

GAS CONCENTRATION MEASUREMENTS IN BOUNDARY LAYERS

E. A. Brun

UDC 532.526:541.12.035

Modern probe and probeless methods of measuring concentration profiles are reviewed. Boundary-layer processes associated with flow over solids, among them the catalysis of an N^+N_2 mixture at a metal wall, and hydrogen and methane combustion, are investigated.

The problem of mass transfer through a boundary layer is being investigated in the Aerothermal Laboratory of the National Research Center. In what follows the techniques used in our wind tunnels are described.

1. Boundary-Layer Mass Transfer

1.1. My object is to review modern methods of measuring the concentration fields in boundary layers on walls. These measurements are based on certain principles of the thermodynamics of irreversible processes, in particular, "localizability." Since to examine them in detail would be to digress too far from my subject, I shall assume that they are valid and known to the reader. Moreover, I consider it useful to start by demonstrating the necessity of boundary-layer concentration measurements.

When a rocket enters the atmosphere, the composition of the air is changed by the action of the shock waves and, as a result of the intense rise in temperature (Fig. 1), such processes as dissociation, nitric oxide formation, and ionization are initiated. Near the wall the temperature falls rapidly, and this leads to the reverse processes, but the local states observable on the porous structure are unable to attain the chemical equilibrium appropriate to the physical conditions, since the time required to complete the reaction in the fluid particle is large compared with the time spent by the particle in the boundary layer.

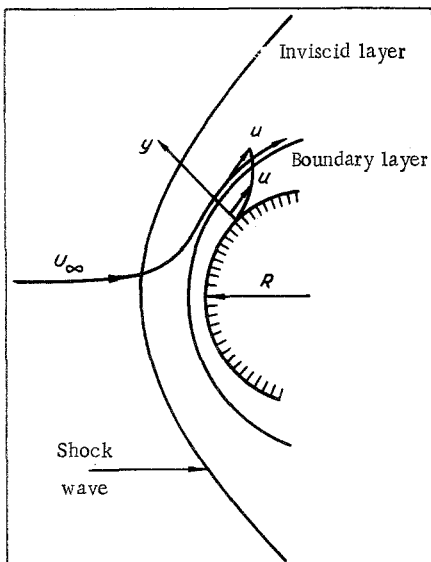


Fig. 1

At the same time, the wall has a catalytic effect, which considerably increases the rate of the reaction and, when in contact with the wall, the particle is at precisely that point where the reaction is almost instantaneous. The concentration of the components is not the same at both edges of the boundary layer, and this leads to diffusion of the components, so that mass transfer is superimposed on heat transfer through the boundary layer.

A simple example illustrating this transfer mechanism is provided by a zero-gradient flow of nitrogen plasma over a flat steel plate at a velocity ~ 800 m/sec. Owing to the low pressure at a temperature of the order of 2000°C the plasma is in the nonequilibrium state, and there is practically no chemical reaction in the free stream or the boundary layer [1]. However, it has been shown that when the flow makes contact with a steel wall, whose temperature is maintained at $\sim 500^\circ\text{C}$, catalysis obviously takes place with the formation of monatomic products.

National Research Center, Aerothermal Laboratory, France. Translated from *Inzhenerno-Fizicheski Zhurnal*, Vol. 19, No. 3, pp. 532-547, September, 1970. Original article submitted April 1, 1970.

© 1973 Consultants Bureau, a division of Plenum Publishing Corporation, 227 West 17th Street, New York, N. Y. 10011. All rights reserved. This article cannot be reproduced for any purpose whatsoever without permission of the publisher. A copy of this article is available from the publisher for \$15.00.

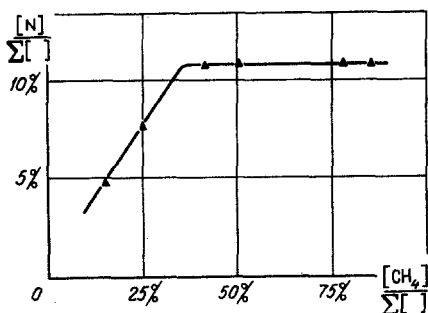


Fig. 2

The mechanism of catalysis has been predicted by Riddell. One atom of nitrogen in the gaseous state is adsorbed and upon collision with another gas atom forms molecular nitrogen, parts of the adsorption surface remaining always saturated with adsorbed atoms



The formation of monatomic products can only be a forward reaction; the law of chemical kinetics is written in the following form

$$-\frac{dx}{dt} = kx, \quad (1)$$

where k is the concentration of monatomic nitrogen at time t . Integration makes it possible to treat k as the reciprocal of the time constant

$$\tau = \frac{x}{dx/dt}. \quad (2)$$

For the plate the time constant is small owing to the presence of catalysis; in the boundary layer, on the other hand, the time constant is large, since the reaction rate tends to zero.

If the steel plate is replaced by a Pyrex one, there is no catalysis. Investigations have shown that reaction-induced luminescence is observed in the case of a steel, but not in the case of a glass plate.

1.2. Let us now consider the situation in the boundary layer in the presence of a chemical reaction accompanied by diffusion.

The diffusion of the i -th component can be characterized by the so-called "mechanical" time

$$\tau_m = \frac{\delta}{v_i}. \quad (3)$$

Here, δ is the thickness of the boundary layer, and v_i is the average diffusion rate of the i -th component in the boundary layer.

