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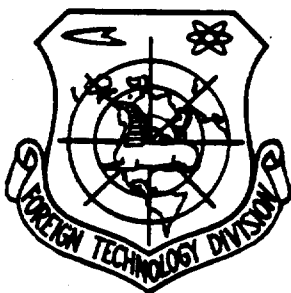
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THERMODYNAMIC AND THERMOPHYSICAL PROPERTIES OF COMBUSTION PRODUCTS

(Selected Pages)

by

V. Ye. Alemasov, A. F. Dregalin, et al.



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TABLE OF CONTENTS

U. S. Board on Geographic Names Transliteration System.....	11
Forward to Volume II.....	1
Basic Designations Adopted.....	5
Chapter I. General.....	7
Chapter II. Initial Data for Calculations.....	10
Chapter III. Accuracy of the Calculation Results.....	38
Chapter IV. Brief Description of Tables and Graphs.....	61
Chapter V. Tables and Graphs of Calculation Results.....	66
Bibliography.....	109

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U. S. BOARD ON GEOGRAPHIC NAMES TRANSLITERATION SYSTEM

Block	Italic	Transliteration	Block	Italic	Transliteration
А а	<i>А а</i>	A, a	Р р	<i>Р р</i>	R, r
Б б	<i>Б б</i>	B, b	С с	<i>С с</i>	S, s
В в	<i>В в</i>	V, v	Т т	<i>Т т</i>	T, t
Г г	<i>Г г</i>	G, g	У у	<i>У у</i>	U, u
Д д	<i>Д д</i>	D, d	Ф ф	<i>Ф ф</i>	F, f
Е е	<i>Е е</i>	Ye, ye; E, e*	Х х	<i>Х х</i>	Kh, kh
Ж ж	<i>Ж ж</i>	Zh, zh	Ц ц	<i>Ц ц</i>	Ts, ts
З з	<i>З з</i>	Z, z	Ч ч	<i>Ч ч</i>	Ch, ch
И и	<i>И и</i>	I, i	Ш ш	<i>Ш ш</i>	Sh, sh
Й й	<i>Й й</i>	Y, y	Щ щ	<i>Щ щ</i>	Shch, shch
К к	<i>К к</i>	K, k	Ъ ъ	<i>Ъ ъ</i>	"
Л л	<i>Л л</i>	L, l	Ы ы	<i>Ы ы</i>	Y, y
М м	<i>М м</i>	M, m	Ь ь	<i>Ь ь</i>	'
Н н	<i>Н н</i>	N, n	Э э	<i>Э э</i>	E, e
О о	<i>О о</i>	O, o	Ю ю	<i>Ю ю</i>	Yu, yu
П п	<i>П п</i>	P, p	Я я	<i>Я я</i>	Ya, ya

*ye initially, after vowels, and after ъ, ы; e elsewhere.
When written as ë in Russian, transliterate as yë or ë.

RUSSIAN AND ENGLISH TRIGONOMETRIC FUNCTIONS

Russian	English	Russian	English	Russian	English
sin	sin	sh	sinh	arc sh	sinh
cos	cos	ch	cosh	arc ch	cosh
tg	tan	th	tanh	arc th	tanh
ctg	cot	cth	coth	arc cth	coth
sec	sec	sch	sech	arc sch	sech
cosec	csc	csch	csch	arc csch	csch

Russian	English
rot	curl
lg	log

THERMODYNAMIC AND THERMOPHYSICAL PROPERTIES OF COMBUSTION PRODUCTS

V. Ye. Alemasov, A. F. Dregalin, A. P. Tishin, V. A. Khudyakov, and
V. N. Kostin

Volume II: Fuels on an Oxygen Base

(Reference book: prepared under the scientific direction of
Academician V. P. Glushko)

FORWARD TO VOLUME II

The second volume of the Reference Book begins a series of volumes which present the thermodynamic and thermophysical properties of combustion products of various groups of fuel compounds. As indicated in volume I of the Reference [6], the basis of the grouping of fuel compounds is classification in accordance with related oxidizers since it is namely the oxidizer which usually is the component determining the special features of the fuel compound. Four typical groups of fuels are distinguished.

In the course of working on the Reference it was learned that the presentation of results from the calculation of each typical group of fuels (12-15 fuel compounds) in one volume is inexpedient. Such a volume turns out to be cumbersome, difficult to produce, and inconvenient to use. In this connection, two volumes are devoted to each characteristic group. Thus, the properties of combustion products of fuels based on oxygen and air are presented in Volumes II and III.

The second volume of the Reference presents thermodynamic and thermophysical properties of the combustion products of four fuel compounds in which oxygen is used as the oxidizer. All the data which are presented were obtained by the authors by calculations in accordance with the original methods and programs described in Volume I.

The necessary initial data on the enthalpy of the fuel components were taken primarily from the Reference Book "Termicheskiye konstanty veshchestv" [Thermal constants of substances] [45-48], and the reference data on thermodynamic properties of the components of combustion products - from the reference "Termodinamicheskiye svoystva individual'nykh veshchestv" [Thermodynamic properties of individual substances] [49]. Supplements and refinements obtained by the authors of Reference [49] when preparing its third edition were also used.

The list of properties of combustion products, range and spacing of change of determining parameters (stagnation pressure at the input to the nozzle p_{co} , excess oxidant ratio α_{ox} , degree of expansion ϵ) correspond to those presented in Volume I.

The data obtained by calculation correspond to the liquid state of oxygen with a boiling temperature of 90.188°K and a pressure of 1 physical atmosphere. In Volume I of the Reference it was shown that using methods of extrapolation for enthalpy it is possible to recalculate results to another initial temperature of fuel components or to their different phase state with high accuracy. The derivatives necessary for these recalculations, just as the derivatives for extrapolation in accordance with p_{co} , ϵ , and chemical composition of the fuel component (content of admixtures), are presented in the tables of the volume.

The results of the calculation are presented in the form of graphs and tables, a detailed description of which is given in Volume I and a brief one - in this volume.

The basic author and editing work in the preparation of the volume was conducted by members of the Editorial Council under the scientific direction of Academician V. P. Glushko.

The composition of the Editorial Council: Academician V. P. Glushko (chairman), V. Ye. Alemasov (deputy chairman), N. V. Illarianov (scientific secretary), A. P. Vanichev, S. D. Grishin, A. F. Dregalin, V. A. Il'inskiy, and A. P. Tishin.

Doctor of Technical Sciences V. Ye. Alemasov, Doctor of Technical Sciences A. F. Dregalin, Doctor of Technical Sciences A. P. Tishin, Candidate of Technical Sciences V. A. Khudyakov, and Junior Scientific Associate V. N. Kostin accomplished the basic work - they obtained all calculation data presented in Volume II from the methods and programs which they developed. As regards the tabular material obtained on the BESM-6 computer, the persons mentioned also stepped forth as editors - compilers. They accomplished: the preparation of the initial data for calculation; a check of the results for conformance with initial data; the logical monitoring of the correctness of the calculation's results in accordance with specially developed algorithms; the introduction of special designations into the tables which are absent in the ATsPU EVM [computer alpha-numeric printer]; checking the quality of the printing and necessary completion work.

On the basis of original calculation data, this same collective prepared all the graphs presented in the second volume except for the graphs on the influence of chemical nonequilibrium (Figs. No. 5.6-5.11, 5.17-5.21, 5.27-5.31). The latter were prepared by Doctor of Technical Sciences U. G. Pirumov from the results of calculations which he conducted jointly with L. F. Kuz'mina, V. S. Chibisova, and A. K. Petrova.

Textual materials of the volume were prepared by: Doctor of Technical Sciences V. Ye. Alemasov and Doctor of Technical Sciences A. F. Dregalin - §§ I, IV, 2.4, 2.5, 3.2-3.5; Doctor of Technical Sciences V. A. Il'inskiy - §§2.1-2.3; Doctor of Technical Sciences U. G. Pirumov - §2.6; Candidate of Technical Sciences V. A. Khudyakov and Junior Scientific Associate V. N. Kostin - §3.1.

Doctor of Technical Sciences A. P. Tishin and Candidate of Technical Sciences V. A. Khudyakov took part in the preparation of materials for §2.1; Z. Kh. Gruzdeva - for §2.5; V. I. Bychenok - for §3.4; and A. S. Lyashev - for §3.5.

The bibliography was prepared by the authors of of the sections from bibliographic sources published primarily prior to 1971.

Scientific editing of the volume was accomplished by Academician V. P. Glushko (responsible editor) and Doctor of Technical Sciences V. Ye. Alemasov. Scientific editing of the volume's sections were conducted by:

Corresponding Member of the Academy of Sciences USSR A. P. Vanichev - sections I, II text, graphs of Figs. 5.1-5.21;

Doctor of Technical Sciences V. A. Il'inskiy - section III of the text;

Doctor of Technical Sciences S. D. Grishin - section IV of the text, graphs of Figs. 5.22-5.35.

Work on systematizing the bibliographic sources, compiling the card files and bibliography, and the extremely laborious work on the technical formulation of Volume II was accomplished by a group of associates of VINITI [All-Union Institute of Scientific and Technical Information] of the Academy of Sciences of the USSR under the overall direction of N. V. Illarionov consisting of: N. V. Akshinska, T. V. Luzina, N. G. Mozhayeva, D. A. Shirinskaya, as well as associates of other organizations L. A. Borisova, A. I. Vinik, Z. Kh. Gruzdeva, G. A. Dekhtyaruk, G. B. Kozina, G. S. Kol'tsova, A. S. Lyashev, I. A. Nikulin, A. P. Panchenko, S. M. Potapova, M. G. Rezyapkina, Candidates of Technical Sciences V. N. Trinos, A. Z. Khamidullin, A. S. Cherenkov, and D. I. Yagudina.

The authors express their profound gratitude to all these people.

A review of the manuscript for Volume II was conducted by Doctor of Chemical Sciences Professor L. V. Gurvich, Doctor of Technical Sciences Professor Ye. A. Sivoldoskiy, Doctor of Chemical Sciences

Professor G. B. Manelis, and Candidate of Physical-Mathematical Sciences L. N. Stesik. Doctor of Technical Sciences Ye. V. Samuylov took part in the discussion and review of §§2.5 and 3.3. The authors are grateful to the reviewers for their valuable remarks and advice. The authors mark with special gratitude the work of Doctor of Technical Sciences V. A. Il'inskiy who, without restricting himself to the duties of editor, rendered active creative assistance in the preparation of new materials for section III.

Basic Designations Adopted

- a - speed of sound;
- α_{ox} - excess oxidant ratio;
- α_p - isobaric coefficient of expansion;
- β - consumption complex (specific pressure impulse);
- β_T - isothermic compression coefficient;
- C_p, c_p - specific heat at constant pressure: molar and weight, respectively;
- C_v, c_v - specific heat at constant volume: molar and weight, respectively;
- $\epsilon = \frac{P_{co}}{P}$ - degree of pressure expansion;
- ζ - coefficient of impulse loss;
- F - area;
- $F = \frac{F}{F_0}$ - geometric degree of expansion (relative area);
- $f = \frac{F}{Q}$ - specific (unit) area;
- Q - per-second flow rate;
- g - weight fraction;
- η - coefficient of dynamic viscosity;
- h, h - specific enthalpy: molar and weight, respectively;
- I_s - specific impulse;
- K - equilibrium constant for partial pressures;
- k_1 - weighted fuel-air ratio;
- k_2 - volumetric fuel-air ratio;
- $\kappa = \frac{c_p}{c_v}$ - ratio of specific heat;
- λ - coefficient of thermal conductivity;
- M - Mach number;
- μ - molecular weight;
- n - number of moles, mean index of isentropy;
- p - pressure;

R - universal gas constant;
 r - radius;
 $\bar{r}$ - relative radius;
 ρ - density;
 s, s - specific entropy: molar and weight, respectively;
 T - temperature;
 v - specific volume;
 w - rate of flow;
 x - molar fraction;
 z - weight fraction of substance in condensed state.

Indices

r - fuel;
 ox - oxidizer;
 τ - propellant;
 n - parameters in a vacuum (superscript);
 0 - deceleration parameters;
 f - parameters of nonreacting mixture;
 $*$ - parameters at input to chamber;
 c - parameters at input to nozzle;
 $*$ - parameters in nozzle throat (subscript);
 a - parameters in exit section of nozzle.

CHAPTER I

GENERAL

1.1. Brief Survey of Published Data

Oxygen as an oxidizer is widely used in various chemical fuels. The most widespread fuel combinations are a combination of oxygen with liquid hydrocarbon fuels of the gasoline and kerosene type.

Some information on the properties of the combustion products of such fuels are presented in [22, 37].

The wide use of natural gas as a fuel required a determination of the properties of the products of natural gas combustion with oxygen and hydrogen. These properties are presented in Soviet and foreign works [20, 55, 76] as applicable to various thermotechnical devices.

Fuel based on natural gas and air-oxygen oxidizers with easily ionized additives are employed to generate electric power by the magnetohydrodynamic method. Some information on the properties of the combustion products from such fuels is contained in [8, 13, 25, 91].

The successful development and employment of jet propulsion systems substantially expanded the list of fuels being employed and investigated. In addition to conventional hydrocarbon fuels, ammonia, asymmetrical dimethylhydrazine, pentaborane, and other fuels are employed in combination with oxygen or are being studied.

One of the most effective fuels is employed with liquid oxygen - liquid hydrogen which was first proposed for ZhRD's [liquid-fuel rocket motors] in 1930 by K. E. Tsiolkovskiy [33].

Calculation data on the properties of combustion products of such fuel combinations are presented in many works.

Usually, information on the properties of combustion products is presented in the form of IS-diagrams [20, 69] or in the form of tables and graphs. The range of change of the determining parameters and the list of properties to be calculated differ substantially in different works. The majority of works encompass narrow intervals of change in the composition of the fuel (α_{ok}), pressure on the input to the nozzle (p_{co}), and degree of gas expansion in the nozzle (ξ). As a rule, only the basic thermodynamic properties of the combustion products are determined. Transfer properties are presented in a few sources [4, 15, 40, 87]. The most complete and systematized information on the properties of the combustion products of a number of fuels is contained in the works of authors [2-4, 10-12]. They present a broad list of thermodynamic properties and examine different versions in the accomplishment of the processes. These data were obtained in a broad range of determining parameters. Thus, the calculations of the fuels of liquid oxygen + kerosene [10] and liquid oxygen + asymmetrical dimethylhydrazine [11] encompass a range of change of the excess oxidant ratio $\alpha_{ok} = 0.1-10$, pressure at the input to the nozzle $p_{co} = 2-25 \text{ MN/m}^2$, and degree of expansion $\xi = 20-5000$. For the liquid fuel of oxygen + liquid hydrogen [2, 12], information on combustion products was obtained in the range of $\alpha_{ok} = 0.05-10$, $p_{co} = 1-30 \text{ MN/m}^2$, and $\xi = 10-10,000$.

Of foreign works, we can note a summary of data on the fuel of liquid oxygen + liquid hydrogen [83] as well as a few works containing fragmentary information on the combustion products of several fuels, for example, [43, 71, 82].

A systematic generalized impression of the materials mentioned above in the form, for example, of a compiled reference book is

(inexpedient. This is hindered by many circumstances: the differences in initial data in various works, different completeness of information, different intervals of change in determining parameters, the absence of accuracy estimates, and so forth.

1.2. Fuels Presented in Volume II

Volume II presents thermodynamic and thermophysical properties of combustion products of fuel groups which are of interest for contemporary and promising thermoenergy engineering and engine building. They are liquid two-component fuels based on oxygen as an oxidizer:

liquid oxygen + liquid hydrogen,
 liquid oxygen + kerosene,
 liquid oxygen + asymmetrical dimethylhydrazine,
 liquid oxygen + liquid ammonia.

The list of properties determined by calculation is the same for all fuels. The range of change in the determining parameters (α_{ok} , p_{co} , ξ) varies in accordance with two types of grids: "large" (B) and "small" (M). More detailed information on the list of properties and grids of parameters are presented in Chapter XIII of Volume I.

Table 1.1 presents a list of fuels which are examined in Volume II and indicates a grid of parameters in accordance with which the calculation was accomplished.

Table 1.1. Fuels examined in Volume II of the Reference Book.

№ п/п	Топливо (1)	$\alpha_{ок}$	$p_{co}, \text{МН/м}^2$	Сетка (2)
1	$O_2 + H_2$	0,3—5,0	0,1—50	Б
2	$O_2 + \text{керосин}$ (3)	0,4—5,0	0,1—50	Б
3	$O_2 + (CH_3)_2NNH_2$	0,3—5,0	0,1—50	Б
4	$O_2 + NH_3$	0,6—2,0	0,2—50	М

KEY: (1) Fuel; (2) Grid; (3) Kerosene..

CHAPTER II

INITIAL DATA FOR CALCULATIONS

2.1. Chemical Composition of Fuel Components

Fuel components are technical products and admixtures are present in them along with the basic substance. The admixture content is regulated in the Standards for a number of technical substances which serve as fuel components.

If the chemical composition of an admixture is close to the composition of the basic substance and its content is low, then in a number of cases the admixture can be identified with the basic substance introducing, where necessary, a correction for heat of formation.

2.1.1. Oxidizers

Liquid oxygen O_2 . The composition is standardized in accordance with GOST [All-Union State Standard] 6331-68, "Liquid oxygen, technical and medical." This standard is extended to liquid oxygen which is obtained from the air by deep freezing.

Depending upon the content of oxygen and admixtures technical liquid oxygen is produced in three varieties. The composition is presented in Table 2.1. In accordance with GOST 6331-68 the content of carbon monoxide, gaseous acids, bases, ozone, and other gas oxidizers is not standardized. However, the quantity of these substances is low and they can be disregarded.

The basic admixture in liquid technical oxygen is nitrogen whose weight content in liquid oxygen does not exceed 0.8%. When performing calculations for the Reference Book only liquid nitrogen was considered as an admixture for liquid oxygen.

Table 2.1. Liquid oxygen, technical and medical.

Наименование показателей (1)	Нормы для сортов (2)		
	1	2	3
1. Содержание кислорода в объемных % не менее (3)	99,7	99,5	99,2
2. Содержание ацетилена в 1 л жидкого кислорода в мл при 20°C и 760 мм рт. ст. не более (4)	—	—	0,04
3. Содержание масла в 1 л жидкого кислорода в мг не более (5)	—	—	0,01
4. Содержание двуокиси углерода в 1 л жидкого кислорода в мл при 20°C и 760 мм рт. ст. не более (6)	3	3	Не нормируется (8)
5. Содержание влаги и механических примесей (7)	—	—	Не нормируется (8)

KEY: (1) Name of indices; (2) Standard for varieties; (3) Oxygen content in volume %, no less than; (4) Acetylene content in 1 liter of liquid oxygen in ml at 20°C and 760 mm Hg, no more than; (5) Oil content in 1 liter of liquid oxygen in mg, no more than; (6) Content of carbon dioxide in 1 liter of liquid oxygen in ml at 20°C and 760 mm Hg, no more than; (7) Content of moisture and mechanical admixtures; (8) Not standardized.

2.1.2. Fuels

Liquid hydrogen H_2 . Liquid hydrogen is obtained from commercial gaseous hydrogen whose chemical composition is regulated in accordance with GOST 3022-61.

In gaseous hydrogen which is obtained by the electrolysis of water and chloride salts as well as by the iron vapor method, oxygen, nitrogen, and water may be present in noticeable quantities; also carbon monoxide in hydrogen obtained by the conversion of methane and other gaseous hydrocarbons. The solubility of nitrogen, oxygen, and water in liquid

hydrogen is very low. With an extremely low hydrogen temperature oxygen, nitrogen, and water are in a solid state, usually fall out as a precipitate, and are removed. Therefore, liquid hydrogen is obtained with an extremely low quantity of admixtures.

At room temperature hydrogen consist of a mixture of approximately 25% para hydrogen and approximately 75% ortho hydrogen which is in equilibrium. At the boiling temperature of liquid hydrogen the equilibrium content of ortho hydrogen is about 0.2% and the content of the para modification is approximately 99.8%.

In this Reference Book it is accepted that there are no admixtures of other substances in liquid hydrogen and the content of the para modification can be greater than the equilibrium. The coefficients of the extrapolation formulas A_4 , B_4 , C_4 , D_4 , L_4 in the calculations of compounds with liquid hydrogen pertain to extrapolation for oxidizer content.

Kerosene. Kerosenes are obtained from petroleum and are a mixture of various hydrocarbons of several homologous series; present in them is a small quantity of heteroorganic compounds which contain nitrogen, sulfur, and oxygen. The content of individual hydrocarbons depends on the method of obtaining the kerosene and the oil deposit. The hydrocarbon content of individual homologous series except for aromatic hydrocarbons is usually not standardized or is standardized indirectly (for example, the content of unsaturated hydrocarbons is limited by the iodine or bromine number). The fractional composition of kerosene is regulated, i.e., the temperatures up to which a given portion of the kerosene is distilled.

Table 2.2 presents the physical-chemical properties of Soviet kerosenes which are employed for rocket motors. In accordance with the indicated GOST's these kerosenes should contain no mechanical admixtures, insoluble resins, hydrogen sulfide, water, water soluble acids, and bases.

Kerosenes contain a small amount of oxygen and nitrogen and a small quantity of sulfur; therefore, they are not considered in

calculations for the Reference Book. It is accepted that at a temperature of 25°C the density of the kerosene equals 0.830 g/cm³; the lowest heat of combustion is 10,300 kcal/kg; the carbon content equals 85.9% by weight and the hydrogen content - 14.1% (conventional chemical formula CH_{1.956}, C/H ratio = 0.5113).

In order to have the opportunity to extrapolate the results of the calculations for kerosenes of various composition, a substance with a conventional chemical composition, an addition of 1% of which changes the C/H ratio by 1%, is taken as the basic admixture. The enthalpy of this conventional substance is taken as equal to the enthalpy of kerosene. The derivatives for the composition of the fuel which are presented in the tables of the reference book are derivatives for the change in the C/H ratio in the fuel expressed in fractions.

Table 2.2. Physical-chemical properties of some kerosenes.

Физико-химические показатели	(2) ГОСТ 10 227-62			(3) ГОСТ 12 308-66		МРТУ-38-1 244-66
	Т-1	ТС-1	Т-2	Т-6	Т-7 (ТС-1Г)	
(3) Плотность при 20 °С, г/см ³ , не ниже	0.800	0.775	0.755	0.840	0.775	0.830
(4) Кислотность, мг KOH/100 мл горючего, не более	0.7	0.7	0.7	0.5	0.5	0.7
(5) Йодное число, г йода/100 г горючего, не более	2.0	3.5	3.5	1.0	0.5	0.5
(6) Содержание ароматических углеводородов, %, не более	20	22	22	10	22	5
(7) Содержание фактических смол, мг/100 мл горючего, не более	6	5	5	6	4	2
(8) Содержание серы, %, не более, в том числе меркаптановой, не более	0.10 —	0.25 0.005	0.25 0.005	0.05 —	0.05 0.001	0.01 —
(9) Зольность, %, не более	0.003	0.003	0.003	0.003	0.003	0.003
(10) Теплота сгорания низшая, ккал/кг, не менее	10 250	10 250	10 300	10 300	10 300	10 300

KEY: (1) Physical-chemical indices; (2) All-Union State Standard; (3) Density at 20°C, g/cm³, no lower than; (4) Acidity, mg KOH/100 ml of fuel, no more than; (5) Iodine number, g iodine/100 g of fuel, no more than; (6) Content of aromatic hydrocarbons, %, no more than; (7) Content of actual resins, mg/100 ml of fuel, no more than; (8) Sulfur content %, no more than, including mercaptan, no more than; (9) Ash content, %, no more than; (10) Lowest heat of combustion, kcal/kg, no more than.

Asymmetrical dimethylhydrazine (CH₃)₂NNH₂. The basic admixtures when obtaining asymmetrical dimethylhydrazine (NDMG) are water, dimethylamine (CH₃)₂NH, and methylene dimethylhydrazine (CH₃)₂NNCH₂. Some quantity of these substances can also be formed with the oxidation of

NDMG with oxygen of the air. The remaining admixtures are present in small quantity and are not considered in this Reference Book.

Table 2.3. The effect of the content of $(\text{CH}_3)_2\text{NH}$ and $(\text{CH}_3)_2\text{NNCH}_2$ on the characteristics of combustion products.

№ п/в	Состав горючего (1)	$T_{\text{св}},$ К	$\rho,$ м/сек	$I_s, \text{ м/сек}$ (2)			$\bar{F}$		
				$\alpha=50$	$\alpha=100$	$\alpha=1000$	$\alpha=50$	$\alpha=100$	$\alpha=1000$
1	98.5% $(\text{CH}_3)_2\text{NNH}_2 + 0.5\% (\text{CH}_3)_2\text{NH} + 1\% (\text{CH}_3)_2\text{NNCH}_2$	3672	1800	3176	3330	3735	8.25	14.40	96.35
2	95.5% $(\text{CH}_3)_2\text{NNH}_2 + 1.5\% (\text{CH}_3)_2\text{NH} + 3\% (\text{CH}_3)_2\text{NNCH}_2$	3674	1799	3175	3329	3734	8.25	14.41	96.45
3	97% $(\text{CH}_3)_2\text{NNH}_2 + 1\% (\text{CH}_3)_2\text{NH} + 2\% (\text{CH}_3)_2\text{NNCH}_2$	3673	1800	3176	3330	3734	8.25	14.40	96.40

KEY: (1) Composition of fuel; (2) m/s.

Special thermodynamic calculations were conducted in order to determine the effect of changes in the content of dimethylamine and methylene dimethylhydrazine in asymmetrical dimethylhydrazine on the basic characteristics of combustion products.

