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FINAL SCIENTIFIC REPORT

Experimental and Theoretical Study of Chemiluminescence in Flames and of Combustion in Solid Propellants

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This research has been sponsored in part by the AIR FORCE OFFICE OF SCIENTIFIC RESEARCH (SREP) through the European Office of Aerospace Research, O.A.R., United States Air Force, under Contract F 61052 — 70 — C — 0016.

Firme L. Wouters
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ABSTRACT

The two parts of the report deal successively with chemiluminescence in flames and with combustion of solid propellants.

1) Relationships between chemiluminescence (CL) and chemi-ionization (CI) on one hand, and the molecular structure of the fuel on the other hand have been put forward, in particular the structure of hydrocarbon fuels has been investigated. The importance of the formation of "energy rich bonds" during the C.L. and C.I. processes has been pointed out not only with hydrocarbon fuels but also with cyanogen and ammonia, where the formation of N-O bond plays an essential role.

2) Applying the multimicrojet burner technique for the simulating study of heat transfer from the reaction zone onto the regressing surface of solid propellants, it has been possible to investigate the dependence of the heat release on parameters such as total flow, distribution modes of gases, dilution and richness of the flammable mixture and to correlate the heat release in function of the burning velocity alone. Moreover, a new reliable technique to prepare "cigarettes" of PMM for hybrid combustion has been developped where one can get rid of any trace of acetone, and where heat losses to the wall of the tube are avoided during the burning process. Mass burning rates of PMM with N_2O and O_2 have been recorded, and the porosity of the sample has been studied.

PART ONE

CHEMILUMINESCENCE AND CHEMI-IONIZATION IN FLAME SYSTEMS

Introduction

The high concentration in excited and ionized species in the flame reaction zone is one of the most striking facts which characterizes the non-equilibrium state prevailing in burning systems. Most approaches of this problem so far have been concerned with experiments carried out at low pressure regime (1, 2). On the contrary, at Louvain, large efforts have been done in order to work with flames burning at atmospheric pressures (3, 4), and extensive use has been made of overall properties such as burning velocity, flame temperature, chemi-ionization rate, ion yield, intensities of band emission, quantum yields of excited species, and mass spectrometric identification of the ions in flames.

This part of the report deals successively with three different approaches to the chemiluminescence (CL) and chemi-ionization (CI) phenomena for flames burning in various mixtures of gaseous fuels and oxygen :

1. - **Intensities of CH-, C_2- and OH-band emission as well as saturation currents of methane-oxygen flames diluted with nitrogen have been recorded in order to study in details the processes responsible for the chemiluminescence and chemi-ionization phenomena induced by methane.**

2. - **Comparison of the same data among several hydrocarbon (paraffinic, olefinic, etc) fuels have been made when hydrocarbons in traces are added to a "basic" flame burning in a slightly rich mixture of hydrogen-oxygen and nitrogen.**

3. - **Less encountered fuels containing (a) nitrogen atom(s) indic**

a peculiar behaviour. The ion yield in those flames is extremely variable depending on the atom to which the nitrogen is bound e.g. traces of cyanogen or ammonia in the same "basic" flame show essential differences by which excited- and primary ions are produced.

Before discussing separately each of these questions, a brief survey of the experimental technique employed and of data reduction will be given now.

All measurements are performed on a Powling-Egerton type of burner consisting of a bundle of 212 inconel minitubes., 4mm in diameter and 16 cm long. These minitubes are set inside an inconel tube with an inner diameter of .78 cm. Flames stabilized on such a burner can be viewed as macroscopically flat. The flame area is then equal to the burner area S. The burning velocities V_o are obtained from the literature (^{5}) and the total gas flow is adjusted accordingly. however slight corrections have to be done to avoid quenching or blow-off effects. One takes so into account the non-adiabatic character when the flame front is too close to the burner surface. The total flow D is therefore equal to k S V_o with k adjusted in such a way to get the maximum ion and quantum yields (for all mixtures so far, k ~ 1.2). Each gas flow of the mixture is monitored by the method of shocked flow using sonic nozzles. But, the components occuring in small quantities, for example, those used as traces added to the basic flammable mixture have been monitored by a different technique. A long narrow pyrex tube with a precisely known volume between two marks is traversed by mercury plug which are moving under the influence of the pushing gas. The transit time is carefully recorded providing us with an excellent measure for gas flow of the order of a few cm^3/s. The burner is mounted so that the flame surface is normal to the optical axis of the entrance path of the spectrometer. The spectra is ana lyzed by a grating in quartz, detected by a 1 P 28 photomultiplier (sensitive from 2800 Å to 7000 Å) and recorded on a Leeds-Northrup Speedomax.

Besides, a potential difference is applied between the burner itself (cathode) and a water-cooled anode in brass, located parallel to the burner at a distance of about . 5 cm. Since the anode is easily removable, it allows the measurement of chemi-ionization and band intensities keeping the flame position and geometry identical. The voltage applied to the electrode can vary between 0 and 3 kv. When an electric field is applied to the flame, the ions and electrons are drifting in opposite directions. In this geometry, the ions migrate to the burner and the electrons to the anode. This migration-process competes with the ion-recombination and when the voltage is sufficiently high all ions and electrons are collected on the electrodes. It corresponds then to a current i_s which doesn't vary anymore with the potential difference, this value of the current is known as the saturation current and does mean that all of the ions produced initially in the reaction zone are removed from it.

The saturation current i_s is therefore a measure of the number of ions produced per unit time in the flame front and it is directly related to the primary chemi-ionization rate V_f as follows :

$$V_f = \frac{i_s}{\varepsilon . S\, e_i} \qquad (1)$$

with ε the elementary charge of an electron and e_i the thickness of the region where the chemi-ionization takes place.

Another interesting parameter describing the chemi-ionization is of course, the ion yield : it is defined as the ratio of the number of ions created to the number of fuel molecules able to induce ionization in the flame. It can be expressed as a function of measurable quanti-

$$\eta_+ = \frac{i_s}{\varepsilon . D_B} \qquad (2)$$

with D_B the flow of fuel in molecules per second.

The ion yield represents also the ratio between the overall chemi-ionization rate and the overall burning rate V_e, when the thickness e_i of the chemi-ionization is directly proportional to the flame front thickness e_o. This has been proved to be correct by WORTBERG (6):

$$\eta_+ = \frac{V_f}{V_e} \qquad (3)$$

In a similar way, from emission spectroscopic data, the band intensities are proportional to the concentration in excited molecules (M^*). The overall chemiluminescence rate $V_{f_{M^*}}$ sounds then :

$$V_{f_{M^*}} = \frac{I_{M^+}}{e_{M^*} . S} = K \frac{(M^*)}{\tau_{M^*}} \qquad (4)$$

where I_{M^*} is the photomultiplier current proportional to the number of photons emitted per unit time in a sone e_{M^*} thick, and τ_{M^*} represents the radiative lifetime of the excited species.

Taking into account as main deactivation processes those by collisions (valid for sure at atmospheric pressures) and assuming a steady state regime for the excited species in the flame front, one derives

$$V_{f_{M^*}} = K' (k_d \frac{n I_M}{e_{M^*}}) \qquad (5)$$

All temperature independent parameters have been gathered in K'. k_d is the deactivation rate constant proportional to $\sqrt{T}$ and n the overa number of molecules per unit volume.

Besides, by definition the quantum yield for the species M^x is :

$$\Phi_{M^*} = \frac{I_{M^*}}{D_B} \qquad (6)$$

when there is equivalence between e_o and e_{M^*}, the quantum yield is also given as a function of the combustion and the chemiluminescence rates as

$$\Phi_{M^*} = K'' \sqrt{T} \; \frac{V_{f_{M^*}}}{V_e} \qquad (7)$$

All equations (1) through (7) are quite general and can be applied to any kind of premixed flames. However, it is worth to discuss in some details flames for which ionization and (or) band emission are induced by small traces of a definite compound in the fresh gases. Provided the additive concentration remains small (less then a per cent of the total volume of the burning mixture) the basic parameters of the flames do not vary : burning velocity and flame temperature remain practically unaltered. But, the slight emission and saturation current are very sensitive even to the smallest amount of specific molecules. This is particularly true when traces of carbon containing molecules are added to burning mixtures such as $CO/O_2/N_2$ or $H_2/O_2/N_2$.

The ion concentration in hydrogen- or carbon monoxide-flames without additives is extremely weak, of the order of 10^{+8} ions/cm^3. Furthermore, for both systems the emitted spectra are very simple : they exhibit either a continuum (CO) or almost uniquely the OH ultraviolet bands (H_2). But, the slightest traces of carbon- or nitrogen containing molecules modify, in a noticeable way, the flame spectrum due to the presence of specific band emissions (CH, NH, CN for instance). At the same time when the spectrum changes, the number of ions generated in the flame increases largely, although the other parameters vary in a much lesser extent.

It is easy to gather information about the "order" dependence of ionic or excited species formation with respect to the additive concentration, by plotting the saturation current or the band emission intensities versus the percentage of traces added. The "order" is intimately related to the number of trace molecules required to build up either the primary ion or the excited species under consideration.

However, if the reactant responsible for chemiluminescence or chemi-ionization in flame is the main fuel, the rate V_f , $V_{f_{M^*}}$ and V_e can be written, at least formally, as follows :

$$V_f = k_f (B)^x . (A)^y e^{-E_i/RT_m} \quad (8a)$$

$$V_{f_{M^*}} = k_{f_{M^*}} (B)^{x^*} . (A)^{y^*} e^{-E_{M^*}/RT_m} \quad (8b)$$

$$V_e = k_e (B)^{x'} . (A)^{y'} e^{-E_e/RT_m} \quad (8c)$$

The exponents are the apparent partial orders with respect to the fuel (B) and to the oxidizer (A) of the rates of ion production (x, y), of excited species M^* formation (x^* , y^*) and of combustion (x' , y'), accordingly. The corresponding overall activation energies are E_i , E_{M^*} and E_e.

The mean temperature T_m of the flame reaction zone has been deduced previously (^{5}) and is approximated to

$$T_m = T_i + 0.74 (T_f - T_i) \quad (9)$$

with T_i fresh gases temperature and T_f the flame temperature.

Likewise, if all thicknesses e_i , e^* and e_o are proportional they can be estimated along the line described elsewhere (^{7}) in terms of the schlieren thickness e_s of the flame front as follows :

$$e_s = e_o \left(\frac{1}{2} + \frac{\pi}{4} \ln \frac{T_m - T_i}{T_i} \right) \quad (10)$$

At least, in the model of a homogeneous reactor representing the flame front, an equation relating V_o , e_o and T_m appears :

$$\frac{V_o}{\sqrt{T_m}} = \frac{Cst}{e_o} \qquad (11)$$

From the equations (8) to (11), the overall activation energy for every process either chemi-ionization or excited species formation or combustion is deduced immediately by plotting the appropriate logarithm versus the reciprocal temperature :

$$\ln \frac{i_s V_o T_m^{(x+y-1)}}{X_B^{x+y}} \qquad \text{for } E_i \qquad (12a)$$

$$\ln \frac{I_{M^*} V_o T_m^{(x^*+y^*-\frac{3}{2})}}{X_B^{x^*+y^*}} \qquad \text{for } E_{M^*} \qquad (12b)$$

and

$$\ln \frac{V_o^2 T_m}{X_B} \qquad \text{for } E_e \text{ when } x' + y' = 2 \qquad (12c)$$

The sums $(x+y)$ and $x^* + y^*)$ are usually close to two.

In a similar way, by applying the equations (9), (10) and (11) to flames where traces of a specific molecule are added to a flammable mixture and if the sums of the partial orders with respect to the fuel and to the oxidizer are identical for combustion, chemi-ionization and chemiluminescence, one derives :

$$\Delta E_i \text{ from } \ln \eta_+ \text{ vs. } 1/T_m \qquad (12d)$$

$$\Delta E_{M^*} \text{ from } \ln \frac{\Phi_{M^*}}{\sqrt{T_m}}, \text{ vs. } 1/T_m \qquad (12e)$$

The "order" dependences and the overall activation energies are generally coupled with mass spectroscopic data which provide us with the nature of the ions, the position of maximum concentration for individual ionic species, their concentration dependence with respect to the initial conditions and also the recombination rates of ions (8, 9, 10). One can put forward, thus, some mechanism responsible for the formation of ions and excited species in agreement with all those experimental results. It is worth to point out here that the mechanism of CL and CI is not necessarily identical in pure flames of a given fuel and in "basic" flames with small traces of the fuel added, although the primary chemi-ionization reaction remains very often unchanged.

Section I

PURE HYDROCARBON FLAMES

(with the collaboration of J. F. LAMBERT)

In order to attempt to present a scheme responsible for the chemiluminescence and chemi-ionization in hydrocarbon flames, it has been choosen to begin with the simplest one : the methane and then to extend the measurements to more complex hydrocarbon fuels. The measurements obtained so far have been extended to the largest range possible for richness and dilution. The relative intensities of the OH, CH and C_2-band emissions are displayed on figures 1, 2 and 3 respectively. Data are presented as a function of the equivalence ratio φ and each curve corresponds to the dilution percentage in nitrogen. The equivalence ratio is defined here as the ratio of the fuel concentration to the oxidizer in the actual mixture, to the same ratio in a stoichiometric mixture.

A direct comparison of intensities measured for different emitters doesn't allow to draw definite conclusions about the eventual relationship among the excited species. However, it is interesting to point out from the evolution of intensities with φ at several dilutions that

- the maximum intensities of the different emitters do not coincide with each other,
- the region of more rapid variation of C_2-band intensity with φ corresponds to a maximum in CH emission
- and the more rapid variation of CH intensity is reached in a region of equivalence ratio where the OH emission maximizes i.e. around the stoichiometry.

Finally, even for the richest mixture studied so far ($\varphi = 1.3$) the maximum of C_2-band emission is not observed. A much easier comparison is gained from the fig. 4 where the logarithms of saturation currents and intensities of band emissions are simultaneously presented as a function of φ. None of the emissions does follow precisely the evolution of i_s which has been taken from the literature (4).

Considering the ratios of the current or emissions intensities as a function of the dilution (α), some quantitative indications can be deduced about the relative values of the overall apparent activation energies for C.L. and C.I. processes. An increase of I_{OH}/i_s is always observed for any mixtures with increasing dilution, but the ratios I_{CH}/i_s and I_{CH}/I_{C_2} evolve differently with nitrogen dilution in rich or in lean mixtures. At last, the increase of I_{CH}/I_{OH} with α is particularly rapid in rich mixture. The data presented on figures 1, 2 and 3 have been processed to get the precise overall activation energies by following the method described briefly in the introduction, but applied to pure flames. The differences ΔE of activation energies of either CL or CI process with the combustion are measured from the slope of the logarithmic plot of either Φ^* or η_+ as a function of the reciprocal temperature. Fig. 5 exemplifies the results for CH emission.

TABLE I

φ	R	CH		C_2		OH		ions	
		ΔE^*	E^*	ΔE^*	E^*	ΔE^*	E^*	ΔE_+	E_+
0.439	0.18	28.4	-	-	-	-	-	-	-
0.532	0.21	25	67.4	-	-	39.9	82.3	31.9	70.6
0.632	0.24	30.7	72.5	-	-	42.9	84.8	29.7	67.6
0.740	0.27	27.0	70.5	-	-	39.5	82.9	28.7	69.9
0.857	0.30	23.0	68.5	41.0	-	41.0	85.9	29.8	77.0
1.000	0.33	18.2	65.5	15.6	-	36.3	83.9	30.0	83.4
1.125	0.36	15.9	62.7	4.1	-	35.3	82.1	26.8	77.5
1.279	0.39	-	55.8	-	-	-	-	24.3	67.0

All results are summarized on Table I where E^* refers to the overall activation energy of the corresponding process. In lean mixtures the values of ΔE in kcal/mole are fairly constant : 30 for ions, 41 for OH^* and 26 for CH^*. For rich mixtures, there is a systematic decrease for any process and the C_2-emission, mainly detected in rich flames, indicates this tendency very strongly. A similar behaviour (variable activation energy) in rich mixtures has already been observed by BURKE and VAN TIGGELEN (11) in their study of the burning mechanism of methane. No definite activation energy could be ascribed to the burning process in rich flames. This similarity is due to the influence of a specific mechanism, more probably pyrolysis processes of the hydrocarbon which then parallels the combustion phenomena. Of course, they are of great importance in the formation of C_2 excited molecules which requires at least a collision of two non-oxidized fragments (CH, C or CH_2) from the original molecule.

Another interesting feature about the emission of the OH excited radical is the equality of the quantum yields Φ_{OH} for mixtures with different equivalence ratio, provided the temperatures are identical. This fact becomes evident from the outlook of a plot similar to fig. 5, but relative to the OH band emission, where almost all data are on the same straight line regardless the value of φ. One gets for instance $\ln \Phi_{OH} = -2.0$ at $T_m = 2000\,^\circ K$. The slight dependence of Φ_{OH} upon the richness of the mixture appears also clearly on figure 6 which presents the log Φ as a function of the logarithm of the ratio of oxygen to methane in the mixture at a mean temperature. The slope gives the difference (b-n) of the partial orders of combustion (b) and chemiluminescence (n) with respect to the methane concentration, at T_m = $2000\,^\circ K$. The behaviour of OH emission can be explained only if, at least one of the main reaction mechanism for OH^* production is intimately related to the combustion process in the flame front. One can suggest for example the following scheme :

	ΔH (kcal/mole)	
$CH_4 + OH \longrightarrow CH_3 + H_2O$	- 16	(11-1)
$CH_3 + O_2 \longrightarrow CH_2O + OH$	- 52	(11-2)
$H_2CO + OH \longrightarrow CHO + H_2O$	- 42	(11-3)
$CHO + O_2 \longrightarrow CO_2 + OH^*$	+ 12	(11-4)

The direct precursor of the excited OH radical would be then the formyl radical which is well known to be involved in the chain mechanism of burning for hydrocarbon fuels. Furthermore, such a sequence of reactions corresponds to the overall stoichiometry of the combustion and finally, the measured activation energy ΔE_{OH} could agree with a slightly endothermic process.

The dependence of Φ_{C_2} and Φ_{CH} upon the ratio $(O_2)/(CH_4)$ has to be put in parallel with the variation of activation energies with the richness of the mixture. It indicates also that the C_2- and CH-chemiluminescence are not directly connected with the burning mechanism. In order to know these processes in more details, it will be necessary to investigate the pressure effects and to use hydrogen-oxygen flames seeded with methane. Any change in the equivalence ratio of the basic hydrogen-oxygen flames induces radical concentration modifications, keeping the CH_4 concentration constant. Some reactions will be therefore enhanced and some other favoured.

The preliminary results gathered on the propane flames show a similar trend as the one observed for CL and CI processes in methane.

