current height of the leg (m); $\Delta\Theta_x = \Theta_0 - \Theta_x$, dimensionless cooling depth; Θ_x, dimensionless temperature of the heat-absorbing junctions; ΔT_{max}, $\Delta\Theta_{max}$, dimensional and dimensionless maximum cooling depth of a conventional thermopile; $z = E^2/(4\rho\lambda)$, Q factor of the thermocouple (T^{-1}); E, total thermo-emf (V/K); ρ, mean electrical resistivity of the thermocouple ($\Omega\cdot$m); λ, mean thermal conductivity of the thermocouple (W/(m$\cdot$K)); $j = (2E\delta I)/(\lambda f)$, dimensionless current density; I, supply current (A); f, cross-sectional area of leg (m^2); $Fo = (at)/(4\delta^2)$, Fourier criterion; a, mean diffusivity (m^2/sec); t, time (sec); $\eta = G_d/G_s$, relative heat content of the thermal load; G_d, heat capacity of the thermal load (J/K); G_s, total heat capacity of the semiconductor thermopile (J/K); Fo_m, Fourier criterion, determining the dimensionless time over which a conventional thermopile attains the maximum cooling depth; d_s, diameter of the semiconductor leg; max ΔQ, maximum cooling capacity of the thermopile.

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VIRIAL COEFFICIENTS OF METHANE, ETHANE, AND PROPANE AT TEMPERATURES UP TO 1500°K

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The second and third virial coefficients are calculated for the (12-7, δ) model pair potential. With their help the fourth virial coefficient is determined from the experimental data for p, $\tilde{V}$, and T. The limit of applicability of the equation of state obtained is indicated.

The second and third virial coefficients of monoatomic (neon, argon, krypton) and diatomic (nitrogen, oxygen, air) gases were previously calculated in [1, 2] for temperatures up to 3000°K. With their help the fourth virial coefficient was determined from the experimental data on p, $\tilde{V}$, and T. The equation of state obtained describes with high accuracy the data on the thermodynamic properties of these gases tabulated in handbooks [3-6].

In this paper we present the virial coefficients of three polyatomic gases, whose molecules have the most diverse symmetry. As previously, the (12-7, δ) model pair potential, proposed in [7]

$$\varphi(r) = \begin{cases} \infty, & r \leqslant r_e, \\ 5{,}1042\varepsilon\left[\left(\dfrac{\sigma^2 - r_e^2}{r^2 - r_e^2}\right)^6 - \left(\dfrac{\sigma^2 - r_e^2}{r^2 - r_e^2}\right)^{7/2}\right], & r \geqslant r_e \end{cases} \qquad (1)$$

(where ε is the depth of the potential well; σ is the "diameter;" and r_e is the "core" of the molecule) was employed in the calculations. The application of this potential to gases consisting of polyatomic molecules with arbitrary symmetry was impeded by the uncertainty in the size of the molecular "core."

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TABLE 1. Values of the Constants for Methane, Ethane, and Propane

Substance	$\frac{\varepsilon}{k}$, K	$\sigma_i \cdot 10^8$, cm	$r_e \cdot 10^8$, cm	δ	ν^*	α	β	T_B, K
Methane	208	3,566	0,896	0,0631	0,100	1,762	2,283	517
Ethane	364	4,120	1,592	0,1493	0,100	2,322	2,819	800
Propane	468	4,600	2,093	0,2070	0,085	2,631	3,003	944

Note. $\nu^* = 3/4\ \alpha C_6/\varepsilon\sigma^9$ is the reduced parameter of the nonadditive tridipole interaction; T_B is Boyle's temperature.

As is well known, molecules of polyatomic gases can have the most diverse form and, therefore, their potential energy (the potential) of intermolecular interaction, generally speaking, will not be spherically symmetric. This difficulty is circumvented by averaging the interaction potential over all possible orientations of the colliding molecules.

Polyatomic molecules have another property which monoatomic molecules do not: the existence of internal degrees of freedom. This property is characterized by an average moment of inertia of the polyatomic molecule:

$$I_{av} = \frac{I_A + I_B + I_C}{n}, \tag{2}$$

where I_A, I_B and I_C are the principal moments of inertia of the molecule and n is the number of rotational degrees of freedom.

In this work the quantity

$$r_e = \sqrt{\frac{4I_{av}}{m}}, \tag{3}$$

which for homonuclear diatomic molecules ($I_{av} = I_A = I_B = 1/4\ mr_e^2$) equals the equilibrium distance between nuclei, is used for the "core" of polyatomic molecules. This quantity was used previously in [2, 7-9] as the "core" for nitrogen and oxygen. For monoatomic molecules the quantity r_e is calculated from the rotational constant of the molecules. Molecules with the same structure and close internuclear distances (for example, methane and carbon tetrafluoride) can have significantly different "cores" and therefore nonsphericity parameter of the molecule

$$\delta = \left(\frac{r_e}{\sigma}\right)^2. \tag{4}$$

The two other constants of the (12-7, δ) pair potential are determined based on a combined analysis of the experimental data on the viscosity [10] and the second virial coefficient [11]. The constants of the (12-7, δ) potential found in this manner for methane, ethane, and propane are given in Table 1.

The computed values of the second virial coefficient are compared with the generalized experimental data [11] in Table 2. As a rule, the results agree within the limits of error indicated in [11].