Table 2.4. Synthetic liquid ammonia.

Наименование показателей (1)	(2) Нормы	
	1-й сорт	2-й сорт
(5) Содержание аммиака в %, не менее	99.9	99.6
(6) Содержание влаги в %, не более	0.1	0.4
(7) Содержание масла в мг/л, не более	10.0	35.0
(8) Содержание железа в мг/л, не более	2.0	Не нормируется (9)

KEY: (1) Name of indices; (2) Norms; (3) 1st grade; (4) 2nd grade; (5) Ammonia content in %, not less than; (6) Moisture content in %, not less than; (7) Oil content in mg/l, no more than; (8) Iron content in mg/l, no more than; (9) Not standardized.

As an example, Table 2.3 presents the results of these calculations for a fuel compound of $\text{O}_2 + \text{NDMG}$ with $p_{\text{co}} = 10 \text{ MN/m}^2$ and $\alpha_{\text{ok}} = 1.0$.

Table 2.5. Chemical composition of fuel compounds taken in calculations.

Топливная композиция (1)		$O_2 + H_2$	$O_2 + \text{керосин}$ (2)	$O_2 + (CH_3)_2NNH_2$	$O_2 + NH_3$
Окислитель (3)	Исходный состав (4)	O_2	O_2	O_2	O_2
	Примесь (5)	N_2	N_2	N_2	N_2
	Содержание примеси по весу до (6)	0,008	0,008	0,008	0,008
	Коэффициенты экстраполяционных формул (7)	A_1, B_1, C_1, D_1	A_1, B_1, C_1, D_1, L_1	A_1, B_1, C_1, D_1, L_1	A_1, B_1, C_1, D_1
Горючее (8)	Исходный состав в % по весу (9)	100% H_2	C—85,9% H—14,1%	97%(CH ₃) ₂ NNH ₂ + + 1%(CH ₃) ₂ NH + + 2%(CH ₃) ₂ NNCH ₂	100% NH_3
	Примесь (5)	—	$CH_{1,956}^{C_n H_m}$	H_2O	H_2O
	Содержание примеси по весу до (6)	—	$\pm 0,06$	0,005	0,004
	Коэффициенты экстраполяционных формул (7)	—	A_1, B_1, C_1, D_1, L_1	A_1, B_1, C_1, D_1, L_1	A_1, B_1, C_1, D_1

KEY: (1) Fuel composition; (2) Kerosene; (3) Oxidizer; (4) Initial composition; (5) Admixture; (6) Admixture content by weight up to; (7) Coefficients of extrapolation formulas; (8) Fuel; (9) Initial composition in % by weight.

As is evident, with an average content of dimethylamine and methylene dimethylhydrazine in the NDMG the deviation of the specific impulse in a vacuum does not exceed 1 m/s of the value with minimum or maximum taken content of $(CH_3)_2NH$ and $(CH_3)_2NNCH_2$. Proceeding from this, asymmetrical dimethyhydrazine with mean weight fractions of dimethylamine and methylene dimethylhydrazine have been taken as the basic composition in the Reference Book.

Water has been taken as the basic admixture for NDMG.

Liquid ammonia NH_3 . The composition is standardized in accordance with GOST 6221-62, "Synthetic liquid ammonia." Liquid ammonia is produced in two varieties depending on the physical-chemical indices. Its composition is presented in Table 2.4.

The basic admixture for liquid ammonia, in which regard in comparatively small quantity, is water. Other admixtures are present in even lesser quantity and are not considered in the calculations.

2.1.3. Fuel Compounds

In summing up the result, to substantiate the fuel components which are adopted in the calculation and the admixtures which are considered we present a generalizing Table 2.5. For each of the fuel compounds examined in Volume II Table 2.5 presents the initial chemical composition of the fuel components (all calculation tables and graphs correspond to it). The admixtures in the fuel and oxidizer which are considered and the ranges of their possible variation are indicated. In these ranges, the effect of the admixtures can be estimated by extrapolation methods with the aid of the derivatives A_4 , B_4 , C_4 , D_4 , L_4 , A_5 , B_5 , C_5 , D_5 , L_5 , which are presented in the Tables.

2.2. Enthalpy of Fuel Components

The parameters of the combustion products of fuels in calculations were determined using the thermodynamic properties of combustion product components presented in the Reference Book [49]. Therefore, similar to the Reference Book [49], it is accepted that the enthalpies of the elements in the standard state at a temperature of 293.15°K are equal to zero. In accordance with this condition, the enthalpy of any substance at temperature T equals

$$I_i^0 = \Delta H_{f293.15}^0 + (H_i^0 - H_{293.15}^0), \quad (2.1)$$

where the heat of formation $\Delta H_{f293.15}^0$ is equal to the change in enthalpy with the transition of the substance's component elements to the substance being considered.

The following standard states of chemical elements have been accepted: oxygen, hydrogen, and nitrogen - diatomic gases; argon - monatomic gas; carbon - graphites. The same standard states of elements are adopted in reference books [45-48, 50, 79, 88] and works [14, 21, 31, 74].

It is also accepted that high-boiling fuel components have a temperature of 298.15°K and low boiling - boiling temperature.

The heats of formation, heat of mixing, boiling temperature, and heats of evaporation of the majority of individual substances which form the fuel components and which are necessary for determining enthalpy are taken from Reference Books [45-48]. These Reference Books present the most reliable and systematized values of the heat constants of inorganic substances. These constants were selected on the basis of a thorough analysis of virtually all published data (in the first edition, up to the middle of 1963; in the second - up to the end of 1964; in the third - up to March 1967; and in the fourth - to the end of 1968).

In the Reference Books [45-48, 88] and other works which were used the heats of formation are given with a temperature of 298.15°K. It is known that the heat of formation at a temperature of 293.15 is determined from the heat of formation with a temperature of 298.15 from the equation

$$\Delta H_{f,293,15}^0 = \Delta H_{f,298,15}^0 + (H_{293,15}^0 - H_{298,15}^0) - \Sigma (H_{293,15}^0 - H_{298,15}^0). \quad (2.2)$$

Here $(H_{293,15}^0 - H_{298,15}^0)$ and $\Sigma(H_{293,15}^0 - H_{298,15}^0)$ - the changes in enthalpy from a temperature of 298.15°K to a temperature of 293.15°K respectively of the given substance and the elements which form it in standard states.

Substituting expression (2.2) into equation (2.1) we find

$$I_f^0 = \Delta H_{f,298,15}^0 + \Sigma (H_{298,15}^0 - H_{293,15}^0) + (H_f^0 - H_{298,15}^0). \quad (2.3)$$

The values of the differences in the enthalpies $(H_{298,15}^0 - H_{293,15}^0)$ for the elements are presented in Reference Book [49].

2.2.1. Heats of Formation of Individual Substances which go into the Fuel Components

Table 2.6 presents the accepted heats of formation $\Delta H_{f298.15}^0$ of individual substances from elements taken in the standard state. The aggregate state of a substance to which the accepted heat of formation pertains is indicated. The reference to the bibliographic source on whose recommendation the heat of formation was selected is given.

Table 2.6. Accepted heats of formation of individual substances.

Наименование индивидуального вещества (1)	Химическая формула (2)	Агрегатное состояние (3)	Теплота образования $\Delta H_{f298.15}^0$, ккал/моль (4)	Литература (5)
(6) Кислород	O ₂	газ	0	
(7) Азот	N ₂	газ	0	
(8) Водород	H ₂	газ	0	
(9) Аргон	Ar	газ	0	
(10) Диметилгидразин несимметричный	(CH ₃) ₂ NNH ₂	жидк.	11,9±0,4	48
(11) Вода	H ₂ O	жидк.	-68,3149±0,0096	45
(12) Диметиламин	(CH ₃) ₂ NH	жидк.	-10,5±0,1	47
(13) Метилендиметилгидразин	(CH ₃) ₂ NNCH ₃	жидк.	28,6	31
(14) Вода	H ₂ O	газ	-57,796±0,01	45
(15) Диоксид углерода	CO ₂	газ	-94,052±0,011	47
(16) Оксид углерода	CO	газ	-26,416±0,031	47
(17) Аммиак	NH ₃	газ	-11,04±0,07	46

KEY: (1) Name of individual substance; (2) Chemical formula; (3) Aggregate state; (4) Heat of formation $\Delta H_{f298.15}^0$, kcal/mole; (5) Bibliography; (6) Oxygen; (7) Nitrogen; (8) Hydrogen; (9) Argon; (10) Asymmetrical dimethylhydrazine; (11) Water; (12) Dimethylamine; (13) Methylene dimethylhydrazine; (14) Water; (15) Carbon dioxide; (16) Carbon monoxide; (17) Ammonia; (18) Gas; (19) Liquid.

The heat of formation of methylene dimethylhydrazine was estimated by V. P. Kolesov and M. P. Kozina [31]. Here, the heat of formation of gaseous methylene dimethylhydrazine was found from the corresponding group contributions which were taken on the recommendation of the article by Benson et al [57] ($\Delta H_{f298.15}^0 = 36.6$ kcal/mole) while the heat of evaporation was estimated from the recommendation by Klager [68] ($\Delta H_{v298.15}^0 = 8$ kcal/mole).

As mentioned earlier, the accepted value of the lowest heat of combustion of kerosene equals 10,300 kcal/kg.

2.2.2. Heat of Mixing of Individual Substances when Forming Fuel Components

Heats of mixing of nonreacting gaseous substances in the ideal state equal zero.

The heat of mixing of liquid nitrogen and oxygen is extremely low and it is disregarded. Heats of solution of water, dimethylamine, and methylene dimethylhydrazine in asymmetrical dimethylhydrazine are unknown; however, it can be assumed that they are not great. The heat of solution of an extremely small quantity of water in liquid ammonia is unknown and is not considered in the Reference Book; however, it may have a noticeable value. Heats of solution of hydrocarbons with the formation of kerosene are low; they are considered in the experimental value of the heat of combustion.

2.2.3. Boiling Temperature and Heat of Evaporation of Low Boiling Fuel Components

Table 2.7 presents the boiling temperatures at which the pressure of saturated vapor is equal to 1 atm and the heats of evaporation which correspond to them for low-boiling individual substances which are part of the fuel components. The boiling temperatures of liquid hydrogen and oxygen are taken from a report [54] which presents some refined data in comparison with Reference Book [54].

In the Reference Book, when determining the enthalpy of solutions of a small quantity of nitrogen ($\leq 1\%$ by weight) in liquid oxygen it is accepted that the solutions have a boiling temperature of liquid oxygen of 90.188°K although the boiling temperature of liquid nitrogen is substantially lower. The error in enthalpy which is caused by this assumption is low and it can be disregarded. For example, in the case of 0.8%* by weight of the nitrogen solution this error equals ~ 3 cal/mole, i.e., less than the error in determining the heat of evaporation of liquid oxygen.

*The maximum possible amount of nitrogen in liquid technical oxygen in accordance with GOST 6331-68.

Table 2.7. Some physical properties of low-boiling individual substances.

Химическая формула (1)	Температура кипения (2)		Теплота испарения при T _{кип} (4)		Изменение энтальпии в состоянии идеального газа (6)			Литература (3)
	T _{кип} , °K	Литература (3)	$\Delta H_{\text{исп}}^0$, $\frac{\text{ккал}}{\text{моль}}$ (4)	Литература (3)	$H_{T_{\text{кип}}}^0 - H_0^0$, $\frac{\text{ккал}}{\text{моль}}$ (6)	Литература (3)	$H_{298,15}^0 - H_0^0$, $\frac{\text{ккал}}{\text{моль}}$ (6)	
O ₂	90.188 ± 0.010	54	1.632 ± 0.004	45	625	54, 88	2075 ± 1	45
H ₂ , норм. ¹⁾ (7)	20.397 ± 0.010	54	0.2190 ± 0.0005	45	355 ⁴⁾	54	2019 ± 1 ¹⁾	45
H ₂ , равн. ²⁾ (8)	20.28 ± 0.01	54	0.2150 ± 0.0005	45	101	54	2019 ± 1	45
NH ₃	239.73 ± 0.04	46	5.576 ± 0.005	46	1913	54	2400 ± 2	46
N ₂	90.188 ⁴⁾	—	1.211 ⁴⁾	88	625 ⁴⁾	88	2072 ± 1	46

KEY: (1) Chemical formula; (2) Boiling temperature; (3) Bibliography; (4) Heat of evaporation at T_{кип}; (5) kcal/mole; (6) Change in enthalpy in the state of an ideal gas; (7) Normal; (8) Equilibrium.

1) Normal hydrogen is a mixture of 25% para hydrogen and 75% ortho hydrogen.

2) Changes in enthalpy are presented for the case where at boiling temperatures and 298.5°K hydrogen is normal, and at a temperature of 0°K - para hydrogen.

3) Equilibrium at 20.4°K hydrogen contains 99.8% para hydrogen and 0.2% ortho hydrogen.

4) These parameters are presented with a nitrogen temperature of 90.188°K.

Let us estimate the enthalpy error being considered in the case of 0.8% by weight of a nitrogen solution.

It is known that the partial pressure of the vapor of some substance above an ideal liquid solution is equal to the pressure of the saturated vapor above a pure substance (at a given temperature) multiplied by the molar fraction of this substance in the liquid phase. Here, it is assumed that the vapor is a mixture of ideal gases. Consequently, the pressure of the saturated vapor above a 0.8% by weight nitrogen solution in liquid oxygen at a temperature of 90.188°K approximately equals

$$p_{\text{с}} = p_{\text{с}, \text{O}_2} n_{\text{O}_2} + p_{\text{с}, \text{N}_2} n_{\text{N}_2} = 1.0238 \text{ атм.} \quad (\text{a})$$

Here $p_{\text{с}, \text{O}_2} = 1 \text{ атм}$ and $p_{\text{с}, \text{N}_2} = 3.160 \text{ атм}$ - the pressure of saturated vapors respectively above liquid oxygen and nitrogen, with 90.188°K, $n_{\text{O}_2} = 0.9909$, and $n_{\text{N}_2} = 9.13 \cdot 10^{-3}$ - the molar fraction in the solution of oxygen and nitrogen respectively.

The approximate amount of reduction in the temperature of the solution necessary to obtain a pressure of saturated vapor above the solution $p_s = 1$ atm is found using the Clapeyron-Clausius equation

$$\frac{\Delta p}{\Delta T} = \frac{p \Delta H_v}{RT^2}, \quad (b)$$

where Δp - the given amount of reduction in the pressure of the saturated vapor.

Substituting in equation (a), which is written through finite differences, the values of Δp for oxygen and nitrogen from equation (b) we find

$$\Delta p_s = (p_{s,O_2} n_{O_2} \Delta H_{v,O_2} + p_{s,N_2} n_{N_2} \Delta H_{v,N_2}) \frac{\Delta T}{RT^2}. \quad (c)$$

From equation (c) it follows that to obtain the pressure of a saturated vapor above a solution with $p_s = 1$ atm it is necessary to reduce the solution's temperature by the amount $\Delta T = 0.23^\circ$ in comparison with a temperature of 90.188°K . Here, the change in the solution's enthalpy equals

$$\begin{aligned} \Delta I &= -\Delta(\Delta H_v) + c_{pn} \Delta T = \\ &= -(c_{pn} - c_m) \Delta T + c_{pn} \Delta T = c_m \Delta T, \end{aligned} \quad (d)$$

where c_{pn} and c_m - the specific heats of the vapor and liquid at constant pressure respectively.

The value of $\Delta I = -2.9$ cal/mole is equal to the unknown error.

2.2.4. Preheating Heat of Vapors of Low-Boiling Components

The heats of preheating of vapors of low-boiling individual substances in the state of an ideal gas from boiling temperature to 298.15° are found from the expression

$$\begin{aligned} H_{T_{\text{кип}}}^0 - H_{298.15}^0 &= (H_{T_{\text{кип}}}^0 - H_0^0) - \\ &- (H_{298.15}^0 - H_0^0). \end{aligned} \quad (2.4)$$

Here $(H_{T_{\text{кип}}}^0 - H_0^0)$ and $(H_{298.15}^0 - H_0^0)$ - the changes in enthalpy of a substance in the state of an ideal gas from 0°K respectively to the boiling temperature or 298.15°K .

The values of changes in enthalpy ($H_{T_{\text{KHH}}}^0 - H_0^0$) and ($H_{T_{\text{KHH}}, 12}^0 - H_0^0$) are presented in Table 2.7 with references to the literature from which they are taken.

The values of the change in enthalpy ($H_{T_{\text{KHH}}}^0 - H_0^0$), are presented in the report [54] obtained for O_2 - by interpolation of Woolley's data [90], for N_2 (normal and equilibrium) - by direct addition in accordance with the levels of energy of molecular hydrogen and for NH_3 - by the interpolation of Haar's data [63].

2.3. Density of Fuel Components

Table 2.8 presents the densities of individual substances which are the basic component parts (content $>96-99\%$) of the corresponding fuel components and of components which are mixtures of substances (kerosene). Also presented is the density of liquid hydrogen with a content of 75% ortho hydrogen (normal hydrogen). The density values presented are given with references to the literature from which they were taken.

In performing precise calculations, for example, when calculating the volumes of fuel tanks or the mass flow rates of fuel components by volumes (especially with the experimental determination of the specific impulse) use should be made of experimental values of the density of fuel components of a given chemical composition.

Table 2.8. Density of fuel components.

Вещество (1)	Плотность г/см ³ (2)	Литература (3)
O_2	1,135	17
(*) Кerosин	0,830	(7) см. табл. 2.2
$(CH_3)_2NNH_2$	0,786	33, 43
H_2 (норм.) ^а (6)	0,0709	44
H_2 (пара) (6)	0,0708	44
NH_3	0,682	17

KEY: (1) Substance; (2) Density, g/cm³; (3) Literature; (4) Kerosene; (5) Normal; (6) Para; (7) see Table 2.2.

*Mixture 25% para hydrogen and 75% ortho hydrogen.

Table 2.8 presents the densities of substances in the liquid state. The densities of high-boiling substances are given at a temperature of 25°C and of low boiling - at boiling temperature.

The density of kerosene depends on the content of individual hydrocarbons in it; the table presents an arbitrarily accepted value.

2.4. Thermodynamic Properties of Individual Substances

2.4.1. Individual substances which are being considered

The components of the combustion products of fuel compounds which are presented in Volume II of the Reference Book include individual substances which are formed from atoms of oxygen, hydrogen, carbon, and nitrogen.

The components of combustion products are presented in Table 2.9. Their list was prepared on the basis of recommendations in Reference Book [49] and with consideration of the data obtained for the third edition of the Reference Book [49] under preparation. When performing the calculations, only the gaseous state of these substances is considered.

Table 2.9. Components of combustion products.

	H ₂ O	NH	CO, CO ⁺	H ₂ CO
O, O ⁺ , O ⁻	H ₂ O ₂	NH ₂	CO ₂	CN
O ₂ , O ₂ ⁺	N, N ⁺	NH ₃	C ₂ O ₂	HCN
O ₃	N ₂ , N ₂ ⁺	N ₂ H ₄	CH	C ₂ H
H, H ⁺ , H ⁻	N ₂	HNO	CH ₂	C ₂ H ₂
H ₂	NO, NO ⁺	C, C ⁺ , C ⁻	CH ₃	C ₂ H ₄
OH, OH ⁺ , OH ⁻	NO ₂	C ₂	CH ₄	C ₂ N ₂
HO ₂	N ₂ O	C ₃	HCO	

Monatomic carbon C is considered not only in the gaseous but also in the condensed state.

2.4.2. Thermodynamic properties of individual substances

The thermodynamic properties (enthalpy, change in enthalpy, entropy, $\log K_p$) of individual substances are presented in tabular form in Reference Book [49] and the thermoconstants of substances - in the Reference Book [45-48]. For use in calculations, the tabular values of enthalpy i_t^0 are approximated by polynomials of the seventh (gaseous substances) and third (condensed substances) orders. The remaining thermodynamic properties of individual substances are determined from known relationships of thermodynamics with the use of the values I_T^0 .

The coefficients of approximating polynomials are presented in Volume I of the Reference Book. In preparing the first volume changes in the thermoconstants of gaseous substances were considered in accordance with the data of the Reference Book [45-48] and the zero of polynomials A_1 and A_5 were corrected accordingly.

2.5. Transfer Properties of Individual Substances

The transfer properties - coefficients of viscosity η and thermoconductivity λ of individual substances and mixtures of individual substances are determined in considerable measure by the integrals of collisions $\sigma^{(2),s,*}$. For the calculation of integrals $\sigma^{(2),s,*}$, model potentials are used in the Reference Book. The types of potentials used in studies and the method for determining their parameters are examined in detail in Volume I of the Reference Book. For convenience in using this volume of the Reference Book, Table 2.10 provides a brief list of these methods.

For all the individual substances which are considered in the calculations, the Lennard-Jones potential is taken as the model of interaction (12-6):

$$\varphi(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right] \quad (2.5)$$

where σ - the intermolecular distance r at which $\varphi(r) = 0$; ϵ - the depth of the potential well.

Table 2.10. Methods for determining the parameters of potentials.

No.	Methods for determining parameters
1.	Approximation of initial potential
Experimental	
2.	Use of transfer properties
3.	Use of p-v-T properties
4.	Use of properties of crystal with 0°K
5.	Rydberg-Klein-Ries method
6.	Method of scattering on gas targets
7.	Use of data on vibrational relaxation
Calculation-theoretical	
8.	Quantum-mechanical calculation
9.	Use of the Thomas-Fermi-Dirac model of the atom
10.	Semiempirical method of valance bonds
11.	Calculation of dispersion energy
Indirect	
12.	Employment of similarity theory
13.	Method of equivalent solid spheres
14.	Use of parameters in the critical point
15.	Use of parameters in the boiling point
16.	Use of parameters in the melting point
Empirical	
17.	$\sigma_A = 0.75\sigma_{A_1} + 0.45$
18.	$\sigma_A = 0.413 + (0.171 + 0.54\sigma_{A_1}^2)^{1/2}$
19.	$\sigma_{A_1} = \frac{4}{3}\sigma_A - 0.6$; $\sigma_{AB} = \frac{4}{3}(\bar{r}_A + \bar{r}_B) + 1.8$
20.	$\sigma_{AB} = (1.849\bar{r}_{AB}^2 + 5.13\bar{r}_{AB} + 3.24)^{1/2}$
22.	$\sigma_{ABC} = \frac{5}{12}(\sigma_{A_1} + \sigma_{B_1} + \sigma_{C_1}) - 0.55$
22.	$\sigma_{AB} = (\sigma_{A_1}\sigma_{B_1})^{1/2}$, $\sigma_{AB} = \frac{1}{2}(\sigma_{A_1} + \sigma_{B_1})$
23.	Linear relationships
24.	Estimate in accordance with the distance between atoms in molecule
25.	$\sigma_{ij} = \frac{1}{2}(\sqrt{\sigma_{ii}^2\Omega_{ii}^{\prime\prime\prime}} + \sqrt{\sigma_{jj}^2\Omega_{jj}^{\prime\prime\prime}})$

For a number of individual substances, especially if their temperature is high ($\sim 2000-3000^\circ\text{K}$), the use of the Lennard-Jones potential is not preferable. In such cases, the "true" and more substantiated potential was approximated by potential (12-6) from the condition of acceptable conformance of the collision integrals $\sigma^{(1)}_{12}$ and $\sigma^{(2)}_{12}$ of potential (12-6) and the "true" potential. Such an approximation is not strictly a method for determining the parameters of the potentials; this method is presented conventionally in Table 2.10.

A list of individual substances (components of combustion products) which are considered when determining the equilibrium composition is presented above in Table 2.9. Depending on the possible content in the combustion products, it is expedient to combine these substances into two groups (Table 2.11 and Table 2.12 respectively). Individual substances whose molar fraction x_q may be more than 0.01-0.05 and atomic substances are separated into the first group; substances with a lesser content in combustion products are combined in the second. Such an arbitrary division was accomplished on the basis of the results of thermodynamic calculations which are available, for example, [2, 10-12], and from the results presented in this volume.

The parameters of the Lennard-Jones potential for individual substances of the first group are presented in Table 2.11. For the majority of substances we determine (estimate) the parameters σ and ϵ/k again. In those cases where parameters σ and ϵ/k are taken from published data, reference to the source (in the brackets) is given in the table directly along side the value of the parameter. The table also indicates the method for determining the parameters of the potential in accordance with the numbering of Table 2.10; given in the corresponding column is the reference to the literature from which the necessary initial values were taken for the employment of the method (for example, $\sigma^{(1)}_{12}$, T_{KD} , v_{KD} , p_{KD} etc.).

We determined the parameters of the potentials for atomic oxygen, hydrogen, and nitrogen and molecules of oxygen, hydrogen, nitrogen, water, carbon dioxide, carbon monoxide, and nitric oxide as a result of the approximation of collision integrals $\sigma^{(1)}_{12}$ and $\sigma^{(2)}_{12}$. The

collision integrals $\sigma^2 \Omega^*$ were obtained by Ye. V. Samuylov and associates in [40, 41] with the involvement of various methods and potentials depending on the nature of the substances and the intermolecular distances. The data from [40] are used in the Reference Book.

Table 2.11. Parameters of the Lennard-Jones potential for individual substances.