Section II

INDUCED CHEMI-IONIZATION AND CHEMILUMINESCENCE BY HYDROCARBONS IN HYDROGEN-OXYGEN-NITROGEN FLAMES

(with the collaboration of Dr. J. PEETERS and P. HERTOGHE)

The study of the CL intensities and of the CI rates in hydrogen-oxygen flames to which small but variable quantities of different hydrocarbons are added represents a versatile approach to throw some light on the CH^* and C_2^* formations and on their eventual relationship with the primary ion formation. Such a trace technique has the outstanding advantage to compare the different hydrocarbons in the same kinetic surroundings. The temperature, the concentrations of the chain carrier radicals in the "basic" hydrogen-oxygen-nitrogen flames are indeed not significantly affected by addition of hydrocarbon fuels in small quantities : for instance, if 1 % in carbon content of hydrocarbon is supplied to the "basic" flame, the variation in burning velocity remains less than 5 %. Therefore, using a trace technique allows to evaluate the contribution of a specific molecule to the chemi-ionization and chemiluminescence phenomena, independently on the burning mechanism itself as long as the characteristics of the "basic" flame are not changed by the amount of additive.

Recent results of CH- and C_2-band intensities for n-butane traces in hydrogen-oxygen flame with variable dilution in nitrogen are displayed on fig. 7 and 8, respectively. The C_2 emission is more sensitive than the CH emission to the amount of butane added. doubling the percentage of butane increases C_2 emission by a factor 4 to 5 and CH emission by a factor 2-3. But, another interesting feature is the composition between both isomers of butane for which the CI and CL intensities are presented on fig. 9a where squares correspond to n.butane and circles to isobutane. As a general remark, intensities and in particular CH and C_2 emission are larger for iso butane. This tends to indicate that the several functions CH_3, CH_2 and CH of the added molecules contribute unevenly to CI and CL processes, although they are, in first approximation, function of the number of carbon atoms in the investigated molecule.

Some preliminary results in a H_2/O_2 flame 60 % N_2 diluted have been presented last August at the thirteenth International Symposium on Combustion(12) and will be published in the proceedings of this meeting in a very near future. Three copies of the manuscript have been forwarded to EOAR in March 70. The experimental observations are summarized now.

The order dependences with respect to the initial hydrocarbon concentration are successively :

- first order for the saturation currents
- second order for the C_2^* band intensities
- first and second order for the CH^* band intensities.

Fig. 9b shows quite clearly these dependences for propane. This becomes also evident from the straight line on fig. 9c where the ratio of $I(C_2^*)/i_s^2$ is plotted against the amount of acetylene added to the "basic" flame.

On fig. 10, a comparison of the C_2-band emission intensities has been done among several hydrocarbons for a 60 % nitrogen diluted H_2/O_2 flame. The nature of the fuel seems to play a very important role on this band emission. From these data and similar ones for CH emission and saturation currents, one does notice that the ratio $I_2(CH^*)/I(C_2^*)$, where $I_2(CH^*)$ stands for the second order component of the CH^* band intensities, remains constant (1.2 ± 0.25) for all eight fuels of fig. 10. But, the ratio $I(C_2^*)/i_s^2$ for the same fuels varies regularly, e.g. in the case of neopentane it is 25 times larger than of methane. Finally, $I_1(CH^*)/i_s$ is not constant either, which means that several processes depending on the initial structure can be responsible for the formation of CH ground state. The preliminary results reported just above allow to conclude that

1. in a first approximation the original C-C bonds do not persist
2. the reaction

$$C_2 + OH \longrightarrow CH^* + CO \qquad (12\text{-}1)$$

proposed by PANNETIER and GAYDON (13) and checked in great details by BULEWICZ et alii (14) for low pressure acetylene-oxygen flames, plays a role in CH chemiluminescence for any hydrocarbon fuels. On the other hand but to a smaller extent the reaction

$$C_2H + O \longrightarrow CH^* + CO \qquad (12\text{-}2)$$

suggested by HAND and KISTIAKOWSKY (15) could also contribute to CH^* band emission.

It has been shown moreover that the reaction

$$2\,CH \longrightarrow C_2^* + H_2 \qquad (12\text{-}3)$$

proposed by FERGUSON (16) doesn't agree at all with the data. Rather, reactions involving carbon atoms such as the one observed in diffusion flames by NAEGLI and PALMER (17)

$$C + CH \longrightarrow C_2^* + H \qquad (12\text{-}4)$$

has to be taken into account.

Afterwards, new results have shown a linear relation between the ion yield and the number of carbon atoms present in the studied fuel. As it appears from fig. 11, slight corrections have yet to be applied in order to take into account the effect of the molecular structure of the hydrocarbon. This last effect is however less important for ion generation than for excitation of radical species. Such a

TABLE II

Activation energies (Kcal/mole)

Fuel	$\Delta E_1(C_2^*)$	$\Delta E_2(C_2^*)$	$\Delta E_1(CH^*)$	$\Delta E_2(CH^*)$	ΔE_+
methane	-	22.0	9.4	15.6	8.7
ethane	-	17.5	14.4	19.9	9.7
propane	20.0	25.8	19.4	24.6	12.7
iso-butane	20.9	26.0	22.4	29.3	12.4
n-butane	18.5	24.3	20.7	26.3	14.7
neo-pentane	19.8	26.0	18.3	24.9	11.4
cyclopropane	17.7	23.4	20.6	26.9	10.7
ethylene	12.5	18.5	7.6	13.2	10.7
propylene	24.3	29.8	19.6	24.3	14.5
cis-butene 2	28.1	34.1	24.0	30.7	14.5
trans-butene 2	31.4	37.2	26.3	32.4	15.1

linear function between ion yield and number of carbon atoms involved in the fuel was already proposed by BULEWICZ ([18]) in the case of low pressure flames, but her conclusion was based upon measurements of the maximum electrons concentration. Our data presented on fig. 11, however, are related directly to the ratio of the rate of chemi-ionization to the rate of consumption of fuel through the burning process. Therefore the parameter η_+ describes precisely the ion yield i.e. the number of ionic species created per fuel molecule burnt, and this irrespective to any thickness of the reaction zone.

The next step in the investigation about CL and CI phenomena will be to determine with accuracy the influence of the initial structure of the fuel concerned. An extensive series of measurements as those presented on fig. 7 and 8, combined with the corresponding for chemi-ionization rates are now under progress. The data reduction of some recent measurements has already been made. It has been noticed that it exists a small contribution to the C_2^* emission, first order with respect to the hydrocarbon concentration. It is specially valid for hydrocarbon fuels with a large number of carbon atoms. It means thus some kind of persistence of the original C-C bonds in the formation of the excited C_2 molecule, which could be called an "hysteresis effect" of the structure in the CL process. Some activation energies of the C_2 and CH quantum yields for both first and second order processes are gathered in table II. It is worth to point out the very low activation energy of the C_2 quantum yield (first order) of cyclopropane. This compound exhibits indeed an extremely intense C_2 band emission and exemplifies particularly well the so-called "hysteresis effect" of the hydrocarbon structure.

Before reaching some definite conclusions about the comparison of CI and CL processes in several hydrocarbon fuels still more data are required. Furthermore, a detailed analysis of the acetylene behaviour will be also undertaken in the future.

Section III

FLAMES SEEDED WITH MOLECULES CONTAINING NITROGEN ATOMS

(with the collaboration of Dr. C. VINCKIER,
MM. Cl. BERTRAND and M. BREDO)

By going through the literature, one does notice immediately the large efforts devoted to the study of CL and CI occurrence in flame systems when one of the reactants is a molecule with one or more carbon atoms. At the opposite, very few observations (19), (20), (21) deal with nitrogen containing molecules burning at atmospheric pressure. A part of the program on CI and CL phenomena has been initiated toward the explanations of the various and specific effects encountered when nitrogen is involved either as fuel or as oxidizer.

A detailed analysis of the primary and secondary chemi-ionization processes induced by cyanogen in carbon monoxide-oxygen-nitrogen flames has been reported already at the thirteenth Symposium on Combustion. Three copies of the manuscript (22) have been forwarded to the EOAR Office in March 70.

Flames burning in mixtures containing cyanogen are characterized by high saturation currents and by intense red and violet CN band emissions. Ion yields (i.e. number of ions created per molecule of cyanogen) amount to 10^{-5} which is about an order of magnitude larger than for methane. The measurements of CI and CL induced by cyanogen in $CO/O_2/N_2$ flames exhibit moreover order dependences on cyanogen concentration of 1.2 for saturation currents and of 1.0 for the CN-violet band intensities. Besides, in carbon monoxide flames seeded with cyanogen traces, the CN^* band intensity and the saturation current are depending also on the total equivalence ratio of the burning mixture, but their ratio $i_+/I(CN^*)$ is a constant over a wide range of φ values (from 0.6 to 1.2). From the above it means that formation processes for primary ions and CN excited radicals are related to each other. The following elementary reactions

$$CN + O + O \longrightarrow CO + NO^{+} + e^{-} \qquad (13\text{-}1)$$
$$CN + O + O \longrightarrow CN^{*} + O_2 \qquad (13\text{-}2)$$

could be responsible for. They are actually two different reaction paths for the same collision partners.

Furthermore, some recent results have been obtained at different dilution percentages in nitrogen. They allow to calculate the difference ΔE_{+} of activation energies between CI and combustion in $CO/O_2/N_2$ flames seeded with cyanogen traces. The quantity ΔE_{+} amounts to 12 Kcal/mole if the sumsof partial orders are identical for CI and combustion processes, or to 6 Kcal/mole if the overall order of CI is one unit larger than the corresponding order for combustion. The computation of activation energy for CN^{*} band emission (or its difference with the combustion process) is uneasy due to the blurring effect of the CO-continuum. The accurate discrimination between violet band and the CO-continuum emissions is difficult since both are varying simultaneously with the temperature. Therefore, we have turned our efforts toward an other type of "basic flame", i.e. flames burning in hydrogen-oxygen-nitrogen mixtures ($\varphi = 1.1$ and with variable dilution). The comparison of both "basic flames" emphasizes the following striking feature : the order of magnitude for ion yields are identical, eventhough other parameters do vary largely (cf. Table III), in particular the nature of the ions as it appears from their identification by mass spectrometric measurements.

As it was shown previously (22), NO^{+} and CO^{+} have to be reckoned as primary ions. So, two distinct processes were assumed to take part in the generation of NO^{+} and CO^{+} :

TABLE III

CYANOGEN

	H_2/O_2 flames	CO/O_2 flames
η_+ $T_m \sim 1500^oK$	1.1 10^{-5} (50 % N_2)	1.6 10^{-5} (25 % $N_2$0
n_+	1	1
ΔE_+ (Kcal/mole)	30.0	12.0
n_{CH^*}	1	1.2
% of most abundant ions	NO^+(80) ; $NH_4{}^+$(15) ; H_3O^+(5)	NO^+(98) ; CO^+(1.5) ; $O_3{}^+$ (.5)

n_+ : partial order of saturation current with respect to the initial concentration in cyanogen.

ΔE_+ : difference in activation energies for CI and combustion processes. Overall orders have been assumed identical.

n_{CN^*} : partial order of CN-violet band intensity with respect to the initial concentration in cyanogen.

$$CN + O + O \longrightarrow CO + NO^+ + e^- \qquad (13\text{-}1)$$

$$CN^* + O + O \longrightarrow CO^+ + NO + e^- \qquad (13\text{-}3)$$

The complete absence of CO^+ in hydrogen-oxygen flames rules out the second process and it leaves the NO^+ as unique primary ion. However the large difference in ΔE_+ encountered in CO- and H_2-flames, forces to give up the reaction (13-1), since the increment of activation energy due to the (O) atom formation required in process (13-1) could not be responsible for a 18 Kcal/mole difference in ΔE_+. Moreover, the high ion yield seems to indicate that the chemi-ionization has to be very efficient, so that a bimolecular step responsible for the primary ion generation would be plausible. The elementary reaction

$$CN^* + O_2 \longrightarrow CO + NO^+ \qquad (13\text{-}4)$$

is endothermic for about 24 Kcal/mole which, indeed, doesn't disagree with the value of ΔE_+ computed from the experimental data. However, to ascertain the chemi-ionization reaction more data are necessary, for instance the dependence of CI on the overall pressure, the simultaneous change of CI and CL with variation of the equivalence ratio of the "basic flame", the occurrence of NO^* emission and its contingent connection with CI.

Besides the cyanogen, experiments on CL and CI of nitrogen-containing compound have been carried on this study with ammonia. New characteristic features in the CI rate and in the spectra emitted can be expected as a consequence of the lack of carbon atoms in the system. All measurements have been [illegible] out with flames burning in hydrogen-oxygen mixtures diluted in nitrogen, since the slightest traces of molecules containing one of more hydrogen atoms influence too much the burning process of a carbon monoxide-oxygen flame. The ion yield recorded in $H_2/O_2/N_2 + NH_3$ traces is extremely small as compared with the one obtained with cyanogen traces.

TABLE IV

Basic flame : H_2-O_2

R = 0. 69 ; variable dilution

	$(CN)_2$	NH_3
η_+	$\sim 10^{-5}$	$\sim 10^{-8}$
n_+	1	1
n_{NH^*}	1	1
n_{CN^*}	1	-
n_{HNO^*}	1	-
ΔE_+ (Kcal/mole)	30	22. 6
ΔE_{NH^*} (Kcal/mole)	-	13. 1
% most abundant ions	NO^+ (80), NH_4^+ (15) , H_3O^+ (5).	NO^+ (80) H_3O^+ (20)

$(\eta_{+(CN)_2}/\eta_{+(NH_3)}$ from 100 to 1000)

Some data are presented on fig. 12 : the partial order with respect to the initial ammonia concentration is around one, regardless the dilution. Intensities for NH-band emission have been processed along the same line as for the previous systems and a ΔE_{NH} of about 13 Kcal/mole has been deduced if the overall orders for combustion and chemiluminescence are identical. A comparison of the kinetical parameters for hydrogen-oxygen flames seeded with either cyanogen or ammonia is given on Table IV.

Besides the small ion yield of NH_3 molecule as compared with the cyanogen, the most characteristic feature in the C.I. process for ammonia is its much smaller value for ΔE_+. This forces us to consider a primary ionization step which will be somehow exothermic or at least not too endothermic. Moreover, due to the lack of CN radical, the only possible mechanism is a three body reaction with an excited NH radical :

$$NH^* + O + O \longrightarrow NO^+ + OH + e^- \qquad (13\text{-}5)$$

This process doesn't disagree at all with the partial order with respect to ammonia and with the computed activation energies ($\Delta E_+ > \Delta E_{NH^*}$). It doesn't preclude however reactions involving the NO^* radical. Another interesting fact is the complete absence of NH_4^+ ion in those identified so far in $H_2/O_2/N_2$ flames seeded with ammonia although the burning mixture was rich (φ = 1.113).

Before to put forward processes (13-4 and 13-5) as unique reactions responsible of CI for cyanogen and ammonia, other experiments have been pursued on flames with $(CN)_2$- or NH_5-traces and more specifically systematic measurements of saturation currents, burning velocities and band intensities as a function of the total pressure and of the equivalence ratio of the "basic flame". At last, a detailed ana lysis of the NO* chemiluminescence will be undertaken.

It is also interesting to point out that in pure ammonia flames (NH_3/O_2/N_2) the ion yield reaches the same order of magnitude as those recorded in hydrogen flames seeded by NH_3 but, in pure flames considered so far the flame temperatures are much higher. The activation energy ΔE_+ of pure flames burning in lean mixture ($\varphi < 1$) amounts to about 50 Kcal/mole. This extremely high value has to be related with the necessity of building-up an oxygen atom concentration large enough to cause reaction (13-5). It must be noticed also that in the dilution and richness range of the pure ammonia flames studied so far, the ion yield is first order with respect to the initial ammonia concentration.

In conclusion, the observations on compounds containing nitrogen atom can be summarized as follows :

- the large ion yield of cyanogen is ascribed to a bimolecular process between CN* and oxygen molecule, it requires a reasonably large activation energy ;
- the much smaller value of η_+ in flames containing ammonia is also related to an excited species NH*, but, here the elementary step responsible for primary ionisation would be exothermic and termolecular with a small activation energy.

Conclusions

In order to specify the most prominent elementary processes responsible for the production of highly energetic species (excited radicals or molecules, ions), an extensive research program, still in progress, has been undertaken about the chemiluminescence and chemi-ionization in a large series of flame systems. Attempts have been made to relate the molecule structure of the original fuel to the intensity of the emitted band spectra and to the rate of chemi-ions formation. The use of techniques such as mass spectrometry, emission spectroscopy and saturation currents allows to follow simultaneously several excited and ionized species and to stress the sequence of events and their connection with some specific atoms in the original fuel molecule. Both types of flames have been carried out :

- "pure flames", where the specific molecule to be studied was the main fuel,
- flames where the CI and CL phenomena were induced by addition of small amounts of a specific molecule to a so-called "basic flame" characterized by extremely low ionization level and without any important band emissions (generally H_2/O_2 or sometimes CO/O_2).

Measurements on a large number of hydrocarbons, detailed analysis of methane, ammonia and cyanogen has been reported above. The data have been compared and the different processes responsible for the production of excited and ionised species have been discussed. Although the complete mechanism of elementary steps starting with the original molecules leading to the final energy-rich species (ions, electronically excited molecules or radicals) is not yet available, the results collected so far indicate the important role played by termolecular reactions (sometimes of the recombination type) in the CI and CL. Both phenomena are intimately connected to each other and related to the large concentration of chain-carriers radicals in the flame front. For hydrocarbon systems the primary ion production is parallel to the chemiluminescence of CH and C_2 band emission, but for flames containing cyanogen or ammonia traces the ionization step requires the preliminary excitation of specific radicals.

The high activity of carbon containing molecules for CI and CL phenomena has been assigned to the amount of energy liberated during the formation of CO bond (bond energy : 256 Kcal/mole) when two or more collision partners are reacting ; the excess of energy released is then employed to bring one of the products to an electronically excited level or eventually to ionize the newly formed bond. In order to explain the direct relationships between η_+ and the number of carbon atom in the fuel, it has been suggested that, to a large extent, the hydrocarbon fuel undergoes a pyrolysis-like process which breaks up the original molecule in fragment with only one carbon atom. Some initial C-C bonds are kept, however, as the C_2-band emission indicates it.

With molecules containing nitrogen atoms the CI and CL behaviour is quite different and moreover, it varies largely depending on how the nitrogen atom is linked to the other atoms in the fuel. However, it has been assessed that, in all cases, NO^+ is a primary ion. It shows therefore that, here again, highly energetic bond NO (bond energy 152 Kcal/mole) is related intimately to the production of excited and ionized species. The ionic yields are 10^3 times larger in cyanogen than in analogous ammonia systems ; it means that for cyanogen the formation of both CO and NO bond are of importance, but that for ammonia, the formation of the energetic NO bond requires a termolecular process for getting ionized species.

