developed to the experimental conditions given showed that flow in the boundary layer of a cooled body with flow around it by the mixture indicated above is markedly nonuniform. This makes it possible, on the basis of the conformity of component concentrations measured and calculated by means of this model in a boundary layer around a cooled body to obtain information about reaction rate constants over a wider temperature range than in studying chemical kinetics in flames [9].

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ASYMMETRIC IMPACT OF A JET WITH AN IDEAL NONCOMPRESSIBLE LIQUID

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The problem of impact of a jet belongs among classical problems. The question of asymmetric impact of a jet is of special importance in view of the development of new methods for treating metals by means of explosive energy and, in the first instance, welding by explosion [1, 2].

We consider steady-state flow as a result of the impact of two planar jets A_1 and A_2 having at infinity prescribed thicknesses h_0 and H_0 and velocity direction v (Fig. 1). It is necessary to determine the parameters of the two jets B_1 and B_2 formed. Concerning values of velocity v at infinity, then in the case of streams of identical density the velocities should be identical for all four jets. This follows from the fact that free lines of the flow A_1B_1 , B_1A_2 , A_2B_2 , B_2A_1 are lines of constant velocities. We shall consider flow with one critical point 0 at which we place the origin of a Cartesian coordinate system, and we set axis x parallel and toward the velocity of the approach stream in jet A_1 . The angle between converging jets A_1 and A_2 is designated in terms of α , and between diverging jets B_1 , B_2 , and axis x in terms of φ and ψ , respectively (see Fig. 1). Let the thickness of jet B_1 be h and that of jet B_2 be H. Then if it is assumed that h_0 , H_0 , and α are given, in order to determine the remaining four unknowns h, H, φ , and ψ we have three equations in all following from the laws of conservation for mass and flow, and impact for an ideal noncompressible liquid:

$$h + H = h_0 + H_0; (1)$$

$$H\cos\psi - h\cos\varphi = h_0 + H_0\cos\alpha; \qquad (2)$$

$H\sin\psi - h\sin\varphi = H_0\sin\alpha. \tag{2}$

Relationships (2) and (3) are projections of the stream impact on the axis of coordinates x and y, respectively. Thus, the problem appears to be indeterminate. An attempt to make it definite by introducing a supplementary arbitrary hypothesis belongs to Platini [3]. It was suggested that straight line B_2 and return line B_1 of the diverging jet at infinity move in opposite directions

$$\overline{\varphi} = \overline{\psi}.$$
(4)

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