Вещество (1)	$\sigma, \text{\AA}$			$\epsilon/k, ^\circ\text{K}$		
	величина (2)	метод (3)	литература (4)	величина (2)	метод (3)	литература (4)
O	2,631	1	40	295,6	1	40
H	2,120	1	40	505,4	1	40
N	2,495	1	40	419,0	1	40
C	3,098	17	—	52,0	11	—
O ₂	3,347	1	40	150,8	1	40
H ₂	2,934	1	40	34,1	1	40
OH	3,846 [28]	10	—	180,8 [28]	10	—
H ₂ O	2,626	1	40	846,7	1	40
N ₂	3,120	1	40	332,6	1	40
NO	3,669	1	40	75,5	1	40
NO ₂	3,765 [61]	2	—	210,0 [61]	2	—
NH ₃	3,016 [29]	2,3	—	311,2 [29]	2,3	—
CO	2,942	1	40	477,8	1	40
CO ₂	3,900	1	40	210,5	1	40
CH ₄	3,784 [30]	2,3	—	148,2 [30]	2,3	—

KEY: (1) Substance; (2) Value; (3) Method; (4) Literature.

Table 2.12. Parameters of Lennard-Jones potential for individual substances.

Вещество (1)	a, Å			a/m, °K		
	величина (2)	метод (3)	литература (4)	величина (2)	метод (3)	литература (4)
O ₂	4,010	2	49	205,0	2	49
HO ₂	3,068	14	—	168,1	14	—
H ₂ O ₂	4,196 [86]	2	—	289,3 [86]	2	—
N ₂	3,745	23	—	247,0	23	—
N ₂ O	3,828 [86]	2	—	232,4 [86]	2	—
NH	3,250	20	49	306,0	22	—
NH ₃	3,133	23	—	308,6	23	—
N ₂ H ₄	3,951	14	49	392,4	14	49
HNO	2,898	14	—	171,4	14	—
C ₂	3,530	20	49	1505,0	22	—
C ₂	3,962	23	—	1958,0	23	—
C ₂ O ₂	4,807	14	—	330,4	15	64
CH	3,360	20	49	640,0	22	—
CH ₂	3,502	23	—	476,0	23	—
CH ₃	3,644	23	—	312,0	23	—
HCO	3,465	14	—	187,4	14	—
H ₂ CO	3,758	14	—	312,0	14	—
CN	3,430	20	49	707,0	22	—
HCN	3,630 [86]	2	—	569,1 [86]	2	—
C ₂ H	3,752	14	—	176,8	14	—
C ₂ H ₂	4,033 [86]	2	—	231,8 [86]	2	—
C ₂ H ₄	4,193 [30]	2,3	—	209,0 [30]	2,3	—
C ₂ N ₂	4,361 [86]	2	—	348,6 [86]	2	—

KEY: (1) Substance; (2) Value; (3) Method; (4) Literature.

An estimate of the errors in the approximation of the collision integrals $\sigma^2\Omega^{1,1}$ and $\sigma^2\Omega^{2,2}$ by the Lennard-Jones potential is presented in Table 2.13 where, depending on temperature, the moduli of relative deviations in percents $\delta\Omega^{1,1}$ and $\delta\Omega^{2,2}$ (the numerator and denominator respectively) are presented in the form of a fraction:

$$\delta\Omega^{1,1} = \frac{\sigma^2\Omega^{1,1} - (\sigma^2\Omega^{1,1})_{\text{Л.Д.}}}{\sigma^2\Omega^{1,1}}, \quad (2.6)$$

$$\delta\Omega^{2,2} = \frac{\sigma^2\Omega^{2,2} - (\sigma^2\Omega^{2,2})_{\text{Л.Д.}}}{\sigma^2\Omega^{2,2}}, \quad (2.7)$$

where $(\sigma^2\Omega^{1,1})_{\text{Л.Д.}}$ - the collision integral calculated using the Lennard-Jones potential.

Table 2.13. Errors in approximating collision integrals.

Взаимодействие (1)	Метод определения $\sigma^2\Omega^{1,1}$ (2)	T=600°K	1000	1400	1800	2200	2600	3000	3400	3800	4200
O—O	10	—	—	—	2/5	0/3	2/2	3/0	5/1	6/2	7/3
H—H	10	—	—	—	4/8	2/6	0/4	2/2	5/0	7/2	9/5
N—N	10	—	—	—	0/6	1/5	3/3	5/1	7/1	8/2	9/3
O ₂ —O ₂	2, 6, 7, 10	0/1	2/3	2/3	2/3	1/3	0/3	2/2	3/1	5/0	7/1
H ₂ —H ₂	2, 6, 10	0/3	3/9	2/10	1/9	4/8	7/6	9/4	12/3	15/1	17/1
N ₂ —N ₂	2, 6, 7, 10	3/3	6/9	5/9	2/8	1/6	4/5	6/3	8/2	10/0	12/1
H ₂ O—H ₂ O	2	1/0	1/1	1/2	1/1	1/1	1/1	1/1	1/1	1/1	1/1
CO—CO	2, 6, 7	1/0	7/9	8/10	6/9	3/6	1/3	5/1	9/5	14/9	18/12
CO ₂ —CO ₂	2, 6	0/0	0/0	0/0	0/0	0/0	0/0	0/0	0/0	0/0	0/0
NO—NO	2, 6, 10	0/0	0/0	0/0	0/0	0/0	0/1	0/1	1/1	1/1	2/1

KEY: (1) Interaction; (2) Method of determining.

The column "Method of determining $\sigma_{ij}^{(2)}$ " in Table 2.13 indicates the methods on the basis of which the collision integrals (numbering of the methods corresponds to Table 2.12) are calculated in [40, 41]. For atomic substances, the results are given only with $T \geq 1800^\circ\text{K}$ since with a lower temperature the content of these substances in the combustion products is insignificant.

In determining the parameters σ and ϵ/k for the remaining individual substances of the first group, use was made of the experimental data on the viscosity coefficient and the virial coefficients (Ar, NO_2 , NH_3 , CH_4) and semi-empirical, indirect, and empirical methods (OH, C).

The parameters of the potentials for individual substances of the second group (see Table 2.12) were determined primarily by indirect and empirical methods. The selection of these methods was conditioned by the absence of direct experimental data on the equilibrium (virial coefficients) and nonequilibrium (collision integrals, η , λ , D) properties for these substances. For molecules HO_2 , HNO , C_3O_2 , HCO , H_2CO , conventional critical constants were first estimated by empirical methods of work [78].

It should be noted that the probable error in calculations of transfer properties here will be comparatively low since the content of the individual substances listed above in the combustion products is low.

It is customary to estimate the constant potentials in the case of the interaction of unlike molecules of combustion products by empirical rules of combination

$$\left. \begin{aligned} \sigma_{ij} &= \frac{1}{2} (\sigma_i + \sigma_j), \\ \epsilon_{ij} &= (\epsilon_i \epsilon_j)^{1/2}. \end{aligned} \right\} \quad (2.8)$$

Some of the results from such an estimate are presented in Volume I of the Reference Book, and we obtained more detailed results using collision integrals $\sigma_{ij}^{(2)}$ from [40].

Table 2.14. Errors in the approximation of potential constants.

Взаимодействие (1)	Множ. определения на Ω , 3° (2)	T=0K K	1000	1400	1800	2200	2600	3000	3400	3800	4200
O—N ₂	6, 10	—	—	—	1/6	1/4	2/3	4/2	5/1	6/0	7/0
O—O ₂	6, 10	—	—	—	0/3	1/2	3/1	4/0	6/1	7/2	9/3
O—NO	10	—	—	—	2/1	4/0	5/0	6/1	8/2	9/3	10/4
O—H ₂	22 (10)	—	—	—	2/8	4/6	6/4	8/2	10/1	12/1	14/2
O—N	10	—	—	—	9/14	7/12*	5/10	3/9	2/7	0/6	1/4
O—H	10				23/27	21/26	20/24	18/22	16/21	15/20	13/18
H—H ₂	6, 10	—	—	—	24/9	28/13	32/16	37/20	40/23	44/26	48/29
N—N ₂	6, 10	—	—	—	2/6	1/5	3/4	5/3	6/2	7/1	8/0
N—O ₂	6, 22 (10)	—	—	—	0/5	1/4	3/3	4/2	5/1	6/0	7/1
N—NO	22 (10)	—	—	—	2/1	3/0	5/0	6/1	7/2	9/3	10/4
N—H ₂	22 (10)	—	—	—	0/10	3/8	5/6	8/3	10/1	13/1	15/3
CO ₂ —CO	6, 22 (2), 25	2/2	3/3	3/4	2/4	1/2	1/1	2/1	4/3	6/4	8/6
CO ₂ —N ₂	2, 6, 22 (2), 25	15/0	9/4	5/4	4/4	4/3	4/2	4/2	4/1	5/0	5/0
CO ₂ —O ₂	2, 6, 22 (2), 25	10/0	12/0	13/2	14/4	15/6	16/7	18/9	19/10	20/12	21/13
CO ₂ —NO	22 (2), 25	1/0	0/0	0/0	0/0	0/0	0/0	0/0	0/0	0/0	0/0
CO ₂ —H ₂	22 (2), 25	7/5	2/0	1/1	1/1	1/1	2/1	3/0	4/0	5/1	6/1
CO ₂ —H ₂ O	22 (2), 25	8/8	5/5	3/3	2/3	2/2	2/2	2/2	2/1	1/1	1/1
CO—N ₂	6, 22 (2), 22 (7, 10), 25	1/1	6/9	6/10	4/9	1/7	2/5	5/3	8/1	10/1	13/3
CO—O ₂	2, 6, 22 (2), 22 (7, 10), 25	6/3	3/7	3/7	5/6	6/5	8/3	10/2	11/0	13/2	14/3
CO—NO	6, 22 (2), 22 (7, 10), 25	5/6	6/7	4/6	3/5	1/4	0/3	2/2	3/1	4/0	5/1
CO—H ₂	22 (2), 22 (7, 10), 25	2/2	7/8	7/9	5/8	3/7	1/6	0/4	2/3	3/2	5/1
CO—H ₂ O	22 (2), 25	15/16	4/4	1/1	0/2	0/1	1/0	3/2	4/4	7/7	9/10
N ₂ —O ₂	6, 10, 22 (2), 25	2/3	4/7	2/7	0/7	3/5	5/5	7/4	9/2	10/1	12/0
N ₂ —NO	6, 10, 22 (2), 25	4/4	4/5	3/4	1/4	0/3	2/2	3/1	4/1	6/0	7/0
N ₂ —H ₂	22 (2), 22 (10), 25	3/4	6/9	5/9	3/8	0/6	2/5	5/4	7/2	9/0	12/1
N ₂ —H ₂ O	22 (2), 25	11/13	2/3	0/1	1/2	0/2	0/1	2/0	3/1	5/2	6/4
O ₂ —NO	6, 10, 22 (2), 25	0/0	1/0	1/1	0/1	0/1	1/1	2/0	3/1	4/0	5/1

Table 2.14 continued.

Взаимодействие (1)	Метод определения (2)	T=600 K	1000	1400	1800	2200	2600	3000	3400	3800	4200
O ₂ -H ₂	2, 22 (2), 22 (10), 25	9/2	7/3	9/0	10/3	12/6	14/9	16/10	18/12	19/14	21/15
O ₂ -H ₂ O	2, 22 (10), 25	13/13	6/6	4/3	3/2	3/2	3/1	3/1	4/2	4/2	5/2
NO-H ₂	22 (2), 22 (10), 25	1/0	1/2	0/3	0/2	1/2	3/1	4/0	6/0	8/1	10/2
NO-H ₂ O	22 (2), 25	5/4	3/3	2/2	2/2	2/2	2/3	2/3	3/3	3/4	3/4
H ₂ -H ₂ O	22 (2), 25	9/17	7/5	15/1	22/1	26/1	30/1	34/0	37/1	39/2	42/3

KEY: (1) Interaction; (2) Method of determining.

Depending on temperature, Table 2.14 gives the moduli of relative errors in percents

$$\delta Q^{1,1} = \frac{\sigma^2 Q^{1,1} \star - (\sigma^2 Q^{1,1} \star)_{//}}{\sigma^2 Q^{1,1} \star}, \quad (2.9)$$

$$\delta Q^{2,2} = \frac{\sigma^2 Q^{2,2} \star - (\sigma^2 Q^{2,2} \star)_{//}}{\sigma^2 Q^{2,2} \star}, \quad (2.10)$$

where the values of $\sigma^2 Q^{i,j} \star$ are taken from [40] and integrals $(\sigma^2 Q^{i,j} \star)_{//}$ are determined using the rules of combination. The table also indicates the methods which were employed in [40] when calculating integrals $\sigma^2 Q^{i,j} \star$ for the case of the interaction of molecules i-j.

Several methods for determining the potential parameters can be recommended for a number of interactions of molecules i-j. In such cases, in [40] the final values of the parameters were determined as a result of averaging. For some interactions, used as initial data for averaging were the rules for combining in combination with the results from measurements of viscosity, with the use of the semi-empirical method, and with the use of measurements of the time of vibrational relaxation and the semi-empirical method (in Table 2.14 designated 22 (2), 2 (10), and 22 (7, 10) respectively).

As is evident from Table 2.14, the errors in the rules of combining are comparative small; in the majority of cases they do not exceed the errors of the experimental data for the intermolecular interaction under high-temperature conditions. Similar data for the

interactions H-O, H-OH, O-OH are presented in Blank's work [16].

Rotational relaxation was considered for a number of individual substances when calculating the coefficient of thermal conductivity. The numbers of the collisions z_{rot} necessary for the exchange of rotational energy were accepted in the Reference Book on the basis of experimental data. The dependence of z_{rot} on temperature was considered by an approximate formula of the type (see Volume I, Chapter VIII):

$$z_{\text{rot}} = z_{\text{rot}}^{\infty} \left[1 + 2.784 \sqrt{\frac{\epsilon T}{e}} + 5.609 \frac{\epsilon T}{e} \right]^{-1}, \quad (2.11)$$

where ϵ/k - the parameter of the Lennard-Jones potential.

Literature presents data on z_{rot} at a temperature $\sim 300^\circ\text{K}$. On the basis of these data, from formula (2.11) we estimated the values of z_{rot}^{∞} , and subsequently for the calculations of $z_{\text{rot}}(T)$ formula (2.11) was used. Table 2.15 presents the numbers z_{rot}^{∞} and z_{rot} with $T = 300^\circ\text{K}$ with the corresponding references to the literature. It is appropriate to note that for the combustion products of the fuels examined in Volume II of the Reference Book, the effect of rotational relaxation is relatively low (see Volume I, Chapter VIII). For the majority of cases, the contribution of rotational energy to the coefficient of thermal conductivity can be considered on the basis of the diffusion mechanism of transfer.

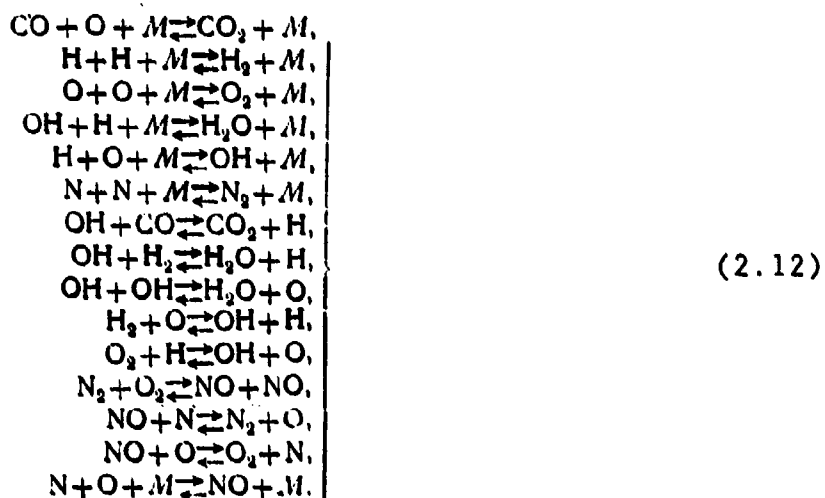
Number: z_{rot}^{∞} , z_{rot} for some individual substances

Вещество (1)	z_{rot}^{∞}	z_{rot}	Литература (2)	Вещество (1)	z_{rot}^{∞}	z_{rot}	Литература (2)
N ₂	60,9	6,0	72,73	C ₂ H ₂	14,0	1,8	73
O ₂	40,5	7,0	72,73	NH ₃	17,9	1,7	85
CO ₂	36,4	5,0	81	H ₂ O	86,0	4,0	70
H ₂	2230,0	250,0	81	CO	94,1	7,0	70
CH ₄	53,8	9,4	73	NO	15,0	3,9	70
C ₂ H ₄	119,6	2,4	73				

KEY: (1) Substance; (2) Literature.

2.6. Constants of Rates of Chemical Reactions

The following system of determining reactions was selected on the recommendations of Academician V. N. Kondrat'yev and in accordance with the data of [32, 36, 52, 65, 75, 80] for the fuels which contain atoms of oxygen, carbon, hydrogen, and nitrogen in their composition and are examined in Volume II of the Reference Book:



The constants of the rates of indicated reactions are presented in Table 2.16. Their values are taken primarily in accordance with the materials of Reference Book [32] and also from the data in [36, 51, 52, 65, 75].

As is known, the rate of reactions which take place with triple collisions depends on the type of catalytic particle M. This question has hardly been studied for the complex mixtures being examined. In this connection, the equations of chemical kinetics for such reactions were written without consideration of the type of catalytic particle although in the selection of a specific constant of the rate of reaction in accordance with the data in Reference Book [32] the dependence of this constant on the type of catalytic particles (with the presence of the corresponding data in the Reference Book) was considered. The rate constant here was selected for such M particles whose concentration is maximum in the combustion products.

Table 2.16. Constants of the rate of direct reactions.

Реакция (1)	Константа скорости (2)	Размерность (3)
$\text{CO} + \text{O} + \text{M} \rightarrow \text{CO}_2 + \text{M}$	$3.5 \cdot 10^{14} \exp \left[-\frac{2.1 \cdot 10^{-2}}{R_0 T} \right]$	$\text{см}^6/(\text{моль})^2 \text{сек}$ (4)
$\text{H} + \text{H} + \text{M} \rightarrow \text{H}_2 + \text{M}$	$1.4 \cdot 10^{10} T^{-1.5}$	»
$\text{O} + \text{O} + \text{M} \rightarrow \text{O}_2 + \text{M}$	$5.5 \cdot 10^{17} T^{-0.87}$	»
$\text{OH} + \text{H} + \text{M} \rightarrow \text{H}_2\text{O} + \text{M}$	$1.2 \cdot 10^{10} T^{-1}$	»
$\text{H} + \text{O} + \text{M} \rightarrow \text{OH} + \text{M}$	$3.3 \cdot 10^{10} T^{-0.5}$	»
$\text{N} + \text{N} + \text{M} \rightarrow \text{N}_2 + \text{M}$	$2.7 \cdot 10^{10} T^{-0.3}$	»
$\text{OH} + \text{CO} \rightarrow \text{CO}_2 + \text{H}$	$2.5 \cdot 10^{14} \exp \left[-\frac{5.1 \cdot 10^{-2}}{R_0 T} \right]$	$\text{см}^6/\text{моль сек}$ (5)
$\text{OH} + \text{H}_2 \rightarrow \text{H}_2\text{O} + \text{H}$	$1.1 \cdot 10^{14} \exp \left[-\frac{8.6 \cdot 10^{-2}}{R_0 T} \right]$	»
$\text{OH} + \text{OH} \rightarrow \text{H}_2\text{O} + \text{O}_2$	$10^{14} \exp \left[-\frac{1.2 \cdot 10^{-2}}{R_0 T} \right]$	»
$\text{H}_2 + \text{O} \rightarrow \text{OH} + \text{H}$	$1.3 \cdot 10^{13} \exp \left[-\frac{9.86 \cdot 10^{-2}}{R_0 T} \right]$	»
$\text{O}_2 + \text{H} \rightarrow \text{OH} + \text{O}$	$2.2 \cdot 10^{14} \exp \left[-\frac{16.5 \cdot 10^{-2}}{R_0 T} \right]$	»
$\text{N}_2 + \text{O}_2 \rightarrow \text{NO} + \text{NO}$	$5.2 \cdot 10^{13} \exp \left[-\frac{0.107}{R_0 T} \right]$	»
$\text{NO} + \text{N} \rightarrow \text{N}_2 + \text{O}$	$3 \cdot 10^{13} \exp \left[-\frac{0.2 \cdot 10^{-2}}{R_0 T} \right]$	»
$\text{NO} + \text{O} \rightarrow \text{O}_2 + \text{N}$	$1.1 \cdot 10^{13} \exp \left[-\frac{7.1 \cdot 10^{-2}}{R_0 T} \right]$	»
$\text{N} + \text{O} + \text{M} \rightarrow \text{NO} + \text{M}$	$3.3 \cdot 10^{11}$	$\text{см}^6/(\text{моль})^2 \text{сек}$ (4)

KEY: (1) Reaction; (2) Rate constant; (3) Dimension; (4) $\text{cm}^6/(\text{mole})^2 \text{s}$; (5) $\text{cm}^3/\text{mole s}$.

In the accomplishment of the calculations it is accepted that the rate constants of a direct and reverse reaction are connected through the equilibrium constants. The latter are taken from data in Reference Book [49].

Calculation of the nonequilibrium flow in the nozzle was conducted in a linear approximation with a given pressure distribution along the length of the nozzle or along the line of current [27]. This pressure

distribution was determined in the following manner. The value of the mean index of isentropy of expansion n was calculated for each fuel from the results of the thermodynamic calculation of equilibrium isentropy expansion. The value of the latter was used for the calculation (by the characteristic method) of pressure distribution along the axis of axisymmetrical nozzles with an angle point and with a uniform flow in the exit section of the nozzle. The pressure distribution which was obtained in this manner was then used in calculations of a unidimensional nonequilibrium flow.

The method for calculating chemically nonequilibrium flows is described in detail in Volume I of the Reference Book. The results for this volume of the Reference Book were obtained on the BESM-4, M-20, and BESM-3M computers in accordance with a special program prepared by V. F. Kolmogorov.

The calculation of a nonequilibrium flow was accomplished from the section in the subsonic part of the nozzle in which the pressure is $p = (0.9-0.95)p_{co}$. From the inlet section of the nozzle and before this section the expansion process is presumed to be equilibrium. Losses in specific impulse ζ_H caused by the nonequilibrium course of the chemical reaction are determined as the difference of the specific impulse of the equilibrium and nonequilibrium flows (with identical values of $\bar{r}$) referred to the specific impulse of the equilibrium flow.

The accuracy of the data obtained was monitored by integral checks for impulse and subdivision of the step. The total error in determining losses of specific impulse ζ_H which arises in connection with the unidimensional approximation, imprecision of the knowledge of constants for the rates of reactions, and errors in numerical integration were estimated at 15-25% of the value of the loss coefficient ζ_H .

As shown in Volume I of the Reference Book, losses in specific impulse ζ_H as a result of the nonequilibrium course of chemical reactions depend on the geometry of the nozzle (diameter of the critical section d_* and the relative radius $\bar{r} = r/r^*$), the type of fuel used, the excess oxidant ratio α_{ok} , and the stagnation pressure

at the inlet to the nozzle p_{co} . In this connection, this volume of the Reference Book presents for a fixed family of nozzles (in the case being examined, this is a family of shortened nozzles which, with full length, have a uniform and parallel axis of flow in the exit section) results for the following range of change in the parameters:
excess oxidant ratio $\alpha_{ok} = 0.2 (0.4) - 1.2 (1.4)$ with a change step of 0.2; diameter of critical section $d_* = 5, 10, 20, 50, 150, 250$ mm;
relative radius $\bar{r} = 1-15$; stagnation pressure at inlet to nozzle $p_{co} = 0.5, 1, 2, 5, 15, 25$ MN/m².

CHAPTER III

ACCURACY OF THE CALCULATION RESULTS

3.1. Effective Changes in the Initial Data on Fuel

The data necessary for the thermodynamic calculation about fuel are the enthalpy and chemical composition of its components. If the interconnection between changes in these data Δx_i is absent, the error in the parameters of the combustion products which arises as the result of changes in the data which are accepted is estimated from the formula:

$$|\Delta \varphi| = \sum \left| \left(\frac{\partial \varphi}{\partial x_i} \right) \Delta x_i \right|.$$

where φ - the parameter of combustion products.

Because of the large volume of information in this volume of the Reference Book, it was not possible to present the errors of each tabular value. However, for the basic properties of combustion products: T_{CO} , β , I_s^n , $\bar{F}$, z - the tables of the Reference Book provide the derivatives $(\partial \varphi / \partial x_i)$, which permit estimating the effect of the discrepancies in the initial data.

The derivatives of the parameters for enthalpy are determined with the use of the differential relationships of thermodynamics which are examined in detail in the first volume of the Reference Book.

The derivatives of the parameters of combustion products T_{co} , β , I_g^n , F , z for the chemical composition of the fuel components are determined numerically in the Reference Book by varying the given weight fraction of the admixture in the component. This varying is conducted in such a way as to ensure the necessary accuracy of linear interpolation for extrapolation for the case of the real admixture content in the fuel components. Examined below is a method for selecting the weight fraction of admixture g from the range $0 < g \leq g_{max}$ for the numerical determination of the derivatives.

Let a change in any parameter depending on the content (for example weight fraction) of the admixture in the fuel component be described by the function $y = f(x)$.

With small quantities of admixture the function $y = f(x)$ can be described with sufficient accuracy by a second-order curve, for example, by the parabola

$$y_1 = ax + bx^2. \quad (3.1)$$

In the Reference Book, the linear approximation of the function $y = f(x)$ is taken, i.e.,

$$y \approx y_2 = kx. \quad (3.2)$$

It is necessary to select point x_1 in such a way that with the approximation of the parabola y_1 with a straight line which passes through point $y = 0$ and $y = y_1(x_1)$ the greatest error in the range $0 - x_{max}$ is minimum.