PART TWO

SIMULATING STUDY OF THE COMBUSTION OF SOLID PROPELLANTS

Introduction

Heat transfer and chemical kinetics are intimately connected in the burning mechanism of solid propellants. Heat conduction, convection or eventually radiation allow to transfer energy from the gaseous burning zone onto the propellant surface. In turn, the transport phenomena induce a change of state at the surface by sublimation, decomposition, depolymerization or pyrolysis of the solid phase. Any of these processes, which are a direct consequence of the heat transfer, is also responsible for the production of the required amounts of gaseous fuel(s) and oxidizer(s) sustaining the exothermic reaction from which part of the heat released is used to set in the surface processes. Such a brief phenomenological description of the combustion of solid propellants points out already that the burning process is an intricate sequence of events with a feed back mechanism and that, by its own nature, it precludes any experimental investigation to discriminate on the spot, the relative importance of the heat transfer and chemical kinetics. Nevertheless, it is possible by adequate measurements to pinpoint the rate determining step of the phenomena.

The above description explains also somehow the difficulties encountered, so far, to reach definite conclusions about the precise mechanism by which some propellants undergo a deflagration, the ammonium perchlorate (AP) decomposition shows a good example of such a situation. Most of the data reported in the literature refer to investigations of decomposition regimes of definite propellants. Among others, combustion of A. P. has been extensively studied these last years, for instance PEARSON (^{23}). Recently, various and highly so phisticated techniques have been applied to A. P. decomposition, they range from Knudsen inlet cell coupled with a Bendix mass spectrometer (24) to laser induced combustion (25). However all these attempts rely upon assumptions about the very first step of A. P. decomposition, i.e. the presence or not of perchloric acid. Although definite experimental evidences of the presence of $HClO_4$ are still lacking, one does observe, indeed, several chlorine oxides which can be considered either as a support of the mechanism (through a subsequent decomposition of the acid) or as an entirely independent decomposition process of the AP which could blur the assumed primary step.

Having this in mind, our research effort on combustion of solid propellants at Louvain University has been deliberately directed toward various and more simple systems where the different facets of the phenomena could be treated almost independently of each other. Two specific approaches have been used :

- Simulating study of heat transfer from the reaction zone onto the regressing surface of composite propellants using the multi micro jet burner for which the description could be found elsewhere (26).
- Systematic investigation of hybrid combustion of a solid bed of fuel with different gaseous oxidizer which are suspected to be involved in the decomposition of AP.

The second section of this program occurs as an extension of the work initiated earlier by BURGER and VAN TIGGELEN (27). It has been carried on more recently by VINCKIER and VAN TIGGELEN (28) with the comparison of burning rates of polymethylmetacrylate (PMM) in mixtures with AP or in hybrid systems when mixed with ammonium chloride. The inhibitor effect of the hydrochloric acid has been put forward to explain the less efficient combustion of PMM-AC mixtures in oxygen, with respect to the PMM-AP systems. In the same trend, a piece of experimental work has been published lately by COMBOURIEU et alii (29) in which the NH_3/ClO_2 flames are described as a combustion analogue of the AP decomposition.

The next two sections discuss in some details the most recent features of the data collected so far on both methods used actually at Louvain, to investigate the burning of solid propellants.

Section I

HEAT TRANSFER STUDIES ON MULTIMICROJET BURNER

(with the collaboration of Mrs. G. LAMBERT)

The so-called analogical burner has been described in great details elsewhere (26), (30). It comprises essentially a double arrays of microtubes (E and I) independently fed by gaseous mixture. The upper edge of the microtubes are soldered on a flat stainless steel grid. Below that surface, a calorimetric water flow renders feasible the accurate measure of the amount of heat transferred from the flame onto the burner surface. As the inner diameter of the tubes is only .5mm, the size of each separate flamelets stabilized on a tiny tube can be considered as the burning zone located above small pellets of propellants in a solid bed and since any regime from pure diffusion to fully premixed flamelets can be achieved, the whole burner simulates reasonably well the state of affair encountered in the burning of solid propellants, but it has the main advantage to allow a direct measure of the heat transfer as a function of the aerodynamical and chemical conditions of the flow of a flammable mixture.

As a matter of fact, if one does consider mixtures involving three gaseous species (fuel, oxidizer and inert), six independent flows have to be monitored which are related to six parameters describing to tally the overall flow conditions for any type of individual flamelets, i.e. :

φ : the overall equivalence ratio
α : the overall degree of dilution
v : the relative flow velocity in both series of tubes
d : the overall flow, usually in cm^3/min.
ϕ : the degree of mixedness of the mixture ; it varies from O for pure diffusion to 1 for fully premixed flames, the morphology of the flame front is extremely sensitive to this parameter. When $\phi = 0$, the I tube system is fed in general with the fuel.

At last, the symbol a characterizes the ratio (fuel to oxidizer concentrations) in a stoichiometric mixture.

The measurement of the heat transferred per unit time $\Delta\dot{H}_s$ is performed by monitoring with great accuracy the calorimetric water flow, and by measuring, at the same time, the in- and outlet temperatures of the water flow.

First observations (30), (31) have exhibited clearly the importance of - the dead space of the flame, i.e. the distance between the burner surface and the lower point of the flame front, as well as of - the degree of wrinkledness of the flame front itself. In a previous paper (31), some measurements on diffusion and premixed flames burning in CH_4-O_2-N_2 mixtures have been carried out.
Now, a comparative study of premixed and diffusion flamelets has been undertaken as a function of the overall dilution (α) for mixtures with an equivalence ratio equal to one and with the same value of the parameter v. Some results related to H_2/O_2 systems are displayed on fig. 14. Similar results have been recorded for methane flames.

Three observations arise from these data :

1) the heat transfer is larger in premixed regime
2) the dependence of the relative heat transfer ($\Delta\dot{H}_s/\Delta\dot{H}_c$) on the

overall dilution is less noticeable for diffusion regime

3) the crossing region of both relative heat transfers for premixed and diffusion flamelets is reached with less diluted mixture in the case of $H_2/O_2/N_2$ flames system.

The first point means that the heat transfer which is maximum in stoichiometric mixture for a <u>premixed flame</u> is essentially controlled by the dead space and that the most important part of the heat transfer process in diffusion regime takes place in the zone where stoichiometry prevails, which, of course, has a lesser extent.
The weaker variation of $\Delta\dot{H}_s/\Delta\dot{H}_c$ in diffusion regime is due to the diffusion process ahead of the burning zone, besides the usual overall dilution effect on the flame temperature which governs the phenomena.
The crossing of $\Delta\dot{H}_s/\Delta\dot{H}_c$ in both regime at 66 % for the hydrogen and at 75 % for the methane is an immediate consequence of the higher diffusion rate of H_2 in the neighbouring jets, with respect to the rate of CH_4.
Such conclusions reinforce those obtained by LYS ([31]) and point out again the value of the approximate model used so far.

However, it is much easier to follow the precise influence of the chemical process on the heat transfer with premixed flames, since we do have then an overall parameter which describes the burning process i.e. V_o. The model of the flamelets downstream the microjets has been put forward earlier and it provides a linear relation between $\Delta\dot{H}_s/\Delta\dot{H}_c$ and the burning velocity V_o :

$$\Delta\dot{H}_s/\Delta\dot{H}_c = M\,V_o - N \qquad (22\text{-}1)$$

Parameters M and N are complicate functions of the overall flow rate (d). So, systematic measurements to check (22-1) have been carried out by varying <u>the overall dilution (α)</u> for hydrogen and methane flames. The data are displayed on fig. 15 and 16, respectively.

One does notice, at once, that the equation is followed on a wide range of flow rate, at last in first approximation. Nevertheless, for a very high flow rate in methane flames, (i. e. flows close to the blow-off limit) a slight positive curvature appears in the lines (fig. 16). Besides, even for small flow rates, the slope of the straight lines and their ordinate at the origin are depending on d.

However, this peculiar behaviour can be explained easily if one does remind (^{31}) that, during the theoretical deduction of the relative heat transfer, the following intermediate equation appears :

$$\Delta\dot{H}_s/\Delta\dot{H}_c = \frac{k\,V_o}{A \exp \frac{B}{V_o} + \frac{k\,E\,V_o}{2R\,T_m b}} \qquad (22\text{-}2)$$

just before expanding the exponential term $A\,e^{B/V_o}$.

The parameter k stands for a complicate function of the heights of the flamelets, and

$$B = P_e\,V_o \qquad (22\text{-}3)$$

with P_e the Peclet number characteristic of the dead space e, and thus depending on the overall flow.

A and b parameters are not flow dependent. Finally, E and T_m have their usual meanings.

Therefore, it is only for not too large flow rate, when P_e is small that the linear expression of e^{B/V_o} is valid. Otherwise, the exponential function has to be developped further. It produces so a slight curvature in the graph of $\Delta\dot{H}_s/\Delta\dot{H}_c$ as a function of V_o , as it is evident from fig. 16, for d $\geqslant$ 8000 cm^3/min. Qualitative agreement between the theoretical model and the experimental variations of M and of N with the overall flow d is also encountered when one does develop the equation (22-2).

But, in order to get a deeper insight of the heat transfer process and to ensure oneself about the dependence of the relative heat release upon the burning velocity, a systematic program is now in progress for measurements of $\Delta\dot{H}_s/\Delta\dot{H}_c$ as a function of V_o when V_o is modified bij varying the equivalence ratio (φ) of the mixture.

However, before dealing with the experiments on rich and lean mixtures, the equipment was adapted in order to avoid the influence of the air. A pyrex cylinder of about 18 cm in diameter and 50 cm long surrounds the multimicrojet burner and is placed on an additional metallic stand shaped as grid through which an inert gas can flow. This type of set up was similar to the Smithells separator which allows to get rid of the influence of the surrounding atmosphere on the burning of very rich mixture.

Some preliminary data are collected on fig. 17. Each series of experiments corresponds to specific external conditions :

1. nitrogen flow around the flame, but without the pyrex cylinder enclosing the burner
2. same set up as 1, but with a flow of dry air
3. nitrogen flow inside the pyrex enclosure (~ 1800 cm^3/min)
4. air flow inside the pyrex enclosure (~ 1800 cm^3/min)
5. only the metallic stand of the pyrex enclosure is kept but no gas is monitored through it
6. the unmodified multimicrojet burner.

As it is clear from the results shown in fig. 17, the presence of a metallic stand modifies to a large extend the heat released to the burner body (Compare curve 6 with the other set up, even in the absence of any gas flow (5)). So, a better insulation is required to decrease the influence of the metallic stand necessary for setting the enclosure.

In other respects, the direct influence of the external atmosphere on the heat transfer remains very small (Compare 3 and 4). That is quite understandable since the largest influence of the surroundings on the flame takes place either on the edges of the flame front, or on the postcombustion zone which is remote from the heat transfer zone. But, before going into more extensive measurements of the influence of φ upon $\Delta\dot{H}_s/\Delta\dot{H}_c$, the insulation of the usual multimicrojet will be improved and, thereafter, the comparison between the overall equivalence ratio effect and overall dilution effects will be carried on further. Anyway, it must be emphasized already now that it exists a striking similarity between the slope of the lines recorded for the variation of $\Delta\dot{H}_s/\Delta\dot{H}_c$ with V_o, when V_o is modified by α, and the slope of the symmetry axis of the parabolic shaped curve of $\Delta\dot{H}_s/\Delta\dot{H}_c$ vs. V_o, by action on the equivalence ratio φ.

Although the experiments on hydrogen and methane seem to follow the model used so far for describing the flames, more work is required not only on the richness study, but also on parameter v characterizing the ratio of flow rates in both series of tubes. At last, this technique of the multimicrojet burner has to be extended to other gaseous mixtures simulating more closely the nature of the decomposition products of definite solid propellants such as A. P. In that respect, the investigation of intermediate regimes with $1 > \phi > 0$ will be of great interest.

Section II

HYBRID COMBUSTION OF POLYMETHYLMETACRYLATE

(with the collaboration of Mr. H. Y. SAFIEH)

In order to pinpoint the gaseous oxidizer responsible for the burning mechanism of A. P. with PMM we have directed our effort to a systematic study of the hybrid combustion of polymethylmetacrylate with different oxidizers such as nitrous oxide and oxygen. It has the aim to measure thus the role and the importance of each decomposition product of A. P. in the overall process, and eventually to decide by taking into account heat losses which one represents the rate determining step.

The technique used previously by BURGER (27) was consisting of the combustion of PMM in a quartz tube, in which the PMM particles were bound together by a solution of 4 g. of PMM in acetone. The acetone was drawn out of the tube by sucking with a water pump. Then, after ignition of the sample, the burning proceeded downwards in the quartz tube. However, there are two major criticisms for this technique : the first refers to the method of cementing the sample in the tube and the second concerns the use of the quartz tubes themselves.

- The use of quartz tubes during the combustion allows, indeed, great losses of heat through the tube which does not regress with the flame front. In particular, combustion of N_2O with PMM was quenched almost at any run.
- As for the question of the binding system, some comments made by McALEVY (32) have been replied by BURGER (33), but anyway, the sucking process of acetone by the water pump alone is not efficient enough and the acetone traces disturb the burning rate measurements of PMM.

Therefore, to remedy to the heat losses through quartz tubes, plexiglass (PMM) tubes have been used. They are 0.05 cm thick and the walls burn with the solid bed at the same rate, being of the same material. Of course, a slow nitrogen flow is surrounding the sample during the run to avoid the influences of the oxygen of air. Moreover, in the cementing technique, after sucking out large amounts of acetone with a water pump, the "cigarette" sample of PMM was kept in a drying room at 60°C and at low pressure for five days.

This procedure has a double aim, first, to get rid of the excess of acetone ; secondly, the samples being kept at a temperature near the melting of PMM provide another choice to bind together the granules of PMM without loosing the porosity of the solid bed.

Comparison of both systems of binding has been performed. The measured rate of burning is about 9 % slower in applying the new method of cementing the sample.

For each experiment, three parameters are representative ; successively the specific weight $\bar{\rho}$, the richness of the burning mixture φ and its mass burning rate $\dot{m}$. Their definition is as follows :

1) $\bar{\rho}$ represents an apparent specific weight of the solid bed

$$\bar{\rho} = \frac{S_t}{S_T}\rho_t + \frac{S_p}{S_T}\rho_p = \frac{1}{D^2}\left[\frac{4(m_T - m_t)}{\pi \ell} + \rho_t(D^2 - d^2)\right] \qquad (22\text{-}3)$$

with S the area of the cross section of the sample (subscripts T, t and p refer to total, tube and powder respectively).

D and d are the outer and inner diameter of the plexiglass tube, ℓ is its length and m is the weight.

2) φ, the equivalence ratio, is defined as the following ratio :

$$\frac{v/D_o}{(v/D_o)_{st}} \qquad (22\text{-}4)$$

where v means the equivalent gaseous flow rate of the solid mass at 20°C, and D_o the flow rate of the oxidizer. Subscript st characterizes the rates for a stoichiometric mixture. Moreover, $v = 241.7\ m/t$ with m the weight of solid PMM burnt, and t the elapsed time during the run.

3) The mass burning rate in $g.cm^{-2}sec^{-1}$ is computed from

$$\dot{m} = \bar{\rho}\, V \qquad (22\text{-}5)$$

with V the linear regression rate.

Last of all, the macroscopie porosity ε of the burning bed is given by

$$\varepsilon = 1 - \frac{\bar{\rho}}{\rho_t} \text{ and } \rho_t = 1.18 \text{ g.cm}^{-3} \qquad (22\text{-}6)$$

By taking into account all constants, the stoichiometric equivalence ratios are

$$\Phi_{O_2} = \frac{1138.8\ D^2\ \dot{m}_{O_2}}{D_{O_2}}$$ for PMM hybrid combustion in oxygen,

and $$\Phi_{N_2O} = \frac{2277.6\ D^2\ \dot{m}_{N_2O}}{D_{N_2O}}$$ in nitrous oxide.

It is worth to point out now that the hybrid combustion of PMM with oxygen is extremely fast as compared to its burning with nitrous oxide.

In what concerns the combustion of PMM with oxygen, some of the data ([34]) are plotted on fig. 18. These experiments have been performed at constant flow rate of oxygen and with size of the granules kept in the same range (.105 - .250 mm). The linear dependence of the mass burning rate $\dot{m}$ on the macroscopic porosity of the sample is quite clear from fig. 18, at least for $0.43 > \varepsilon > 0.30$. Provided that the relationship is still valid for extreme porosities, a fictitious $\dot{m}_{ext}$ can be deduced by extrapolation from fig. 18. It will correspond to the situation encountered at the surface of a composite propellant. It would be of some interest, for each gas flow rate, to perform series of measurements with different porosities, so as to deduce the dependence of $\dot{m}_{ext}$ on the gaseous flow rate and, as a consequence, on the equivalence ratio φ.

Experiments with variable flow rate of N_2O have been carried out for two different but constant granulometry range, both series of data are displayed on fig. 19. The maximum mass burning rates are achie ved in rich mixture (φ = 1.55). It could be a consequence of the different ways by which the oxidizer and fuel species are leaving the solid bed : the oxidizer as a gas but the fuel, sometimes, as microparticles. From then, some PMM pellets of large size are carried away from the flame region leaving the inside unburnt. Moreover, the incomplete burning has to be put in parallel also with the soot formation in the flame. The equivalence ratio φ is not the richness of the mixture, but an apparent one, due to the fact that the reactants are not fully premixed. Nevertheless, the increase of the mass burning rate by decreasing the granulometry does agree with the measurement performed earlier (27) by using the old cementing technique.

The new technique for preparation of polymethylmetacrylate samples in plexiglass tubes has the advantage, by reducing largely the heat losses, to enable the study of slow hybrid combustion for instance polymethylmetacrylate with nitrous oxide. Besides, by making use of "cigarettes" consisting of a bundle of narrow rods of polymethylmetacrylate in a plexiglass tube, a real possibility seems to exist for the investigation of the macroscopic porosity. This type of combustion of a solid propellant would be also similar to the burning process above a multimicrojet burner. Future work in that field has to extend the data gathered so far to some other gaseous oxidizers such as chlorine, nitric oxide, chlorine oxides, which are usually encountered in variable amounts as decomposition products of ammonium perchlorate.

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REFERENCES

(1) W. J. MILLER : Oxidation and Combust. Reviews 3, p. 97 (1968).

(2) E. M. BULEWICZ, P. J. PADLEY and R. E. SMITH : Proc. Roy. Soc. A 315, p. 129 (1970).

(3) L. AGLAVE : unpublished results.

(4) J. PEETERS, Ch. VINCKIER, A. VAN TIGGELEN : Oxidation and Combust. Reviews 4, p. 93 (1969).

(5) A. VAN TIGGELEN et alii : Oxydations et Combustions, Technip, Paris, 1968.

(6) G. WORTBERG : 10th Intern. Symp. on Combustion, p 651 (1965).

(7) P. J. VAN TIGGELEN and A. DUVAL : Bull. Cl. Sci. Acad. Roy. Belg. (5) 53, p. 326 (1967).

