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The Use of Mass Spectrometry to Study the Structure of Flames and Combustion Processes

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The general characteristic methods of the mass-spectrometric study of flames and combustion processes, and the latest achievements in experimental technique in the molecular-beam diagnostics of flames have been examined. The problems associated with the use of probe methods—the effects of freezing the chemical reactions, translational-vibrational relaxation, and perturbations introduced by the probe in the combustion process—have been analysed. The possibilities provided by the technique have been demonstrated for various examples in the study of the combustion of gaseous, liquid, and solid fuels, including that in various technical arrangements—internal combustion engines and liquid rocket motors. Questions related to the use of mass-spectrometric probes for the study of the mechanism and kinetics of chemical reactions in flames and for the determination of the rate constants of the elementary stages have been discussed. The bibliography contains 53 references.

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I. INTRODUCTION

Mass spectrometry provides one of the most popular and effective methods of studying flames and combustion processes[1,2]. One reason for this is the universal character of the method, by means of which it is possible: 1) to identify the components present in flames, 2) to determine their quantitative composition (concentrations), and 3) to measure the distribution of these components in the combustion zones (to study the structure of flames) and on this basis to calculate the component fluxes and reaction rates.

Flames involve high-velocity fluxes of reactive gases with high temperature gradients and concentrations of the original components and final and intermediate reaction products. The gaseous components in flames can be classified as stable or highly active—atoms, radicals, ions, and excited species. Their typical maximum concentrations in flames are given below.

Species	N, mole fraction
Stable (CH_4, O_2, H_2O)	0.1—1
Atoms and free radicals (H, O, OH)	10^{-1}—10^{-2}
Ions (CHO^+, H_3O^+)	10^{-7}—10^{-12}
Excited (HF^*)	10^{-5}

The first important problem in the mass spectrometry of flames is the removal of the particles from the combustion zone and their introduction into the ion source of the mass spectrometer. The maximum temperatures in flames lie in the range 1000–3000 °C, and the characteristic times of chemical reactions under these conditions are 10^{-4}–10^{-7} s. To ensure preservation of the particles, the times taken to remove them from the combustion zone must be much shorter than their lifetimes. In the process of probe sampling, it is necessary to lower the temperature rapidly. With "quenching" in this way, it is easiest to preserve stable particles, and most difficult to preserve active species.

Comparison of the mass-spectrometric probe method with non-contact spectroscopic methods reveals two advantages of the former for probing flames: 1) the possibility of recording all species (this is particularly important for such complex systems as flames); and 2) the greater spatial resolving power. For example, in the latest method of laser Raman spectroscopy, the limiting sensitivity of the measurement amounts to 10^{11} particles[3], which for a pressure of 25 mmHg, $T = 2000$ K, and an accuracy of recording of 1% corresponds to a zone with characteristic dimensions of 2 mm. The spatial resolving power of infrared spectroscopy under the same conditions is not better than 0.1 mm.[4] Moreover, in the last case the probing is not local, but is carried out along a straight line, so that the method is applicable only to uniform one-dimensional systems with rigorously parallel fronts—lines of equal concentration (with deviations from the parallel arrangement $\ll 0.1$ mm).

Because of the complexity of the spectrum, the spectroscopic method cannot detect many of the particles existing in flames. At the same time, the spectroscopic method has the important advantage over mass spectrometry that it is a non-contact method, and does not perturb the process being studied. Thus the two methods supplement one another, and to achieve best results in the study of flames and combustion processes it is necessary to use both methods.

Mass spectrometry has for several decades been used successfully to study flames and combustion processes. The monograph by Fristrom and Westenberg[1] described the results of studies in this field obtained up to 1965. In recent years, as a result of the rapid development of experimental technique, new achievements and promising possibilities have appeared in the mass-spectrometric study of flames and combustion processes, but these developments have not yet been adequately reflected in the literature.

II. ANALYSIS OF PROBLEMS ASSOCIATED WITH THE USE OF THE MASS-SPECTROMETRIC METHOD OF PROBING FLAMES FOR THE STUDY OF THE STRUCTURE OF FLAMES AND COMBUSTION PROCESSES

1. Technique for Removing the Specimen

Probe sampling is an extremely simple process. Two types of apparatus are used as probes. The first are the so-called "isokinetic" micro-probes—cones with a small aperture angle (10–20°), which remove a specimen of gas with the velocity of the advancing flux; the aperture in the apex of the probe being ~10–100 μm. The advantages of samplers of this type are the small aerodynamic and thermal perturbations of the flame; their disadvantages are the poor conditions for quenching the chemical reactions and preserving active species. Samplers of this type are used to study systems which react slowly. Probes of the second type are sonic probes, at the inlet to which the velocity of the gas is equal to the velocity of sound; they consist of cones having an aperture angle of 30–40° or more. As a result of the expansion of the flow at the inlet into the cone, a supersonic stream is formed. The decrease in temperature and the quenching of the chemical reactions take place at a distance of several times the diameter of the opening in the probe. After the sample has been removed, it is necessary to introduce it without distortions into the ion source of the mass spectrometer. The input systems are of two types. In the first, the gas being analysed is introduced into the ion source in the form of a molecular beam, and in the second it is introduced in the form of a supersonic stream, from which the molecular beam may subsequently be formed.

2. Application of the Molecular-beam System for Specimen Removal

Molecular beams represent the most effective system for transporting the particles removed from the flame to the ion source of the mass spectrometer, since the absence of collisions of the particles of the beam with one another and with the walls of the sampling and input system ensures the best conditions for preserving the particles. There are two types of source of molecular beams: effusion and gas-dynamic (supersonic). The molecular beam is formed as a result of the flow of the gas into a vacuum through a small opening of diameter d. Depending on the value of the Knudsen number $\mathrm{Kn} = \lambda/d$ (where λ is the mean free path of the gas molecules in the source), it is possible to have two flow conditions: effusive for $\mathrm{Kn} \gg 1$, and supersonic for $\mathrm{Kn} \ll 1$.[5]

The most important advantage of the gas-dynamic source compared with the effusion source is that it can be used to obtain beams which are two orders of magnitude more intense than those obtained using the effusion source.

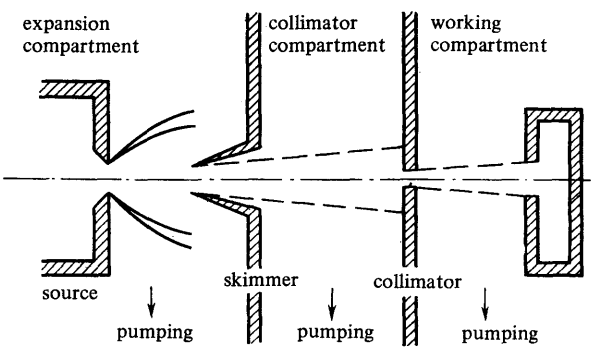


Figure 1. Basic elements of the beam created by a gas-dynamic source.