From the condition for the intersection of curves at point $x = x_1$ we find the value of k :

$$k = a + bx_1. \quad (3.3)$$

Now the error in the linear approximation can be calculated from the formula:

$$\Delta y = y_1 - y_2 = bx(x - x_1). \quad (3.4)$$

It can be shown that the value of x_2 which corresponds to the extremum of the function Δy in the range $0 \leq x \leq x_1$ is equal to $1/2 x_1$.

Thus, the least maximum error of linear approximation arises in the case

$$|\Delta y(x)_{\max}| = \left| \Delta y \left(\frac{x_1}{2} \right) \right|. \quad (3.5)$$

From this condition we obtain that the value of x_1 does not depend on the parameters of a parabola and equals $\sim 0.83 x_{\max}$.

With consideration of this, when determining the derivatives for each fuel component the weight fraction of the admixture was designated from the range $0 \leq g \leq g_{\max}$. The estimate of the accuracy of extrapolation or interpolation when using the derivatives found in this manner was conducted by special thermodynamic calculations. Several illustrating results of these calculations are presented in Tables 3.1-3.4. The following designations are adopted in the Tables: $g_{\max}$ - the maximum weight fraction of the admixture in the component (%),

Δ_1 - the absolute change in the parameter with a change in the admixture content from $g = 0$ to $g = g_{\max}$ (T_{co} °K, β , I_s^n - m/s),

Δ_2 - the maximum absolute error in determining Δ_1 when using the derivatives (T_{co} °K, β , I_s^n m/s).

The values of Δ_1 are found from the results of thermodynamic calculation with $g = 0$ and $g = g_{\max}$.

For the fuel compounds being examined in this volume, the derivatives for the chemical composition of components permit a determination of the change in parameters in the ranges of change of weight fractions of admixtures taken with the same accuracy as the accuracy in presenting the parameters themselves in the tables of the Reference Book.

Variations in pressure at the inlet of the nozzle p_{co} and the excess oxidant ratio in the ranges adopted in the Reference Book

have a weak influence on the accuracy of calculating the change in parameters.

With an increase in the degree of reduction of pressure ε the error in determining the change in relative area is usually increased. The accuracy in determining the change in specific impulse in a vacuum is virtually unchanged with a change in ε .

Tables 3.1-3.4 illustrate these conclusions.

Table 3.1. Accuracy in calculating the properties of combustion products with extrapolation for the composition of components.

$\varphi_{ok} = 1$, $p_{co} = 10 \text{ MN/m}^2$

№№ п/в	Компоненты (1)	Примеси (2)	$\varepsilon_{\max}$ (3)	$T_{co}, ^\circ\text{K}$		$\beta, \text{ м/сек}$ (5)		$I_s, \text{ м/сек } (\varepsilon=100)$ (4)		$\bar{P}, (\varepsilon=100)$	
				Δ_1	Δ_2	Δ_1	Δ_2	Δ_1	Δ_2	Δ_1	Δ_2
1	O ₂	N ₂	0,8	3,3	<0,1	0,1	<0,1	0,8	<0,1	0,012	<0,001
	(CH ₃) ₂ NNH ₂	H ₂ O	0,5	4,7	<0,1	2,4	<0,1	4,5	<0,1	<0,1	<0,001
2	O ₂	N ₂	0,8	6,4	0,4	0,8	0,3	1,3	0,3	0,004	0,002
	Керосин (5)	Изменение C/H (6)	± 6	0,4	0,1	11,4	1,0	20,8	1,8	0,007	0,002
3	O ₂	N ₂	0,8	5,7	0,4	0,7	0,1	1,8	0,1	0,008	0,003
	H ₂	—	—	—	—	—	—	—	—	—	—
4	O ₂	N ₂	0,8	5,7	0,1	1,0	0,1	7,5	0,7	0,121	0,006
	NH ₃	H ₂ O	0,4	3,7	0,1	2,3	0	5,3	0,4	0,026	0,008

KEY: (1) Components; (2) Admixtures; (3) m/s; (4) m/s; (5) Kerosene; (6) Change.

When conducting calculations with the use of derivatives, it is necessary to keep the following in mind. The derivatives for the content of admixtures in the fuel components are calculated with a constant relationship of the fuel components k_1 which is presented in the table. Thus, the thermodynamic parameters which are calculated by extrapolation for components which contain an admixture in the range of $0 \leq g \leq g_{\max}$ correspond to the constant value k_1 and to the value φ_{ok} which varies depending on the weight fraction of the

admixture g. The value of α_{ok} should be determined in such cases from formulas (1.8) and (1.10) of Volume I of the Reference Book after the composition of the fuel components, i.e., the weight fractions of the admixtures, has been selected.

Table 3.2. Accuracy of calculation of properties of combustion products with extrapolation for composition of components $\alpha_{ok} = 1$, $P_{co} = 10 \text{ MN/m}^2$.

Компоненты (1)	Примеси (2)	$\varepsilon_{\text{max}}, \%$	$I_g^{\text{н}}, \text{м/сек}$ (3)						F					
			$g=20$		$g=100$		$g=1000$		$g=20$		$g=100$		$g=1000$	
			Δ_1	Δ_2	Δ_1	Δ_2	Δ_1	Δ_2	Δ_1	Δ_2	Δ_1	Δ_2	Δ_1	Δ_2
O_2	N_2	0,8	1,3	0,2	1,4	0,2	1,8	0,1	<0,001	<0,001	0,002	0,001	0,061	0,024
Керосин (4)	Изменение C/H (5)	± 6	18,5	1,8	20,8	1,8	23,1	1,8	<0,001	<0,001	0,005	0,002	0,113	0,067

KEY: (1) Components; (2) Admixtures; (3) m/s; (4) Kerosene; (5) Change.

Table 3.3. Accuracy of calculation of properties of combustion products with extrapolation for composition of components $\alpha_{ok} = 1.0$; $\varepsilon = 100$.

Компоненты (1)	Примеси (2)	$\varepsilon_{\text{max}}, \%$	$P_{co}, \text{MN/m}^2$	$T_{co}, ^\circ\text{K}$		$\beta, \text{м/сек}$ (3)		$I_g^{\text{н}}, \text{м/сек}$ (3)		F	
				Δ_1	Δ_2	Δ_1	Δ_2	Δ_1	Δ_2	Δ_1	Δ_2
O_2	N_2	0,8	0,1	4,3	0,4	0,5	0,1	0,9	0,2	0,002	0,001
Керосин (4)	Изменение C/H (5)	± 6		0,5	0,1	10,9	1,1	20,6	2,0	0,006	0,001
O_2	N_2	0,8	10	6,6	0,6	0,9	0,1	1,4	0,2	0,002	0,001
Керосин (4)	Изменение C/H (5)	± 6		0,4	0,1	11,4	1,0	20,8	1,8	0,007	0,002
O_2	N_2 (5)	0,8	50	8,9	0,7	1,1	0,1	1,8	0,2	0,002	0,002
Керосин (4)	Изменение C/H (5)	± 6		<0,1	0,2	11,6	1,1	20,9	1,8	0,008	0,003

KEY: (1) Components; (2) Admixtures; (3) m/s; (4) Kerosene; (5) Change.

Table 3.4. Accuracy of calculation of properties of combustion products with extrapolation for composition of components $p_{CO} = 10$ MH/m², $\epsilon = 100$.

Компо- ненты (1)	Примеси (2)	ϵ_{max} %	α_{ok}	T_{CO_2} °K		ρ , м/сек (3)		I_p^0 , м/сек (3)		F	
				Δ_1	Δ_2	Δ_1	Δ_2	Δ_1	Δ_2	Δ_1	Δ_2
O ₂	N ₂	0,8	0,4	32,7	<0,1	10,7	<0,1	12,6	0,1	0,107	<0,001
			1,0	6,6	0,6	0,9	0,1	1,4	0,2	0,002	0,001
			1,2	5,4	0,6	0,9	0,2	0,8	0,2	0,010	0,002
Керосин (4)	(5) Измене- ние C/H	± 6	0,4	19,0	1,2	8,7	0,8	17,2	1,6	0,031	0,001
			1,0	0,4	0,1	11,4	1,0	20,9	1,8	0,007	0,002
			1,2	3,2	0,2	10,5	1,1	19,7	1,8	0,006	0,002

KEY: (1) Components; (2) Admixtures; (3) m/s; (4) Kerosene; (5) Change.

3.2. The Effect of Errors in Thermodynamic Properties of Individual Substances

Sources of errors in calculated values of properties of combustion products were examined in the first volume of the Reference Book. In particular, the absence of methods which permit making a substantiated evaluation of the error in calculations which arises as a result of errors in the thermodynamic properties of individual substances in the literature was noted. In preparing this volume of the Reference Book, a special method was worked out which permits estimating the errors [5].

With a constant elementary chemical composition of fuel any parameter of the combustion products, we will designate it additionally by ϕ , can be represented by the function of enthalpy i and entropy s of the mixture. The latter, in turn, are determined by the elementary chemical composition, pressure of the combustion products, thermodynamic properties (by enthalpy I_q^0 and entropy S_q^0 of the individual substances), and the enthalpy of the fuel. Consequently, the error $\Delta\phi$ which arises

due to the errors in the thermodynamic properties of individual substances can be expressed by ΔI_q^0 and ΔS_q^0 in the final analysis.

The following expressions which describe the enthalpy and entropy of the q-th substance in the gaseous state are known:

$$I_q^0 = \Delta H_{f,298,q}^0 + (H_T^0 - H_0^0)_q - (H_{298}^0 - H_0^0)_q, \quad (3.6)$$

$$(H_T^0 - H_0^0)_q = R_0 T^2 \left(\frac{\partial \ln Q_q}{\partial T} \right)_p, \quad (3.7)$$

$$S_q^0 = R_0 \ln \frac{Q_q}{N} + R_0 T \left(\frac{\partial \ln Q_q}{\partial T} \right)_p, \quad (3.8)$$

where Q_q - the statistical sum for the states of the molecules.

As is evident, the errors ΔI_q^0 and ΔS_q^0 are determined by the errors of a number of values, for example, $\Delta H_{f,298,q}^0$, $R_0 \ln Q/N$ and so forth which are arbitrarily designated further as ω_{qk} ($k = 1, 2, 3, \dots n$).

Consequently, the error of any parameter φ with small errors ω_{qk} is a linear functional relative to $\Delta \omega_{qk}$:

$$\Delta \varphi = \sum_q \sum_k \left(\frac{\partial \varphi}{\partial \omega_{qk}} \right)_{i_{co}, p_{co}, p} \cdot \Delta \omega_{qk}. \quad (3.9)$$

To calculate $\Delta \varphi$ in the general case it is necessary to solve the problem of linear programming since interconnections exist for certain ω_{qk} .

Of greatest practical interest is the estimate of errors in the calculation of specific impulse in a vacuum I_s^n and also of the flow-rate complex β , temperature T_{co} , and molecular weight μ_{co} . In particular, differentiating the well-known expression for specific impulse I_s^n , we can write with i_{co} , p_{co} , $p = \text{const}$ (the subscript "k" is omitted here and subsequently):

$$\left(\frac{\partial I_s^n}{\partial \omega} \right)_{p_{co}, i_{co}, p} = \frac{1}{\omega} \left(\frac{\partial I}{\partial \omega_{qco}} \right)_{i_{co}, p_{co}, p} \times \\ \times [f^2 p p - 1] - f^2 p \omega (\partial p / \partial \omega_{co})_{i_{co}, p_{co}, p} \quad (3.10)$$

where f - the specific area of the nozzle's exit section.

We present the entropy of the combustion products at the inlet to the nozzle S_{co} and in the exit section of the nozzle S in the form of the functions

$$\begin{aligned} S_{co} &= S_{co}(p_{co}, i_{co}, \omega_{qco}), \\ S &= S(p, \varphi, \omega_q), \end{aligned} \quad (3.11)$$

where φ - any parameter of combustion products in the nozzle, for example, T , ρ , I_s^n , μ , and so forth.

Equating the total differentials of the functions (3.11) for the isentropic process of expansion ($s = \text{const}$) with i_{co} , p_{co} , $p = \text{const}$, we obtain

$$\begin{aligned} \left(\frac{\partial \varphi}{\partial \omega_{qco}} \right)_{i_{co}, p_{co}, p} &= \left[\left(\frac{\partial s_{co}}{\partial \omega_{qco}} \right)_{p_{co}, i_{co}} - \right. \\ &\quad \left. - \left(\frac{\partial s}{\partial \omega_q} \right)_{p, \varphi} \cdot \xi_q \right] / \left(\frac{\partial s}{\partial \varphi} \right)_{p, \omega_q}, \end{aligned} \quad (3.12)$$

where the given relationship

$$\xi_q = \frac{d\omega_q}{d\omega_{qco}} \approx \frac{\Delta \omega_q}{\Delta \omega_{qco}}. \quad (3.13)$$

Expression (3.12) can be reduced to a more rational form using the equality

$$\left(\frac{\partial s}{\partial \varphi} \right)_{p, \omega} \cdot \left(\frac{\partial \varphi}{\partial \omega_q} \right)_{s, p} \cdot \left(\frac{\partial \omega_q}{\partial s} \right)_{p, \varphi} = -1. \quad (3.14)$$

As a result, we obtain

$$\begin{aligned} \left(\frac{\partial \varphi}{\partial \omega_{qco}} \right)_{i_{co}, p_{co}, p} &= \left(\frac{\partial s_{co}}{\partial \omega_{qco}} \right)_{p_{co}, i_{co}} \left(\frac{\partial \varphi}{\partial s} \right)_p + \\ &\quad + \left(\frac{\partial \varphi}{\partial \omega_q} \right)_{p, s} \cdot \xi_q. \end{aligned} \quad (3.15)$$

Equation (3.15) coincides with equation (11.39) obtained in Volume I of this Reference Book and which describes the change in the thermodynamic function φ with a change in content of the chemical element b_{T_r} in the fuel. This agreement is caused by the circumstance that in both cases the thermodynamic function φ is a function of the type $\varphi = \varphi(\alpha, \beta, \xi)$, where α and β are any two other thermodynamic functions and ξ is the content of the chemical element in the fuel, the error in calculating the function or any parameter of a nonthermodynamic character, which determines the function φ .

The derivatives $(\partial\varphi/\partial s)_p$ are determined using known thermodynamic relationships presented, for example, [6]. To determine the derivatives $(\partial s_{co}/\partial \omega_{qco})_{p,co,l,co} = (\partial\varphi/\partial \omega_q)_{p,s}$ it is expedient to obtain additional relationships which permit finding derivatives as a result of a differentiation with $p, T = \text{const}$. These relationships substantially simplify the computing scheme of the calculation.

Any parameter of the combustion products φ can be represented by the functions

$$\begin{aligned}\varphi &= \varphi(p, T, \omega_q), \\ \varphi &= \varphi(p, \psi, \omega_q),\end{aligned}\tag{3.16}$$

where ψ - is some thermodynamic function, for example, enthalpy or entropy.

Equating the total differentials of the functions φ expressed through both systems of arguments, with $p, \psi = \text{const}$ we obtain:

$$\left(\frac{\partial\varphi}{\partial\omega_q}\right)_{p,\psi} = \left(\frac{\partial\varphi}{\partial\omega_q}\right)_{p,T} + \left(\frac{\partial\varphi}{\partial T}\right)_p \cdot \left(\frac{\partial T}{\partial\omega_q}\right)_{p,\psi}.\tag{3.17}$$

To determine the derivative $(\partial T/\partial \omega_q)_{p,\psi}$ we write the total differential of the function $\psi = \psi(p, T, \omega_q)$. With $p, \psi = \text{const}$, we have:

$$\left(\frac{\partial T}{\partial\omega_q}\right)_{p,\psi} = - \frac{(\partial\psi/\partial\omega_q)_{p,T}}{(\partial\psi/\partial T)_p}.\tag{3.18}$$

Substituting this result into equality (3.17), we finally obtain

$$\left(\frac{\partial \varphi}{\partial \omega_q}\right)_{p, \psi} = \left(\frac{\partial \varphi}{\partial \omega_q}\right)_{p, T} - \left(\frac{\partial \psi}{\partial \omega_q}\right)_{p, T} \left(\frac{\partial \varphi}{\partial \psi}\right)_p. \quad (3.19)$$

For derivatives which enter into the formula for $(\partial \varphi / \partial \omega_{qco})_{pco, pco, p}$ on the basis of (3.15) with consideration of the differential relationships of thermodynamics we can write: for enthalpy i (with $\psi = s$):

$$\left(\frac{\partial i}{\partial \omega_q}\right)_{p, s} = \left(\frac{\partial i}{\partial \omega_q}\right)_{p, T} - T \left(\frac{\partial s}{\partial \omega_q}\right)_{p, T}; \quad (3.20)$$

for density of combustion products $\rho = \mu_T M_T / R_0 T$ (with $\psi = s$):

$$\left(\frac{\partial \rho}{\partial \omega_q}\right)_{p, s} = \rho \left[\left(\frac{\partial \ln M_T}{\partial \omega_q}\right)_{p, T} + \frac{\alpha_p T}{c_p} \left(\frac{\partial s}{\partial \omega_q}\right)_{p, T} \right]; \quad (3.21)$$

for entropy S_{co} (with $\psi = i_{co}$):

$$\left(\frac{\partial S_{co}}{\partial \omega_{qco}}\right)_{pco, i_{co}} = \left(\frac{\partial S_{co}}{\partial \omega_{qco}}\right)_{pco, Tco} - \frac{1}{Tco} \cdot \left(\frac{\partial i_{co}}{\partial \omega_{qco}}\right)_{pco, Tco} \quad (3.22)$$

Here M_T - the number of moles of fuel which ensures the equality $p = \sum n_q$ (see Volume I, Chapter V).

As is evident, the determination of derivatives $(\partial \varphi / \partial \omega_{qco})_{pco, i_{co}, p}$ in the final analysis is reduced to the calculation of derivatives $(\partial \psi / \partial \omega_q)_{p, T}$ ($\psi = i, s$) in the corresponding sections of the nozzle. Derivatives $(\partial \psi / \partial \omega_q)_{p, T}$ are determined as a result of differentiation of expressions for specific enthalpy and entropy. In particular, for homogeneous combustion products we obtain:

$$\left(\frac{\partial i}{\partial \omega_q}\right)_{p, T} = \frac{\sum_n n_n \cdot i_n^0 \cdot \left(\frac{\partial \ln n_n}{\partial \omega_q}\right)_{p, T} + n_q \left(\frac{\partial i_q^0}{\partial \omega_q}\right)_{p, T}}{\mu_T \cdot M_T} - i \left(\frac{\partial \ln M_T}{\partial \omega_q}\right)_{p, T}, \quad (3.23)$$

$$\left(\frac{\partial s}{\partial \omega_q}\right)_{p, T} = \frac{\sum_n n_n \left(\frac{\partial \ln n_n}{\partial \omega_q}\right)_{p, T} \cdot [S_n^0 - R_0 (1 + \ln n_n)] + n_q \left(\frac{\partial S_q^0}{\partial \omega_q}\right)_{p, T}}{\mu_T M_T} - s \left(\frac{\partial \ln M_T}{\partial \omega_q}\right)_{p, T} \quad (3.24)$$

where n - the subscript of any component of the combustion products,
 q - the subscript of the component of the combustion products, the
effect of whose errors in the thermodynamic functions is being studied.

To determine the partial derivatives $(\partial \ln n_n / \partial \omega_q)_{p, T}$ and $(\partial \ln M_T / \partial \omega_q)_{p, T}$
we differentiate the system of equations for thermodynamic equilibrium
with respect to ω_q with $p, T = \text{const}$. As a result, we obtain closed
systems of equations for the calculation of derivatives:

$$\left(\frac{\partial \ln n_l}{\partial \omega_q}\right)_{p, T} - \sum_j a_{lj} \left(\frac{\partial \ln n_j}{\partial \omega_q}\right)_{p, T} = \delta_{jq} R_j + \delta_{lq} \cdot R_l, \quad (3.25)$$

$$\sum_j a_{lj} n_j \left(\frac{\partial \ln n_j}{\partial \omega_q}\right)_{p, T} + n_l \left(\frac{\partial \ln n_l}{\partial \omega_q}\right)_{p, T} - \\ - B_l \left(\frac{\partial \ln M_T}{\partial \omega_q}\right)_{p, T} = 0, \quad (3.26)$$

$$\sum_n n_n \left(\frac{\partial \ln n_n}{\partial \omega_q}\right)_{p, T} = 0, \quad (3.27)$$

where $B_l = \sum_j a_{lj} n_j + n_l$, i - the subscript of atomic substance, j - the sub-
script of molecular substance, a_{ij} - the stoichiometric coefficient
of the dissociation reaction to the atoms, δ_{iq} , δ_{jq} - the Kronecker
symbols. The values of R_i , R_j and also the derivatives $(\partial S_q^0 / \partial \omega_q)_{p, T}$,
 $(\partial I_q^0 / \partial \omega_q)_{p, T}$ are obtained respectively by differentiation of the expression
for the equilibrium constant and formulas (3.6) - (3.8).

A similar approach can be used to determine errors of parameters
in the combustion chamber. Writing the total differential of the
function $i = i(p, \varphi, \omega_q)$ with $p = p_{co} = \text{const}$ and $i = i_{co} = \text{const}$,
we obtain:

$$\left(\frac{\partial \varphi}{\partial \omega_q}\right)_{p, i} = - \left(\frac{\partial i}{\partial \omega_q}\right)_{p, \varphi} \cdot \left(\frac{\partial \varphi}{\partial i}\right)_p. \quad (3.28)$$

An expression of the type (3.19) is valid for the derivative
 $(\partial i / \partial \omega_q)_{p, \varphi}$, consequently,

$$\left(\frac{\partial \varphi}{\partial \omega_q}\right)_{p, t} = -\left(\frac{\partial \varphi}{\partial t}\right)_p \left(\frac{\partial t}{\partial \omega_q}\right)_{p, T} + \left(\frac{\partial \varphi}{\partial \omega_q}\right)_{p, T} \quad (3.29)$$

For the stagnation temperature at the inlet to the nozzle ($\varphi = T_{co}$) and molecular weight ($\varphi = \mu_{co}$) expression (3.29) takes the form:

$$\left(\frac{\partial T_{co}}{\partial \omega_{qco}}\right)_{p_{co}, t_c} = -\frac{1}{c_p} \left(\frac{\partial t_{co}}{\partial \omega_{qco}}\right)_{p_{co}, T_{co}} \quad (3.30)$$

$$\begin{aligned} \left(\frac{\partial \mu_{co}}{\partial \omega_{qco}}\right)_{p_{co}, t_{co}} &= -\frac{\mu_{co}(\alpha_p T_{co} - 1)}{c_p T_{co}} \left(\frac{\partial t_{co}}{\partial \omega_{qco}}\right)_{p_{co}, T_{co}} + \\ &+ \mu_{co} \left(\frac{\partial \ln M_r}{\partial \omega_{qco}}\right)_{p_{co}, T_{co}} \end{aligned} \quad (3.31)$$

where $(\partial t_{co}/\partial \omega_{qco})_{p_{co}, T_{co}}$ is calculated from a formula of the type (3.23).

The arguments ω_{qk} should be selected on the basis of an analysis of known expressions for the thermodynamic properties of individual substances, for example, (3.6)-(3.8). The errors $\Delta \omega_{qk}$ can be selected on the basis of published data. In particular, for such arguments of ω_{qk} , as $\Delta H_{f, 298, q}$, $R_0 \ln \frac{Q_q}{N}$, heat of fusion (polymorphic transformations) and others, systematic data are presented in Reference Books [45-49]. For some values, for example, $R_0 \left(\frac{\partial \ln Q_q}{\partial T}\right)_p$, reliable data are absent. Information on the interconnection among ω_{qk} both for the given substance ($k = 1, 2, 3 \dots n$) as well as among ω_{qk} for various substances ($q = 1, 2, 3, \dots 1$) is also extremely limited.

3.3. The Effect of Errors in the Thermophysical Properties of Individual Substances

As is known, the procedure for determining the transfer properties - coefficients of viscosity, heat conductivity, and diffusion - is based on the following mandatory conditions.

1. Information on the composition of the combustion products is necessary.

This information is provided by methods presented in Volume I of the Reference Book.

2. A kinetic theory which is applicable for the combustion products systems being examined must be developed.

We cannot fail to note that despite the considerable theoretical studies, a rigid kinetic theory is virtually absent for actual combustion products systems (nonspherical molecules, the presence of internal degrees of freedom and excited molecules, dense gases). Consequently, the basic source of information on transfer properties is the molecular-kinetic theory of monoatomic rarefied gases which is also used in the Reference Book. Here, an estimate of the corresponding corrections for actual special features of combustion products systems is necessary.

The first volume of the Reference Book provides an estimate of the effect of density and internal degrees of freedom. It was adjudged expedient not to consider the effect of density and to consider the effect of internal degrees of freedom (except for several individual substances) on the basis of the diffusion transfer mechanism. This leads to the corresponding errors in transfer coefficients which, as shown in Volume I of the Reference Book, do not exceed several percent. Also insignificant is the error which arises as a result of the use of excited molecules and atoms of the same interaction potentials as for molecules and atoms in the basic state.

3. Quantitative information on the intermolecular interaction which, at the present time, it is customary to give in the form of an empirical function (potential) of interaction $\varphi(r)$ is necessary. For the temperature region of 2000-4000°K, which is most characteristic for combustion products of chemical fuels, the parameters of the potential in the majority of cases cannot be found using direct experimental data. Virtually the only way is the extrapolation of low-temperature data ($T \lesssim 1000^\circ\text{K}$) on the properties of transfer to the region of high temperatures or the extrapolation of high-temperature experimental data ($T \sim 5000^\circ\text{K}$) on the scattering of molecular beams

to the region of low temperature with subsequent matching of the extrapolation results with each other.