(8) A. VAN TIGGELEN : Ionisation in Flames and Identification of the Negative Flame Ions ; Scientific Report No 4, May 1964. Contract AF-61(052)-398.

(9) A. VAN TIGGELEN and S. DE JAEGERE : Experimental Study of Chemi-Ionisation ; Final Scientific Report, May 1967, Grant AF-EOAR-65-82.

(10) A. VAN TIGGELEN and S. DE JAEGERE : Ions produced by chemically Reacting Systems ; Final Scientific Report, May 1969, Grant AF-EOAR-67-53.

(11) R. BURKE and A. VAN TIGGELEN : Bull. Soc. Chim. Belg. 74, 426 (1965).

(12) J. PEETERS, J. F. LAMBERT, P. HERTOGHE and A. VAN TIGGELEN : Thirteenth Symposium on Combustion, to be published.

(13) G. PANNETIER and A. G. GAYDON : C. R. Acad. Sci., Paris 225, 1300 (1947).

(14) E.M. BULEWICZ, P.J. PADLEY and R.E. SMITH : Proc. Roy. Soc. A 315, 129 (1970).

(15) C.W. HAND and G.B. KISTIAKOWSKY : J. Chem. Phys., 37, 1239 (1962).

(16) R.E. FERGUSON : J. Chem. Phys., 23, 2085 (1955).

(17) D.W. NAEGLI and H.B. PALMER : J. Chem. Phys., 48, 2372 (1968).

(18) E.M. BULEWICZ : Comb. and Flame 11, 297 (1967).

(19) J. VAERMAN, G. NENQUIN and A. VAN TIGGELEN : Bull. Soc. Chim. Belg., 65, 435 (1956).

(20) G. NENQUIN, P. THOMAS and A. VAN TIGGELEN : Bull. Soc. Chim. Belg. 65, 1072 (1956).

(21) A. VAN TIGGELEN : Progr. in Astronautics and Aeronautics, 12, Academic Press, 165 (1963).

(22) A. VAN TIGGELEN, J. PEETERS and C. VINCKIER : Thirteenth Symposium on Combustion, Salt Lake City, Aug. 1970 (to be published).

(23) A.R. HALL and G.S. PEARSON : Oxidation and Combust. Reviews 3, 129 (1968).
P.W. JACOBS and G.S. PEARSON : Comb. and Flame 13, 419 (1969).

(24) N.A. GUILLORY and M. KING : A.I.A.A. Journal 8, 1134 (1970).

(25) M. HERTZBERG : Combustion Science and Technology 1, 449 (1970).

(26) J. BURGER, A. VAN TIGGELEN and J. PONCELET : Astronautica Acta 11, 57 (1965).

(27) J. BURGER and A. VAN TIGGELEN : Mém. Acad. Roy. Belg. Cl. Sci. 34 (8), 1 (1964) ; Bull. Soc. Chim. France 3122 (1964). J. BURGER : Rev. Inst. Franç. Pétrole, 20 (9), 1 (1965).

(28) C. VINCKIER and A. VAN TIGGELEN : Astronautica Acta 14, 261 (1969).

(29) J. COMBOURIEU, G. MOREAU, R. MOREAU and G.S. PEARSON : A.I.A.A. Journal 8, 594 (1970).

(30) A. VAN TIGGELEN et alii : Oxydations et Combustions, p. 723, Technip, Paris (1968).

(31) X. LYS and A. VAN TIGGELEN : Combustion Science and Technology 1, 233 (1969).

(32) R.F. McALEVY III et alii : A.I.A.A. Journal 6, 1243 (1968).

(33) J. BURGER : A.I.A.A. Journal 7, 988 (1969).

(34) H.Y. SAFIEH : unpublished results, Thesis Louvain 1970.

FIGURE CAPTIONS

1. Intensities of OH-band emission vs. the equivalence ratio φ for methane-oxygen-nitrogen flames.
2. Intensities of CH-band emission vs. the equivalence ratio φ for methane-oxygen-nitrogen flames.
3. Intensities of C_2-band emission vs. the equivalence ratio φ for methane-oxygen-nitrogen flames.
4. Comparison of the relative band intensities and saturation current for several flames burning in CH_4-O_2-N_2 mixtures.
5. Differences of activation energies ΔE between the CH-chemiluminescence and the burning processes for CH_4-O_2-N_2 mixtures with variable equivalence ratio φ.
6. Difference of overall orders Δn between chemiluminescence and combustion process for OH-, CH- and C_2-band emission at a constant mean temperature $T_m = 1815^\circ K$.
7. CH-band emission of normal butane traces in hydrogen-oxygen flames with variable dilution.
8. C_2-band emission of normal butane traces in hydrogen-oxygen flames with variable dilution.

9a. Dependence of saturation currents and relative band intensities. CI and CL are induced either by normal butane or isobutane in a rich H_2/O_2 flame diluted with 50 % N_2.

9b. Saturation current and band emission intensities vs. the propane content of a hydrogen-oxygen flame with $\varphi = 1.11$ and diluted with 60 % N_2.

9c. Ratio of the C_2-band intensity to the square of the saturation current vs. the initial acetylene content in a rich H_2/O_2 flame (φ = 1.11 and 60 % N_2).

10. Dependence of the C_2^* emission intensities on the carbon content of different hydrocarbons added to a H_2/O_2 flame (φ = 1.11 and 60 % N_2).

11. The ion yield η_+ as a function of the number of carbon atoms in the hydrocarbon molecule added to the H_2/O_2 flame (φ = 1.11 and 60 % N_2).

12. Order dependence of saturation current with respect to the ammonia traces added to H_2/O_2 flame (φ = 1.11 and with variable dilution).

13. Difference ΔE of activation energies between the NH chemiluminescence and the burning process for a slightly rich hydrogen-oxygen flame with 3 % ammonia traces.

14. Comparison of the relative heat transfer in premixed (ψ = 1) and diffusion regimes (ψ = 0) for stoichiometric hydrogen-oxygen-nitrogen flames.

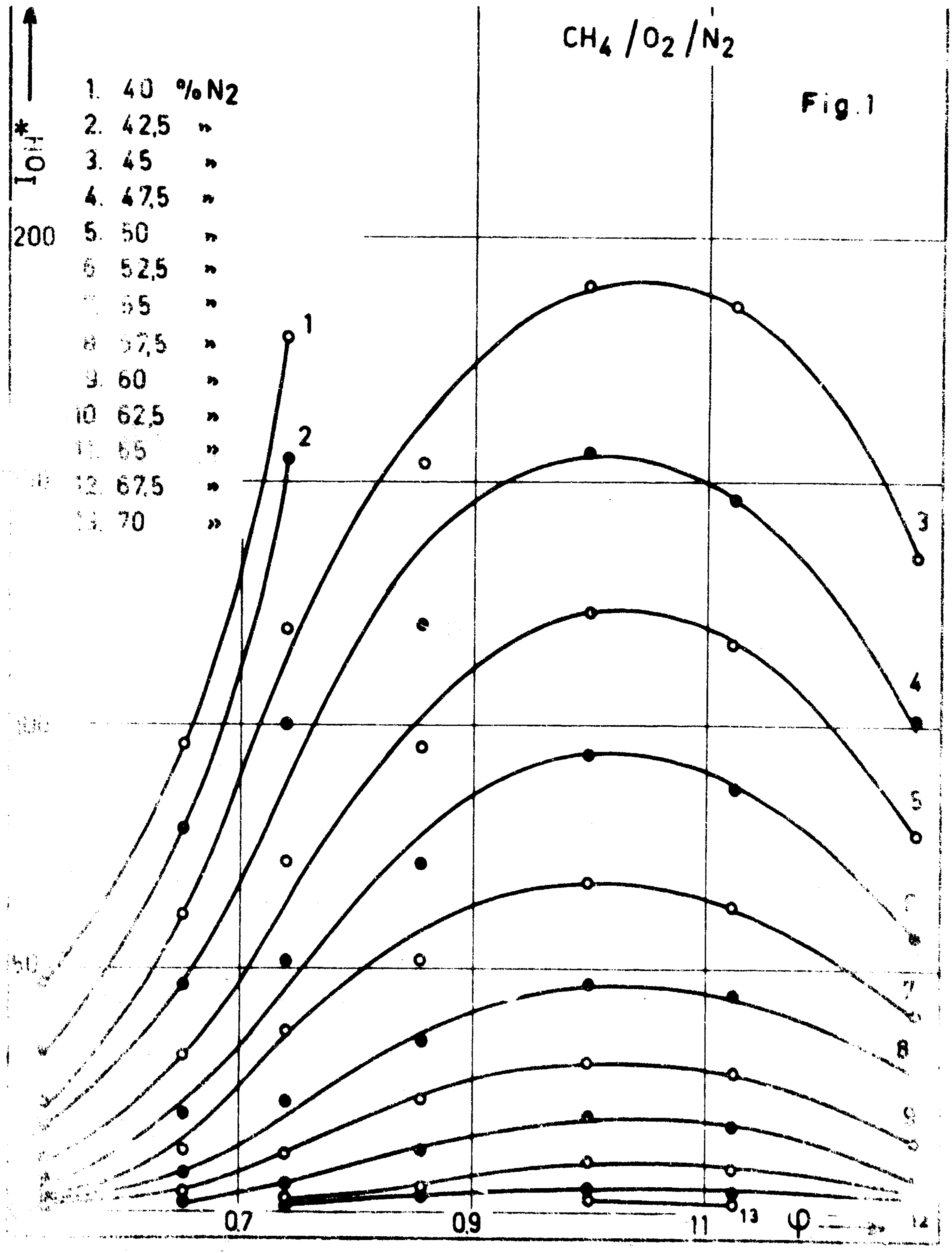
15. Dependence of the relative heat transfer on the burning velocity for premixed hydrogen-oxygen flames with variable dilution in nitrogen and with variable overall flow of the gaseous mixtures.

16. Dependence of the relative heat transfer on the burning velocity for premixed methane-oxygen flames with variable dilution in nitrogen and variable overall flow of the gaseous mixtures.

17. Influence of the external conditions upon the relative heat transfer for methane-oxygen flames when the burning velocity is altered by changing the equivalence ratio. (See text for the various external conditions).

18. Mass burning rate of the hybrid combustion of polymethylmetacrylate with nitrous oxide as a function of the equivalence ratio for two different granulometries.

19. Mass burning rate $\dot{m}$ of PMM vs. porosity (ε) at a constant flow of oxygen.

CH$_4$ /O$_2$ /N$_2$
Fig. 1
I_{OH}^*
200
150
100
50
1. 40 %N2
2. 42,5 »
3. 45 »
4. 47,5 »
5. 50 »
6. 52,5 »
7. 55 »
8. 57,5 »
9. 60 »
10 62,5 »
11. 65 »
12. 67,5 »
13. 70 »
1
2
3
4
5
6
7
8
9
13
12
0.7
0.9
1.1
φ

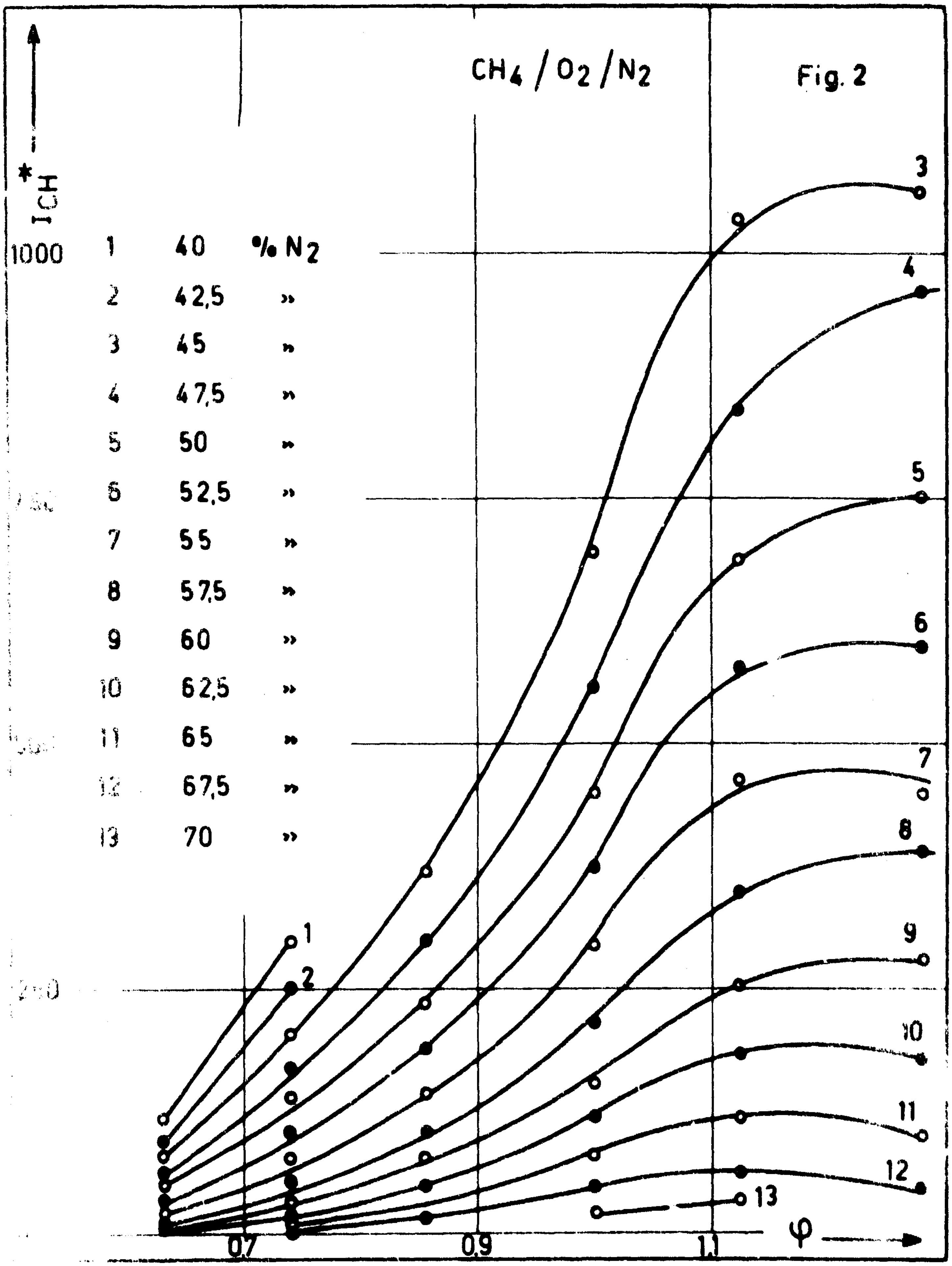
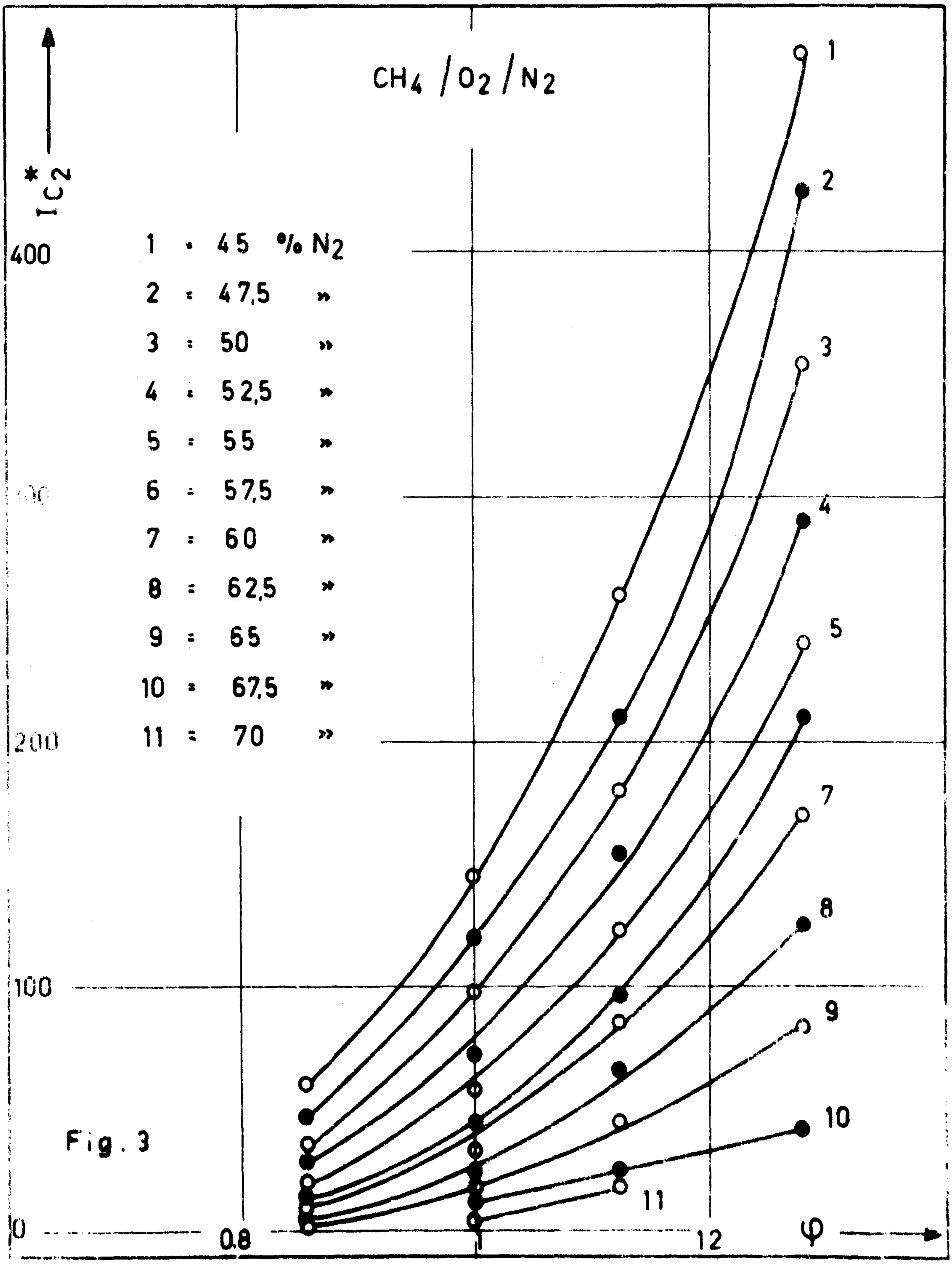

CH₄ / O₂ / N₂
I*CH
1000
750
500
250
1 40 % N2
2 42,5 »
3 45 »
4 47,5 »
5 50 »
6 52,5 »
7 55 »
8 57,5 »
9 60 »
10 62,5 »
11 65 »
12 67,5 »
13 70 »
1
2
3
4
5
6
7
8
9
10
11
12
13
0,7
0,9
1,1
φ