The principal elements of the beam created by a gas-dynamic source are represented in Fig. 1. The flux expands, flowing through the opening, and forms usually a hypersonic free stream in the expansion compartment, which is evacuated to 10^{-2}–10^{-4} mmHg.[5,6] The purpose of the conical separator (skimmer) is to pass the main body of the free stream without perturbations and with a highly ordered motion into the collimator compartment, in which a high vacuum (typically ~10^{-6}–10^{-7} mmHg) to exclude scattering, is created. The collimator

is designed to separate the working beam, which passes into the working compartment of the mass spectrometer.

The general idealised characteristics of the system have been determined[7], with the following assumptions: 1) the expansion is isentropic as far as the skimmer; 2) the flux passes unperturbed through the skimmer; and 3) collisions between the molecules do not take place after the skimmer. For Mach numbers greater than 3, these assumptions lead to the following basic equations defining the characteristics of the beam[5].

The flow rate through the skimmer N_S (molecule s^{-1}) is

$$N_s = \frac{1}{4}\pi d_s^2 n_s a_0 M_s \{1 + [(\gamma - 1)/2] M_s^2\}^{-1/2},$$

where a_0 is the velocity of sound in the gas at rest, γ the ratio of the specific heats, d_S the diameter of the opening in the skimmer, and M_S and n_S the Mach number and density of the molecules at the inlet to the skimmer, related isentropically to the parameters in the source. These quantities can be calculated, and are functions of the distance between the sonic opening and the skimmer. The rate of flow of gas through the collimator N_C is

$$N_c = \frac{1}{2} n_s a_0 \left(\frac{\pi}{4} d_c^2\right)\left(\frac{\pi}{4} d_s^2\right) \frac{M_s (3 + \gamma M_s^2)}{\pi L_s^2 \{1 + [(\gamma - 1)/2] M_s^2\}},$$

where d_C is the diameter of the collimator, and L_S the distance from the collimator to the skimmer.

The picture of the flow given above relates to the ideal case where the scattering of the molecules of the beam is negligible. These conditions can be established only in an assembly in which a high degree of evacuation of the background and scattered gases is ensured by the use of: a) highly efficient pumps and the required geometry of vacuum compartments having a high transmitting capacity at all stages of the evacuation; b) sufficiently large openings in the skimmer and aperture angles of the cone of the skimmer; and c) sufficiently sharp edges of the opening in the skimmer and a high degree of cleanliness in the mechanical treatment of its surface. Otherwise, the formation of shock waves, the penetration of the background gas into the beam, can occur, leading to scattering of the molecules of the beam, etc.

According to calculated data, the intensity of the molecular beam should increase continuously with decrease in the distance between the openings of the jet and the skimmer. In practice, however, decrease in this distance is accompanied by an increase in the pressure between the jet and the skimmer, as a consequence of the decrease in the transmitting capacity of the gap between the jet and the skimmer (particularly in the case where a cone having a small aperture angle is used as jet–sampler). This in turn leads to decreased intensity of the beam due to scattering.

3. Effects of Freezing the Chemical Reactions

To obtain a representative sample, it is necessary that effective freezing of the chemical reactions and the internal state of the particles takes place during their removal. In a typical case, the expansion takes place in several microseconds and involves several thousand bimolecular collisions. Relaxation of the translational temperature is achieved; at the end of the expansion, the rotational temperatures are considerably higher than the translational temperatures; the vibrational relaxation is much less complete than the rotational relaxation. In molecules frozen as a result of the expansion, unimolecular reactions may take place along the path of their track in the detector compartment. The disappearance of active species, atoms, radicals, and ions may take place during the expansion of the gas, as a result of bimolecular reactions. Calculations have been carried out[8], which make it possible to estimate the probability of the disappearance of particular species during the expansion of the flux in the removal of a sample, if the rate constants of the reactions taking place are known. These calculations give encouraging results, which make it possible to neglect the above effect in many cases of interest.

It should be borne in mind that the above applies fully only to the molecular-beam method of removing the specimen using samplers in the form of a cone having an aperture angle of 30° and with a sufficiently large opening at the apex. In this case the main body of the stream from which the molecular beam is subsequently formed is unperturbed. This is due to the small dimensions (compared with the diameter of the stream) of the width of the boundary layer, which is formed on the inner walls of the probe during the expansion of the specimen and in which chemical reactions may take place with a high probability (including heterogeneous catalytic reactions on the walls of the probe). When capillary micro-probes having cones with small aperture angles (10°) are used, freezing of the chemical reactions does not take place effectively.

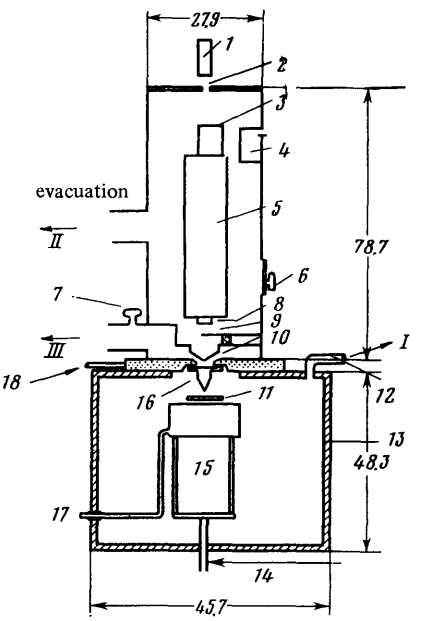


Figure 2. Apparatus of Biordi and coworkers[10]: *1*) laser, *2*) window, *3*) detector, *4*) cold trap, *5*) detector of the mass spectrometer, *6,7*) ionisation lamps, *8*) ion source, *9*) beam modulator, *10*) skimmer, *11*) flame, *12*) copper flange, *13*) combustion chamber, *14*) device for moving the burner in the combustion chamber, *15*) planar burner, *16*) probe, *17*) inlet for the gaseous components of the fuel, *18*) cooling water; *I*) to booster pump. *II,III*) to diffusion pump.

4. Apparatus with Molecular-beam Removal of Specimens from the Flames and Mass-spectrometric Detection

In recent years, with the development of experimental technique in various laboratories throughout the world (the National Bureau of Standards[9], the Bureau of Mines[10,11], the

Institute of Gas Technology[12], etc.[13] in the USA, the Rocket Propulsion Establishment[14] in England, in Belgium[15], etc.), assemblies have been produced with molecular-beam removal of the sample and subsequent mass-spectrometric analysis of the flames, making it possible to record atoms and radicals in the flames.

In the USSR there are assemblies for studying the kinetics of the reactions of atoms and radicals under isothermal conditions in the stream (the "diffusion cloud in the flux" method[16]). An important contribution to the molecular-beam mass spectrometry of flames (particularly atmospheric flames) was made by Greene and Milne[17], whose review systematised work carried out in this field up to 1968.