We assume that at some point the concentration of the i -th component is equal to C_i , while the "chemical" time

$$\tau_c = \frac{C_{ie} - C_i}{dC_i/dt}, \quad (4)$$

i. e., τ_c is equal to the ratio of the deviation from the equilibrium concentration to the reaction rate. In the particular case of a first-order reaction proceeding in only one direction, τ_c is nothing other than the time constant given by Eq. (1).

The definition of these two characteristic times enables us to classify flows.

If $\tau_c \ll \tau_m$, then the reaction proceeds very rapidly and at all points the boundary layer is in a state of equilibrium.

If $\tau_c \gg \tau_m$, then the reaction is unable to proceed and the boundary layer remains frozen.

If τ_c and τ_m are equal in magnitude, then relaxation effects take place in the boundary layer.

Thus, it is important to investigate the concentration profiles in the boundary layer: this makes it possible not only to establish the composition of the boundary layer but also to determine the nature of the flow in the boundary layer and the mechanism of the boundary-layer reactions.

2. Measurements by the Sampling Method

2.1. The sampler is often a cylindrical tube with the axis tangential to the streamlines. Owing to the pressure drop in the tube the sample is delivered to a gas analyzer located outside the flow. Sampling methods have serious disadvantages.

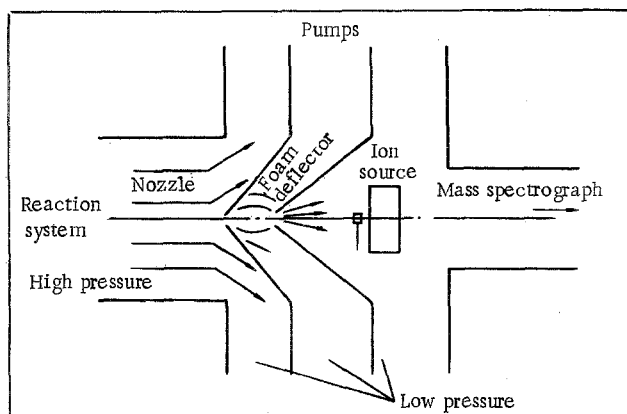


Fig. 3

As a rule, the composition of the sample differs from that existing at the sampling point when the sampler is absent.

Certain precautions must be taken to minimize the random interference caused by the sampler.

a) Obviously, the probe must be made as small as possible [3]. In fact, the disturbances are related with the ratio of the tube diameter to the thickness δ of the boundary layer and this can be reduced by increasing δ ; in particular, for precisely this reason the above-mentioned experiments were conducted at low pressures.

b) The tube axis must be tangential to the streamline that existed before the introduction of the probe; otherwise the disturbance of the velocity field is superimposed on the density profile (if there is one).

c) The variation of velocity along the outer boundary of the probe during sampling will be minimal if the sampled mass is equal to the mass flow rate through a cross section equal to the cross section of the probe before it was introduced into the boundary layer (isokinetic sampling). This precaution makes it possible to avoid distortions of the diffusion flux and chemical reaction rate near the tube and, in particular, where the sample is taken.

d) It is necessary to make sure that the probe is not the principal source of heat in the boundary layer and that thermal equilibrium is established between the probe wall and the fluid flowing over it. A heat source would distort not only the temperature distribution but also the concentration gradient and hence would affect the reaction rate.

e) The probe wall should not have any chemical effect on the composition of the gas mixture (for example, catalytic in the case of a nonequilibrium gas mixture); it should not undergo any transformations (melting, sublimation, etc.).

f) Finally, the specimen should not change during the transport process; if a chemical reaction takes place along the channel, the transport time should be as short as possible as compared with the duration of the reaction; if adsorption is possible, it should be reduced to a minimum by avoiding the use of metals (use Teflon walls, drill holes with sapphire drills, etc.); the measurement should be made in a continuous flow, which enables the analysis to be made after equilibrium adsorption has been established [4].

2.2. We will examine the last condition in more detail, since it is the most important from our standpoint, especially when the specimen is not in chemical equilibrium.

We return to the case of the boundary layer in a nonequilibrium nitrogen plasma. The probe consists of a quartz tube. This material has such a low catalytic reaction constant that it does not cause any changes in atomic nitrogen; accordingly, we may assume that the concentration gradient in the boundary layer varies very little. At the same time, the transfer of atomic nitrogen to the analyzer takes long enough for the catalytic action to have an appreciable effect. The problem consists in bringing all the nitrogen to the same stable state at the sampling point.

Hydrocarbons react with active nitrogen to form cyanohydrin oxides, a series of CN radicals, and cyanogen C_2N_2 [5, 6]. If the hydrocarbon is methane, then the basic reaction may be written as follows