Fig. 2



$I^*_{C_2}$
$CH_4/O_2/N_2$
1 : 45 % N_2
2 : 47,5 »
3 : 50 »
4 : 52,5 »
5 : 55 »
6 : 57,5 »
7 : 60 »
8 : 62,5 »
9 : 65 »
10 : 67,5 »
11 : 70 »
400
300
200
100
0
0.8
1
12
φ
1
2
3
4
5
6
7
8
9
10
11

Fig. 3

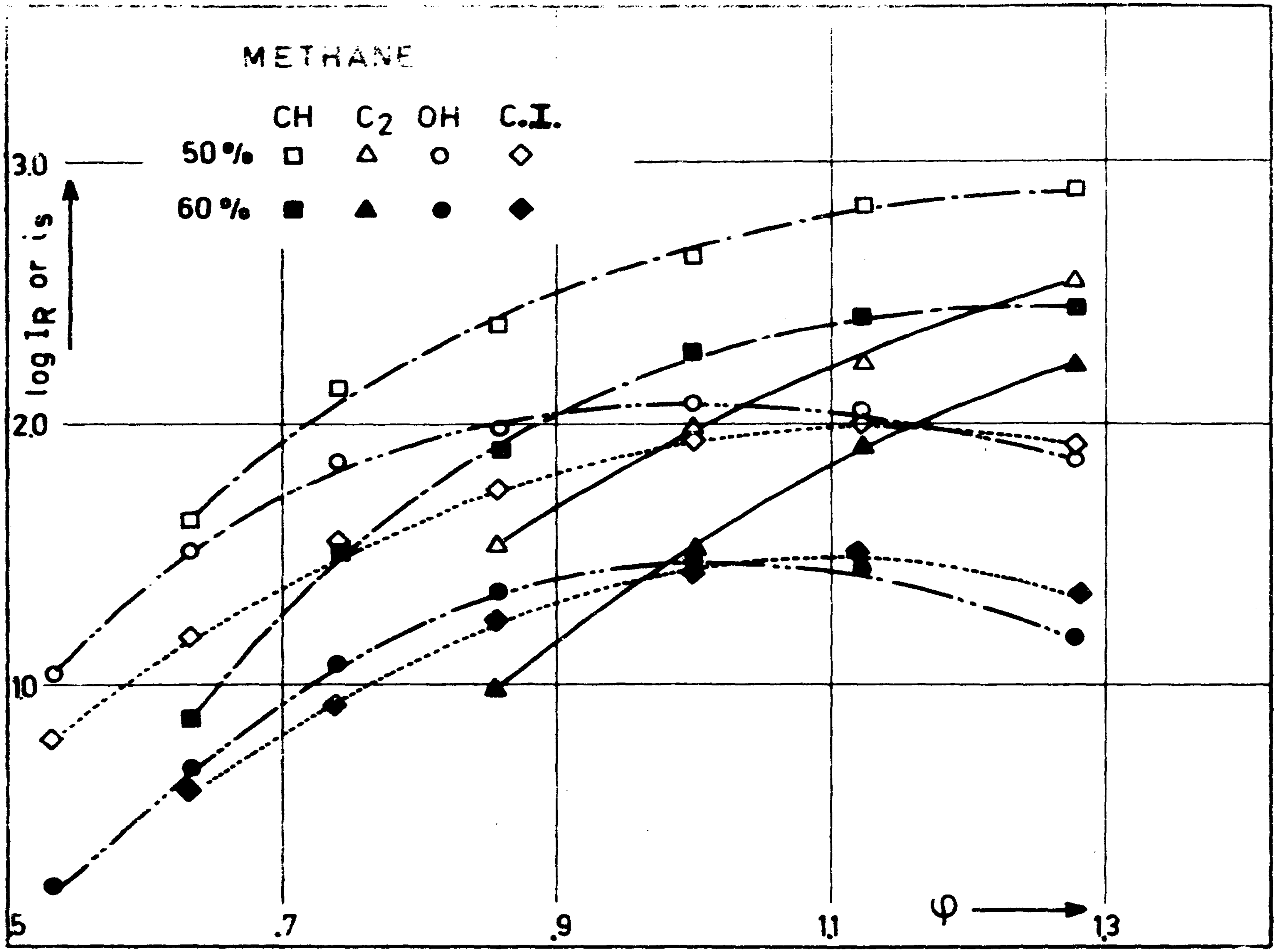
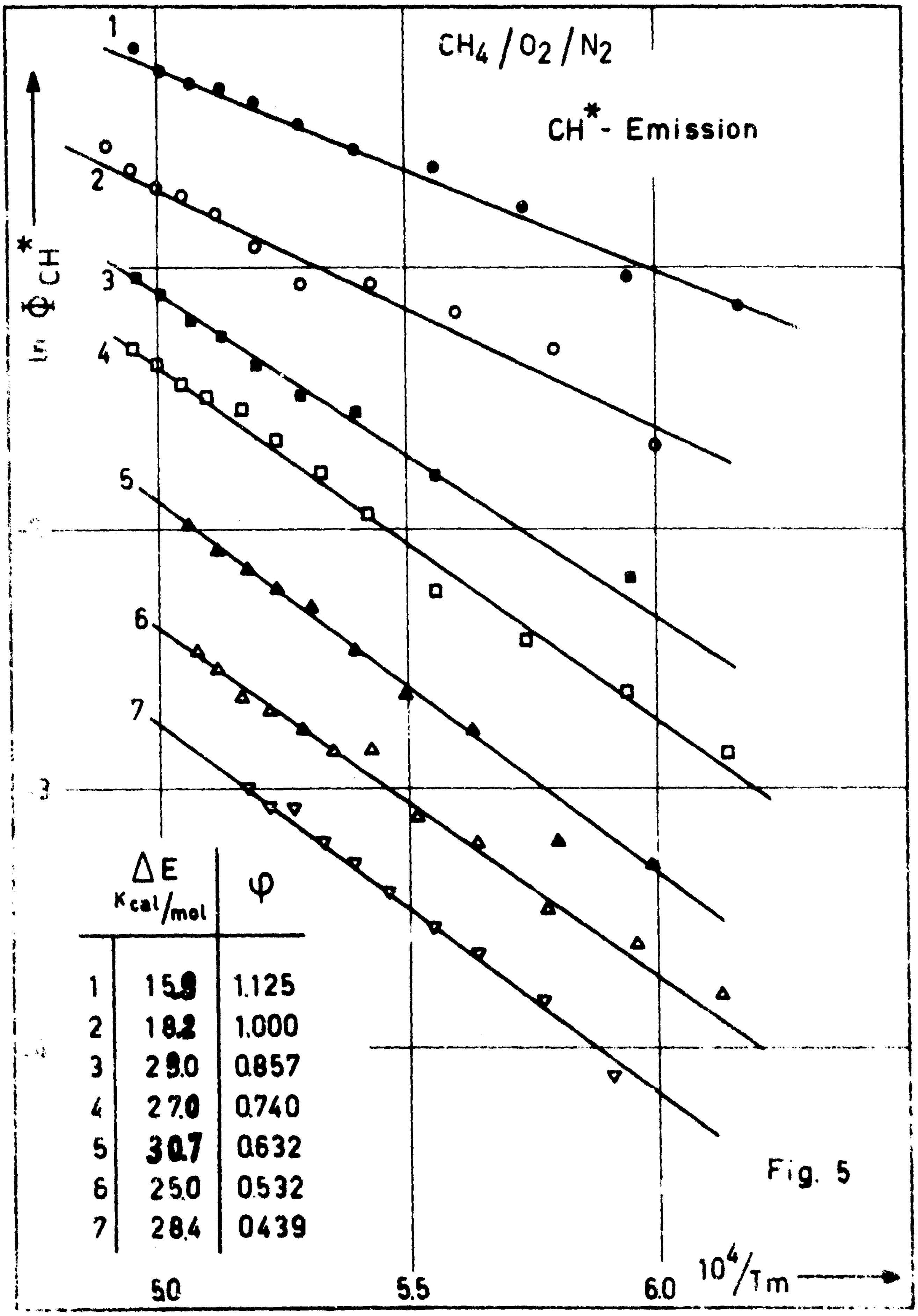
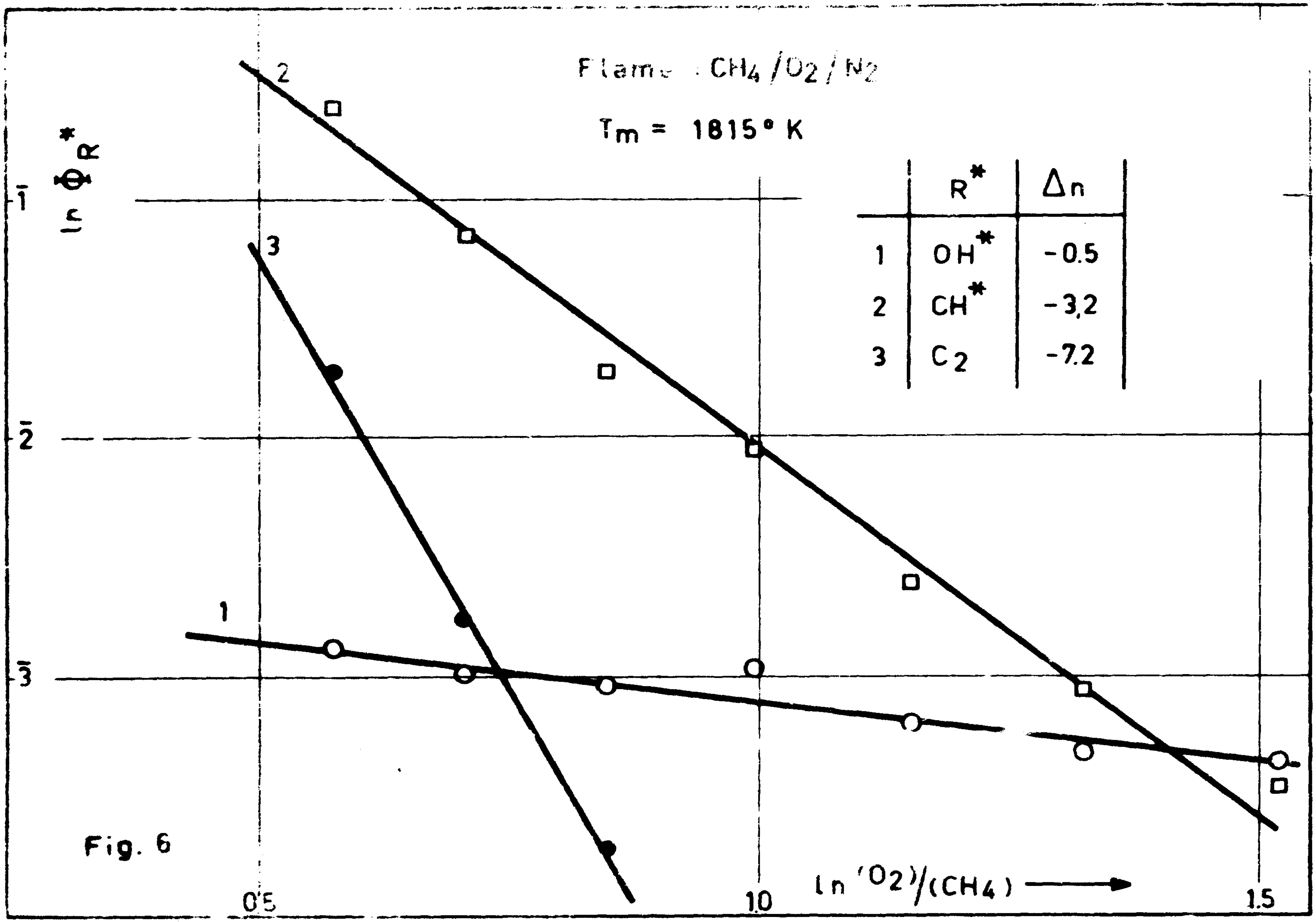


Fig. 4



	ΔE Kcal/mol	φ
1	15.8	1.125
2	18.2	1.000
3	29.0	0.857
4	27.0	0.740
5	30.7	0.632
6	25.0	0.532
7	28.4	0.439

Fig. 5



Flame : $CH_4/O_2/N_2$
T_m = 1815° K
R^* | Δn
1 OH^* -0.5
2 CH^* -3,2
3 C_2 -7.2
$\ln \Phi^*_R$
$\bar{1}$
$\bar{2}$
$\bar{3}$
1
2
3
0.5
1.0
1.5
$\ln (O_2)/(CH_4)$ →

Fig. 6

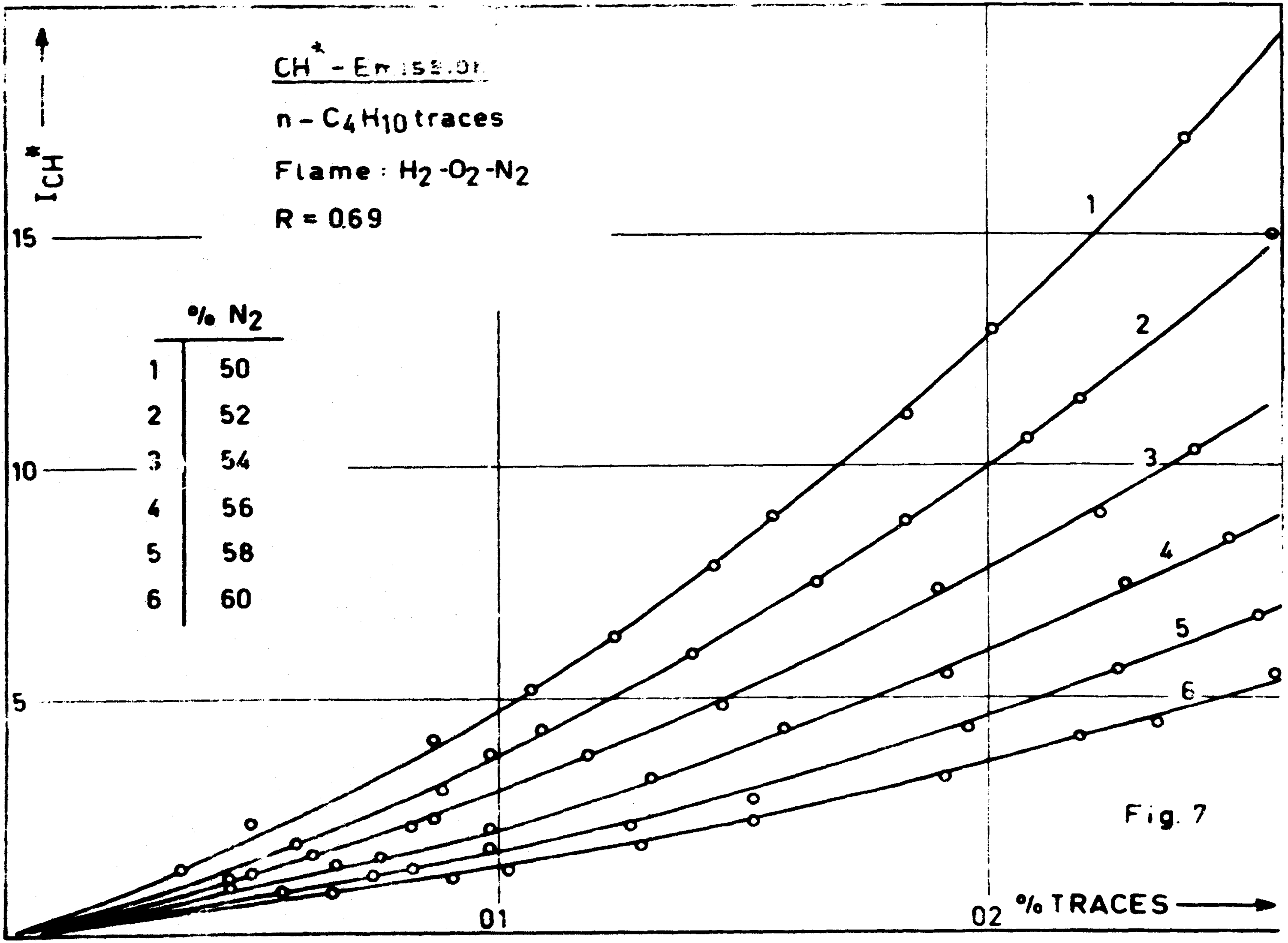

CH* - Emission
n - C_4H_{10} traces
Flame : H_2-O_2-N_2
R = 0.69
I_{CH^*}
15
10
5
% N_2
1 50
2 52
3 54
4 56
5 58
6 60
1
2
3
4
5
6
01
02
% TRACES

Fig. 7

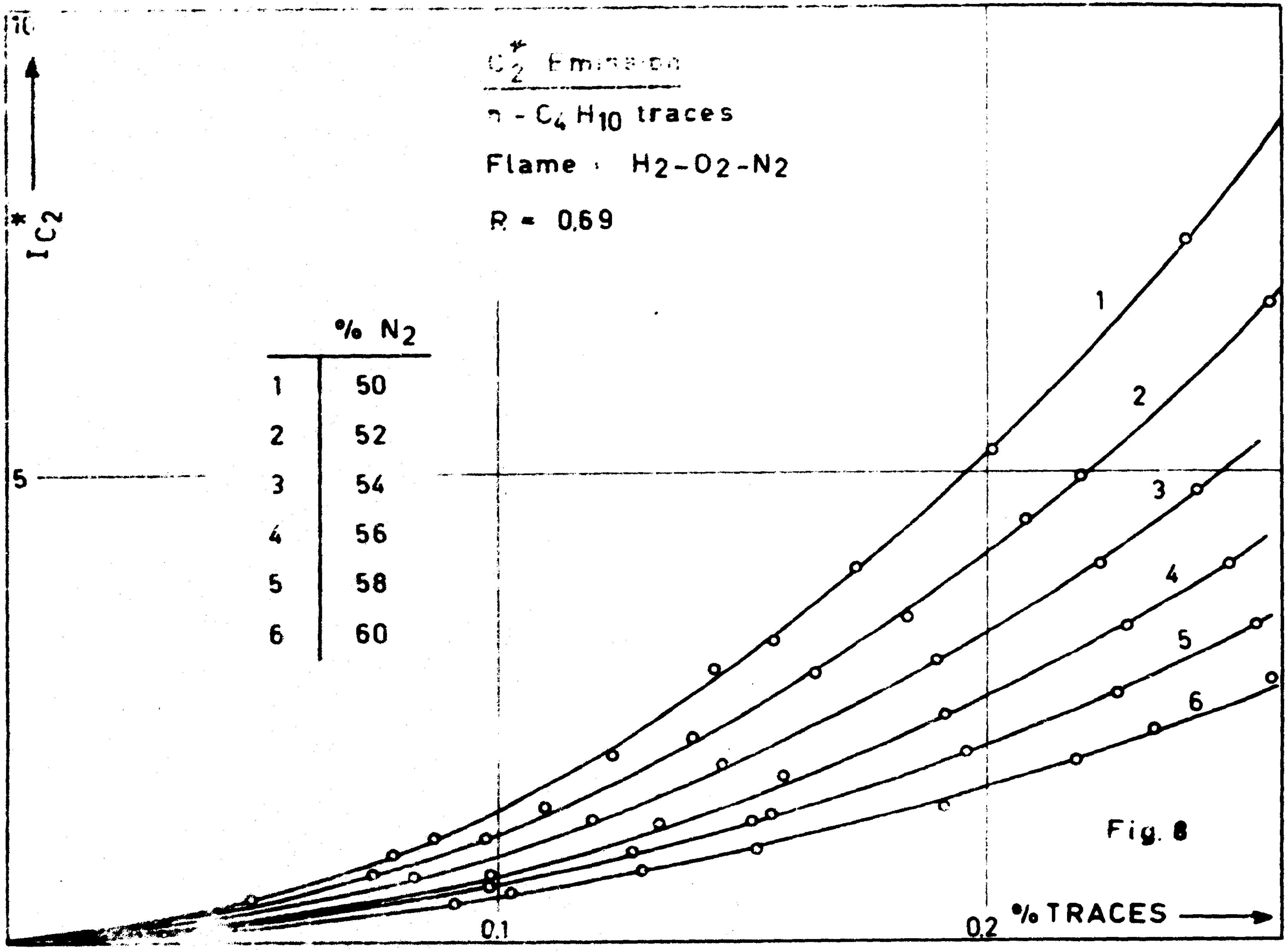

C_2^* Emission
n - C_4H_{10} traces
Flame : H_2-O_2-N_2
R = 0,69
% N_2
1 50
2 52
3 54
4 56
5 58
6 60
$I_{C_2^*}$
10
5
0.1
0.2
% TRACES
1
2
3
4
5
6