Fig. 2 represents a typical assembly (that of Biordi and coworkers[10,11]) used to study the structure of gaseous flames and the mechanism of their inhibition. It includes a combustion chamber with a stationary planar burner, capable of moving relative to the probe, which consists of a quartz cone. The assembly also includes a system for forming and detecting the molecular beam (skimmer, modulator, etc.). A quadrupole mass spectrometer was used as detector.

Similar assemblies have been used to study the distribution of the concentrations of atoms, molecules, and radicals in flames. Quadrupole and time-of-flight mass spectrometers are mainly used as detectors. The choice of quadrupole mass spectrometers is related to their very high sensitivity (reaching 10^{-15} mmHg). Time-of-flight mass spectrometers, which have a lower sensitivity than quadrupole instruments, have a much higher speed of operation, which makes it possible to use them to study fast processes. To separate the signal of the beam against the background of the molecules scattered by the walls of the compartment, mechanical modulation of the beam (by chopping it) and subsequent synchronous detection are used; the frequency of the modulation varies from several tens to several hundred Hertz. When modulation of the beam is used, the signal : noise ratio increases by a factor of 10^2–10^4. When this technique is used, the sensitivity of the detecting apparatus also increases considerably. A tendency to use computer control with mass spectrometers can be observed.

An important problem is to increase the heat resistance of the material of the probe. The maximum temperatures in the combustion zone amount to 1000–3000 °C, and are often higher than the melting point of the material used as sampler. The material of the sampler should satisfy the following requirements: 1) it should have a high melting point, and 2) it should be inert, and should not be broken down in the high-temperature active gaseous medium. The materials most frequently used for samplers are quartz, corundum, and refractory metals (platinum, tantalum, and a tantalum–hafnium alloy). Probes consisting of metals having a much higher coefficient of thermal conductivity than quartz and corundum, however, remove heat from the combustion zone much more rapidly than probes of quartz and corundum, and hence introduce greater thermal distortions into the flame. High-temperature ceramics can be recommended as probe materials. Difficulties arise in the construction of microprobes, however, when ceramics are used. The opening at the apex of the probe should be small and have a small wall thickness, and the length of the channel should be less than the diameter of the opening in the probe. The skimmer should have sharp edges, and the walls a small roughness factor, to prevent the production of reflected shock waves.

To select the optimum parameters for the assembly (in particular the distance between the sampler and the skimmer L), a number of authors have studied the dependence of the intensity of the beam I on L/d (for a fixed pressure p in the source; d is the diameter of the opening in the sampler) or the relationship $I = f(p)$ for different L/d. The data obtained by different authors do not show satisfactory agreement. According to some workers[18,19], the $I = f_1(L/d)$ curve has a maximum at $L/d = 30$–100, whereas according to others[12], the intensity increases continuously with decrease in L/d to 2–3. In the apparatus of Greene and Milne[18], the intensity of the molecular beam reached 10^{17} molecule cm^{-2} s^{-1} at a pressure of 1 atm in the source. The authors cited carried out detailed studies with individual gases and their mixtures, and showed that the intensity of the peak I_i of a component in a mixture is proportional to its partial pressure in the source p_i and its molecular mass M_i:

$$I_i = kp_iM_i.$$

5. Perturbations Introduced by the Probe

This question is one of the basic factors determining the quantitative aspect of the mass-spectrometric probing of flames. It is therefore not surprising that a large number of experimental and theoretical studies have been devoted to its examination. The most important perturbations introduced by the probe in the combustion process are aerodynamic and thermal. The probe acts as a material and heat sink, and this leads to the distortion, close to the probe, of the lines of equal concentrations and temperature in the flow. Since the component of the gas velocity along the axis of the probe is, close to it, greater than the gas velocity in the advancing flux, the lines of equal concentrations will be displaced in the direction of the probe (bent towards it) by an amount proportional to the diameter of the opening in the probe. This feature must be taken into account when matching the temperature (generally measured without the probe) and concentration profiles.

It should also be noted that with change in the temperature distribution in a flame without a probe as a result of the flow around the thermocouple, an aerodynamic track is formed; this produces a displacement of the lines of equal concentrations and temperatures by an amount proportional to several times the diameter of the thermocouple junction; an analogous effect is observed when the flux flows around the probe. These displacements must also be taken into account when matching the temperature and concentration profiles. It should be noted, however, that up to the present there has been insufficient quantitative study of these questions. A method for matching temperature and concentration profiles has been proposed[20], but it requires a more rigorous quantitative basis.

The aerodynamic perturbations introduced by a point sink into an advancing plane-parallel flux were calculated by Rosen[21], who found the velocity field close to the sink and calculated the dependence of the distance z (in units of the radius of the sink r) at which the vertical component of the velocity v_y/v_∞ is 5% on the sample removal factor $\alpha = Q/\pi r^2 v_\infty$ (where Q is the bulk velocity of the sink). For example, for $\alpha = 2$ (determined experimentally[22]), $z/r = 2$, that is breakdown takes place at a distance from the probe smaller than the diameter of its opening. A real probe, however, consists not only of a sink but also of an obstacle in the form of the walls of the probe, the thickness of which may be many times the diameter of the opening. Allowance for this feature in the quantitative examination of sampling problems may lead to results different from those obtained by Rosen[21].

In calculations of the isentropic flow of a gas close to and inside a probe[13], it was found that cooling as a result of the expansion of the gas specimen being analysed takes place even before the aperture of the probe (where the gas velocity is equal to the velocity of sound) at a distance of

~(1–1.5)d. Thus the gas temperature decreases by 5% at a distance d from the aperture upstream along the flux, and by 20% in the cross-section of the aperture. Thus the freezing of the chemical reactions in the gas specimen being removed begins even before its entry into the probe; the result of the analysis therefore refers to a point separated from the probe by a distance equal to its diameter.

A more important effect than that examined above is the cooling of the gas in front of the probe by the removal of heat by the latter. This question has been examined theoretically[23]; it was shown that the decrease in temperature may reach 8.5% under typical experimental conditions. The question has also been studied experimentally[24]. The experiments were carried out as follows: a thermocouple was placed at a definite point in the flame front, and the probe was placed at different distances from the thermocouple. When the probe was situated at a considerable distance from the thermocouple (greater than the width of the combustion zone), it had no influence on the thermocouple readings. As the probe approached the thermocouple, the temperature decreased; the maximum effect was ~150 K. The distribution of the temperature of the flame of the planar burner was measured by the thermocouple without the probe and with the probe placed at a distance of 2d from the thermocouple (the aperture angle of the probe was varied). The experimental results (Fig. 3) show that a probe with a cone aperture angle smaller than 40° does not distort the temperature profile in the flame zone (except for temperatures close to the flame temperature), but displaces it as described above. In the case given, this displacement amounted to 0.5 mm, which is one tenth of the width of the combustion zone, and was much greater than the diameter of the opening in the probe (which was equal to 0.1–0.14 mm).