It should be noted, however, that such an approach is possible now only for a narrow range of individual substances, primarily components of carbon fuel combustion products. Only an empirical estimate of the parameters of the potential is possible for the remaining components of combustion products, especially of those containing atoms of metal, as a result of the absence of experimental data.

The method of matching experimental data on properties of the transfer and scatter of molecular beams in the work of Samuylov and Tsitelauri [41] was used to determine the section of collisions $\sigma_{Q' \cdot Q''}$ for the interactions $O_2 - O_2$, $H_2 - H_2$, $N_2 - N_2$, $CO - CO$, and $CO_2 - CO_2$. In this volume of the Reference Book this method is realized as a result of the approximation of the sections of collisions $\sigma_{Q' \cdot Q''}$ by the Lennard-Jones potential (the approximation error is characterized above in Table 2.13).

It is of interest to estimate the errors of the transfer coefficients for the substances mentioned above and several others in comparison with the experimental data and which were calculated in the Reference Book. Presented as an example in Tables 3.5 and 3.6 are the results of such an estimate for the coefficients of viscosity η and heat conductivity λ in the form of errors:

$$\delta\eta = \frac{\eta - \eta_{\text{эксп}}}{\eta_{\text{эксп}}} \cdot 100\%,$$

$$\delta\lambda = \frac{\lambda - \lambda_{\text{эксп}}}{\lambda_{\text{эксп}}} \cdot 100\%.$$

The values of $\eta_{\text{эксп}}$, $\lambda_{\text{эксп}}$ are taken from the data in Reference Book [17, 18]. As is evident from the tables, the error of the coefficients η and λ is permissible in the case where these coefficients are used in calculations of the processes of heat- and mass exchange in engines which use chemical fuel.

For higher temperatures ($T \sim 3000-4000^\circ\text{K}$) the errors in the transfer coefficients of the individual substances mentioned above as well as of atoms and free radicals of O, H, N, and OH, and molecules of NO comprise approximately 30% ($\sim 20\%$ - the error in the method for scattering molecular beams and the semi-empirical method of valence bonds for OH, $\sim 10\%$ - the error in the approximation of $\sigma_{12}^{1,2}$ by the Lennard-Jones potential).

It is not possible to provide a reliable estimate of the errors in calculating the properties of the transfer of mixtures because of the practical absence of experimental data for combustion products of the fuels examined in the Reference Book. The following approximate relationship was taken to estimate the errors in the viscosity coefficient in the Reference Book (Volume I, Chapter XIV):

$$\delta\eta = \frac{\eta}{\mu} \sum \frac{\mu_i x_i}{\eta_i} \delta\eta_i. \quad (3.32)$$

Table 3.5. Error in the viscosity coefficient of several gaseous substances.

H ₂		H ₂ O		CO		CO ₂		CH ₄		N ₂		NH ₃		O ₂	
T° K	δη%	T° K	δη%	T° K	δη%	T° K	δη%	T° K	δη%	T° K	δη%	T° K	δη%	T° K	δη%
373	1,5	373	7,8	373	15,4	500	1,1	373	0,8	500	4,2	373	7,8	500	1,9
473	0,9	473	1,3	473	9,3	700	0,9	473	1,1	700	3,2	423	6,8	700	0,4
573	0,2	573	1,6	573	3,7	900	0,7	573	1,3	900	8,6	473	6,1	900	0,9
673	0,3	673	3,8	673	0,5	1100	0,1	673	1,6	1100	12,1	523	5,5	1100	2,0
773	0,6	773	4,8	773	3,6	1300	0,2	773	0,4	1300	14,0	—	—	1300	3,1
873	0,8	873	6,0	873	6,5	1500	0,6	873	0,5	1500	17,3	—	—	1500	4,2
973	2,1	973	7,3	973	8,0	1700	1,1	973	0,4	1700	19,5	—	—	1700	5,3
1073	1,7	—	—	1073	9,8	1900	1,7	1073	0,2	1900	21,2	—	—	1900	6,3
1173	1,4	—	—	1173	10,6	2000	1,9	1173	0,2	—	—	—	—	2000	6,8
1273	2,3	—	—	1273	11,5	2500	3,5	1273	0,5	—	—	—	—	2500	9,1

Table 3.6. Error in the coefficient of heat conductivity of gaseous substances.

H ₂		H ₂ O		CO ₂		CH ₄		N ₂		NH ₃		O ₂	
T° K	δλ%	T° K	δλ%	T° K	δλ%	T° K	δλ%	T° K	δλ%	T° K	δλ%	T° K	δλ%
400	2,0	393	9,6	400	4,1	373	3,3	400	11,0	400	9,2	400	1,0
600	1,5	443	11,5	500	0,6	393	2,7	500	4,9	450	10,2	500	0,5
800	3,0	493	12,8	600	2,0	433	1,6	600	0,4	500	8,0	600	2,1
1000	3,8	543	13,4	700	2,5	493	0,7	700	4,2	550	9,7	700	4,7
1200	5,7	593	13,6	800	2,7	533	0,1	800	8,4	600	8,6	800	5,3
1400	7,6	—	—	900	2,6	573	0,1	900	10,7	—	—	900	5,4
1600	9,6	—	—	1000	2,5	623	0,3	1000	12,5	—	—	1000	4,7
1800	11,5	—	—	1100	2,2	773	0,4	1100	13,6	—	—	1100	5,9
2000	12,2	—	—	1200	1,5	—	—	1200	13,1	—	—	1200	5,2
—	—	—	—	1300	1,5	—	—	1300	13,8	—	—	1300	5,2
—	—	—	—	1400	1,8	—	—	1400	12,6	—	—	1400	5,2

For the fuel compounds being examined in this volume, the basic components of the combustion products are H₂, O₂, H₂O, CO, CO₂, N₂, OH, H, O; the molar fraction of O, H, and OH for the majority of values of α_{ok} , p_{so} , and ϵ is no more than 10%. Consequently, the basic error in calculating the viscosity coefficient of a mixture is introduced by the errors in $\delta\eta_i$ of molecules H₂, O₂, H₂O, CO, CO₂ and N₂. Considering the approximate nature of relation (3.32), it is expedient to take the values of $\delta\eta_i$ for these substances as identical, as approximately 20-30%. Thus, the possible error in the viscosity coefficient of the combustion products in the tables of the Reference Book is 20-30%; the error in the coefficient of heat conductivity is estimated as

$$\delta\lambda \approx (1,0 - 1,2) \delta\eta. \quad (3.33)$$

3.4. Extrapolation Accuracy

The tables in the Reference Book present derivatives which, with a constant elementary chemical composition of the fuel, permit the extrapolation of stagnation temperature on the inlet to the nozzle T_{co} ,

the flow-rate complex β , the specific impulse in a vacuum I_g^* , and the relative area (the geometric degree of expansion) of the nozzle $\bar{F}$. These values can be extrapolated in accordance with the pressure in the combustion chamber p_{co} , according to the degree of the nozzle's expansion, according to pressure $\mathcal{E}$, and according to the fuel's enthalpy i_T . The data in Volume I of the Reference Book can be used to calculate the derivatives which are necessary for extrapolation in accordance with the geometric degree of expansion $\bar{F}$ and to determine the coefficients of interpolation polynomials.

The expansion of the function of several independent variables into a Taylor series is used for extrapolation. The accuracy of the extrapolation depends on the type of fuel, the accepted form of functional dependence of parameters on p_{co} , i_T , or $\mathcal{E}$, the number of terms considered in the series, and the amount of change in the argument with extrapolation. The latter is determined by the intervals of values p_{co} and $\mathcal{E}$. The logarithmic form of expansion into a series and linear extrapolation are recommended on the basis of the studies which have been conducted (see Volume I, Chapter XI).

As numerous calculations have shown, the accuracy of extrapolation for all fuels is determined primarily by the values α_{ok} , p_{co} , and $\mathcal{E}$ in the vicinity of which the extrapolation is accomplished. Extrapolation for fuel enthalpy with p_{co} , $\mathcal{E} = \text{const}$ in all cases of interest to us (for example, even with a change in the aggregate state of the fuel components) provides acceptable accuracy (see Volume I, Chapter XV).

3.4.1. Estimate of extrapolation errors

As a result of the variety of fuels which are presented in the Reference Book and the broad range of changes in parameters α_{ok} , p_{co} , and $\mathcal{E}$, it is not possible to provide an estimate of the errors in extrapolating values for each fuel and for each value of α_{ok}^0 , p_{co}^0 , $\mathcal{E}^0$. When necessary, to determine possible errors in extrapolation for a selected tabular interval $\ln p_{co}^{(1)} - \ln p_{co}^{(2)}$ or $\ln \mathcal{E}^{(1)} - \ln \mathcal{E}^{(2)}$ the error in extrapolation can be estimated from the value of the second term in the Taylor expansion which is discarded:

temperature T_{co}

$$\delta T_{co}\% = \frac{1}{2} 10^{-1} \frac{A^{(1)} - A^{(2)}}{\ln \frac{p_{co}^{(1)}}{p_{co}^{(2)}}} \left[\ln \frac{p_{co}}{p_{co}^{(2)}} \right]^2; \quad (3.34)$$

flow-rate complex β

$$\delta \beta\% = \frac{1}{2} 10^{-1} \frac{B^{(1)} - B^{(2)}}{\ln \frac{p_{co}^{(1)}}{p_{co}^{(2)}}} \left[\ln \frac{p_{co}}{p_{co}^{(2)}} \right]^2; \quad (3.35)$$

specific impulse in a vacuum I_s^* with $p_{co} = \text{const}$

$$\delta I_s^*\% = \frac{1}{2} 10^{-1} \frac{C^{(1)} - C^{(2)}}{\ln \frac{s^{(1)}}{s^{(2)}}} \left[\ln \frac{s}{s^{(2)}} \right]^2; \quad (3.36)$$

geometric degree of expansion of nozzle $\bar{F}$

$$\delta \bar{F}\% = \frac{1}{2} 10^{-1} \frac{D^{(1)} - D^{(2)}}{\ln \frac{s^{(1)}}{s^{(2)}}} \left[\ln \frac{s}{s^{(2)}} \right]^2. \quad (3.37)$$

In expressions (3.34) and (3.37) the superscripts "1" and "2" designate the amounts of the values on the boundary of the selected interval, without superscripts - in the middle of the interval, and coefficients A, B, C, D - the corresponding partial derivatives which are presented in the tables of the Reference Book.

To estimate possible errors in extrapolation, we can also recommend third-power interpolation polynomials whose coefficients are determined from the value of the function and its first derivative with $p_{co}^{(1)}$ and $p_{co}^{(2)}$ or $s^{(1)}$ and $s^{(2)}$. A method for determining coefficients is given in the first volume of Reference Book [5]. Another possible method for estimating is calculation of errors in the middle of the interval $p_{co}^{(1)} - p_{co}^{(2)}$ or $s^{(1)} - s^{(2)}$ in accordance with values δT_{co} , $\delta \beta$, δI_s^* , $\delta \bar{F}$ on the boundaries of the interval. For example, using tabular data with $p_{co}^{(1)}$ or $s^{(1)}$, we can determine from extrapolation formulas the parameters with $p_{co}^{(2)}$ or $s^{(2)}$ and find the errors δT_{co} , $\delta \beta$, δI_s^* , $\delta \bar{F}$ by comparison with

tabular data with $p_{co}^{(1)}$ or $\epsilon^{(2)}$. The error in the middle of the indicated intervals p_{co} or ϵ is approximately 0.25 of the amounts of the values δ found.

An impression about the possible errors in extrapolation is provided by the materials in Chapter XV of the Reference Book's first volume as well as by the data in [2].

3.4.2. Regions of greatest extrapolation errors. Some recommendations

Temperature in the combustion chamber T_{co} . The maximum errors in extrapolation for p_{co} should be expected in the region of values of the excess oxidant ratio which corresponds to the greatest rate of change in the composition of the combustion products. Usually this occurs with $(T_{co})_{max}$. Since the position of the maximum of the function $T_{co} = f(\alpha_{ok})$ usually depends very weakly on the temperature in the combustion chamber, it is sufficient to provide an estimate of possible extrapolation errors with one value of p_{co} . The degree of dissociation is decreased with an increase in pressure in the combustion chamber; therefore the rate of change of the function $T_{co} = f(p_{co})$ is somewhat greater in the region of low pressures in the combustion chamber than in the region of high pressures. Consequently, large extrapolation errors are possible with low pressures p_{co} .

Flow-rate complex β . Just as in the case of temperature T_{co} , the greatest errors should be expected in the region of the excess oxidant ratio which corresponds to the maximum β . The rate of change in the function $\beta = f(p_{co})$ is determined by the rate of change in the combustion products composition depending on p_{co} . With an increase in pressure the degree of dissociation decreases and the effect of p_{co} is weakened. Therefore, with comparatively low pressures ($p_{co} \approx \approx 10 \text{ MN/m}^2$ or less) a higher extrapolation accuracy is given by an expansion of the type $\ln \beta = f(\ln p_{co})$, and with high - $\beta = f(p_{co})$.

The step of pressure change p_{co} adopted in the Reference Book permits us to extrapolate β in accordance with p_{co} with high accuracy (see Volume I, Chapter XV). The employment of one or another form of expansion is dictated by convenience in performing the calculations.

Specific pulse in a vacuum I_s^n . The greatest errors in extrapolating I_s^n in accordance with p_{co} and ε should be expected with values of α_{ok} which correspond to the maximum I_s^n . These values of α_{ok} usually correspond to the greatest deviation of the relation $I_s^n(\varepsilon)$, $p_{co} = \text{const}$ and $I_s^n(p_{co})$, $\varepsilon = \text{const}$ from linear values as a result of the joint influence of dissociation and recombination.

A numerical analysis shows that the greatest values of the derivatives $(\partial I_s^n / \partial p_{co})$ with $\varepsilon = \text{const}$ is observed in the case of low values of p_{co} and ε . With values of pressure p_{co} selected in the Reference Book the relative changes in I_s^n depending on p_{co} between any adjacent values, i.e., $\frac{1}{I_s^n} \left(\frac{\Delta I_s^n}{\Delta p_{co}} \right)$, usually do not exceed 1%. Consequently, in this case the extrapolation error in the middle of the interval, as a rule, does not exceed 0.25%.

A change in the degree of expansion for pressure ε can be caused by a change in p_{co} or p_a as well as of both parameters simultaneous. It should be noted that in the case of $\varepsilon = \text{const}$ the value of I_s^n depends comparatively weakly on the value of p_{co} . With a simultaneous change in p_{co} and p_a , the extrapolation of I_s^n can be accomplished for two parameters: for p_{co} with $p_a = \text{const}$ and for ε or (p_a) with $p_{co} = \text{const}$.

Calculations and their analysis show that the greatest errors in extrapolation should be expected with low values of ε and p_{co} . However, the interval in pressure values p_{co} and ε adopted in the Reference Book permits avoiding large errors in certain measure: with $p_{co} < 2 \text{ MN/m}^2$ the interval of change $\varepsilon \sim 2.5$ and with $p_{co} \geq 2 \text{ MN/m}^2$ this interval is ~ 6 .

A comparison of the results of thermodynamic calculations in accordance with extrapolation formulas shows that with the use of the first derivatives alone with a 2.5-fold change in ε the error in extrapolation in accordance with ε does not exceed 1%. For example, for the fuel $O_2 + NH_3$ in the case of initial parameters $p_{co}^0 = 2 \text{ MN/m}^2$, $\varepsilon^0 = 5$ with extrapolation to the limit of the interval $p_{co} = 2 \text{ MN/m}^2$,

$\varepsilon = 10$ we obtain a relative error $\delta/\bar{F} = 0.89\%$. With extrapolation to the middle of the interval the extrapolation error is substantially reduced.

The geometric degree of expansion of the nozzle $\bar{F}$. With a constant degree of pressure reduction in the nozzle ε relative changes of adjacent values of $\bar{F}$ depending on p_{c0} in the tables of the Reference Book are comparatively low and comprise 1-2%. Under these conditions, employment of only the first two derivatives in formulas with extrapolation in accordance with pressure p_{c0} with $\varepsilon = \text{const}$ provides acceptable accuracy.

Calculations and their analysis show that with extrapolation in accordance with ε with $p_{c0} = \text{const}$ the greatest errors should be expected in the region of low p_{c0} and low ε . The accuracy in extrapolation of $\bar{F}$ in accordance with ε with the use of only the first derivatives is lowest in comparison with the extrapolation of other parameters; here, a large error should be expected with extrapolation from high ε in the direction of low.

Above we examined the most unfavorable cases of extrapolation where we should expect the greatest errors. Basically, these are the extreme points of parameters p_{c0} and ε in the tables of the Reference Book. With mean values of the parameters the accuracy of extrapolation with the use of the first derivatives is rather high for the use of extrapolation results in practical calculations.

When necessary, extrapolation accuracy can be increased by using second finite differences.

3.5. Accuracy of Graphic Representation

The graphic representation of functions in semilogarithmic and logarithmic coordinates is used in the Reference Book.

Inaccuracies in the construction of graphs lead to errors in the values being represented on them. An estimate of such errors with the construction of graphs in the indicated coordinates is offered below.

Let the function $y = f(\log x)$ be represented graphically in semi-logarithmic coordinates on a graph with height H_y . The scale of the function y

$$M_y = \frac{y_{\max} - y_{\min}}{H_y} \quad (3.38)$$

is constant and the same for any point on the graph. An inaccuracy in constructing $\overline{\Delta y}$ entails an error Δy of the function

$$\Delta y = M_y \overline{\Delta y}. \quad (3.39)$$

The maximum relative error with $\overline{\Delta y} = \text{const}$ equals

$$\delta y_{\max} = \frac{\Delta y}{y_{\min}}. \quad (3.40)$$

When presenting a function in decimal logarithmic coordinates $\log y = f(\log x)$ the scale of logarithmic values will be

$$M_y = \frac{1}{l}, \quad (3.41)$$

where l - the length of a segment ($\log 10 - \log 1$) on the graph.

Inaccuracy in the construction of the graph $\overline{\Delta \log y}$ causes the error

$$\Delta \log y = (\overline{\Delta \log y}) M_y. \quad (3.42)$$

Consequently, the error Δy of the function y is

$$\Delta y = y [10^{(\overline{\Delta \log y}) M_y} - 1]. \quad (3.43)$$

From expression (3.43) with a constant error $\overline{\Delta \log y}$ it follows that

$$\delta y = \frac{\Delta y}{y} = 10^{(\overline{\Delta \log y}) M_y} - 1 = \text{const}, \quad (3.44)$$

where δy - the relative error.

As an example, we estimate the errors in the functions T_{co} , I_s , β and $\log F$ for the case $H \approx 160$ mm, $l = 50-80$ mm.

In constructing the graphs, one can "err" by approximately 0.5-1.0 mm, i.e., $\Delta y, \Delta l_{gy} \sim 1$ mm. In the region of values $T_{co} = 3000^\circ\text{K} - 1000^\circ\text{K}$ and $I_s = 4000-2000$ m/s according to expressions (3.39)-(3.40) we obtain

$$\begin{aligned} M_T &\approx 12.8^\circ\text{K/mm}, \Delta T = 12.8^\circ\text{K}, \\ \delta_{T_{\max}} &= 1.2\%; M_{I_s} \approx 12.8 \frac{\text{m/s}}{\text{mm}}, \Delta I_s \approx 12.8 \text{ m/s}, \\ \delta_{I_{s\max}} &= 0.6\%. \end{aligned}$$

In the region of values of $\log F = \log 1000 - \log 1$ the results are presented in Table 3.7.

Table 3.7. Estimate of errors in the construction of the relation $\log \bar{F} = f(\log \varepsilon)$

$l, \text{ mm}$	50	80
$M_{I_s \bar{F}}$	0.02	0.0125
$\delta \bar{F}, \%$	2.3	1.9
$\Delta \bar{F}, \bar{F}=10$	0.23	0.19
$\Delta \bar{F}, \bar{F}=100$	2.3	1.9
$\Delta \bar{F}, \bar{F}=1000$	23	19

When determining a function from its graph, the values of the quantities are obtained with an error which depend on an erroneous determination of both n of the coordinates of the graph of the function. In this case, the errors in determining the values exceed the errors in constructing the graph of the function.

CHAPTER IV

BRIEF DESCRIPTION OF TABLES AND GRAPHS

A detailed description of the tables and graphs and instructions are presented in Chapter XIII, Volume I. Presented below is a brief description of the tables and graphs which are necessary for convenience in using each volume separately.

4.1. Tables

The columns of the table (from left to right) present the following information.

First column - conventional designations of the values being presented.

Second column - values pertaining to conditions at the inlet to the nozzle (stagnation pressure p_{co}).

Third column - values pertaining to conditions in the critical section of the nozzle (pressure $p_* = p_{co}/s_*$).

Fourth and subsequent columns - values pertaining to sections in the supersonic portion of the nozzle (pressure in the section corresponds to the current stage of expansion ϵ and comprises $p = p_{co}/\epsilon$).

The lines of the table (from top to bottom) present the following information.

The first line contains some information on the fuel and combustion products, and namely:

- λ_{ok} - excess oxidant ratio;
- k_1 - coefficient of the fuel component ratio, kg oxidizer/kg fuel;
- ρ_T - the mean fuel density, g/cm³;
- i_T - specific enthalpy of the fuel, kJ/kg;
- s - specific entalpy of the combustion products which is constant on the section from the inlet to the nozzle to the exit section, kJ/kg deg.

The group of lines under the heading "General Values" contains the following data:

- $\epsilon = \frac{p_{co}}{p}$ - the degree of nozzle expansion with pressure;
- p - pressure, kN/m²;
- T - temperature, OK;
- μ - mean molecular weight, kg/mole;
- a, M - speed of sound in equilibrium-reacting mixture (a), m/s, in the second column; Mach number (M) for the values $\epsilon > \epsilon_*$;
- n - the mean index of isoentropy of expansion in the interval from p_{co} to $p = p_{co}/\epsilon$;
- w - the speed of flow, m/s;
- β, I_s^* - the flow-rate complex β , m/s, for values $\epsilon = \epsilon_*$; specific impulse in a vacuum I_s^* , m/s, for values $\epsilon > \epsilon_*$;
- $F = \frac{F}{F_*}$ - the geometric degree of expansion of the nozzle (relative area);
- c_{pf} - specific "frozen" specific heat of combustion products at constant pressure, kJ/kg deg;
- c_p - equilibrium specific heat of combustion products at constnat oressure, kJ/kg deg;
- $\eta \cdot 10^4$ - coefficient of dynamic viscosity of gas phase of mixture, n s/m²;
- λ_f - the coefficient of "frozen" specific heat of the gas phase of combustion products, W/m deg;
- λ - coefficient of equilibrium heat conductivity of the combustion products gas phase, W/m deg;
- $\gamma = \frac{c_p}{c_v}$ - the ratio of the equilibrium specific heats with constant pressure and constant volume;

$\alpha_p \times T$ - the product of the isobaric expansion coefficient times temperature;

$\beta_T \times p$ - the product of the isothermal contraction coefficient times pressure;

z - the total fraction by weight of substances in a condensed state.

In the group of lines under the heating "coefficients of extrapolation formulas" the following partial derivatives are presented.

$$A_1 = \left(\frac{\partial \ln T_{co}}{\partial \ln p_{co}} \right)_{T,e} \cdot 10^3 - \text{in the second column;}$$

$$C_1 = \left(\frac{\partial \ln I_s^n}{\partial \ln p_{co}} \right)_{T,e} \cdot 10^3 - \text{in the fourth and subsequent columns;}$$

$$A_2 = \left(\frac{\partial \ln T_{co}}{\partial I} \right)_{p_{co},e} \cdot 10^3 - \text{in the second column;}$$

$$C_2 = \left(\frac{\partial \ln I_s^n}{\partial I} \right)_{p_{co},e} \cdot 10^3 - \text{in the fourth and subsequent columns;}$$

$$B_1 = \left(\frac{\partial \ln \beta}{\partial \ln p_{co}} \right)_{T,e} \cdot 10^3 - \text{in the third column;}$$

$$C_3 = \left(\frac{\partial \ln I_s^n}{\partial \ln s} \right)_{p_{co},T} \cdot 10^3 - \text{in the fourth and subsequent columns;}$$

$$B_2 = \left(\frac{\partial \ln \beta}{\partial I} \right)_{p_{co},e} \cdot 10^3 - \text{in the third column;}$$

$$\left. \begin{aligned} D_1 &= \left(\frac{\partial \ln F}{\partial \ln p_{co}} \right)_{T,e} \cdot 10^3 \\ D_2 &= \left(\frac{\partial \ln F}{\partial I} \right)_{p_{co},e} \cdot 10^3 \\ D_3 &= \left(\frac{\partial \ln F}{\partial \ln s} \right)_{T,p_{co}} \cdot 10^3 \end{aligned} \right\} - \text{in the fourth and subsequent columns;}$$

$$A_4 = \left(\frac{\partial T_{co}}{\partial g_1} \right)_{p_{co}} - \text{in the second column;}$$

$$C_4 = \left(\frac{\partial I_s^n}{\partial g_1} \right)_{p_{co},e} - \text{in the fourth and subsequent columns;}$$

$$B_4 = \left(\frac{\partial \beta}{\partial g_1} \right)_{p_{co}} - \text{in the third column;}$$

$$D_4 = \left(\frac{\partial F}{\partial g_1} \right)_{p_{co},e} - \text{in the fourth and subsequent columns;}$$

$$L_1 = \left(\frac{\partial g}{\partial k_1} \right)_{p_{co}, t} - \text{in the second column;}$$

$$A_1 = \left(\frac{\partial T}{\partial k_1} \right)_{p_{co}}$$

$$C_0 = \left(\frac{\partial I_0''}{\partial i_0} \right)_{p_{co}, t} - \text{in the fourth and subsequent columns;}$$

$$B_0 = \left(\frac{\partial I_0''}{\partial k_0} \right)_{p_{co}} - \text{in the third column;}$$

$$D_0 = \left(\frac{\partial P}{\partial k_0} \right)_{p_{co}, t} - \text{in the fourth and subsequent columns;}$$

$$L_0 = \left(\frac{\partial g}{\partial k_0} \right)_{p_{co}, t}$$

The group of lines under the heading "equilibrium composition" presents the molar fractions of gaseous individual substances (designated by the symbols of chemical compounds and atoms) and the fractions by weight of individual substances in the condensed state (chemical symbols have the additional sign*). The zero of whole numbers and the decimal point have been omitted in writing decimal fractions.