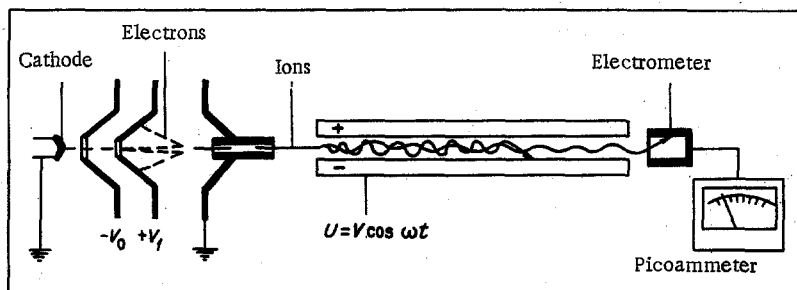


Fig. 4

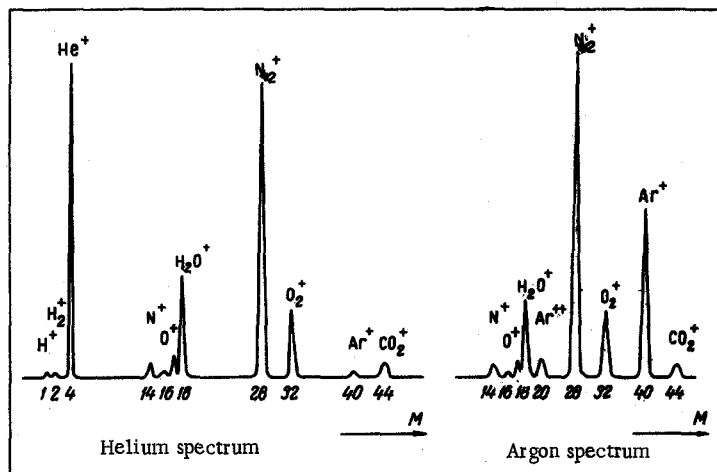


Fig. 5



The rate of the reaction is high enough for it to be regarded as instantaneous [7]. It is necessary to make the atomic nitrogen react with the hydrocarbon and then transfer the stable mixture to the analyzer.

The gases are mixed at the entrance to the probe and sucked through by a vacuum pump connected to the analyzer. Obviously, the ratio of methane and nitrogen flow rates must be such as to ensure a complete reaction, but there is no need to dilute the samples with a large amount of methane, since the analyzer gives measurements that are the more accurate, the higher the content of nitrogen and hydrogen cyanide in the mixture. Then the methane flow rate is increased proportionally: an analysis has shown that at first the atomic nitrogen content increases in proportion to the methane flow rate, then becomes constant (Fig. 2). At this point the conversion of atomic nitrogen is complete and the results corresponding to the minimum methane flow rate ensuring the conversion of all the N to HCN are retained. This method is presented as an example, but, as we shall see, there are other cases where an auxiliary fast reaction may direct the composition of the mixture or when the possibility of the existence of a reaction between the mixture components, the probe, and the analyzer is unknown.

3. Various Types of Remote Analyzers

Without dwelling on the question of chemical analysis I shall briefly describe some of the methods that have been used.

3.1. Mass Spectrograph. This apparatus is the one most often used in our laboratory. The analysis is made at a very low pressure on the interval 10^{-5} - 10^{-11} torr. This is especially important in the analysis of liquefied gas flows.

The gas molecules introduced into the chamber at very low pressure (Fig. 3) are ionized by electron bombardment, for example:



The ions thus formed pass through a series of openings in plates at electric potentials designed to focus the ions. The electron beam then penetrates into the separating element.

In the separators it is possible to employ electric or magnetic fields (Omegatron), a grid under a variable electric potential (topatron) or a quadrupole tube, to whose electrodes a variable-frequency voltage is applied (Varian). In the latter case, which is the most convenient from our standpoint, at a given frequency only the trajectory of the ions on a narrow interval has a regular sinusoidal shape. The other particles undergo transverse oscillations of increasing amplitude until they reach the surface of the quadrupole. This leads to their deionization and elimination and only the ions with the resonant frequency of the quadrupole (Fig. 4) reach the electron multiplier connected with the recording instrument. When the frequency is varied, all the M/g values are erased except for those corresponding to the ions contained in the beam. These form peaks whose height is proportional to the molar concentration (Fig. 5). The mass spectrograms are interpreted with respect to the ratio $M/\Delta M$, where M is the ion mass, and ΔM is the mass variation corresponding to the width of the peak measured at half-height. For molecular mass measurements on the interval 1-50 the solution gives ~ 50 , whereas for higher molar masses it is ~ 20 .

If the sensitivity is very high, a partial pressure equal to 10^{-14} torr of one component is sufficient to detect nitrogen.

The mass spectrograph is now widely employed for investigating the reactions of all kinds of gases [8, 3]. However, it is not being used extensively enough for determining the concentration profiles in boundary layers with and without chemical reactions.

If all the necessary precautions are taken, then in most cases the sampling method gives good results, which in our laboratory can also be checked by other methods.

3.2. Chromatography. The composition of the specimen can be determined by chromatography. Chemists, in particular, frequently employ this method. However, for many reasons it is less useful than mass spectrography. In the first place, the pressure in the analyzer must be greater than 5 mm Hg and the mass flow rate in the chromatograph is correspondingly higher than in the mass spectrograph. In certain cases this has undesirable consequences (for example, in the case of free diffusion). Moreover, interpretation takes much longer than for the mass spectrograph.

Finally, the chromatograph must be calibrated in relation to the composition of the mixture, whereas the mass spectrograph indicates the component content at the time of sampling, and, in particular, is very useful for analyzing a gas containing atoms, free groups, etc.

3.3. Other Types of Analyzers. There are also other analyzers based on various physical principles, but all have certain disadvantages: high flow rate, time-consuming experiments, reading times ~ 1 min, etc.