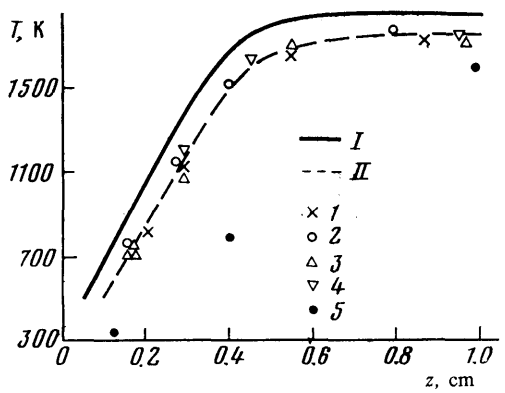


Figure 3. Temperature distribution in the flame of a planar burner (z is the distance from the burner surface) without a probe (*I*) and with probes (*II*) having different hole dimensions d and aperture angles α' of the cone. The distance between the thermocouple and the probe was equal to twice the diameter of the opening in the probe; α': *1*, *2*) 10–15°; *3*) 40°; *4*) 64°; *5*) 78°; d, μm: *1*) 137.5; *2*) 51; *3*) 114; *4*) 100; *5*) 87.5.

In the experiments described above, the aperture angle of the cone of the probe was varied. When the aperture angle of the cone is greater than 40°, it influences the concentration and temperature distributions[24]. Increase in the aperture angle of the cone apparently increases the heat losses into the probe, and the flame front is no longer one-dimensional. On the other hand, decrease in the aperture angle of the cone of the probe below 40° leads to an increase in the thickness of the boundary layer inside the probe near the inlet hole. This leads to an increase in the probability of the disappearance of the active species (particularly atoms, radicals, and ions) on the walls of the probe. Thus the optimum aperture angle of the cone of the probe is 30–40°.

The distortions of the concentration gradient during sampling with a probe under isothermal conditions have been studied theoretically and experimentally[22]. It was concluded that the effect of distortion of the concentration gradient can be neglected if the ratio of the dimensions of the opening in the probe to the width of the reaction zone is much less than unity. Thus to decrease the distortions it is possible to recommend a reduction in the size of the opening in the probe. Decrease in the size of the opening in the probe, however, leads to an increase in the proportion of the boundary layer and hence to an increase in the distortion of the composition of the gas in the specimen (chiefly the concentrations of the active species, for which the probability of disappearance increases in the boundary layer as a result of homogeneous and heterogeneous-catalytic reactions).

To estimate how the composition and concentration profiles of the specimen are distorted during its removal, a number of authors have carried out independent measurements of various parameters by other non-contact methods. For example, the distributions of the concentrations of hydrogen in an H_2–O_2–N_2 flame have been determined by mass-spectrometric and optical methods (Fig. 4).[9] The concentrations of OH radicals in the flame for 10.3% CH_4–21.6% O_2–68.1% Ar ($p = 0.042$ atm, $T = 1835$ K), measured optically (from the absorption), by mass spectrometry, and by the method of balanced reactions (from the data in Ref. 9) at a point 3 cm above the surface of the burner were 7.8×10^{14}, 15.5×10^{14}, and 16.9×10^{14} particles cm^{-3} respectively.

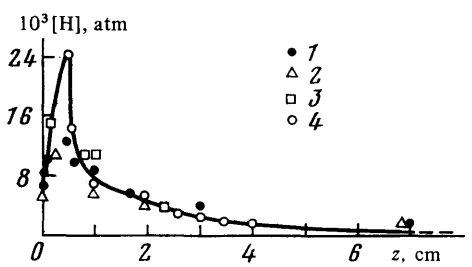


Figure 4. Concentration profiles of hydrogen atoms in an H_2–O_2–N_2 flame, measured by the mass-spectrometric method using ceramic (*1*) and metallic (*2*, *3*) probes and by an optical method (*4*).

As shown below, the constants for a number of elementary chemical reactions, found by the treatment of data obtained by mass-spectrometric probe methods, show satisfactory agreement with published data[25] and data obtained independently by other methods. Thus in spite of the perturbations introduced by the probe method, it can be used to determine with sufficient accuracy the chemical structure of the flame front, the concentrations of the reacting components, and the kinetics of chemical reactions in flames.

III. STUDIES OF THE MICROSTRUCTURE OF FLAMES AND THE MECHANISM AND KINETICS OF CHEMICAL REACTIONS IN GASEOUS FLAMES

1. Equations Describing a Planar Laminar Flame

The equations defining the behaviour of a one-dimensional (planar) laminar flame are given below[1].

1. Equation for the conservation of mass:

$$\rho v = \rho_0 v_0 = \text{const},$$

where v is the velocity of the flux, and ρ the density.

2. Equation for the conservation of the fluxes of the individual compounds:

$$\frac{d}{dz}[N_i(v+V_i)] = \sum_{j,k=1}^{N'} k_{jk} N_k N_j;$$

Thus the derivative of the flux of a compound at any point in the flame should be equal to the rate of the appearance or disappearance of this compound as a result of the chemical reaction; k_{jk} is the rate constant for the reaction of the two compounds j and k; the sign of k_{jk} depends on whether the compound i appears or disappears in this reaction; N_i is the concentration of the ith component; V_i the diffusive flux of the ith component; N' the total number of components; and z the coordinate in the direction of which all the characteristics change.

3. The equation of state:

$$p = NRT; \quad N = \sum_{i=1}^{N'} N_i .$$

The velocity of the diffusive flux of the ith component is defined as

$$V_i = \frac{N^2}{N_i \rho} \sum_{j=1}^{N'} M_j D_{ij}^* \frac{d}{dz}\left(\frac{N_j}{N}\right) - \frac{D_i^{*T}}{N_i M_i} \frac{d}{dz} \ln T .$$

Here, D_{ij}^* and D_i^{*T} are the coefficients of binary diffusion and thermal diffusion, and M_i is the molecular mass of the ith component. This is the equation of Fick's law, applied to multi-component systems, with an additional term (the last) which takes account of thermal diffusion.

These equations are the basic equations describing the change in the characteristics in a laminar planar flame. In the analysis of data on the structure of flames, it is sometimes convenient to use an additional variable. This is the fraction of the flux of the mass of the ith component G_i, defined as

$$G_i = \frac{N_i M_i}{\rho v}(v + V_i).$$

It characterises that fraction of the total mass flux through unit area due to the diffusion and convection of the compound i.

The basic equations of a one-dimensional flame can be written in a more compact form using the variable G_i. For a planar flame, the equations for the conservation of the compounds can be written in the form:

$$\frac{\rho_0 v_0}{M_i} \frac{dG_i}{dz} = \sum_{j,k=1}^{N'} k_{jk} N_j N_k = R_i. \qquad (1)$$

If the concentration and temperature distributions are measured experimentally, the differential equations (1) can be used to find the rates of formation or disappearance of the compounds, and then the velocities and rate constants of the elementary reactions in flames for different experimental conditions.