4.2. Graphs

The following standard graphs are presented for each of the fuel compounds examined in the volume:

- 1) $I_0'' = f(\alpha_{ok}, p_{co}, t)$ and $p_T = f(\alpha_{ok})$.
- 2) $\beta = f(\alpha_{ok}, p_{co})$.
- 3) $T_{co} = f(\alpha_{ok}, p_{co})$ and $\alpha = f(\alpha_{ok})$.

Since, in addition to the scale α_{ok} there are the scales k_1 and k_2 , other ties are also illustrated, for example, $T_{co} = f(k_1, p_{co})$ and so forth.

- 4) $\bar{F} = f(t, \alpha_{ok}, p_{co})$.

Since the dependence of the relative area $\bar{F}$ on pressure p_{co} is weak, each line with $\alpha_{ok} = \text{const}$ is approximately valid for the pressure interval indicated in the graph.

The results of the calculation of losses in specific impulse in a vacuum (ζ_{vac}), which are caused by chemical disequilibrium of the flow in the nozzle are presented in the form of graphical relationships for three fuel compounds ($\text{O}_2 + \text{H}_2$, kerosene, and asymmetrical dimethylhydrazine). This information is limited to only three fuels in connection with the great labor intensity in the calculation of nonequilibrium flows and, primarily, in connection with the absence of much data on the mechanism and constants of the reaction rates in a gas phase.

The results of calculations of chemically nonequilibrium flows are presented in the form of graphical dependences of the coefficient of loss in specific impulse ζ_{v} on the relative radius $\bar{r}$ for a series of fixed values α_{ok} , p_{co} , d_* .

Six figures are presented on each page for the given value of excess oxidant ratio α_{ok} . Each figure on a page corresponds to one selected value of stagnation pressure at the input to the nozzle p_{co} whose value in MN/m^2 is indicated on the graph, and the series of values of d_* is mm.

To find ζ_{v} with values of α_{ok} , p_{co} , and d_* which are not presented on the figures, graphical interpolation should be conducted. Here, it is expedient to construct additional graphs of the type:

- a) $\zeta_{\text{v}} = f(\alpha_{\text{ok}})$ with $\bar{r}$, p_{co} and $d_* = \text{const}$,
- b) $\zeta_{\text{v}} = f\left(\frac{250 \text{ MH}}{d_*}\right)$ with $\bar{r}$, p_{co} and $\alpha_{\text{ok}} = \text{const}$,
- c) $\zeta_{\text{v}} = f\left(\frac{25 \text{ MH/m}^2}{p_{\text{co}}}\right)$ with $\bar{r}$, d_* and $\alpha_{\text{ok}} = \text{const}$,

considering the natural condition that with d_* , $p_{\text{co}} \rightarrow \infty$, $\zeta_{\text{v}} \rightarrow 0$.

1) In this regard, also see Figs. 18.20 and 18.21 in the first volume of the Reference Book.

CHAPTER V.

TABLES AND GRAPHS OF CALCULATION RESULTS

FUEL - OXYGEN + HYDROGEN ($O_2 + H_2$)

	$c_{ox} = 0.3 - 5.0$	
	$P_{ox} = 0.1 - 50 \frac{MN}{m^2}$	
	OXIDIZER	FUEL
CHEMICAL FORMULA	O ₂	H ₂
ENTHALPY $\frac{kJ}{kg}$	-398.3	-4353.9
DENSITY $\frac{g}{cm^3}$	1.135	0.07076
ADMIXTURE	LIQUID NITROGEN N ₂	NONE
Range of change in admixture content, by weight	0.008	—
Coefficients of extrapolation formulas	A, B, C, D,	—

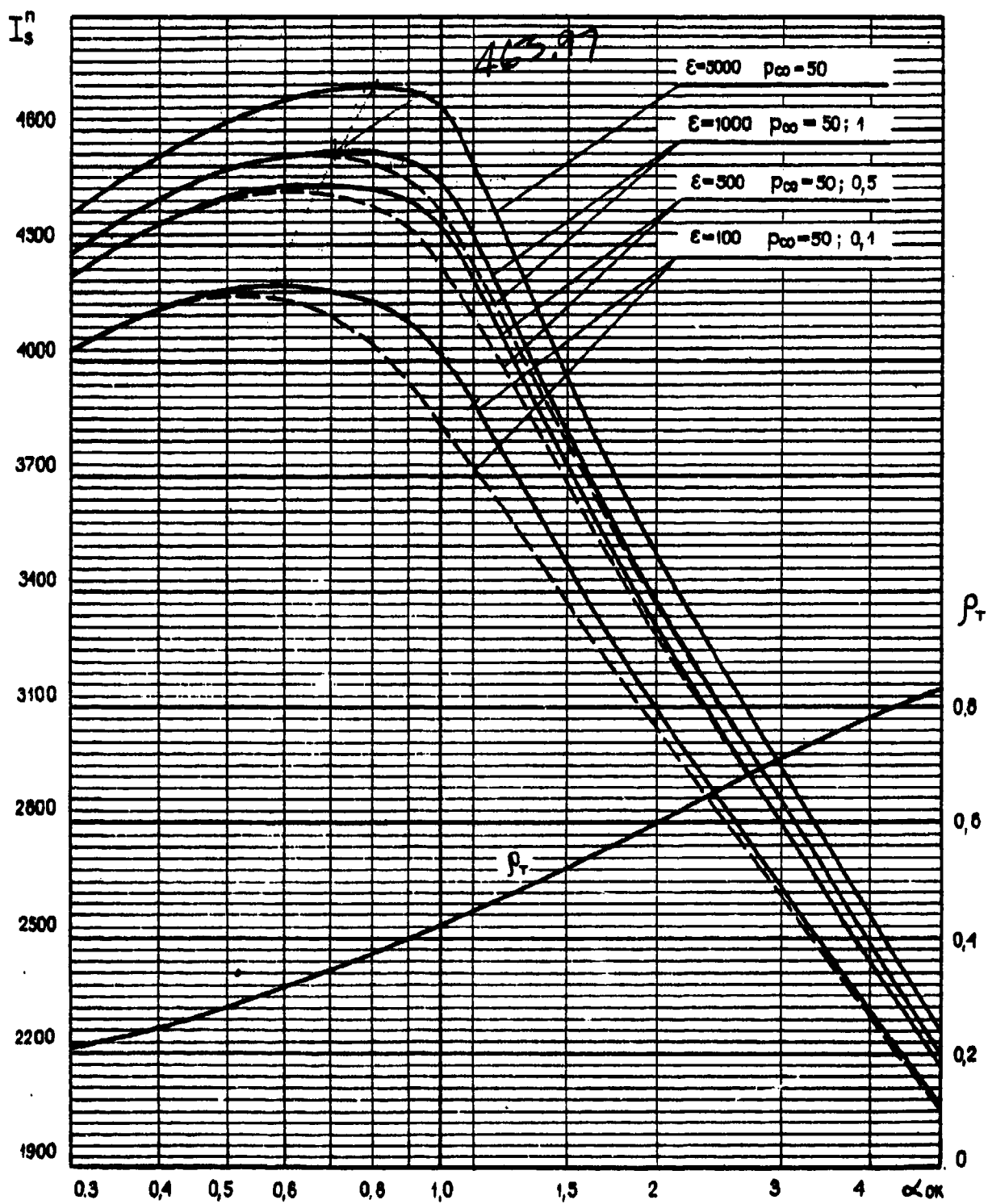


Fig. 5.1.

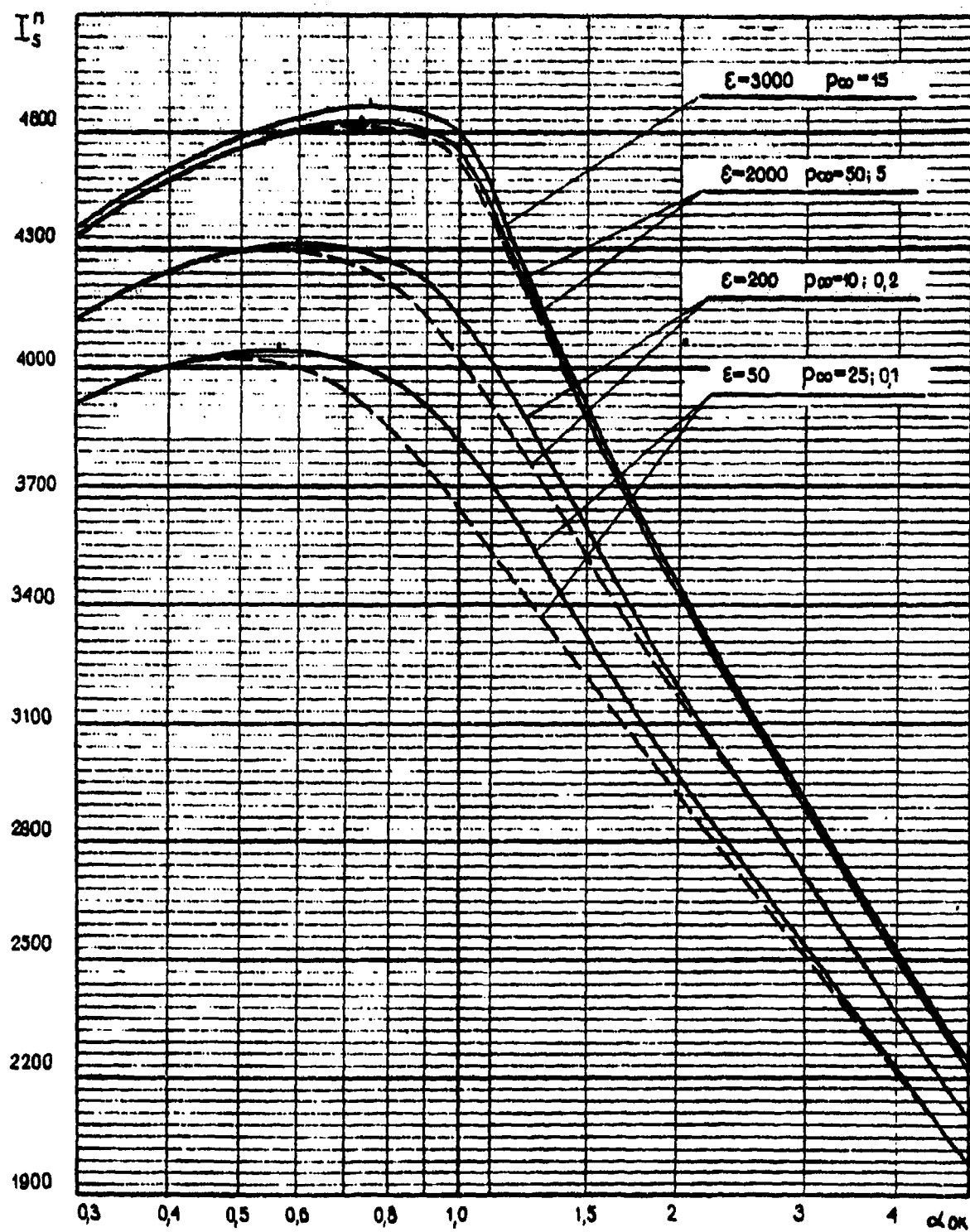


Fig. 5.2.

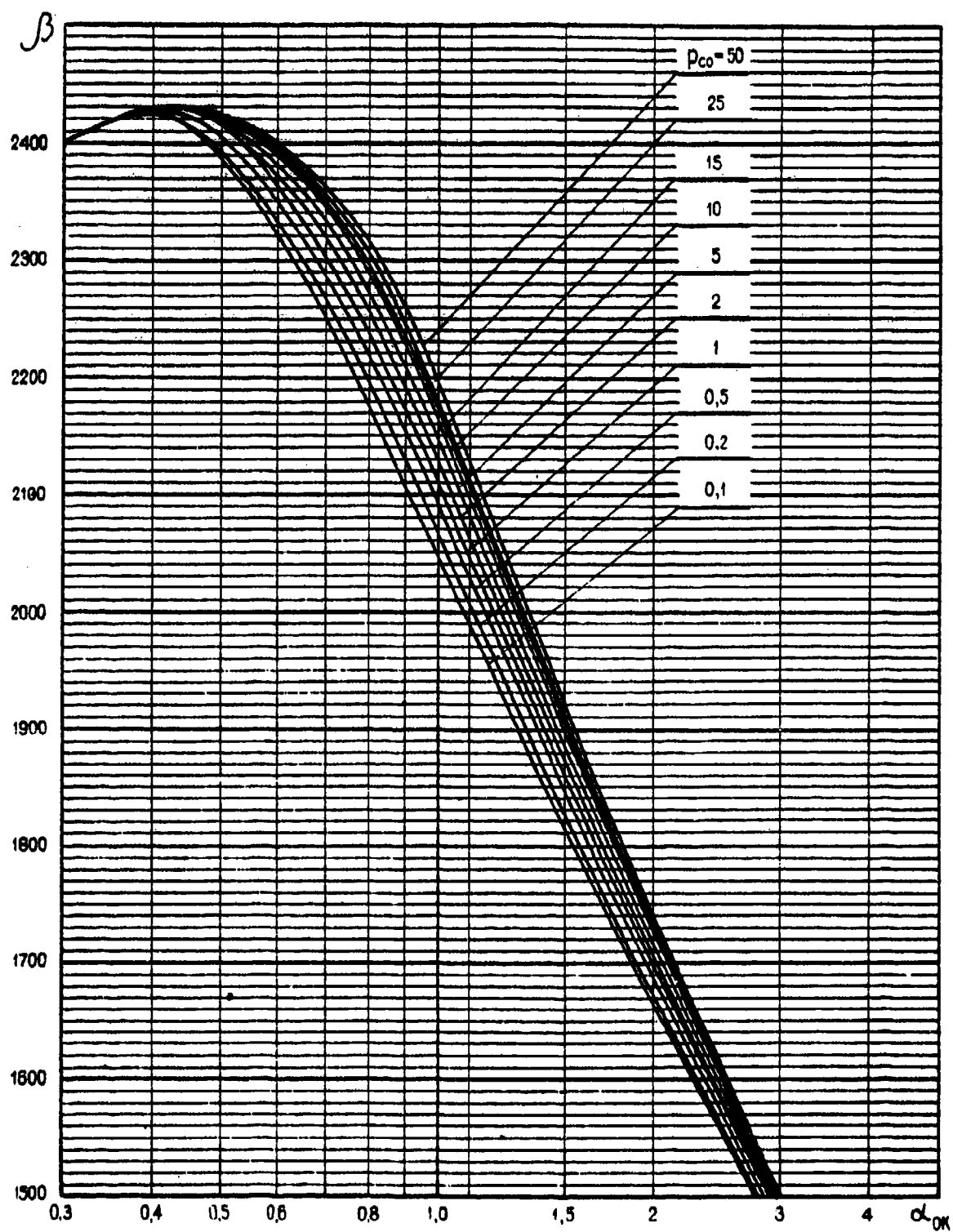


Fig. 5.3.

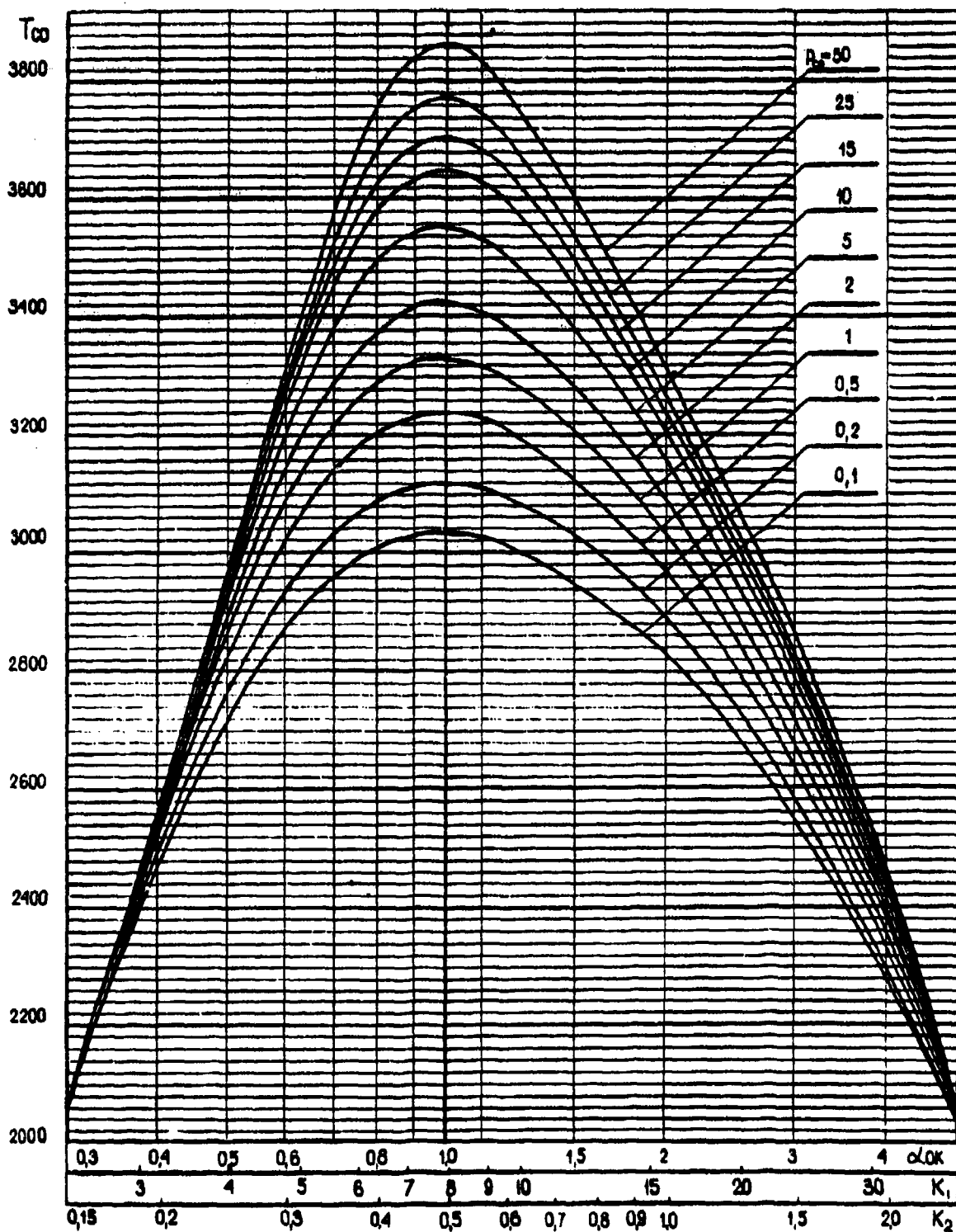


Fig. 5.4.

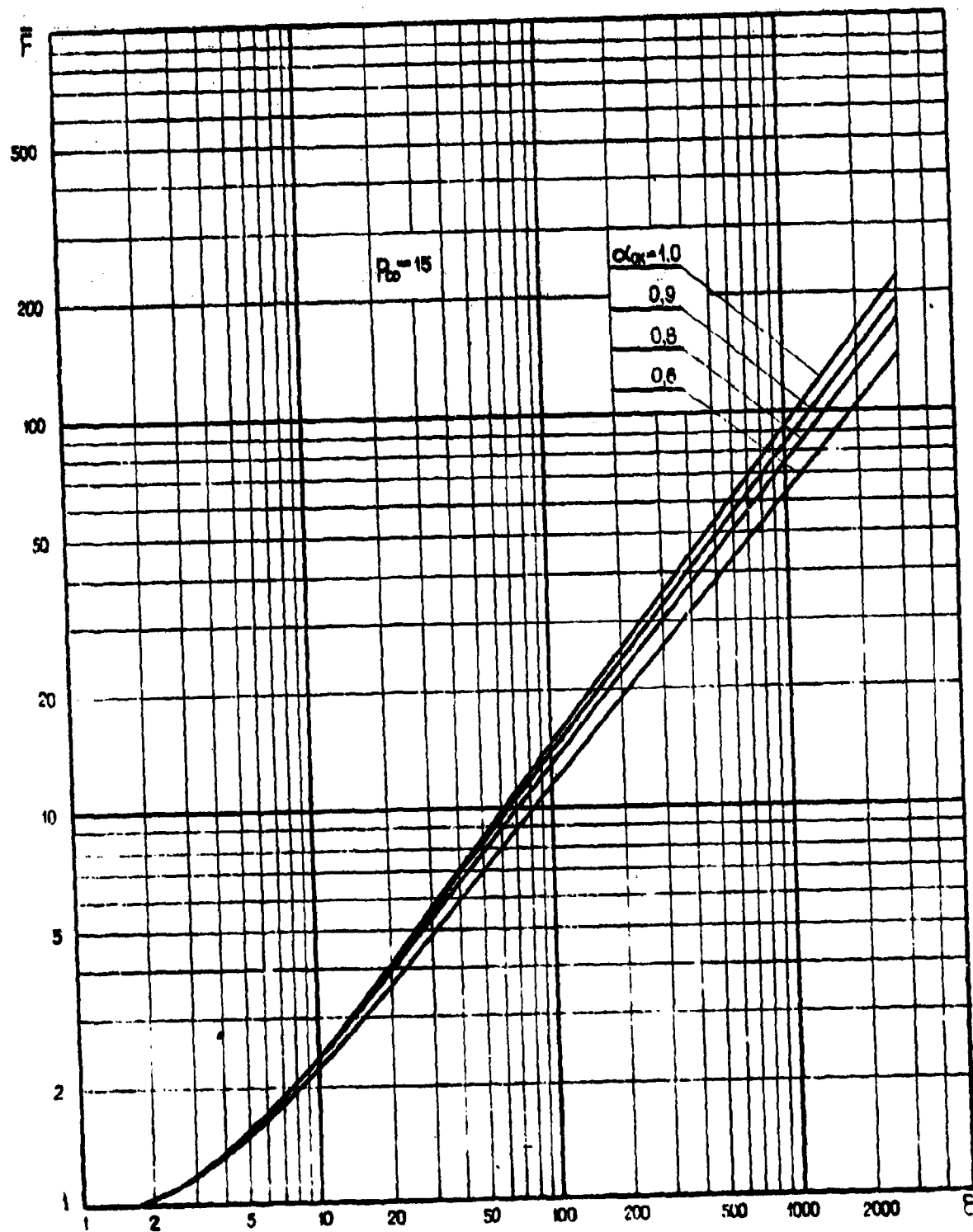
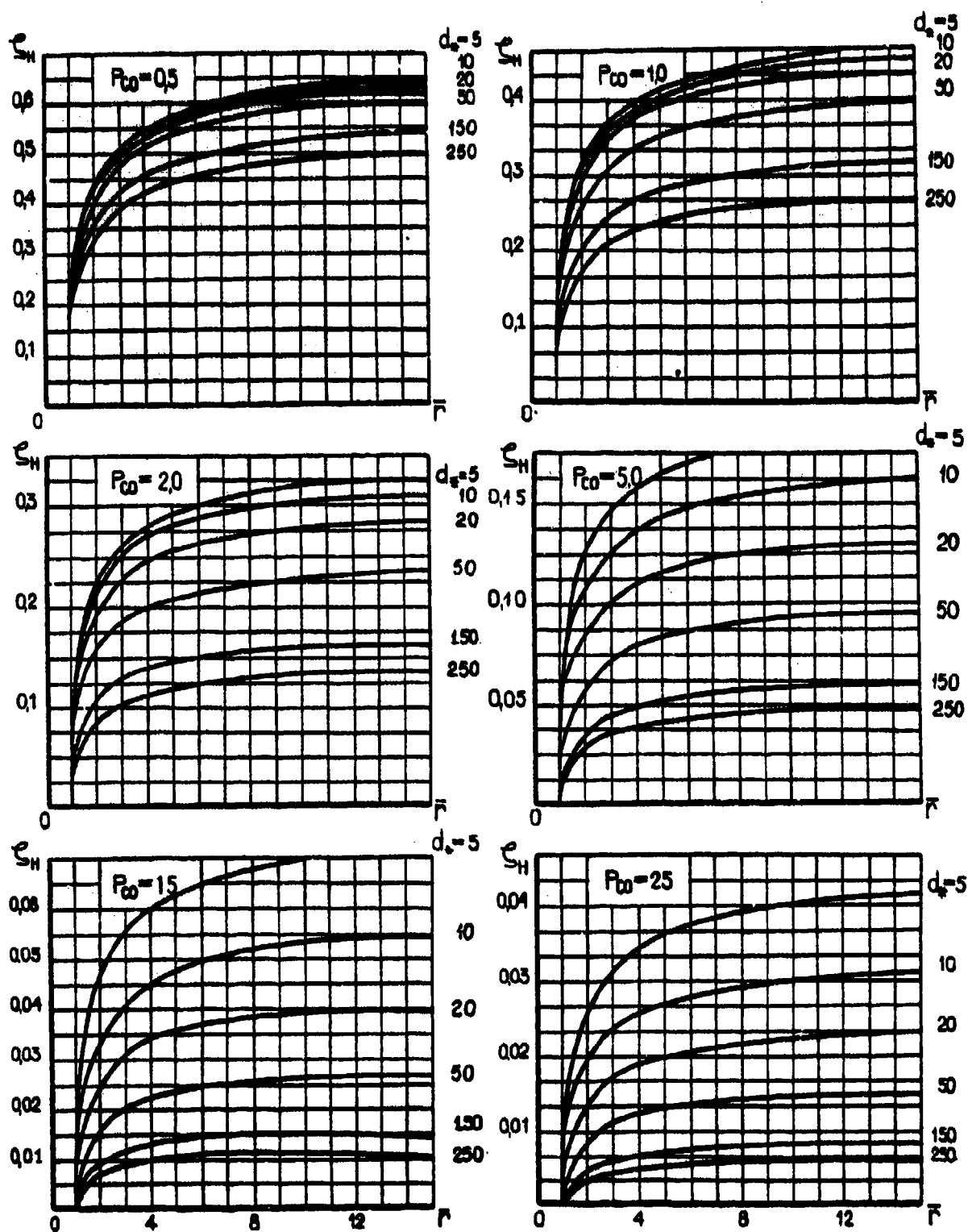


Fig. 5.5.



$$\alpha_{OK} = 0.4$$

Fig. 5.6.