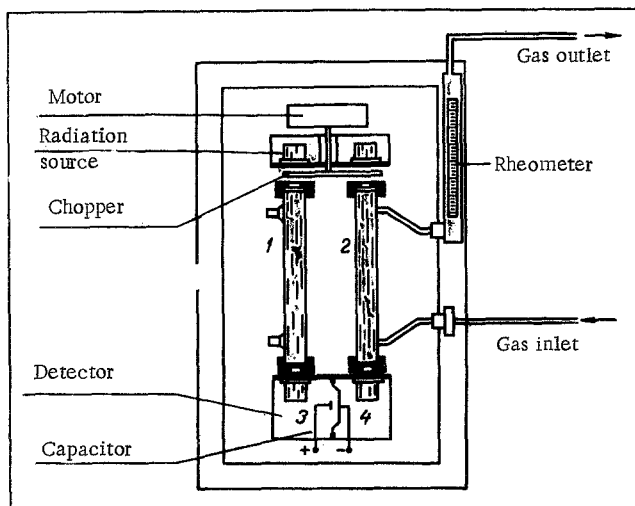


Fig. 6

a) The infrared absorption analyzer is based on the principle that many gases (CO , CO_2 , SO_2 , NH_3 , hydrocarbons) have absorption lines in the infrared region of the spectrum, while the absorbing component attenuates infrared radiation of a certain wavelength characteristic of the gas irrespective of its temperature and pressure to a degree proportional to its concentration.

The measurements are differential, since the energies involved are low. For example, take two tubes of equal length; dry, pure air is circulated in one (comparison tube 1, Fig. 6) and a gas mixture containing a sample with the component in the other (analytical tube 2, Fig. 6). Both tubes are placed in the zone of infrared radiation, which is received in two identical cells 3, 4 separated by a thin membrane. One of these contains the sampled mixture with component i . The gas in the cells absorbs the radiation characteristic of the component i . The radiation is interrupted once a second by the rotation of a bladed chopper; accordingly, the temperature and hence the pressure in both cells is related with the frequency of the chopper blades. The membrane is used to measure the instantaneous pressure drop, which is proportional to the selective attenuation of one of the radiations in tube 2, which holds the mixture containing component i .

b) The katharometer or analyzer based on the different thermal conductivities of gases is also a differential instrument; four conductors, whose resistance varies with temperature, form a Wheatstone bridge and are so arranged that two facing conductors are bathed by the investigated gas mixture and the other two by a reference gas. The difference in thermal conductivities is sufficient to produce a current proportional to the measured concentration. In order to avoid corrosion and catalysis, the measuring conductors are insulated by means of perfectly airtight glass capillaries (Fig. 7).

c) for oxygen it is possible to employ a magnetic analyzer, since it is characterized by paramagnetism.

4. Probeless Techniques

These methods are superior in that they do not require sampling of the gas in the boundary layer. They necessarily involve optical measurements and, unfortunately, for this reason cannot always be employed.

4.1. Emission Line Intensity. This method is suitable only for investigating plane flow or for a gas mixture at a rather high temperature (for example, a plasma). A plane is selected in the boundary layer parallel to the velocity and perpendicular to the wall (Fig. 8). An image is focused by a lens L on the slit of a spectrograph parallel to the target plane and perpendicular to the wall. The spectral lines of the i -th component of the gas mixture are formed on the plate and their intensity is studied with a microphotometer. The intensity is proportional to the concentration of the i -th component of the mixture and thus we can directly obtain the dependence of the concentration on the distance to the plate. The instrument optics must be adjusted as follows:

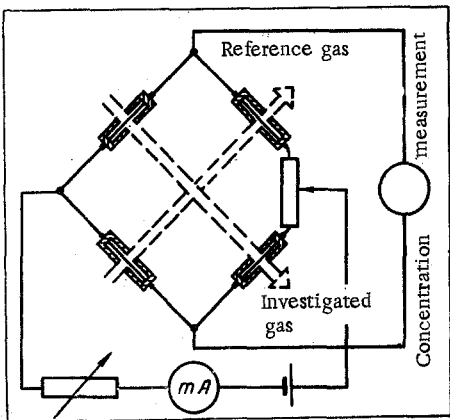


Fig. 7

a) The emission of the entire thickness of the boundary layer must fall on the spectrograph slit;

b) Not only the target plane but almost all points of the boundary layer irradiating the slit must be considered, as it were, located at infinity, which provides a basis for assuming that the width of the boundary layer, on the one hand, and the focal length of the lens, on the other, are small as compared with the distance from the lens to the boundary layer;