2. Microstructure of Flames and Determination of the Rate Constants of the Elementary Stages

Figs. 5 and 6 give as examples the results of the mass-spectrometric study of the microstructure of the flame CH_4 (9.62%)–O_2 (21.4%)–Ar (68.97%) at a pressure of 32 mmHg.[10] Fig. 7 gives the rates of the reaction of the principal stable compounds in the zone of the flame, obtained by computer treatment of the data in Fig. 5 using the equations given above and specially developed programs[26]. Subsequent treatment of the data on the reaction rates of the stable components in the flame makes it possible to determine the rate constants of the elementary reactions if their mechanisms are known.

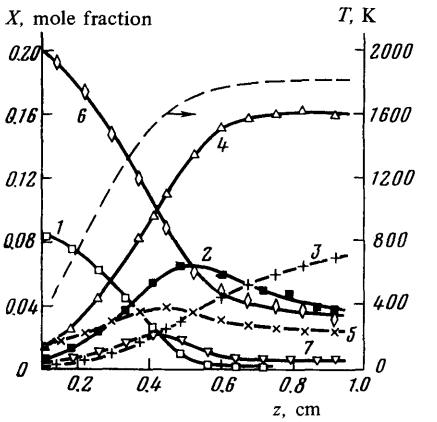


Figure 5. Temperature and concentration profiles for the principal stable components of the flame: *1*) CH_4; *2*) CO; *3*) CO_2; *4*) H_2O; *5*) H_2; *6*) O_2; *7*) CH_2O (× 20).

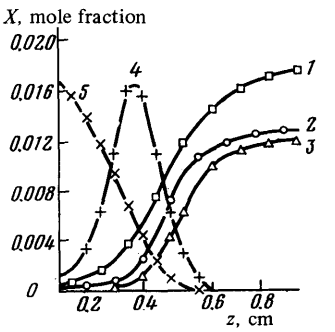


Figure 6. Concentration profiles for the principal intermediate products of the flame: *1*) H (× 0.8); *2*) OH; *3*) O; *4*) CH_3 (× 5); *5*) CH_4 (× 0.2).

Baulch and coworkers[26] give as an example the determination of the rate constant of the forward reaction

$$H + O_2 \underset{k_r}{\overset{k_f}{\rightleftarrows}} OH + O$$

from the data obtained by probing a CH_4–O_2 flame. The rate of the reaction of molecular oxygen in the flame, found from the concentration profile of O_2, is defined by the equation:

$$R_{O_2}=k_f[H]\cdot[O_2]-k_r[OH]\cdot[O].$$

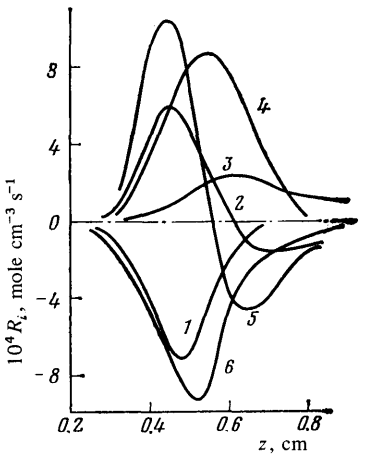


Figure 7. Profiles of the velocities of the reactions of the principal stable components in the flame: *1–6*) see Fig.5.

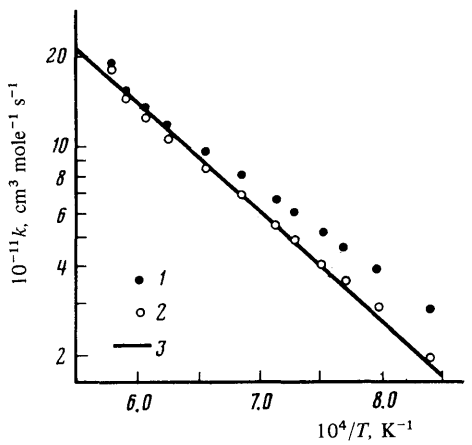


Figure 8. Arrhenius relationship for the rate constant of the reaction $H+O_2\rightarrow OH+O$; *1*) calculation from Eqn.(2) using experimental data; *2*) calculation using a more complex equation, taking account of the consumption of O_2 in its reaction with the radical HCO; *3*) straight line obtained from a critical analysis of published experimental data.

The square brackets denote the concentrations of the corresponding compounds. From the equilibrium constant of the above reaction K_{equil}, the quantity R_{O_2} can be expressed in terms of the mole fractions of oxygen and the radicals X_{OH}, X_{O_2}, X_H, and X_O, the profiles of which are known:

$$R_{O_2}=(p/RT)^2k_f(X_{OH}X_O/K_{equil}-X_HX_{O_2}). \qquad (2)$$

Fig.8 gives in Arrhenius coordinates the results of the calculation of k_f from this equation using experimental data[26], the results of a calculation using a more complicated equation taking account of the consumption of O_2 in the reaction with the radical HCO (using the published values of the rate constant of this reaction), and also the results of a critical analysis of published experimental data obtained independently over a wide range of temperatures using other experimental methods. It can be seen that the agreement is satisfactory.

Table 1. Magnitudes of the errors in the determination of the rate constants of the elementary reactions from mass-spectrometric studies of the microstructure of flames[25].

No.	Reaction	Temp. range, K	Smoothing, %	Matching of the temperature and concentration profiles, %	Temp. dependence of the intensities of the peaks of the fragment ions, %
1	$H+O_2\rightarrow OH+O$	1300—1500	20	35	—
	»	1500—1700	5	20	—
2	$H+CH_4\rightarrow CH_3+H_2$	1325—1500	30	35	20
	»	1500—1700	40	25	10
3	$CO+OH\rightarrow CO_2+H$	1425—1575	20	30	3
	»	1575—1725	10	30	3
4	$CH_3+O\rightarrow H_2CO+H$	1550—1650	20	25	5
	»	1650—1750	30	25	15
5	$H+CF_3Br\rightarrow HBr+CF_3$	1000—1300	15	25	—
	»	1300—1600	20	20	—

Table 2. Comparison of reaction rate constants determined from mass-spectrometric studies of the microstructure of flames[25] and found by other methods (see Table 1 for the numbering of the reactions).