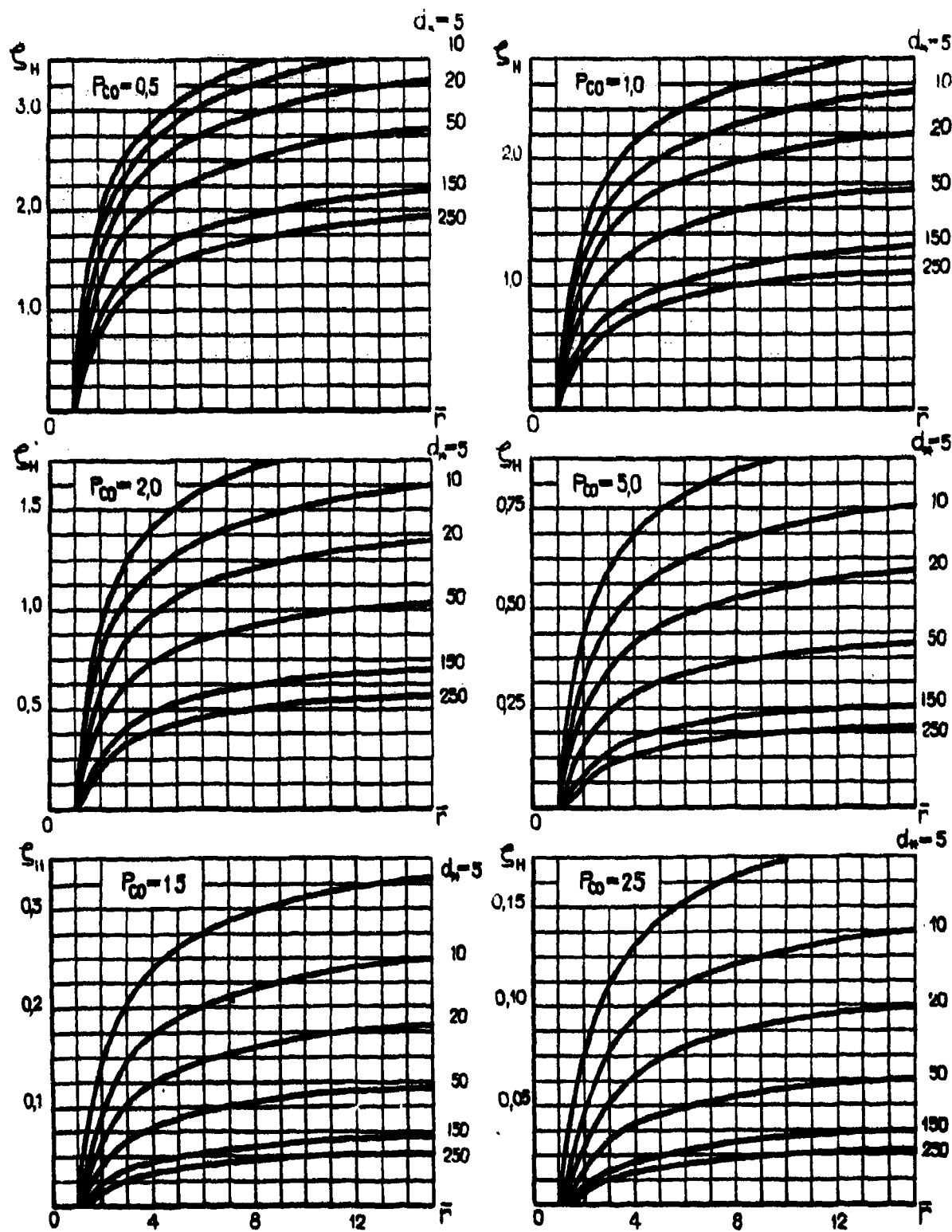


Fig. 5.7. $\alpha_{0K} = 0.6$

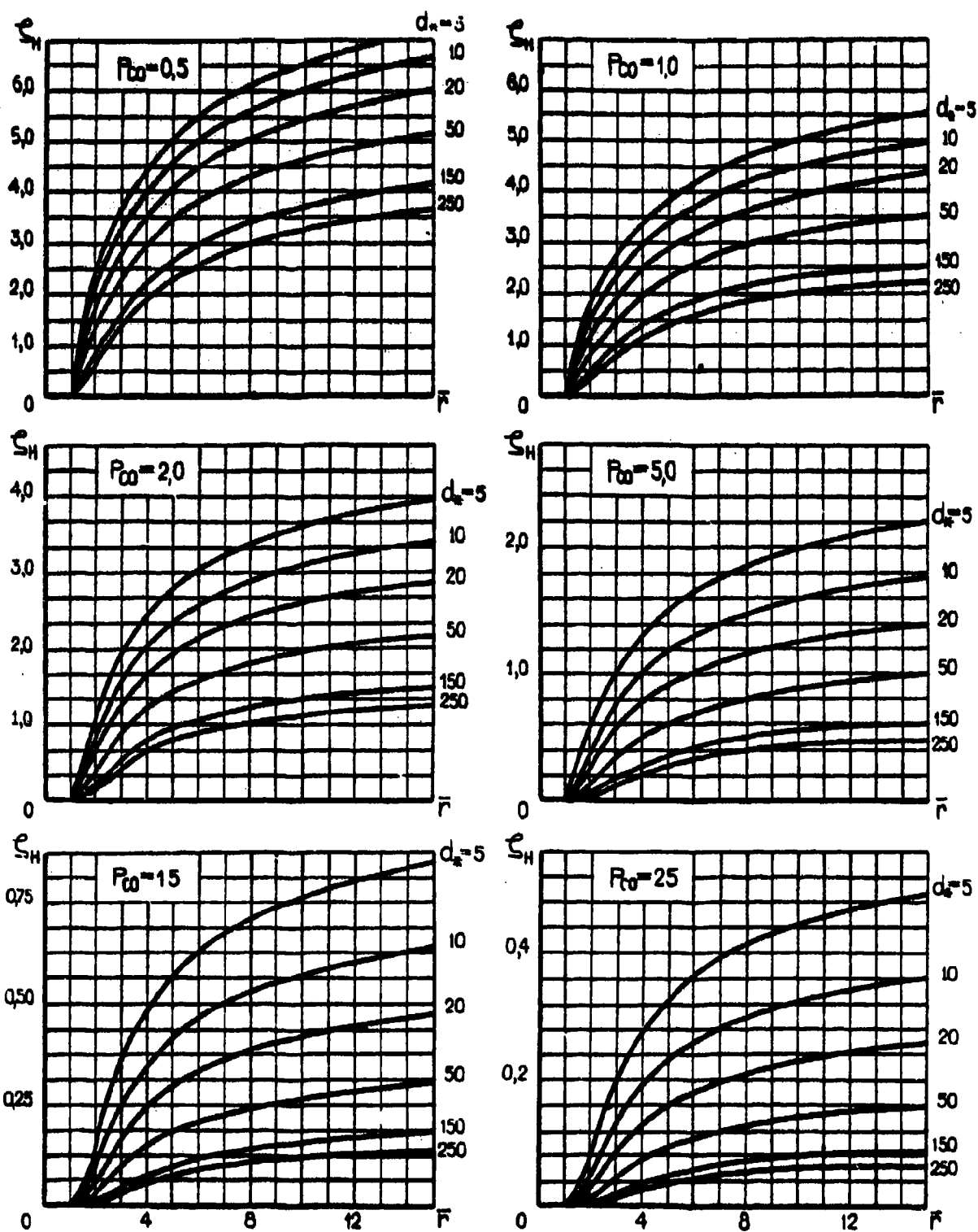
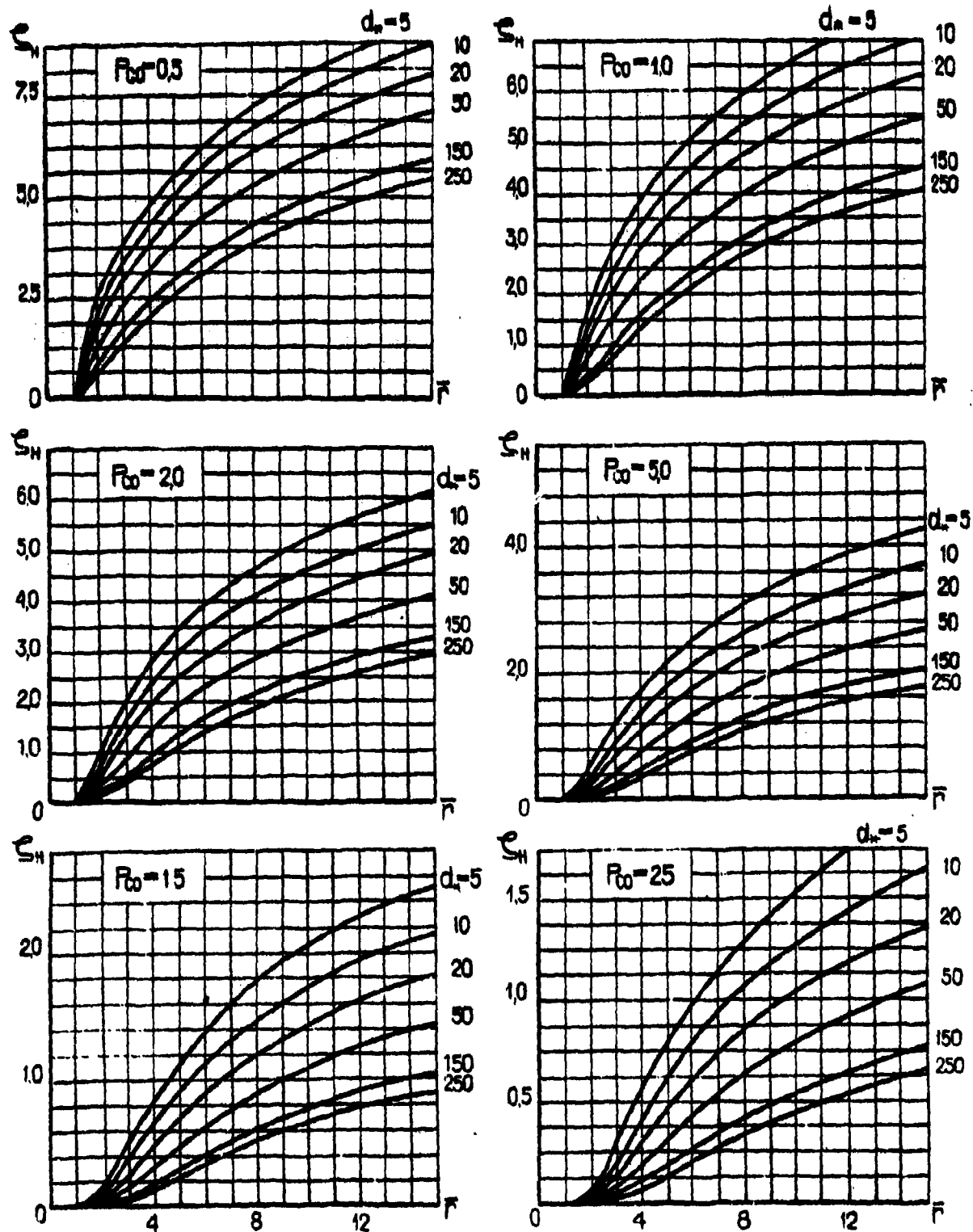


Fig. 5.8. $\alpha_{0K} = 0.8$



$\alpha_{0K} = 1.0$

Fig. 5.9.

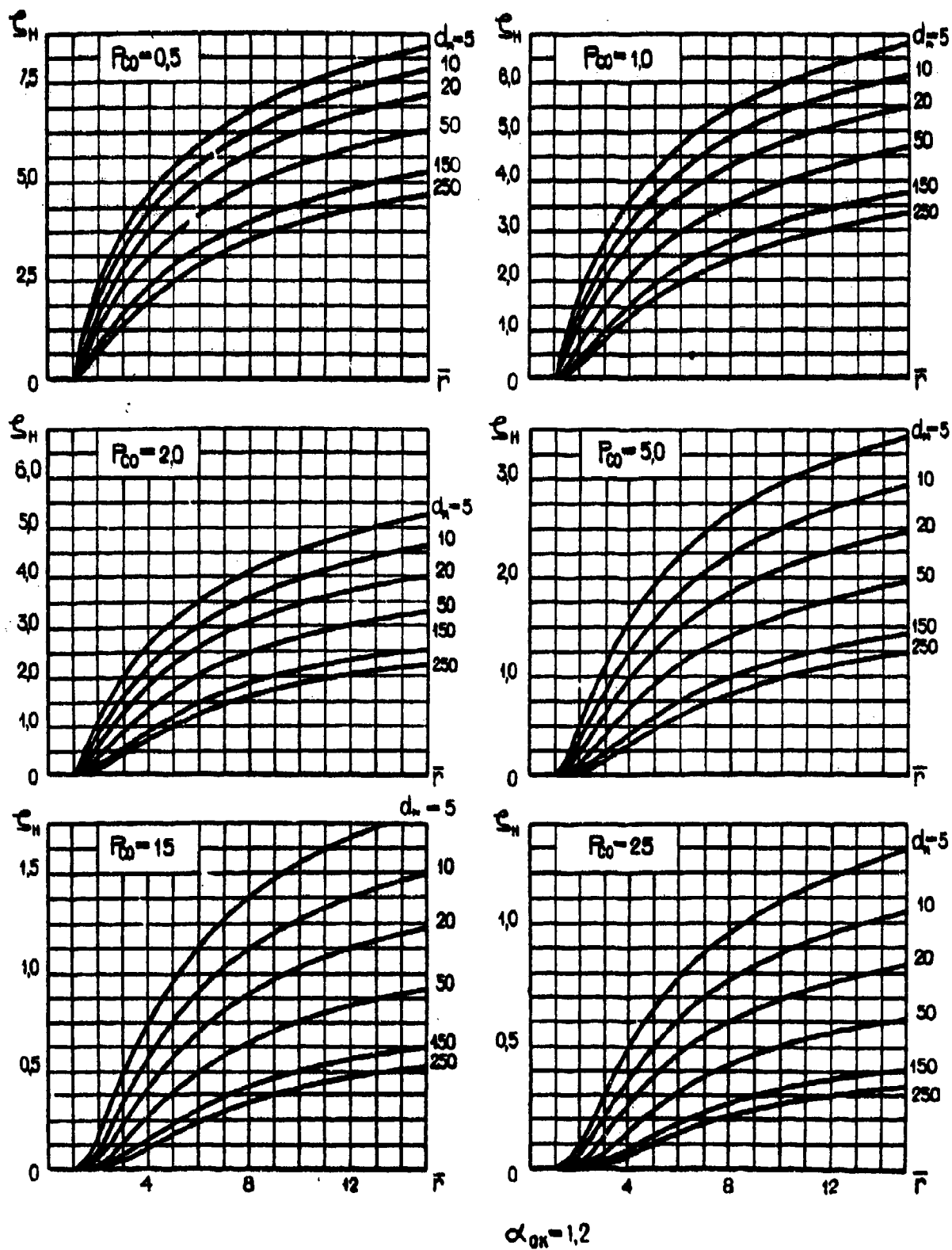
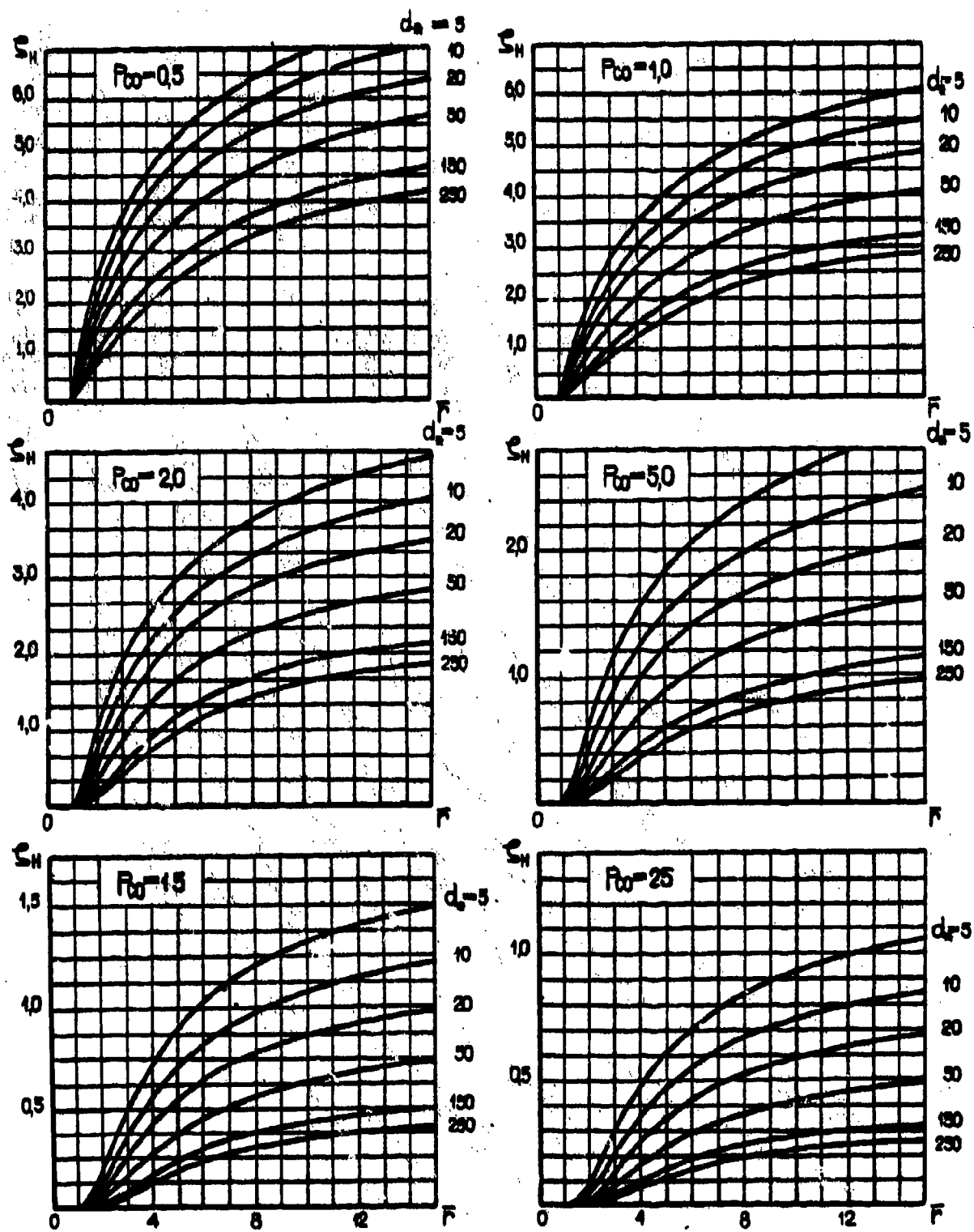


Fig. 5.10



$$\alpha_{0K} = 1.4$$

Fig. 5.11.

FUEL - OXYGEN + KEROSENE (O_2 + KEROSENE)

$$\epsilon_{\text{ex}} = 0.4 - 5.0$$

$$P_{\text{ex}} = 0.1 - 50 \frac{\text{MN}}{\text{m}^2}$$

CHEMICAL
FORMULA

OXIDIZER

FUEL

O_2

$\text{CH}_{1.87}$

(C-85.9%, H-14.1%)

ENTHALPY $\left(\frac{\text{kJ}}{\text{kg}} \right)$

-398.3

-1948

DENSITY $\left(\frac{\text{g}}{\text{cm}^3} \right)$

1.135

$T = 90.188^\circ\text{K}$

0.83

$T = 298.15^\circ\text{K}$

ADMIXTURE

LIQUID NITROGEN, N_2

Change in C/H
ratio given

Range of change in
admixture content,
by weight

0.008

Change in C/H by 28%

Coefficients of
extrapolation formulas

$A_0 B_0 C_0 D_0 L_0$

$A_0 B_0 C_0 D_0 L_0$

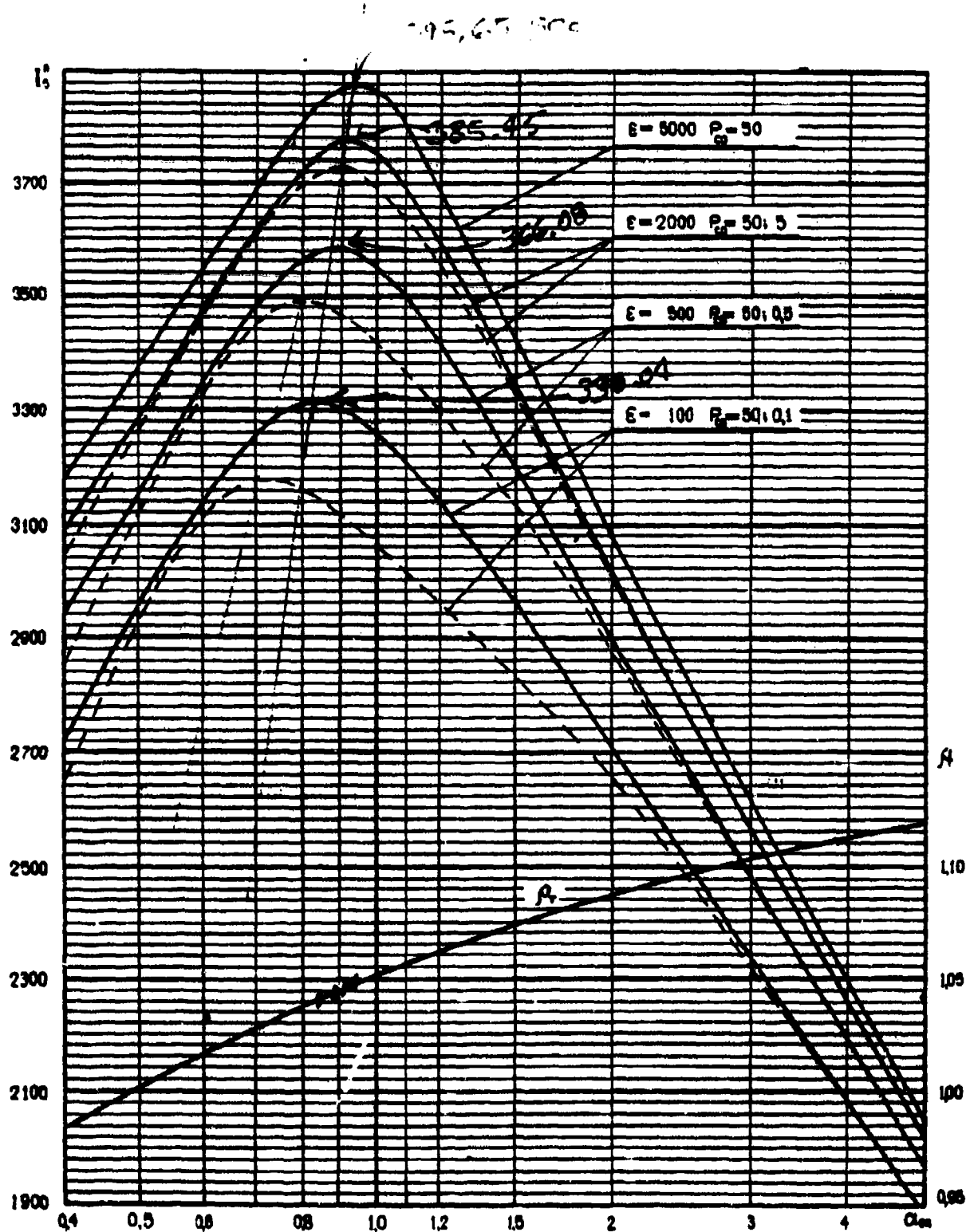


Fig. 5.12.