Fig. 8

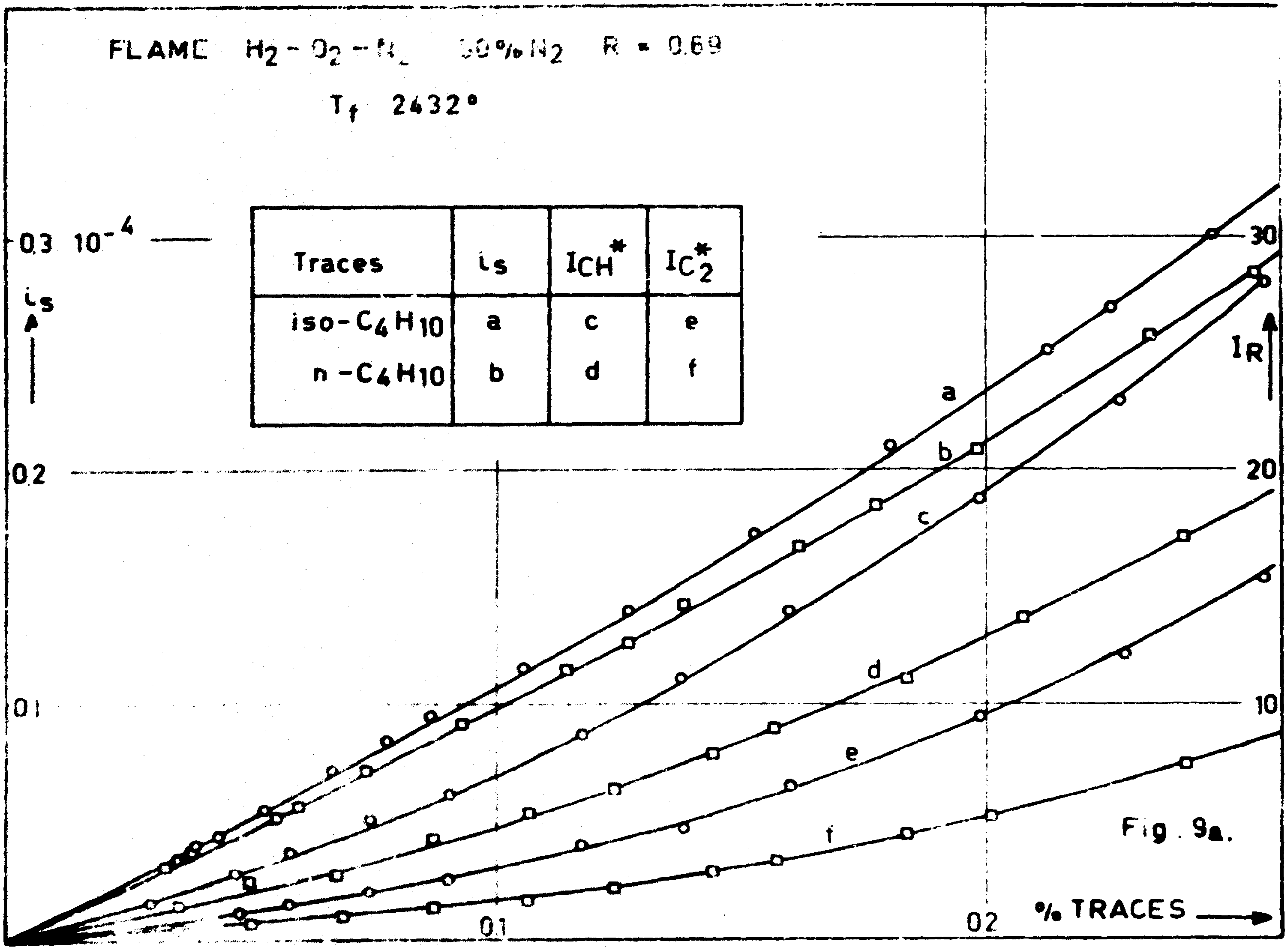

FLAME $H_2 - O_2 - N_2$ 50 % N_2 R = 0.69
T_f 2432°
Traces
i_s
I_{CH}^*
$I_{C_2}^*$
iso-C_4H_{10}
a
c
e
n-C_4H_{10}
b
d
f
i_s
0.3 10^{-4}
0.2
0.1
I_R
30
20
10
0.1
0.2
% TRACES
a
b
c
d
e
f

Fig. 9a.

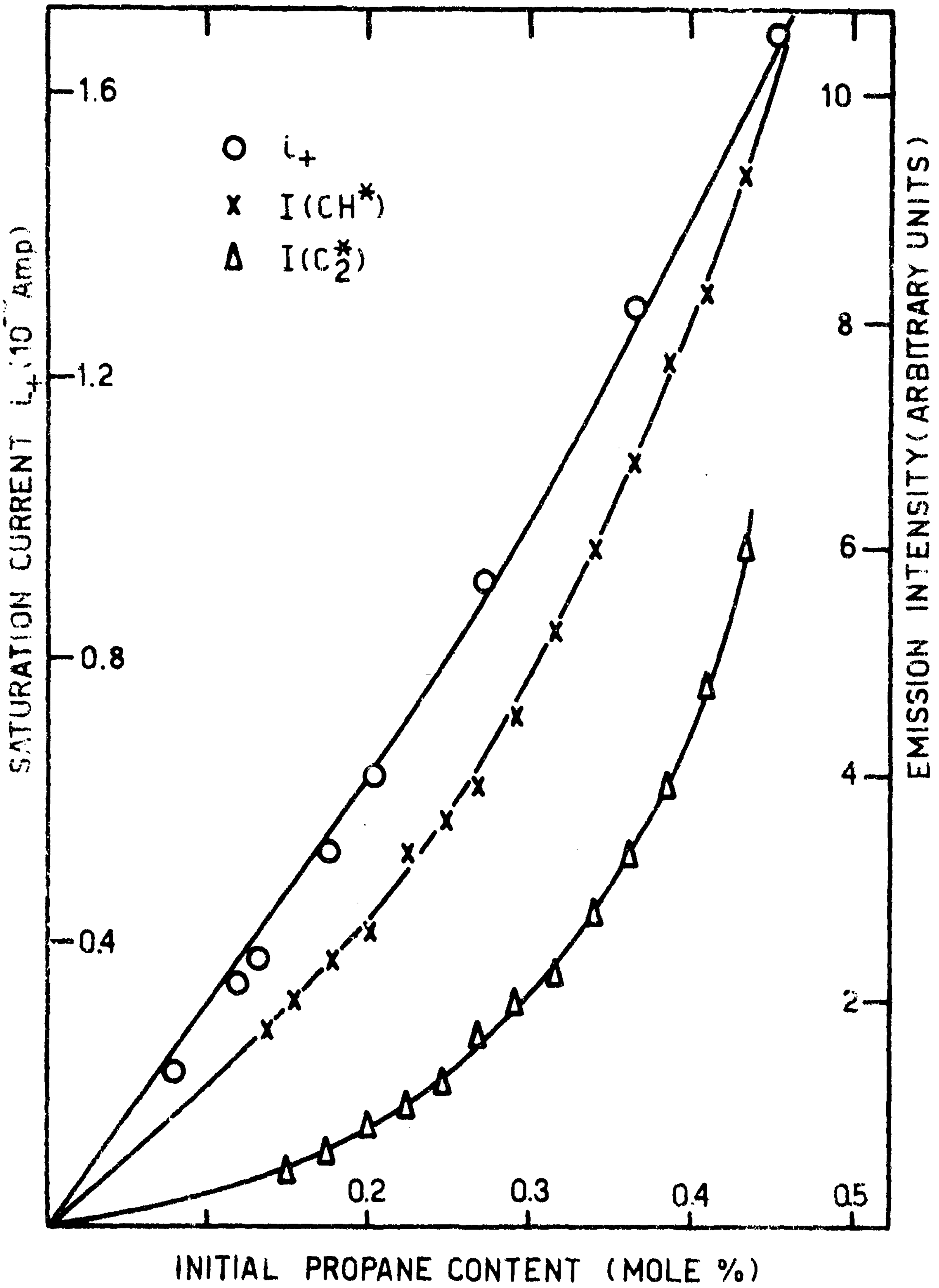

1.6
1.2
0.8
0.4
SATURATION CURRENT i_+ (10^{-8} Amp)
10
8
6
4
2
EMISSION INTENSITY (ARBITRARY UNITS)
0.2
0.3
0.4
0.5
INITIAL PROPANE CONTENT (MOLE %)
○ i_+
x I(CH*)
Δ I(C_2^*)

Fig. 9b.

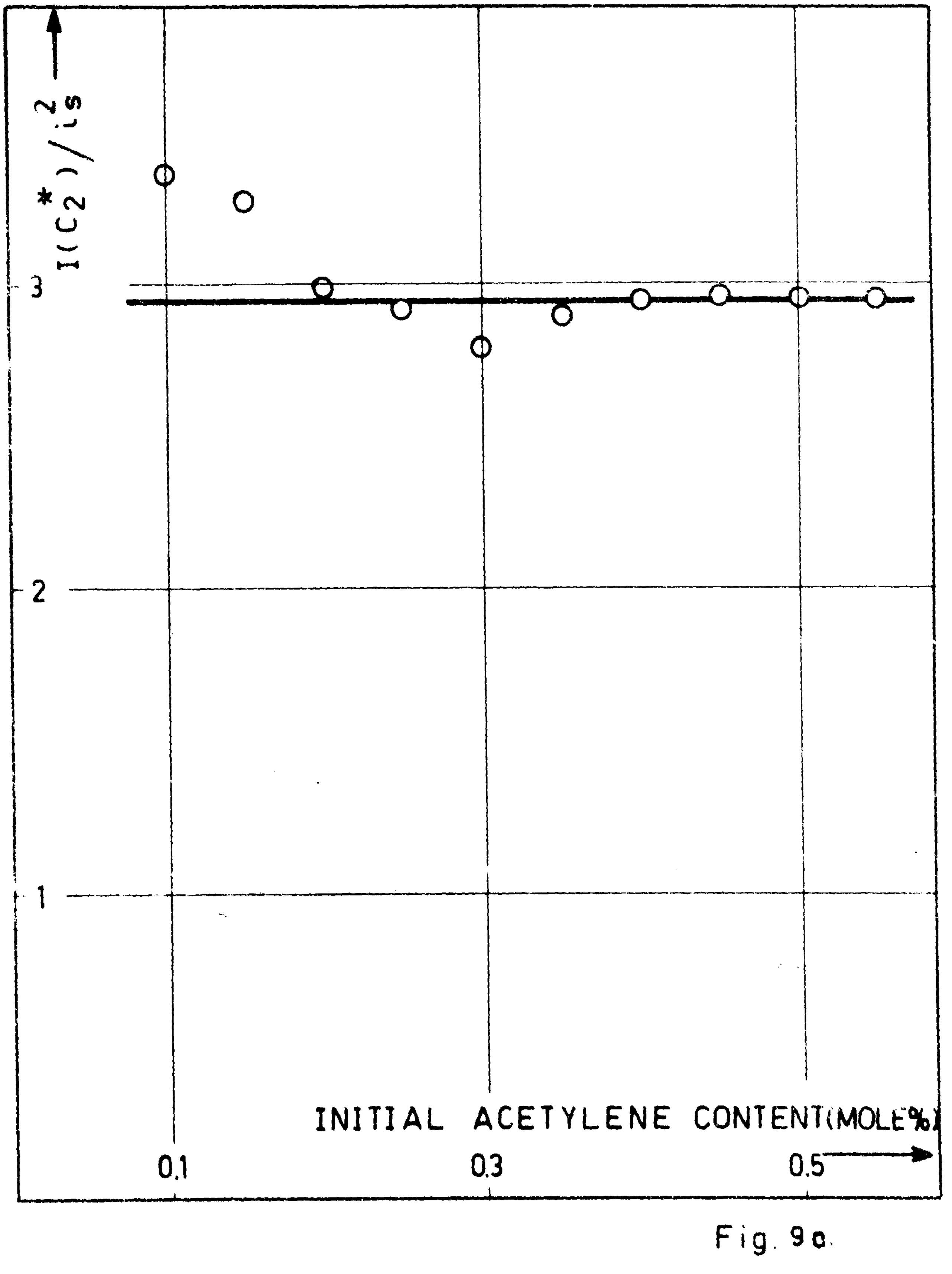


Fig. 9a.

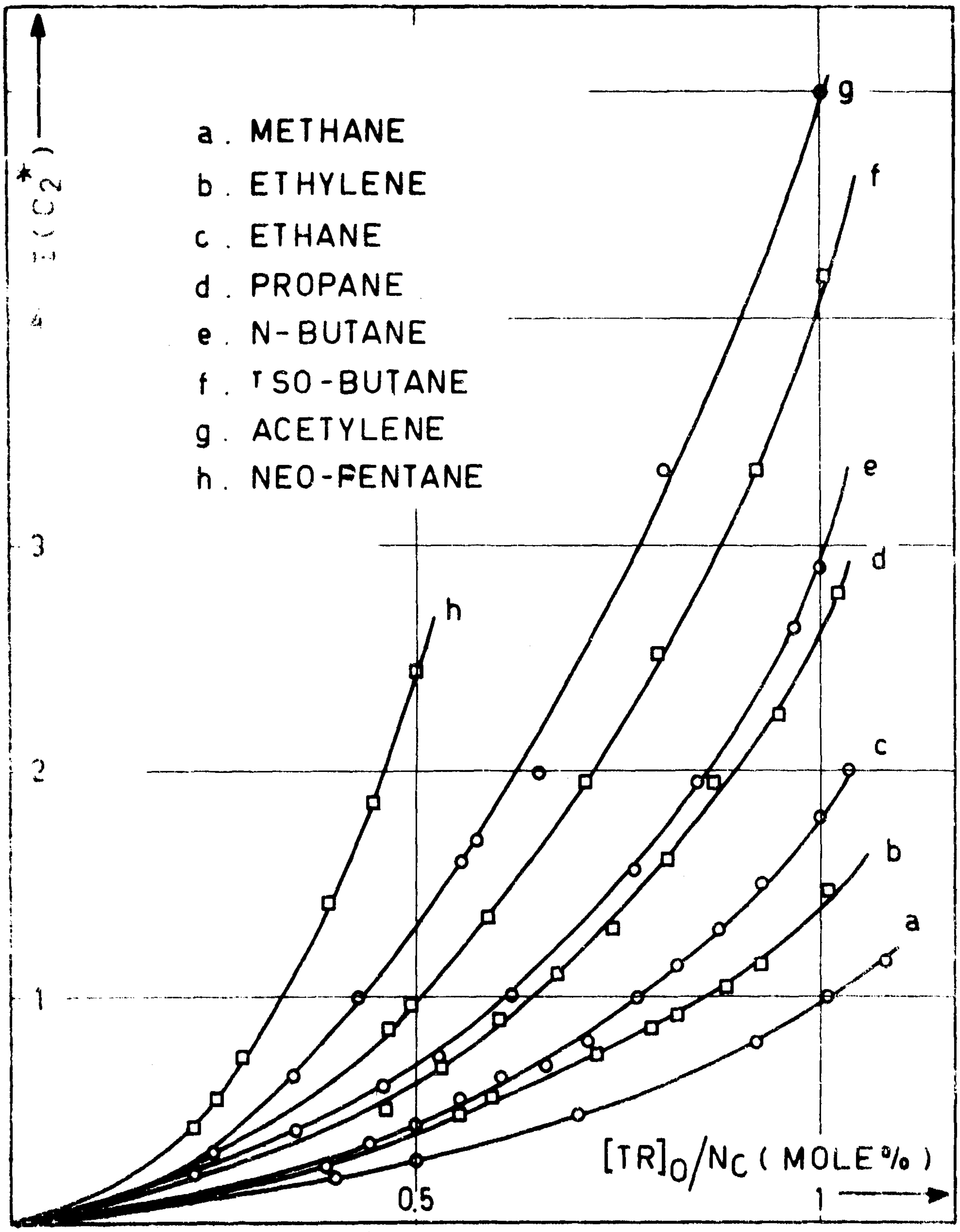

a . METHANE
b . ETHYLENE
c . ETHANE
d . PROPANE
e . N-BUTANE
f . ISO-BUTANE
g . ACETYLENE
h . NEO-PENTANE
E(C2*)
1
2
3
4
0.5
1
[TR]0/NC (MOLE %)
a
b
c
d
e
f
g
h

Fig. 10.