Reaction No.	T, K	Rate constant (Ref.25)	Data obtained by other methods	Refs.
1	1300—1700	$7.5\cdot10^{13}\exp(-13500/RT)$	$2.2\cdot10^{14}\exp(-16900/RT)$; 700—2000K	26
2	1325	$7\cdot10^{11}$	$3.1\cdot10^{13}\exp(-8200/RT)$; 1200—1800K	27
2	1540	$2\cdot10^{12}$		
2	1665	$4.7\cdot10^{12}$	$(3.2\pm0.6)\cdot10^{12}$; 1600 K	15
2	1700	$7.5\cdot10^{12}$		
3	1425—1725	$4.6\cdot10^{11}$	$k=10.83\pm3.9\cdot10^{-4}\ T$	28
4	1550—1750	$8.2\cdot10^{13}$	$2.6\cdot10^{14}\exp(-2000/RT)$; 1000—2000K	29
4	—	—	$7.4\cdot10^{13}$, 297K	30
5	1000—1600	$2.3\cdot10^{14}\exp(-9200/RT)$	$4.36\cdot10^{15}\exp(-17450/RT)$	31

The problems arising in the determination of the rate constants of elementary reactions from data obtained by probing flames have been listed and analysed[25]: 1) the problem of smoothing the curves drawn through the experimental points, arising from the need for double differentiation of the concentration profiles; 2) the matching of the concentration and temperature profiles; 3) the temperature dependence of the intensities of the peaks of the fragment ions; and 4) the problem of calibrating the mass spectrometer with respect to radicals and atoms. Table 1 gives the magnitudes of the errors arising in the determination of the rate constants of elementary reactions from the results of mass-spectrometric studies of the microstructure of a flame (with the exception of the errors associated with the determination of the absolute concentrations of atoms and radicals in the calibration, which amount to 100%). Table 2 gives the rate constants of elementary reactions, determined from the results of mass-spectrometric studies of the microstructure of flames using probe

removal of samples, and also calculated from experimental data obtained using other methods. It can be seen that the agreement is satisfactory; thus the mass-spectrometric method can ensure the determination of the rate constants of elementary reactions with an accuracy which at the present time is not less than the accuracy of the measurement of the rate constants by other methods (particularly in the high-temperature range).

3. Vibrational–translational Non-equilibrium in Flames

It is necessary to deal particularly with the question of translational–vibrational non-equilibrium in the reaction zone of a methane–oxygen flame[25] and its study by molecular-beam mass spectrometry. The existence of vibrational disequilibrium for certain diatomic radicals in the reaction zone of a flame has been proved directly by spectroscopic methods[32]. The mass-spectrometric probing of flames makes an additional contribution to the study of this question. The translational–vibrational disequilibrium of molecules is revealed in a change (compared with the equilibrium case) in the ratio of the intensities of the mass peaks of the "parent" and fragment ions, since the rate of fragmentation of a complex molecule depends on the degree of vibrational excitation.

In the molecular-beam mass-spectrometric probing of flames and the analysis of the data obtained, three questions are closely related: 1) the above-mentioned temperature dependence of the intensities of the peaks of the fragment ions; 2) vibrational–translational relaxation in the flame; and 3) vibrational–translational relaxation in the expansion of the gas during the removal of the specimen from the flame.

These questions have been analysed[25] for CO_2 and CH_4 molecules in a CH_4–O_2–Ar flame. Account was taken of data on the temperature dependence of the peaks of the fragment ions in the mass spectra of CO_2 and CH_4, obtained using effusion and gas-dynamic molecular beams. From the analysis of the experimental data, it was concluded[25] that translational–vibrational disequilibrium exists for the methane molecule both in the flame and in the process of gas expansion during the removal of the specimen from the flame. For CO_2, in both cases, vibrational–translational equilibrium can be established.

To explain this, the following estimates are given[25]. Under the conditions of the flame, the molecules undergo 10^8 collisions per second. The vibrational–translational relaxation times in a CH_4–Ar mixture were measured, and are equal to 3×10^{-5} s under flame conditions, which corresponds to an average of 3000 collisions. With allowance for diffusion, the flow velocity of methane in the flame is 2500 cm s^{-1}, which corresponds to a delay in the establishment of vibrational–translational equilibrium at a distance of 0.07 cm, comparable with the width of the chemical reaction zone and the high spatial resolving power of the probe. For the CO_2 molecules, however, the velocity of the flux under the same conditions is smaller by an order of magnitude than that for the CH_4 molecules (since the diffusion flux of CO_2, unlike that of CH_4, takes place in the opposite direction to the overall flux) and amounts to 300 cm s^{-1}. Thus the spatial lag of the vibrational relaxation for CO_2 is smaller by an order of magnitude and amounts to ~0.007 cm.

4. Mechanism of Inhibition in Flames

The flame probe method also makes it possible to study the mechanism of the action of additives introduced into a flame, for example to inhibit them. The results of studies of the microstructure of a methane–oxygen flame containing the added inhibitor CF_3Br have been used[26] to calculate the rates of consumption of the inhibitor in the chemical reaction zone of the flame.

The possible reactions involving the consumption of the inhibitor, and their contribution to the total rate of consumption of the inhibitor (CF_3Br) in the flame, as percentages of the experimentally observed maximum rate, are given below:

$CF_3Br \rightarrow CF_3 + Br$	8
$CF_3Br + CH_3 \rightarrow CH_3Br + CF_3$	2
$CF_3Br + O \rightarrow BrO + CF_3$	0.1
$CF_3Br + Br \rightarrow Br_2 + CF_3$	0.1
$CF_3Br + H \rightarrow HBr + CF_3$ + 25 kcal $mole^{-1}$	100

The rate of consumption of the inhibitor at a given point in the combustion zone by each of the possible reactions was determined by multiplying the corresponding rate constant, taken from published data, by the experimentally measured[25] concentration of the inhibitor and the radical at this point. The contribution of the reaction to the total maximum rate of consumption of the inhibitor was determined at the point of maximum rate by dividing the rate of consumption, calculated as described above, by the rate of consumption obtained by mathematical treatment of the concentration and temperature profiles in the flame. The data given show that the principal path in the consumption of the inhibitor is its reaction with hydrogen atoms, which are the main chain carriers in the branched chain reaction of methane oxidation. As a result of this reaction, there is a decrease in the concentration of hydrogen atoms; this leads to a decrease in the rate of the oxidation process and hence in the rate of propagation of the flame.

A cycle of studies has been carried out[33] to investigate the structure of the front of hydrocarbon flames (chiefly propane) and the mechanism of their inhibition. A knowledge of the mechanism of chemical reactions in the flame zone and the mechanism of inhibition makes it possible to develop methods for calculating flame propagation velocities and to establish methods for finding effective combustion inhibitors, which are of considerable importance for preventing fires and explosions.

The technique described above has been used to study the structure of the rarefied flames CH_4–O_2,[10,11] $HClO_4$–CH_4,[14] N_2O–H_2,[34] and C_2H_4–O_2[15] and the atmospheric flames CH_4–O_2 and H_2–O_2.[9,12,13] As a result of these studies, it has been possible in a number of cases not only to establish the mechanisms of the chemical reactions in the flames but also to find various previously unknown rate constants of elementary reactions.

IV. NON-STATIONARY PROCESSES

Dynamic mass spectrometry has found extensive application in the study of non-stationary processes in gaseous and condensed systems: in the study of the propagation of flames and shock waves, the kinetics of fast decomposition reactions, processes in internal combustion engines, etc. The propagation of atmospheric cold flames of butane in a tube (at a velocity of 4 cm s^{-1}) has been studied[35]; the products passed directly into the ion source of a time-of-flight mass spectrometer through a hole made in the wall of the tube by means of a laser.