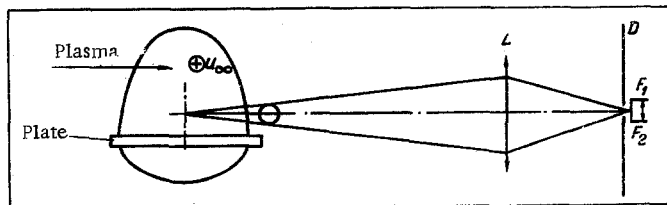


Fig. 8

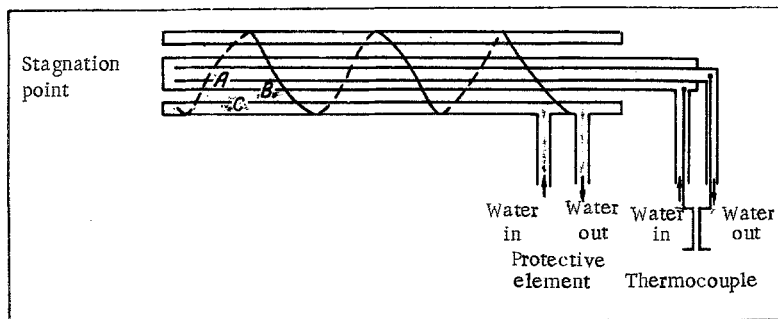


Fig. 9

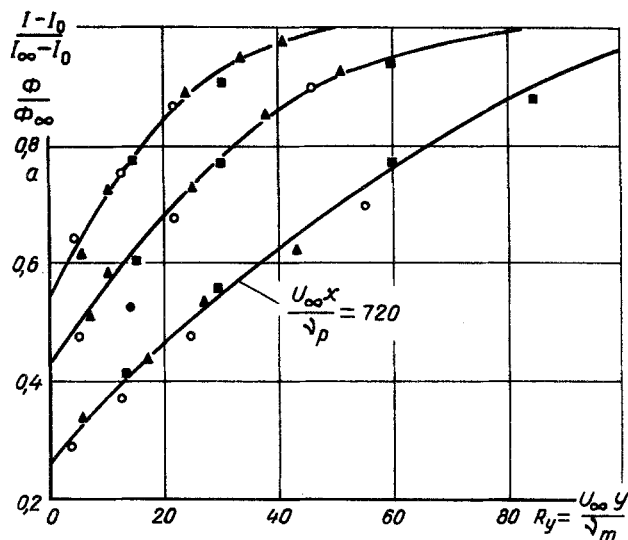


Fig. 10

c) Since the spectrograph integrates all the radiation from the boundary layer, the thickness of the boundary layer must be sufficiently large as compared with the zone disturbed by the edges of the wall.

This method is recommended, in particular, for investigating plasma [9]. It can be used to determine the distribution up to the wall and, moreover, the concentration of electrons, atoms, and ions in the boundary layer along plane walls.

The interpretation of the spectra is single valued if a boundary layer in the equilibrium state is involved. Instead of the optical spectrum it is possible to use a Raman spectrum or electron paramagnetic resonance.

4.2. Light Beam Absorption. This method is applicable to plane flows. A cylindrical light beam intersects the boundary layer parallel to the wall and perpendicular to the velocity. The diameter of the light beam is small as compared to the thickness of the boundary layer. If the i -th component of the gas mixture absorbs an optical or infrared band, the change of optical absorption is investigated as a function of the distance to the wall; this absorption is proportional to the concentration C of the i -th component. In this way, we obtain C_i as a function of y .

This method is less practical than the emission method, since the beam must remain perfectly parallel during the intersection of the boundary layer. As with the emission method, the intersection zone must be large enough to reduce the influence of edge effects. This method has been employed in the infrared region for measuring the concentration of the OH radical.

5. Probe Measurements

5.1. Photochemical Concentration Determination. I. Determination of Nitrogen Concentration. We have already mentioned the total reaction of atomic nitrogen and methane with the formation of the substance

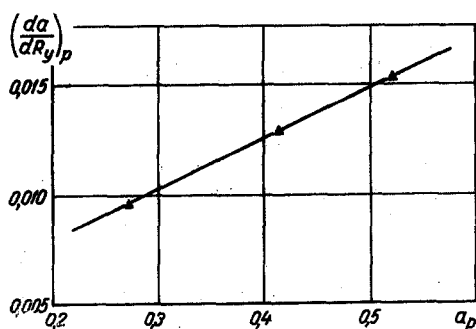


Fig. 11

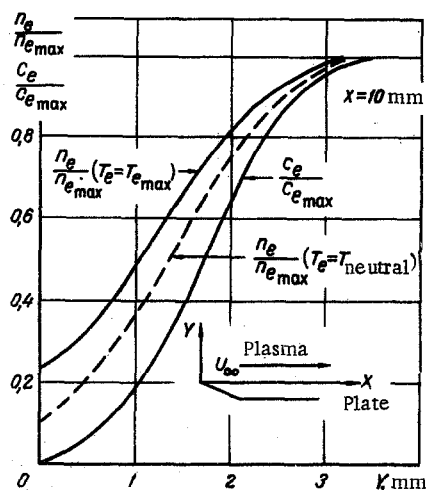


Fig. 12

HCN, whose molar concentration is proportional to the nitrogen concentration. This reaction causes luminescence and gives the CN lines a blue coloration [10]. If the CN concentration is high enough, the energy radiated during the reaction is proportional to the atomic nitrogen concentration [11].

The probe employed is a quartz tube with axis perpendicular to the wall through which the methane is supplied. In order to measure the luminous intensity of the reaction, an image of the region near the probe is received by a photomultiplier. The measurements will be accurate only if the fraction associated with the chemical reaction predominates in the radiation detected by the photomultiplier, in other words, the ratio of the intensity I obtained with injection to the intensity I_0 obtained without injection must be high. It can be taken ≈ 6 if the appropriate spectral region is selected. The relative molar concentration of atomic nitrogen is written thus:

$$\frac{C_N}{C_{N\infty}} = \frac{I - I_0}{I_\infty - I_0}, \quad (5)$$

where I_∞ and $I_{0\infty}$ are the intensities outside the boundary layer.