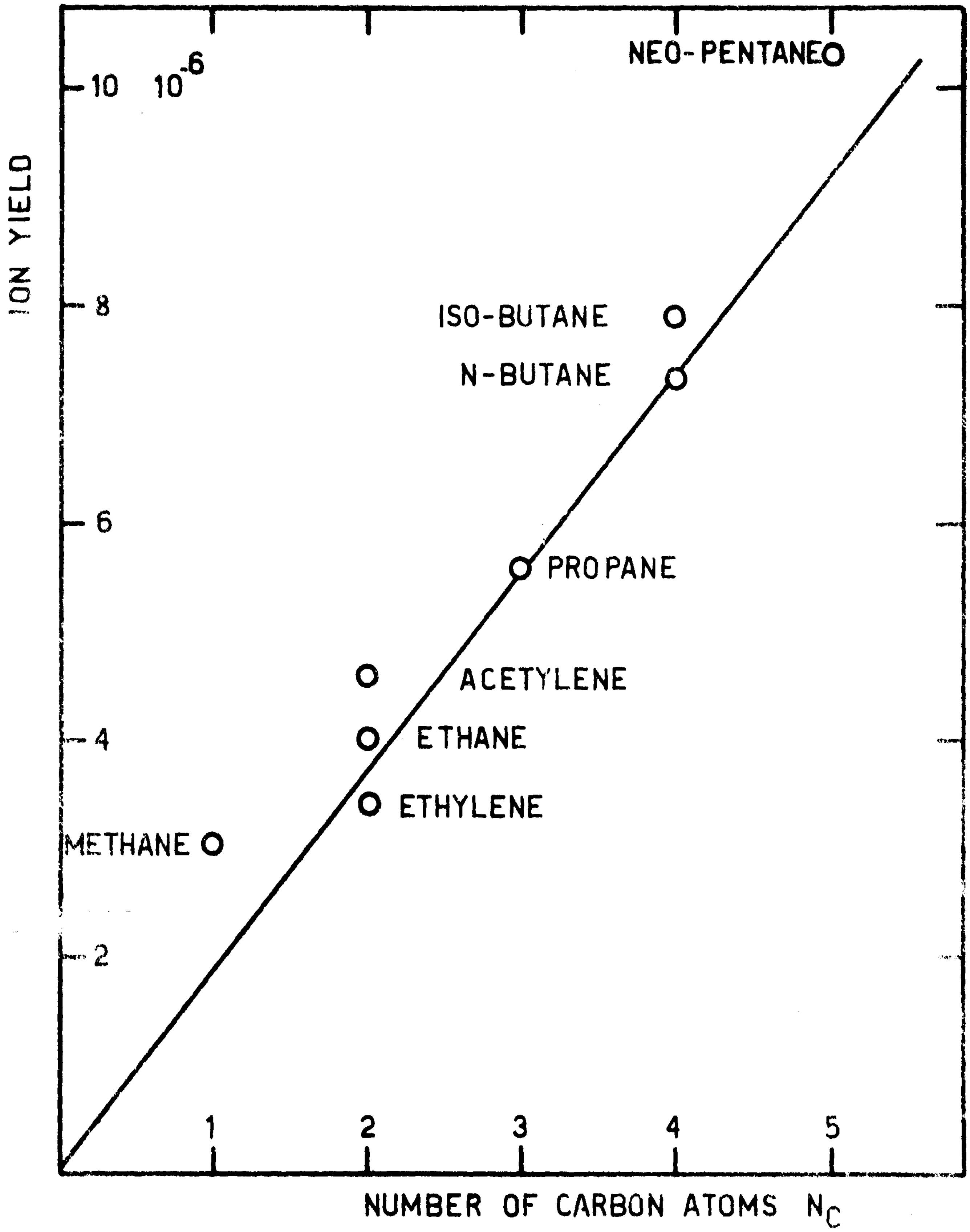

ION YIELD
10
10^-6
8
6
4
2
NEO-PENTANE
ISO-BUTANE
N-BUTANE
PROPANE
ACETYLENE
ETHANE
ETHYLENE
METHANE
1
2
3
4
5
NUMBER OF CARBON ATOMS N_C

Fig 11.

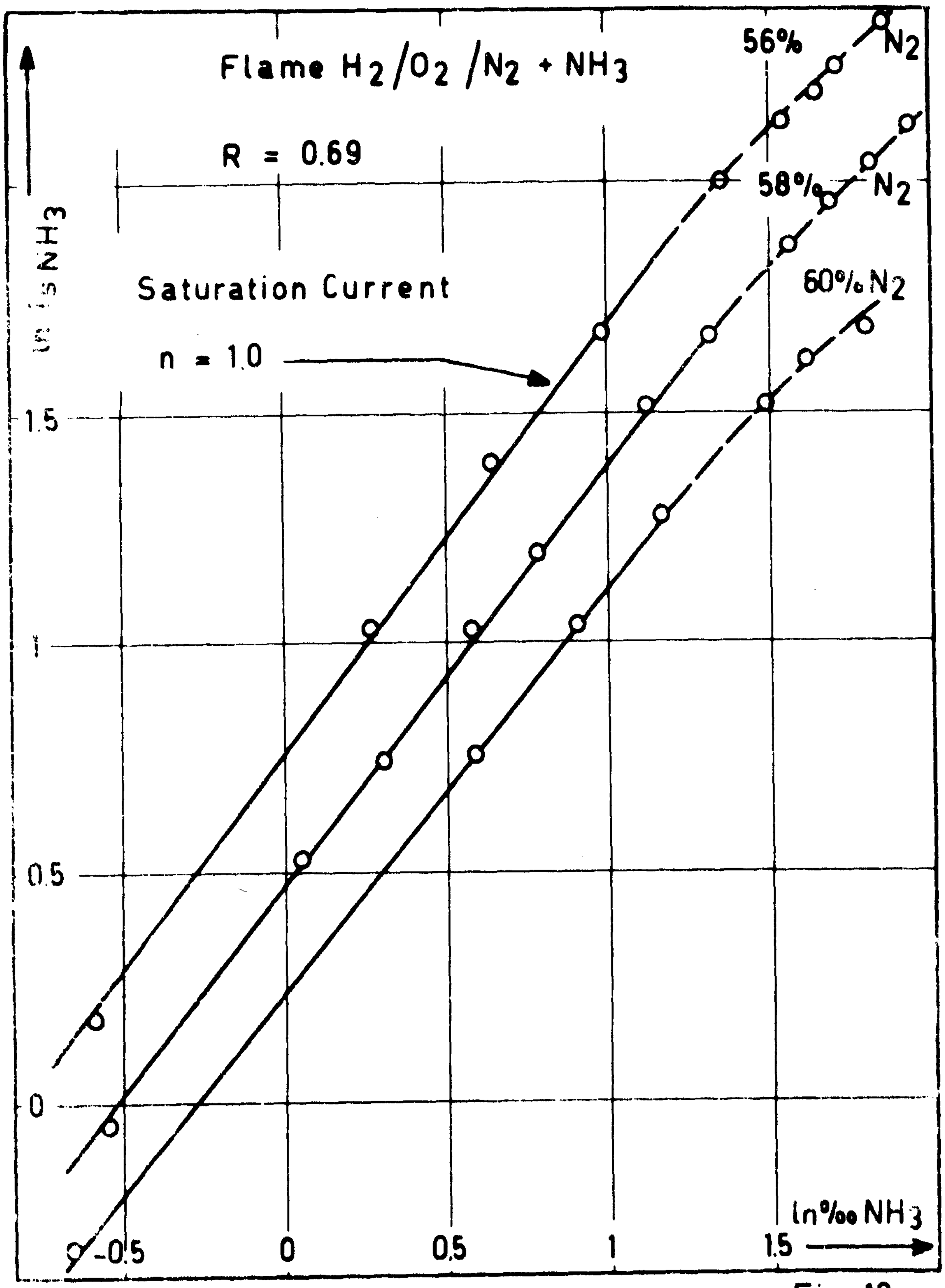

Flame H2/O2/N2 + NH3
R = 0.69
Saturation Current
n = 1.0
56% N2
58% N2
60% N2
ln is NH3
ln ‰ NH3
1.5
1
0.5
0
-0.5
0
0.5
1
1.5

Fig. 12

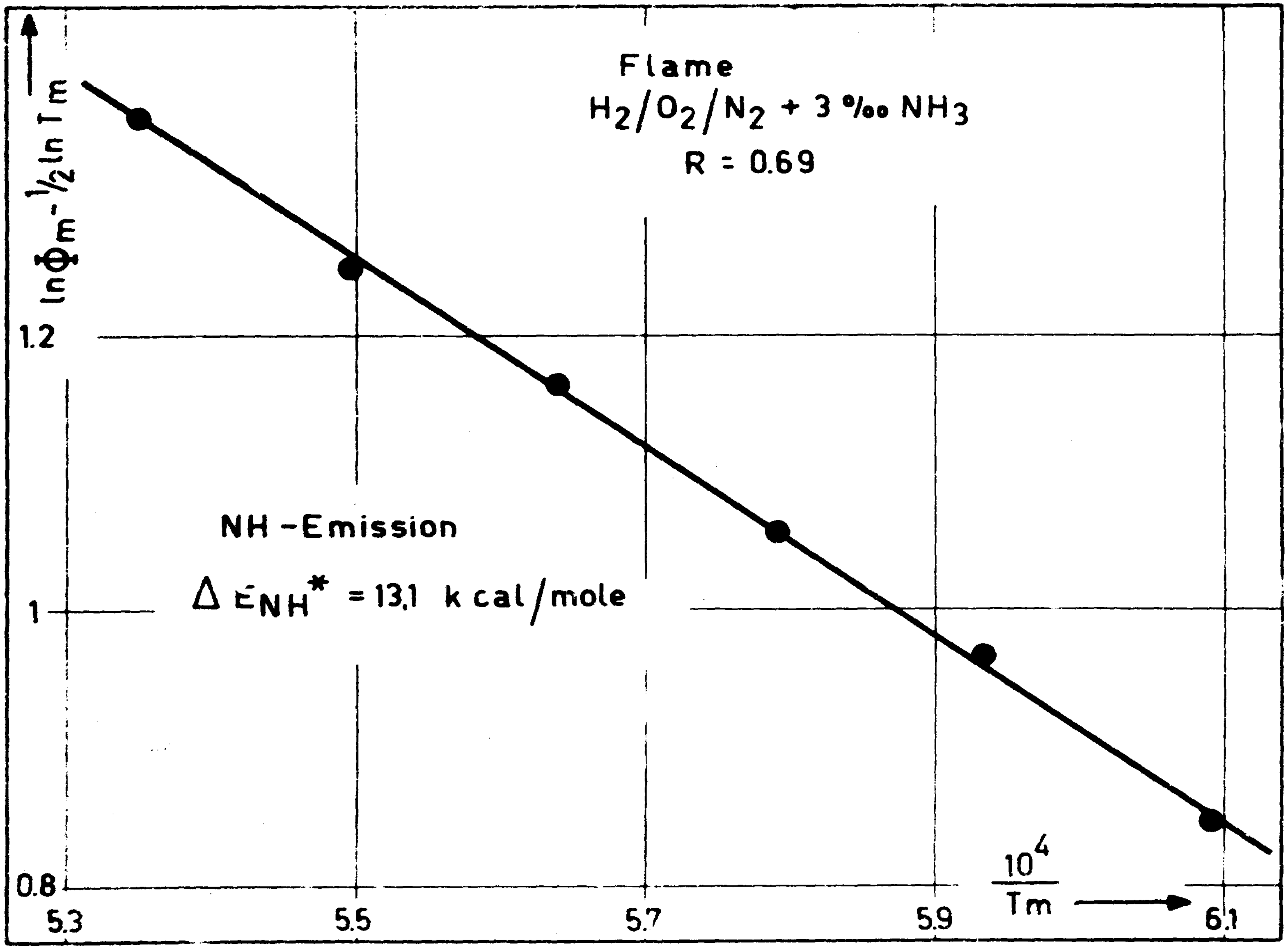

$\ln \Phi_m - \frac{1}{2} \ln T_m$
1.2
1
0.8
5.3
5.5
5.7
5.9
6.1
$\frac{10^4}{T_m}$
Flame
$H_2/O_2/N_2$ + 3 ‰ NH_3
R = 0.69
NH -Emission
$\Delta E_{NH}^* = 13{,}1$ k cal/mole

Fig. 13

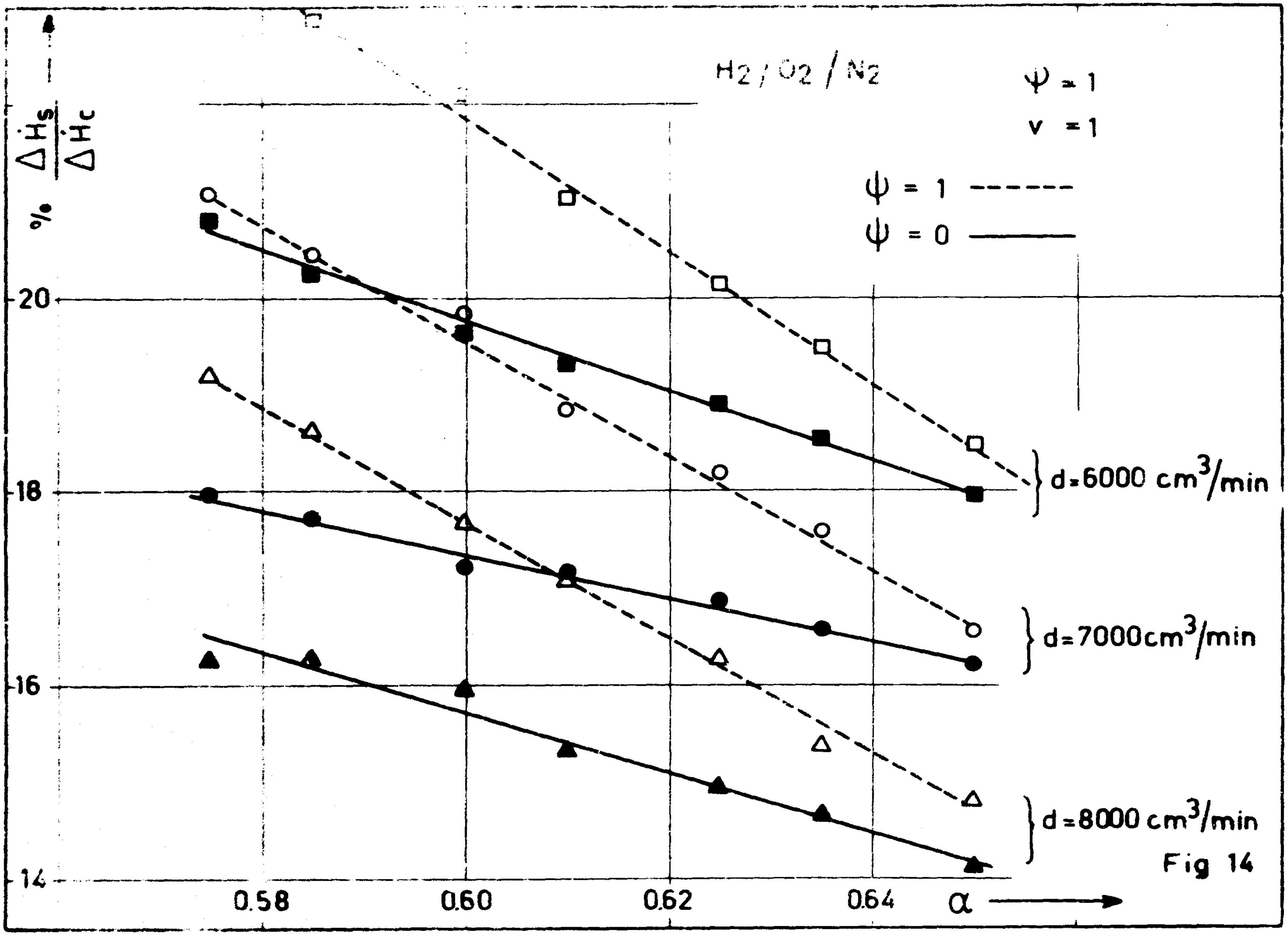

H2 / O2 / N2
Ψ = 1
v = 1
ψ = 1 ------
ψ = 0 ——
% ΔḢs / ΔḢc
20
18
16
14
0.58
0.60
0.62
0.64
α
d=6000 cm³/min
d=7000cm³/min
d=8000 cm³/min

Fig 14

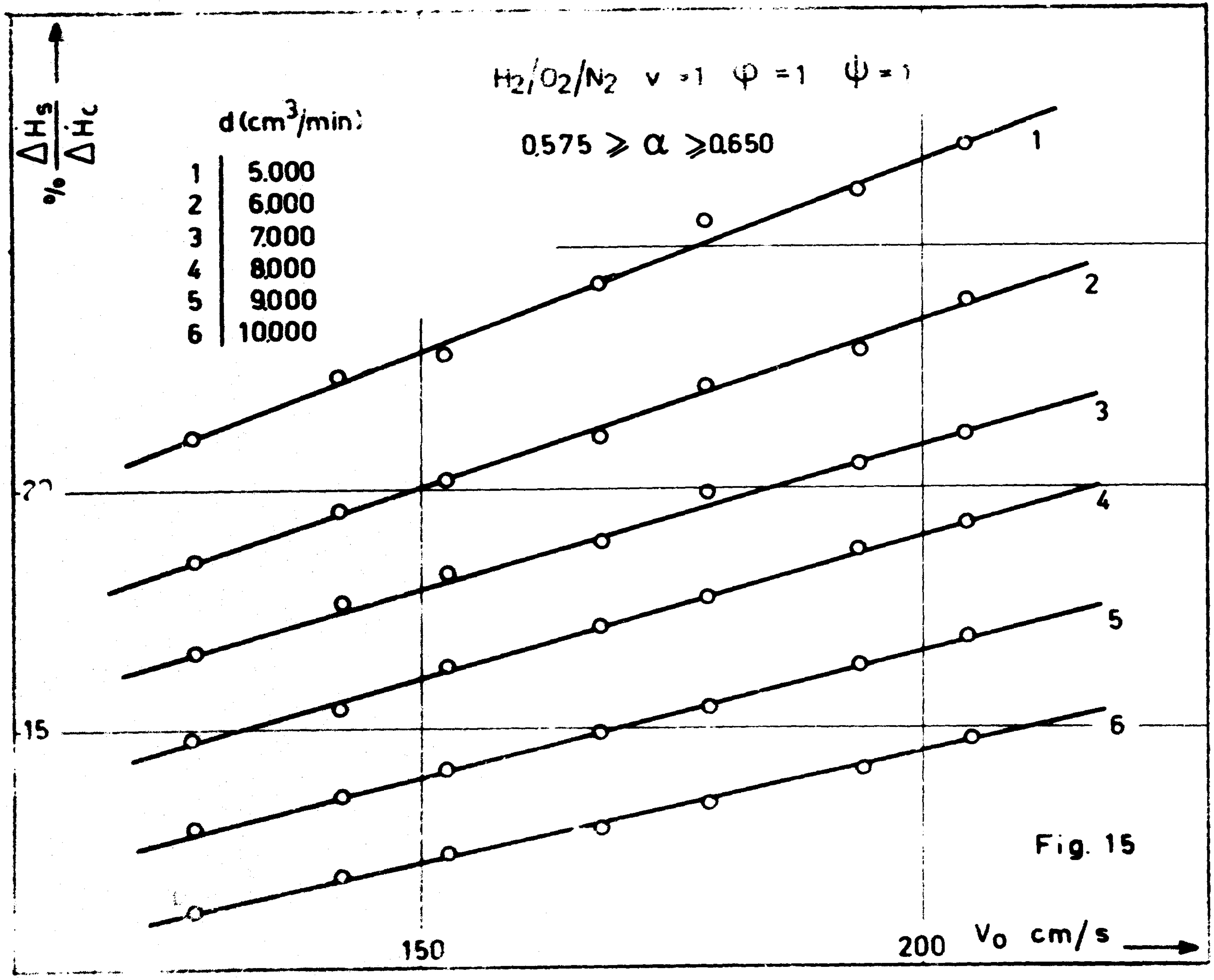

$\frac{\Delta H_s}{\Delta \dot{H}_c}$ %
$H_2/O_2/N_2$ v = 1 φ = 1 ψ = 1
0,575 ⩾ α ⩾ 0,650
d (cm³/min)
1 | 5.000
2 | 6.000
3 | 7.000
4 | 8.000
5 | 9.000
6 | 10.000
1
2
3
4
5
6
20
15
150
200
V_0 cm/s