The computed values of the second and third virial coefficients were then employed to determine the fourth virial coefficient from the p, $\tilde{V}$, and T data [12-17]. As previously [1, 2], the expression

$$D^* = \frac{D}{(b_0)^3} = \frac{\alpha}{(T^*)^{3/4}} - \frac{\beta}{(T^*)^{3/2}}, \tag{5}$$

where $b_0 = 2/3\ \pi N\sigma^3$; $T^* = kT/\varepsilon$, was employed to approximate the fourth virial coefficieint for $T \geqslant 0.5T_B$. The constants α and β are given in Table 1.

Taking into account the fourth virial coefficient made it possible to approximately double the region of applicability of the equation of state. The boundary of the region of applicability increases with the temperature and can be approximately described in the form

$$\rho \leqslant \frac{0{,}55}{B + T\frac{dB}{dT}}, \tag{6}$$

TABLE 2. Comparison of the Computed Values of the Second Virial Coefficient of Methane, Ethane, and Propane with the Generalized Experimental Data of [11] $-B$, cm^3/mole

T, K	Methane		Ethane		Propane	
	[11]	calculation	[11]	calculation	[11]	calculation
120	273±5	273,2				
140	207±3	203,2				
160	161±3	157,6				
200	105±2	102,3	410±10	410,5		
220	—	84,3	336±5	338,6		
240	—	70,1	282±3	284,7		
260	—	58,7	243±2	242,9	526±20	506,4
300	42±1	41,3	182±2	182,3	382±15	377,2
350	26±1	26,3	130,5±1,5	132,4	276±10	274,9
400	15±1	15,6	96,0±1	98,4	208±10	207,6
450	—	7,7	71,0±1	73,9	—	160,1
500	+0,5±1	+1,5	52,0±0,5	55,4	124±5	125,0
550	—	−3,3	36,5±0,5	41,0	97±5	97,9
600	−8,5±1	−7,3	24,5±0,5	29,5	—	76,5
700	—	−13,0	—	+12,2	—	44,8
800	—	−17,2	—	0	—	22,5
900	—	−20,3	—	−9,2	—	+6,0
1000	—	−22,7	—	−16,3	—	−6,6
1100	—	−24,6	—	−21,7	—	−16,6
1200	—	−26,1	—	−26,1	—	−24,8
1300	—	−27,3	—	−29,8	—	−31,5
1400	—	−28,3	—	−32,9	—	−37,1
1500	—	−29,1	—	−35,5	—	−41,3

TABLE 3. Computed Values of the Third Virial Coefficient and the Limit of Applicability of the Proposed Equation of State

T, K	C, $cm^6/mole^2$			P_{max}, MPa		
	methane	ethane	propane	methane	ethane	propane
200	3920	−6681				
220	3513	+6760				
240	3136	11460	−21810			
260	2817	12710	+7800	11,2		
300	2338	11860	24790	16,7		
350	1956	9710	34800	24,6	6,6	
400	1719	7936	21060	33,4	10,0	
450	1567	6657	17550	42,7	14,1	6,9
500	1465	5750	14820	52,3	18,8	9,4
550	1394	5101	12780	62,0	23,9	12,4
600	1345	4629	11260	71,8	29,5	15,7
700	1279	4016	9261	96,2	41,3	23,2
800	1239	3658	8082	119	53,8	31,5
900	1212	3438	7356	143	66,5	40,3
1000	1191	3298	6890	167	79,3	49,3
1100	1175	3198	6583	191	95,1	58,5
1200	1160	3128	6376	216	110	67,7
1300	1148	3078	6234	241	124	76,9
1400	1136	3039	6135	266	139	86,1
1500	1125	3008	6034	293	154	99,2

where B is the second virial coefficient.

The computed values of the third virial coefficient and the pressure corresponding to the boundary of the region of applicability of the equation of state obtained are given in Table 3. Within the indicated pressure range the discrepancies between the computed values of the compressibility factor and the data in handbooks [12-14], as a rule, do not exceed ±0.5%.

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EFFECT OF CHEMICAL REACTIONS ON FLOW AND MASS TRANSFER IN A LIQUID FILM IN THE PRESENCE OF SURFACE-ACTIVE MATERIALS

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To the thin-film approximation an investigation is made of the effect of surface-active materials on the hydrodynamics and mass transfer in liquid films falling under gravity in the presence of surface chemical reactions.

In many chemical engineering processes which occur in film reactors and packed and tray absorbers mass transfer takes place under conditions in which the surface tension at the interface between the liquid film and the adjacent gas stream is not constant, which is caused in particular by the presence of surface-active materials [1]. The surface tension gradients which arise in this case and the shear stresses connected with them as a result of the Marangoni effect can have an important effect on the hydrodynamics and rate of mass transfer of materials dissolving in the film [2]. In a number of industrial processes (such as, for instance, the purification of gases by chemisorption) mass transfer into the film is accompanied by chemical reactions with the participation of surface-active reagents and products [3].

An effect of surface-active materials on mass transfer can arise as follows. In the first place both the material itself and also the chemical reactions can lead to a loss of stability of the flow and to the appearance of convective cells which intensify transfer close to the free surface [4]. Such effects have been investigated, for instance, in [5, 6]. In the second place, the surface-active material can significantly change the velocity at the film surface, which can also influence the mass transfer characteristics. An investigation of the effect of insoluble surface-active materials on mass transfer in a laminar film with a slowly varying thickness not allowing for chemical reactions was carried out in [7].

The aim of the present work was to investigate the effect of surface chemical reactions involving the participation of a surface-active material on the hydrodynamics and mass transfer in a liquid film within the framework of the second of the mechanisms indicated above. Here a film in laminar flow along an inclined plane under the influence of gravity forces is considered, where the film is almost planar and its free surface is in contact with an adjacent gas. The flow rate of the liquid in the film is regarded as being constant and equal to Q.

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