II. Determination of Oxygen Concentration. The addition of a small amount of nitric oxide NO to atomic oxygen gives a greenish-yellow luminescence as a result of the series of slow reactions



but the atomic oxygen quickly reacts with NO_2 according to the following scheme



as a result of which nitrogen peroxide is restored, i. e., in the presence of a small amount of nitric oxide the luminescence associated with the chemical reactions is proportional to the concentration of atomic oxygen. If the mixture is admitted to the tube after adding NO, then a decrease in luminous intensity is observed along the tube axis (x axis)

$$-\frac{dI}{dx} = -\frac{dC_0}{dx}. \quad (6)$$

In order to determine the absolute concentration C_0 of atomic oxygen at any point of the tube, it is sufficient to add nitrogen peroxide in an amount such that luminescence ceases at the point of admission. Then, in accordance with reaction (i), the molar concentration will be equal to the concentration of NO_2 , whose value is known, since the NO_2 flow rate is measured.

III. Determination of Hydrogen Concentration. In exactly the same way it is possible to measure the molar concentration of atomic hydrogen using nitric oxide in the slow reactions

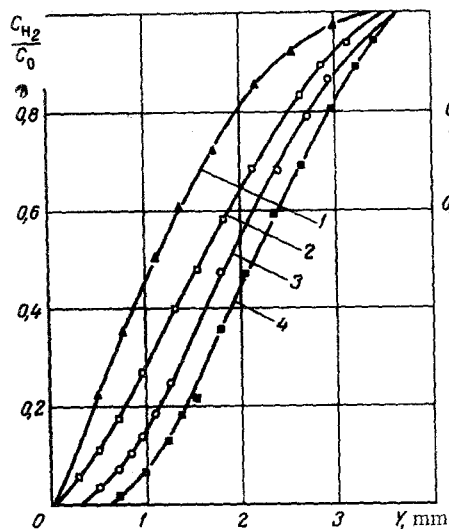


Fig. 13

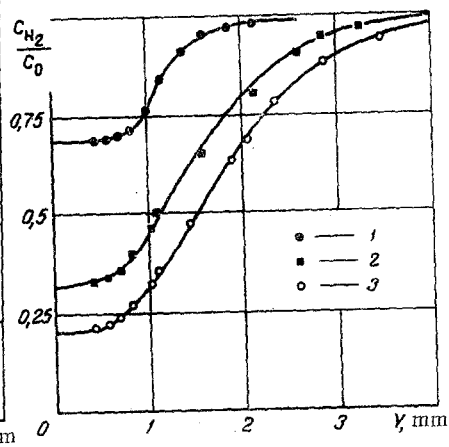


Fig. 14

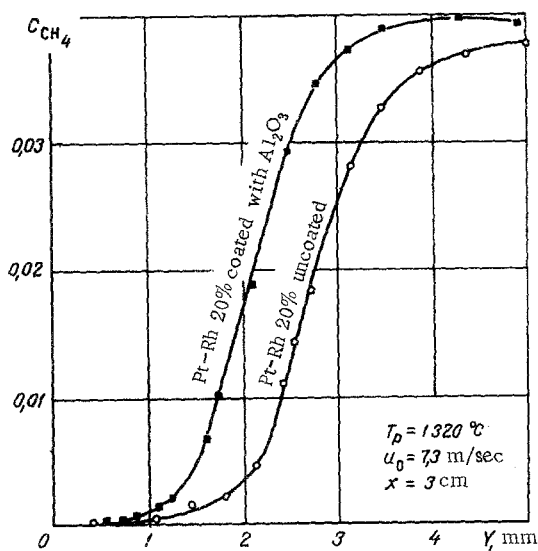
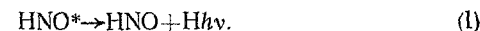
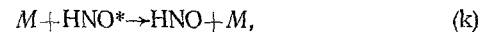
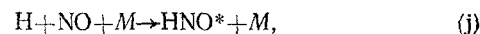
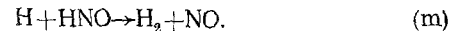


Fig. 15



These reactions are accompanied by red luminescence.

Thus, if the amount of nitric oxide is small, the reaction rate will be proportional to the molar concentration of atomic hydrogen, since nitric oxide is very rapidly restored in accordance with the scheme



5.2. Microcalorimetric Determination of Composition. With the aid of a microcalorimeter mounted in the flow it is possible to measure the amount of heat released in the course of a complete chemical reaction accompanied by total consumption of one of the components of the mixture [13]. We will investigate only the case of catalytic reactions. The probes employed are small,

which makes them most suitable for studying the boundary layer. Here we are concerned with systems in the nonequilibrium state [14, 15]. Even in this case the size of the probe is of great importance in connection with the possibility of using it in the immediate vicinity of the wall. The results of the microcalorimetric measurements coincide completely with data obtained by other methods. The principle of this technique can be briefly described as follows.

The energy of decomposition of nitrogen N_2 is liberated in the course of the recombination of N atoms. From the amount of heat released in the recombination reaction in a sample of the mixture at some point of the boundary layer it is possible to determine the atomic nitrogen concentration in the mixture. A sample can be obtained by means of an isokinetic probe. A certain amount of gas is blown through an annular tube, in which it transmits heat to water circulating in the tube. By measuring the rates of flow of the water and the injected gas and the inlet and outlet temperatures of the water it is possible to determine the heat flow through the walls of the annular tube. Obviously, it is also necessary to take into consideration the other heat-transfer components (heat conduction, radiation). A rarefied gas at high temperature cannot be injected into the probe owing to its high viscosity. Stagnation measurements can be made with this probe (Fig. 9).