Fig. 15

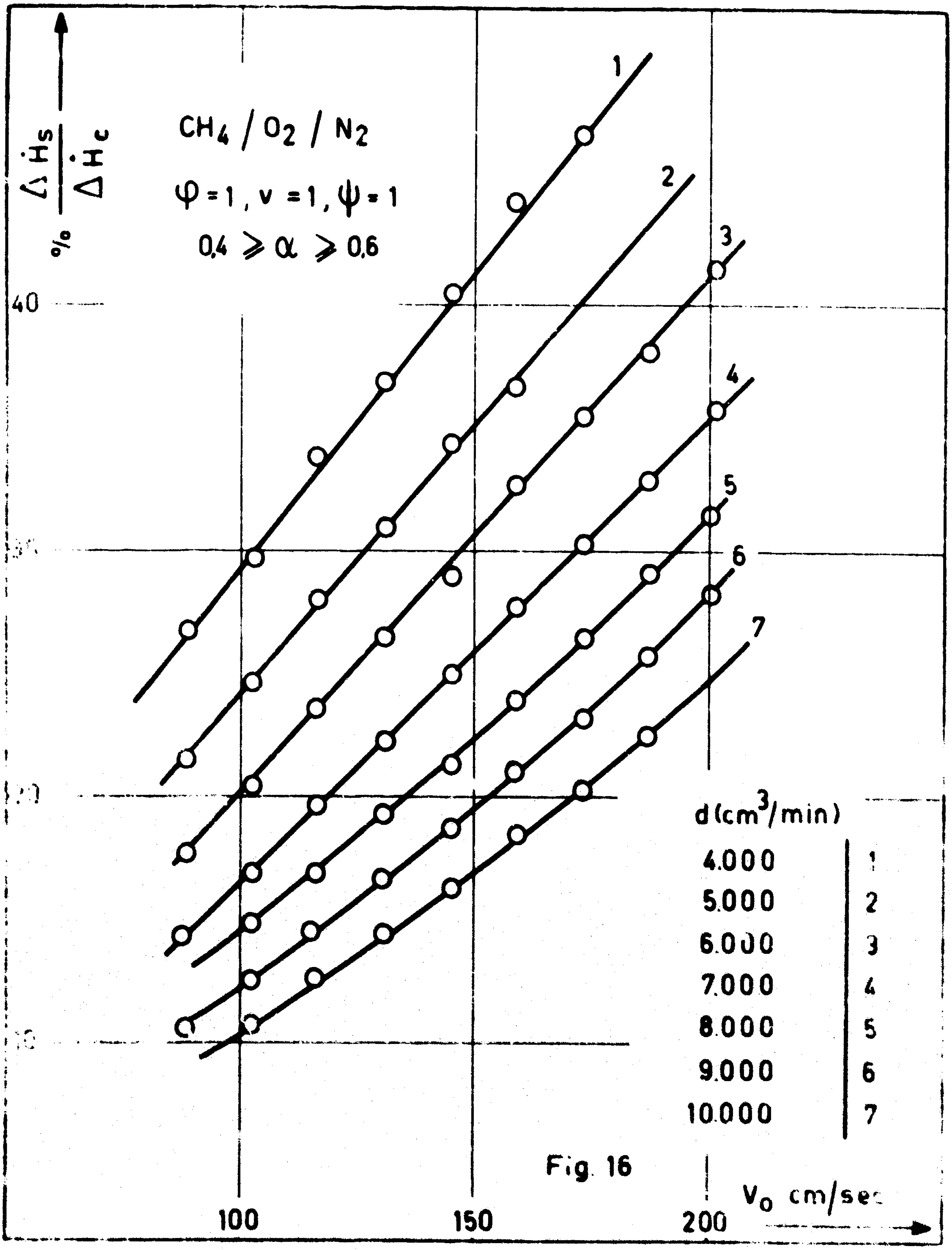

% ΔḢs / ΔḢc
CH4 / O2 / N2
φ = 1 , ν = 1 , ψ = 1
0,4 ⩾ α ⩾ 0,6
40
30
20
10
1
2
3
4
5
6
7
d (cm³/min)
4.000 1
5.000 2
6.000 3
7.000 4
8.000 5
9.000 6
10.000 7
100
150
200
V0 cm/sec

Fig. 16

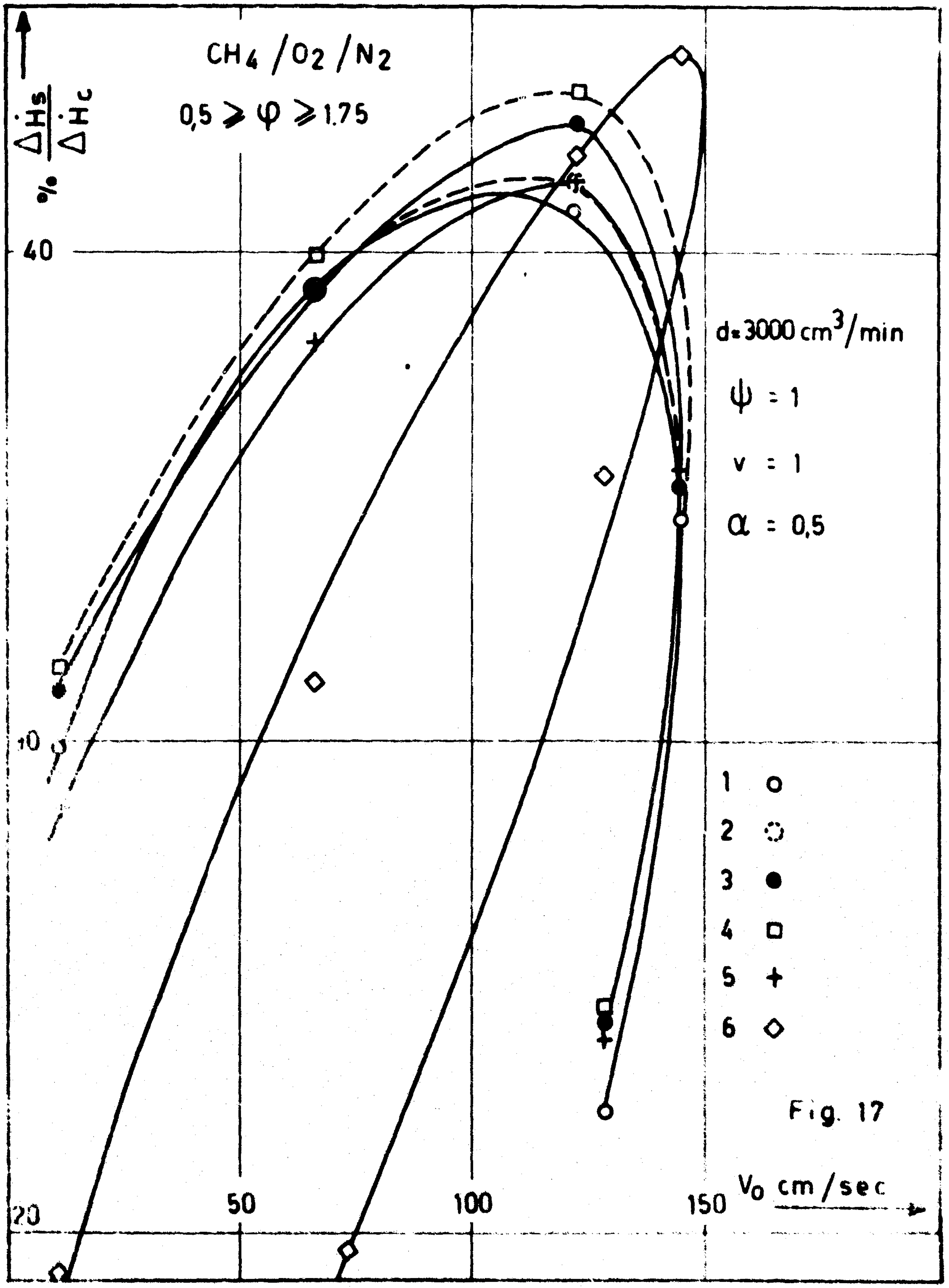

CH4 /O2 /N2
0,5 ⩾ φ ⩾ 1.75
% ΔḢs/ΔḢc
40
10
20
50
100
150
Vo cm/sec
d=3000 cm³/min
ψ = 1
v = 1
α = 0,5
1 ○
2 ◌
3 ●
4 □
5 +
6 ◇

Fig. 17

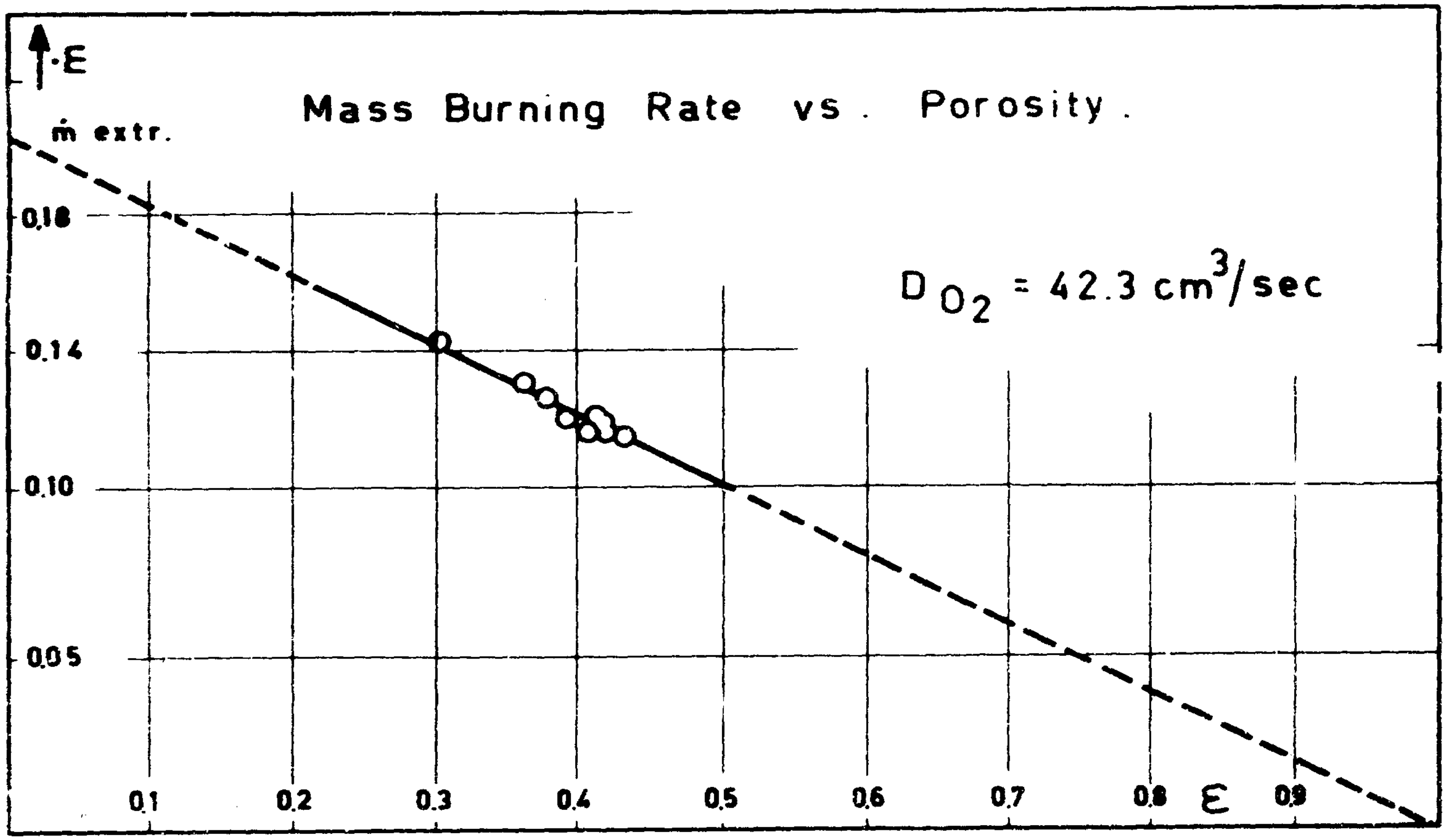

Mass Burning Rate vs. Porosity.
$\dot{m}$ extr.
$\uparrow \cdot \varepsilon$
$D_{O_2} = 42.3\ cm^3/sec$
0.18
0.14
0.10
0.05
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
ε

Fig .18

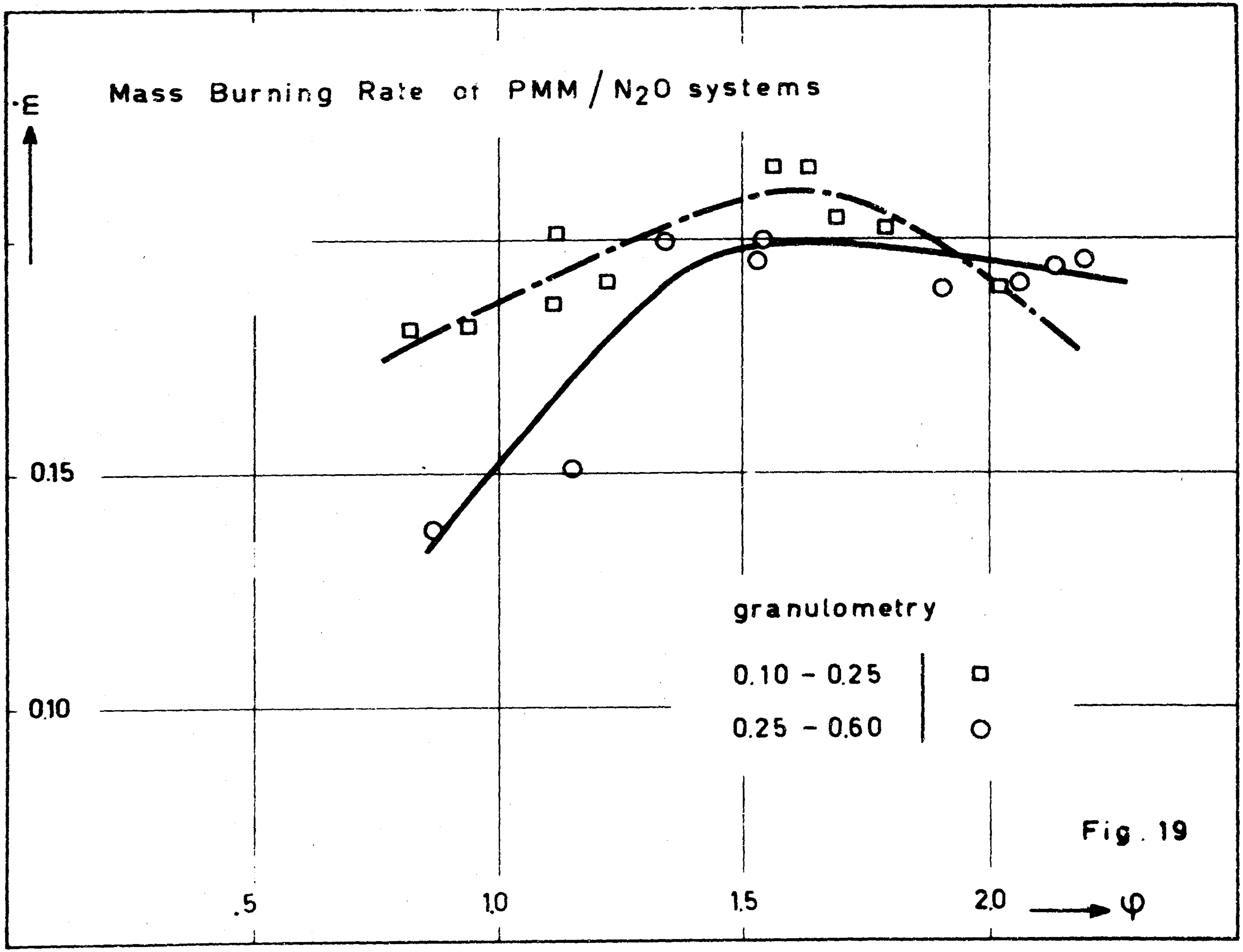

Mass Burning Rate of PMM / N2O systems
·E
0.15
0.10
.5
1.0
1.5
2.0
φ
granulometry
0.10 - 0.25 □
0.25 - 0.60 ○

Fig. 19

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1400 Wilson Boulevard (SREP)
Arlington, Va. 22209

The two parts of the report deal successively with chemiluminescence in flames and with combustion of solid propellants.

1) Relationships between chemiluminiscence (CL) and chemi-ionization(CI) on one hand, and the molecular structure of the fuel on the other hand have been put forward, in particular the structure of hydrocarbon fuels have been investigated. The importance of the formation of "energy rich bonds" during the CL and CI processes has been pointed out not only with hydrocarbon fuels but also with cyanogen and ammonia where the formation of N-O bond plays an essential role.

2) Applying the multimicrojet burner technique for the simulating study of heat transfer from the reaction zone onto the regressing surface of solid propellants, it has been possible to investigate the dependence of the heat release on parameters such as total flow, distribution modes of gases, dilution and richness of the flammable mixture and to correlate the heat release as a function of the burning velocity alone. Moreover, a new reliable technique to prepare "cigarettes" of PMM for hybrid combustion has been developped where one can get rid of any trace of acetone, and where heat losses to the wall of the tube are avoided during the burning process. Mass burning rates of PMM with N_2O and O_2 have been recorded, and the porosity of the sample has been studied.

DD form 1473
1 nov 65

UNCLASSIFIED
Security Classification

14. KEY Words	Link A		Link B		Link C	
	Role	WT	Role	WT	Role	WT
-Chemiluminescence in flames						
-Spectrum emitted in flames						
-Chemi-ionization in flames						
-Hydrocarbon structure and chemi-ionization or chemiluminiscence in flames						
-Cyanogen flames						
-Ammonia flames						
-Simulating study of solid propellants						
-Multimicrojet burner						
-Hybrid combustion in PMM						

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13. ABSTRACT

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-Ammonia flames				
-Simulating study of solid propellants				
-Multimicrojet burner				
-Hybrid combustion in PMM				