The rarefied flame in mixtures of chlorine azide and hydrogen, being propagated along a tube at a velocity of 6 m s^{-1} has been studied[36]. The mixture was ignited at one end of the tube, and the probe placed at the other end. A Bendix Aviation Corporation time-of-flight mass spectrometer was used to record the change with time in the intensity of the mass peaks as the combustion wave passed the point where the specimen was consumed (the transit time amounted to

several milliseconds). Considerable concentrations of intermediate products—radicals and atoms—were detected.

The formation of nitric oxide in air in a spark discharge, which is important for investigating the mechanism of spark ignition, has been studied in a flow reactor[37]. The molecular-beam removal of specimens from the working compartment of an internal combustion engine during its operation is also of considerable interest[38]. The dependence of the concentration of propane on the angle of rotation of the crankshaft was measured experimentally. The results make it possible to understand the processes of combustion of the fuel in the engine, and this is important for developing measures to improve its operation.

The chemical structure of the turbulent track produced during the flight of a projectile at supersonic velocity has been studied[39]. A sphere of diameter 16 mm was projected in air at a pressure of 60 mmHg and a velocity of 6 km s^{-1} close to a probe having a molecular-beam system for extracting the sample. The formation of NO in the track was detected, and the time dependence of the concentration of nitric oxide in the track was measured: the decrease in [NO] was recorded over a period of several milliseconds after the flight of the sphere.

One of the most striking examples of the application of time-of-flight mass spectrometry to the study of high-temperature chemical processes is the study of the kinetics of reactions in shock waves[40] and in pulse flash photolysis[41-43] (the reaction times amount to tenths or hundredths of a microsecond).

In spite of the efficiency of the method, however, the time-of-flight mass spectrometer does not yet ensure the accuracy of recording required for carrying out kinetic studies of processes lasting for hundredths of a microsecond. Recently, therefore, new systems have appeared for the mass-spectrometric study of fast processes[44], in which the separation of the ions according to mass is carried out in a magnetic field, and each type of ion is recorded by means of its own collector. The dynamic mass spectrometer has also found extensive application in the study of the kinetics of the fast reactions involved in the decomposition of solid fuels (S.F.) as one of the stages of the combustion process. Work carried out in this field up to 1969 has been reviewed in detail[45].

Mass-spectrometric methods for studying the fast processes involved in the decomposition of solid fuels have continued to develop in recent years. Fig. 9 shows an assembly[46] used to study the fast processes involved in the decomposition of specimens of solid fuels at a pressure of 1 atm under isothermal (time ~ 1 s) and non-isothermal conditions (rate of heating 100–1000 K s^{-1}, close to the rate of heating in the combustion wave of the solid fuel). The assembly contains a heating system, a flow reaction vessel, a pumping system, a time-of-flight mass spectrometer (TFMS), and an automatic recording system, which includes a specially developed device, "Strob", which converts the mass-spectrometric information into digital form, and a PL-150 punch machine.

Examples have been given[46,47] of the study of the decomposition of catalyst-containing mixtures, based on ammonium perchlorate, under conditions of rapid heating, close to the rate of heating in the combustion wave. Correlations have been found between the decomposition and combustion processes.

The use of an automatic system for recording mass-spectrometric information has made it possible to reduce by an order of magnitude the time taken to process the results of measurements and to increase by an order of magnitude the accuracy of the measurement.

V. COMBUSTION OF CONDENSED AND HETEROGENEOUS SYSTEMS

The mass-spectrometric method can be used successfully to study the combustion of solid fuels and the flame structures and kinetics of the chemical reactions in solid fuel flames[48-50].

In the probing of solid fuel flames, additional difficulties arise (compared with gaseous flames); one of these is the difficulty of stabilising the combustion surface relative to the probe. The measurement process should therefore be rapid (several seconds) and have a low inertia. These difficulties have been overcome[48-50].

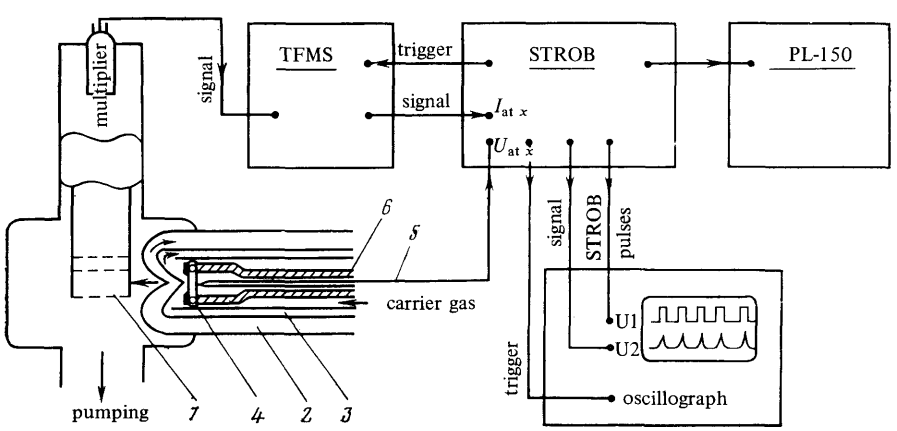


Figure 9. Diagram of the apparatus for studying the fast processes involved in the decomposition of solid fuels: *1*) ion source of the time-of-flight mass spectrometer; *2*) low-pressure compartment; *3*) high-pressure compartment (1 atm); *4*) cell for heating the specimen rapidly; *5*) thermocouple; *6*) current-carrying leads.

As an example, Fig. 10 gives the results of a study of the distribution of the concentration of the reacting components in the flame of a model solid fuel mixture based on ammonium perchlorate (84%) and polymethyl methacrylate (16%) at a pressure of 50 mmHg and an initial temperature of 180 °C.[50] The burning solid fuel specimen was moved in the direction of the stationary probe at a velocity greater than the velocity of combustion. As a result, the probe passed through all the combustion zones, including the reaction layer of the *K*-phase. As the combustion surface approached the probe, in the zone of the flame there was a decrease in the concentrations of the combustion products HCl ($m/e = 36$), $CO_2 + N_2O$ (44), and NO + N_2O (30), and also CO + N_2 (28) and H_2O (18), not shown in Fig. 10, and an increase in the concentrations of the products of the gasification of the oxidant, $HClO_4$, ClO_2 (67), O_2 (32), and NH_3 (16), and the fuel, methyl methacrylate (41).