5.3. Comparison of Methods. All three methods used by Lassau – sample analysis in a mass spectrograph, photochemical measurements, and microcalorimeter measurements – gave closely similar

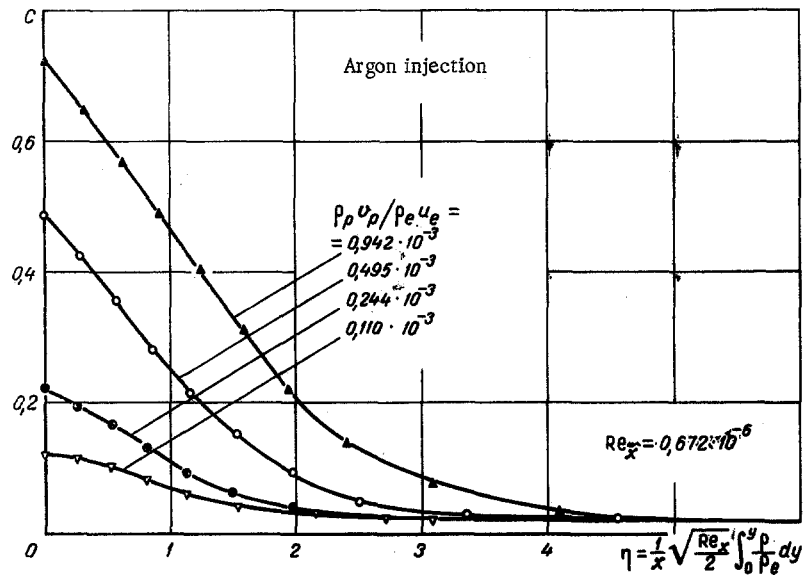


Fig. 16

results for the relative concentrations (see Fig. 11). The kinematic viscosity is calculated from the mean wall temperature (1200°C) and used to determine the Re number based on the distance to the wall. In the data presented in the graphs the temperature of the plate has been taken as the reference temperature. Mass spectrograph data are denoted by circles, photochemical data by squares, and calorimetric data by triangles.

In conclusion it should be noted that the relative concentration profiles can be determined experimentally with high accuracy.

6. Results and Their Application

6.1. Catalysis of a N + N₂ Mixture at a Wall. It follows from Fig. 10 that the concentration profiles are almost linear; this quasilinearity was predicted in the boundary layer calculations made in [16]. By extrapolating the profiles it is possible to determine the concentrations $a_p = (C_N/C_{N\infty})_p$ at the wall from the expression given in [17]. It should be noted that the mass flow at the wall $(da/dR_y)_p$ is proportional to the concentration at the wall a_p (Fig. 11), which confirms the conclusion that the atomic nitrogen dissipation reaction is a first-order reaction, as previously pointed out. In Fig. 14 the ordinates are the dimensionless number da/dR_y , where $R_y = u_\infty y / \nu_m$. From the known mass flux and the wall concentration we obtain a catalysis rate ~ 45 m/sec for a steel plate under experimental conditions.

6.2. Investigation of an Argon Plasma. In investigating an argon plasma [10] it was found possible to determine the concentration distribution profile over the thickness of the layer at a distance of 10 cm from the edge of the plate by measuring the luminous intensity (Fig. 12). The quantity $C_e/C_{e\max}$ is the electron concentration in the core, which was equal to $2 \cdot 10^{21}$ e/m³. The dashed curve corresponds to an electron temperature equal at any point to the neutral-atom temperature. The figure also includes the concentration profile when it is assumed that the electron temperature is equal to the neutron temperature.

6.3. Hydrogen Combustion. A platinum plate was placed in a wind tunnel parallel to the flow of a mixture of cold air and hydrogen at a low hydrogen content (on the interval 0.02–0.06) and a low velocity (~ 6.5 m/sec). The flow was laminar along the plate and as a result of the Joule effect had a temperature that fluctuated from 300 to 1500°C [18].

In Fig. 13 the relative molar percentage content has been plotted as a function of the distance to the wall. If the wall temperature is below 600°C (curve 1) ($u_0 = 6.5$ m/sec; $T_p = 500^\circ\text{C}$; $C_0 = 0.028$), the diffusion profile is determined as follows: hydrogen diffuses to the wall and burns only at the wall. This is catalytic combustion at a surface. Curves 3 ($u_0 = 6.5$ m/sec; $T_p = 920^\circ\text{C}$; $C_0 = 0.052$) and 4 ($u_0 = 6.5$ m/sec; $T_p = 1000^\circ\text{C}$; $C_0 = 0.052$), corresponding to the highest temperatures (of the order of 900°C), have a zero concentration gradient at the wall. This shows that the hydrogen is completely burned in the boundary layer. The intermediate process, in which some of the hydrogen burns in the boundary layer and the

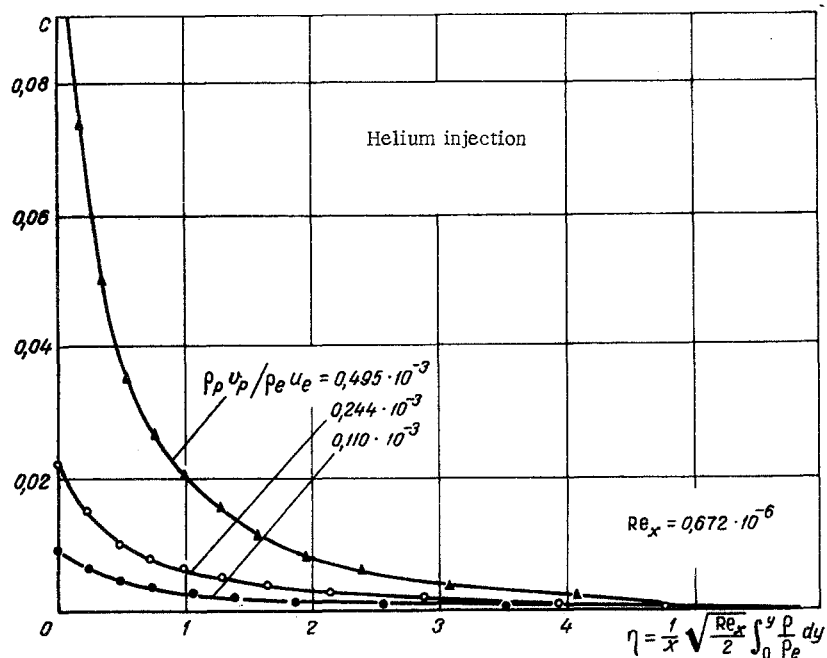


Fig. 17

rest at the surface of the plate, is illustrated by curve 2 ($u_0 = 6.5$ m/sec; $T_p = 880^\circ\text{C}$; $C_0 = 0.052$) corresponding to a temperature of 880°C . In all cases combustion was complete. If the wall is not catalytic (for example, a platinum plate coated with aluminum or gold), then a partial reaction in the boundary layer is not completed at the wall. The relative concentration profiles presented in Fig. 14 were obtained in various sections of the plate at a temperature $T_p = 800^\circ\text{C}$, a velocity $u_0 = 6.6$ m/sec, and an initial content $C_0 = 0.0185$ [1) $x = 2$ cm; 2) 3; 3) 3.5].

6.4. Methane Combustion. The results obtained for methane combustion in a boundary layer do not coincide with the data obtained for hydrogen combustion [18]. In addition to combustion in the homogeneous phase and catalytic concentration at the surface, it was found that there is catalytic combustion in the homogeneous phase, obviously caused by vaporization of the plate [19]. This is confirmed by the fact that the nature of combustion in the homogeneous phase depends on the plate material (Fig. 15). The temperature of the plate (1320°C) was such that the reaction was completed in the boundary layer irrespective of the plate material.

6.5. Wall Injection. It is important to investigate the concentration profiles in the boundary layer not only when a reaction takes place near the wall but also in the presence of sublimation, evaporation, ablation of the wall and wall injection. In this case the wall is the source of a component that diffuses through the main gas. An example is provided by experiments [20] on the injection of argon or helium through a flat plate into a supersonic air flow ($M = 5$). The thickness of the dynamic and diffusion boundary layers increases in the presence of argon injection from 1.5 to 2.5 at a mass-transfer parameter $\rho_p v_p / \rho_e u_e = 1.58 \cdot 10^{-3}$, while the thickness of the diffusion boundary layer changes from 1.2 to 1.6 for argon and from 1.5 to 2.5 for helium as the mass-transfer parameter varies from 0.11 to $0.495 \cdot 10^{-3}$ (Figs. 16, 17). It can be stated that at the same relative flow rate the thickness of the diffusion boundary layer is greater for helium than for argon injection and, conversely, at equal flow rates of the injected gas the concentration at the wall is lower for helium.

LITERATURE CITED

1. Lassau, *Chimie et Industrie, Genie Chimique*, 100, 7 (1968).
2. Le Goff, Cassuto, and Pentenero, *Industrie Chimique Belge*, No. 4 (1964).
3. Tine, *Agardograph* 47, Pergamon Press (1961).
4. Fristrom, Grunfelder, and Favin, *J. Phys. Chem.*, 65, 587 (1961).
5. Herron, Franklin, and Bradt, *Canad. J. Chem.*, 37, 539 (1959).
6. Fontijn, Rosner, and Kurzius, *Aerochem. Res. Lab.*, No. 8 (1962).

7. Blades and Winkler, *Canad. J. Chem.*, 29, 1022 (1951).
8. Stevenson, *Ion-Molecule Reactions*, McDowell (editor), McGraw-Hill (1963).
9. Valentin, Piar, and Lacase, *J. Phys.*, 29, No. 4, 3-44 (1968).
10. Young and Shappless, *J. Chem. Phys.*, 39, 4 (1963).
11. Van Tiggelen and Feugier, *Revue de l'I. F. P.*, 20, 7 (1965).
12. Melville and Gowenlock, *Experimental Methods in Gas Reactions*, MacMillan and Co. (1964), p. 248.
13. Au and Sprengel, *Z. Flugwiss.*, 14, 4 (1966).
14. Haenig, *ARS J.*, 29, 5 (1969).
15. Rosner, *AIAA J.*, 2, 4 (1964).
16. Lassau, *C.R. Acad. Sci.*, 261, 4617 (1965).
17. Valentin, *Annales Phys.* (1961).
18. Cabannes and Valentin, *Bulletin de la Societe Chimique de France*, 166 (1962).
19. Devore, Eyraud, and Prettre, *C.R. Acad. Sci.*, 248, 1227 (1958); 248, 2345 (1959).
20. Cornil, *C.R. Acad. Sci.*, *Seance du 16 Juillet* (1969).