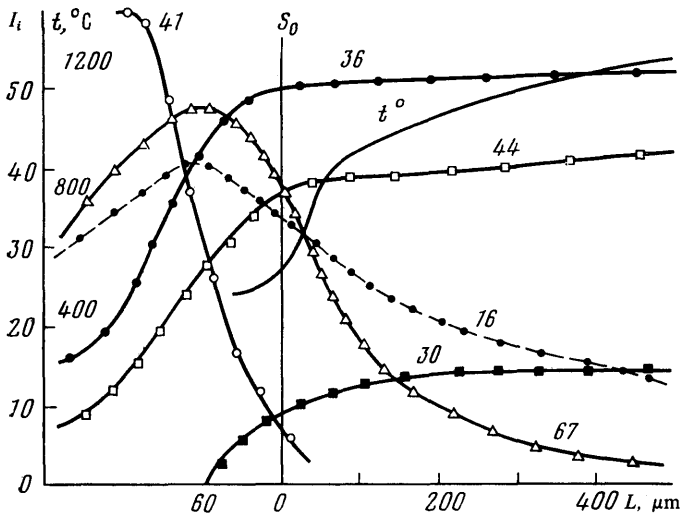


Figure 10. Profiles of the intensities of the peaks of the reacting components I_i in the combustion zone of a solid fuel mixture; S_0 is the combustion surface, $t°$ the temperature, L the distance to the combustion surface, and the figures next to the curve give the values of m/e.

On further movement of the specimen, the probe enters the reaction layer of the condensed phase, making it possible to record (qualitatively at least) the concentrations of gaseous components in the reaction layer of the solid fuel; this cannot yet be done by any other method. As the probe moves into the reaction layer away from the combustion surface, the concentration of oxidant increases, reaches a maximum, and then decreases, whereas the concentration of the products of the gasification of the fuel continue to increase, indicating that the decomposition takes place by a stepwise mechanism. The chemical structure of the combustion wave has also been studied[49,50] for ammonium perchlorate, ballistic powder, and mixtures containing added combustion catalysts.

The results obtained make it possible to deepen and broaden existing ideas regarding the mechanism of the combustion of solid fuels and to obtain data on the kinetics of chemical reactions in solid fuel flames, which can be used to develop mathematical models of their combustion.

There has recently been an increase in interest in the study of the mechanism of the combustion of polymers in connection with the search for polymer combustion inhibitors and methods for decreasing the combustibility of polymers. Mass spectrometry has been used[51] to determine the concentration profiles of the components in the combustion zone of polymethyl methacrylate in air (Fig. 11). The first results have been published[52] on the probing of the diffusion flame of an epoxide resin; the results show the variety of the chemical reactions accompanying the combustion of polymers. Further studies should assist in the investigation of the mechanism of the combustion of polymers.

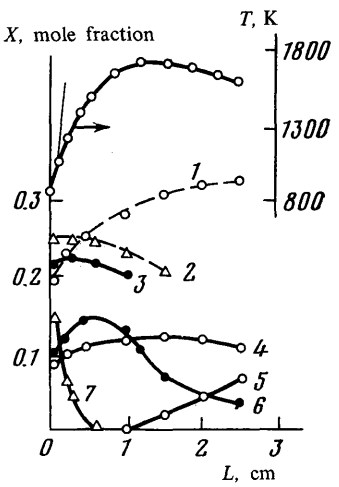


Figure 11. Dependence of the temperature and concentration of the products of the combustion of polymethyl methacrylate in air on the distance L (cm) from the combustion surface of the polymer: *1*) Ar (× 0.5); *2*) H_2 (+0.2); *3*) hydrocarbons (+0.2); *4*) CO_2; *5*) O_2; *6*) CO; *7*) methyl methacrylate.

VI. LIQUID ROCKET MOTORS

The possibilities provided by dynamic mass spectrometry for the study of the processes involved in the mixing of the components and their combustion in liquid rocket motors (LRM) have been demonstrated[53]. An assembly has been developed[53] which makes it possible to study the processes involved in the mixing and combustion of the oxidant (N_2O_4) and the fuel (N_2H_4) in the combustion compartment of a small LRM. Since the final aim of the studies was to analyse the combustion of a system containing the extremely aggressive components F_2–N_2H_4, an attempt was made to create a molecular-beam sampling system. In spite of the fact that a molecular beam was not established in the specimen-removal system, because of the insufficient rate of pumping of the skimmer compartment, it was possible to obtain a number of experimental facts of importance for understanding the processes taking place in the motor.

Fig. 12 shows the experimental assembly, which includes the combustion chamber of the LRM and the sampling system. To study the local concentrations of the components in the combustion compartment of the motor, the jet was replaced by a plate having 29 holes of diameter 0.21 cm, with centres

separated by 1.14 cm. The sampler could be placed at the centre of any of the holes, with a high accuracy. The pressure in the space in which the flow of the combustion products took place was 1 atm.

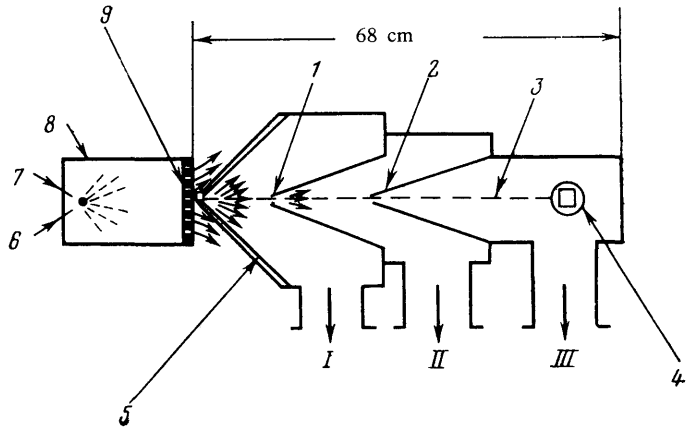


Figure 12. Removal of a specimen from the gases flowing from the combustion chamber of a liquid rocket motor: *1*) skimmer, *2*) collimator, *3*) supersonic molecular beam, *4*) quadrupole mass spectrometer, *5*) water-cooled heat shield, *6*) oxidant, *7*) fuel, *8*) combustion chamber, *9*) water-cooled multi-jet end plate; *I*, *II*, and *III*—evacuation stages.

Preliminary experiments established that the hole in the sampler was closed by fusion when the motor was operated for 6 s, but remained undamaged for a duration of operation of 3–3.5 s, which was found to be sufficient to obtain and record the required experimental results. Treatment of the results of the mass-spectrometric studies established significant non-uniformity of the oxidant/fuel ratio over the cross-section of the combustion chamber of the motor. It was shown that the phenomenon of so-called "stream penetration", previously detected in experiments with cold components, also takes place in the hot working motor. The large quantities of nitric oxide (compared with equilibrium) detected in the mass spectra indicate inadequate efficiency of the combustion in the motor. The results obtained indicate the need to improve the sampling system. The authors cited[53] subsequently intend to increase the rate of pumping the skimmer compartment and to obtain a molecular beam at a pressure at the point of sampling up to 6 atm.

Thus the mass-spectrometric method provides a powerful instrument for studying combustion processes. The possibilities provided by the method have not yet been fully revealed, and are far from exhausted. Mass spectrometry occupies an important position among other methods for studying flames and combustion processes, such as optical, radiospectroscopic, calorimetric, chromatographic, and other methods, each of which has its own advantages and disadvantages. Best results can undoubtedly be achieved by the simultaneous use of the above methods.

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