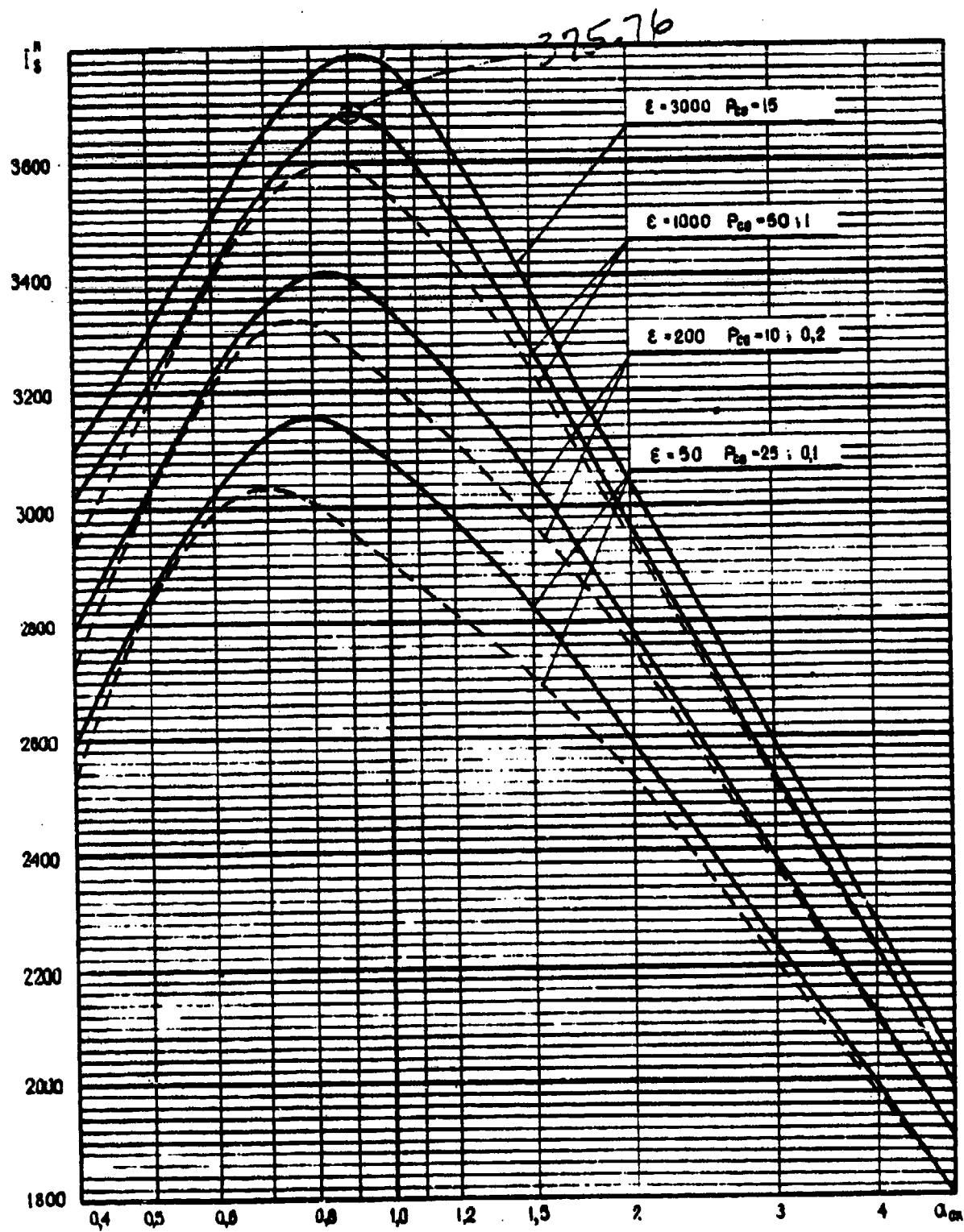


Fig. 5.13.

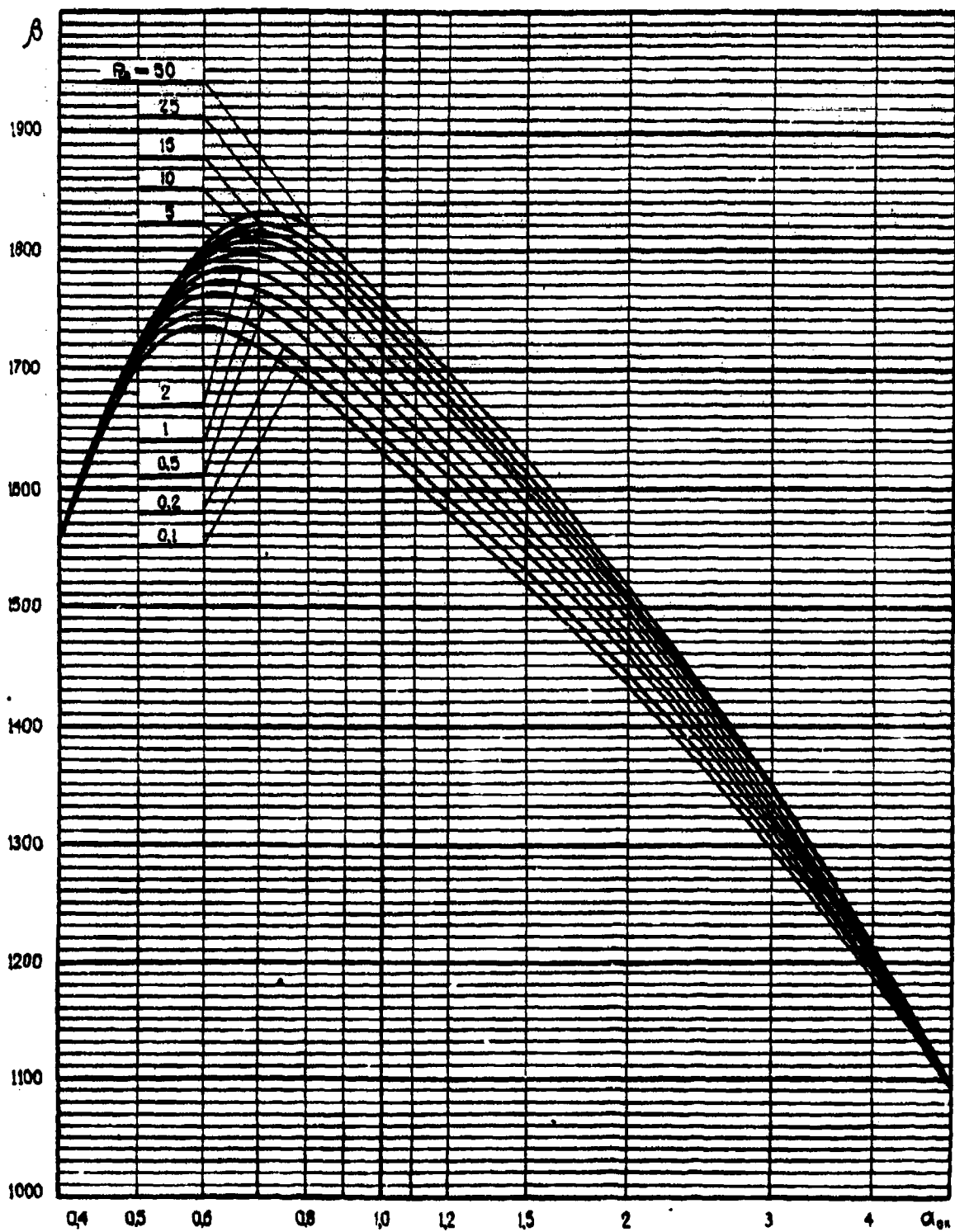


Fig. 5.14.

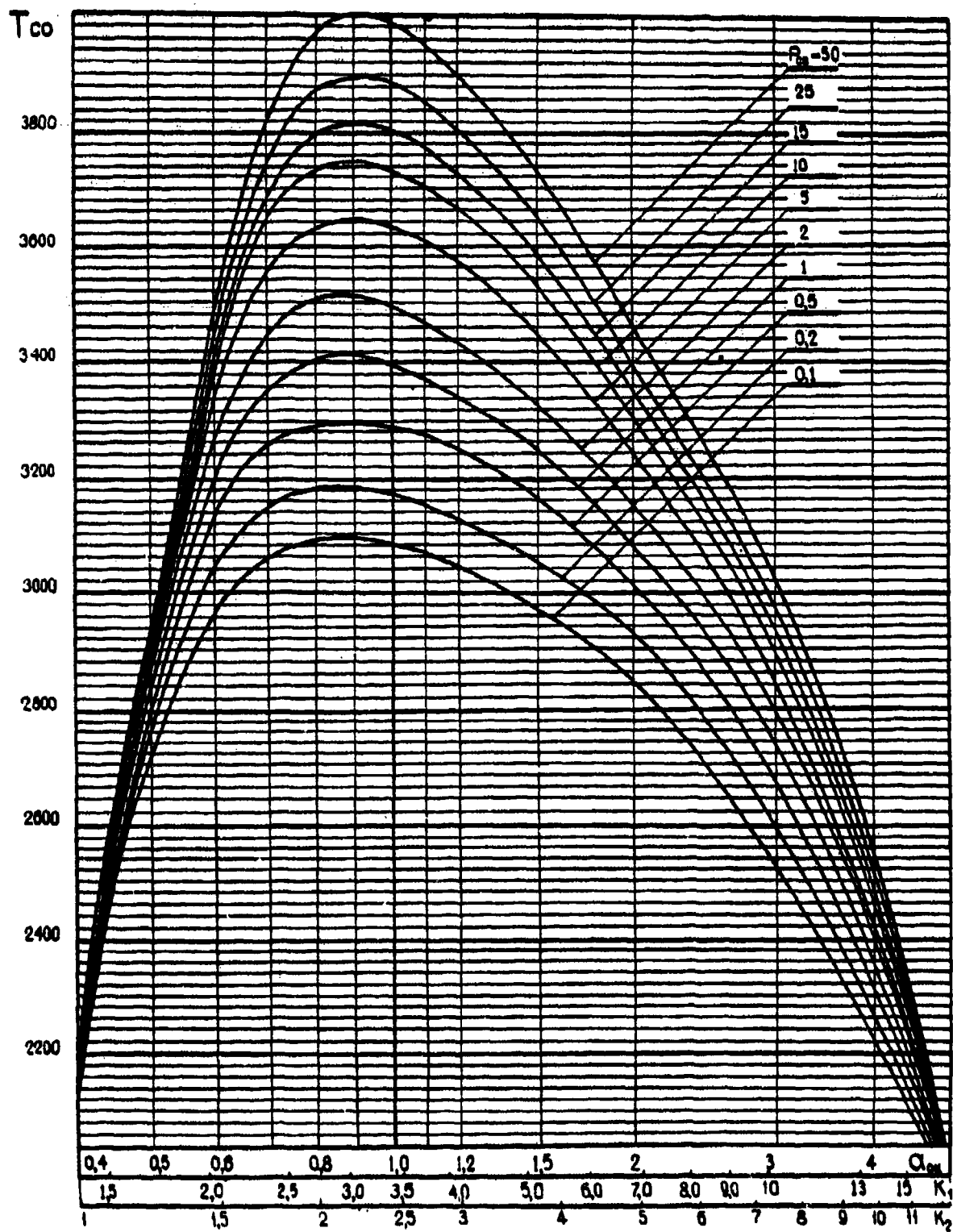


Fig. 5.15.

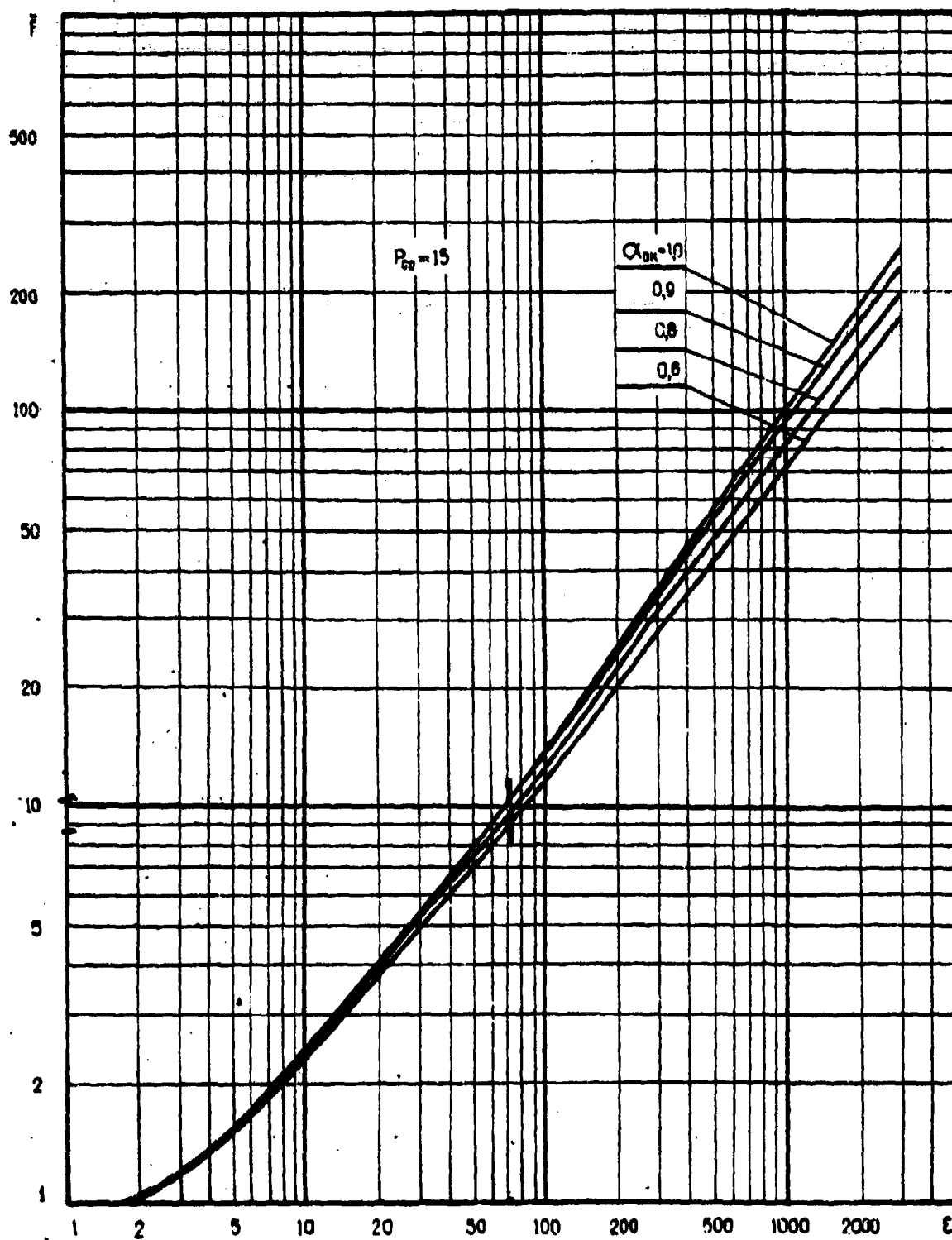
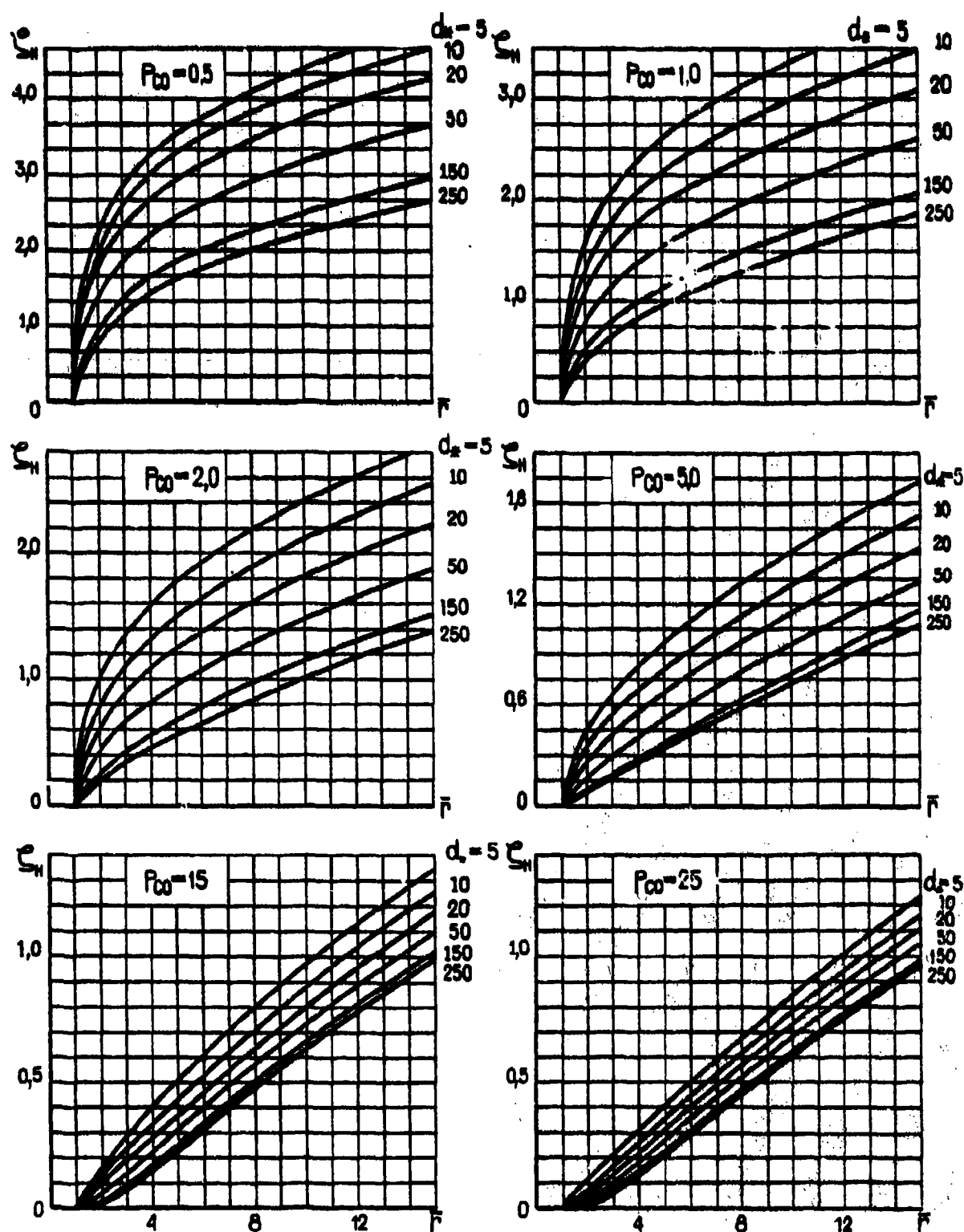
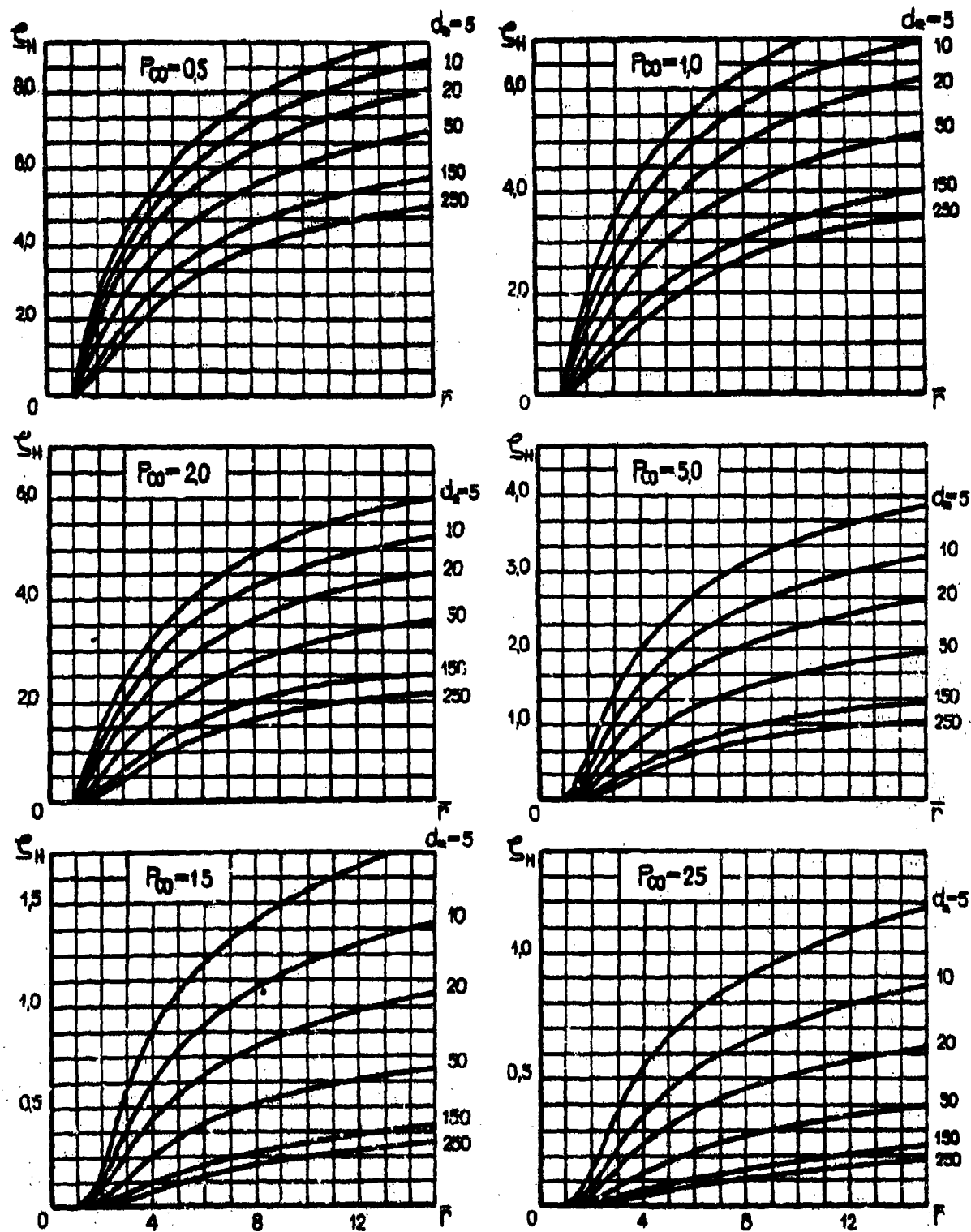


Fig. 5.16.



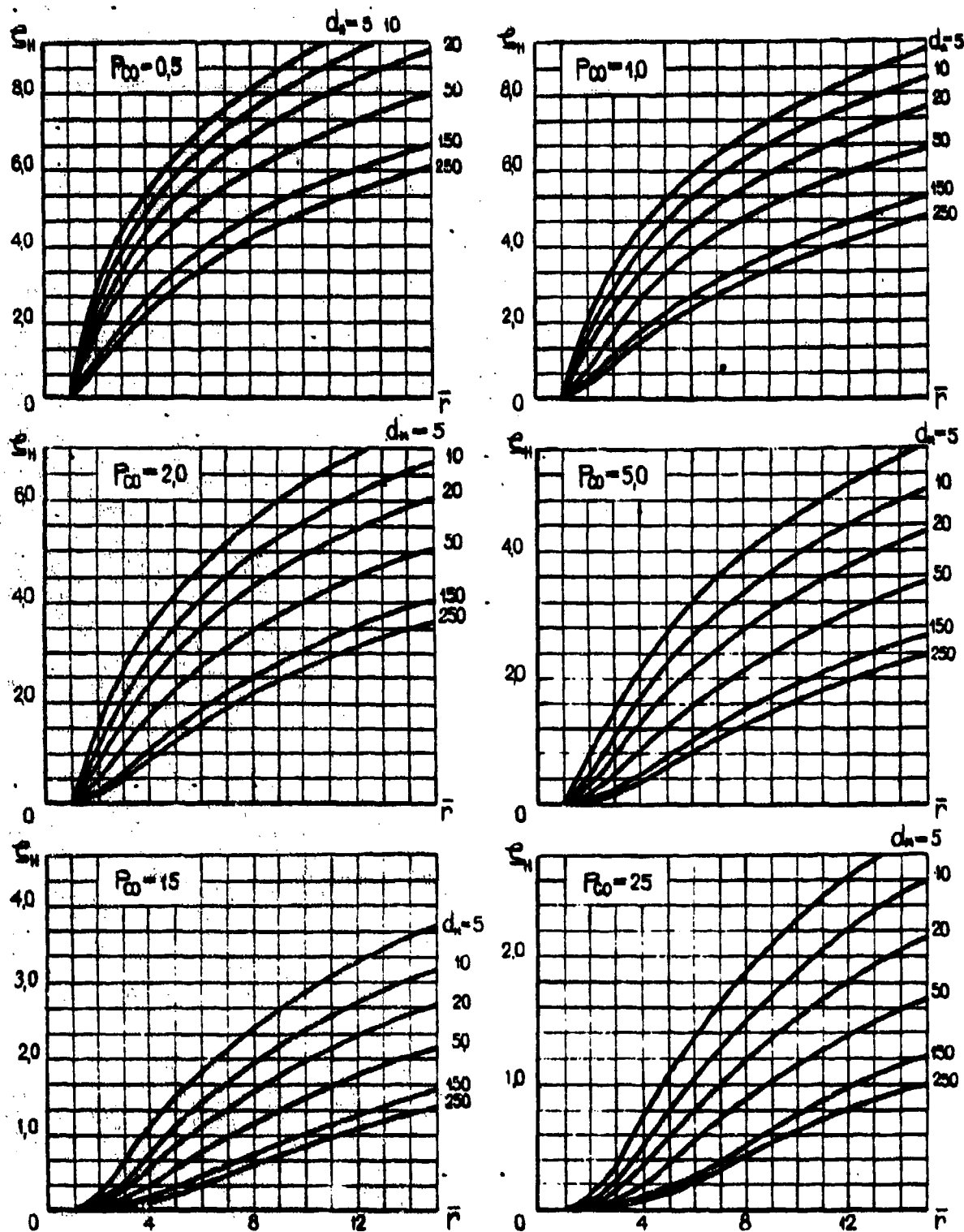
$$\alpha_{0K}=0.6$$

Fig. 5.17.



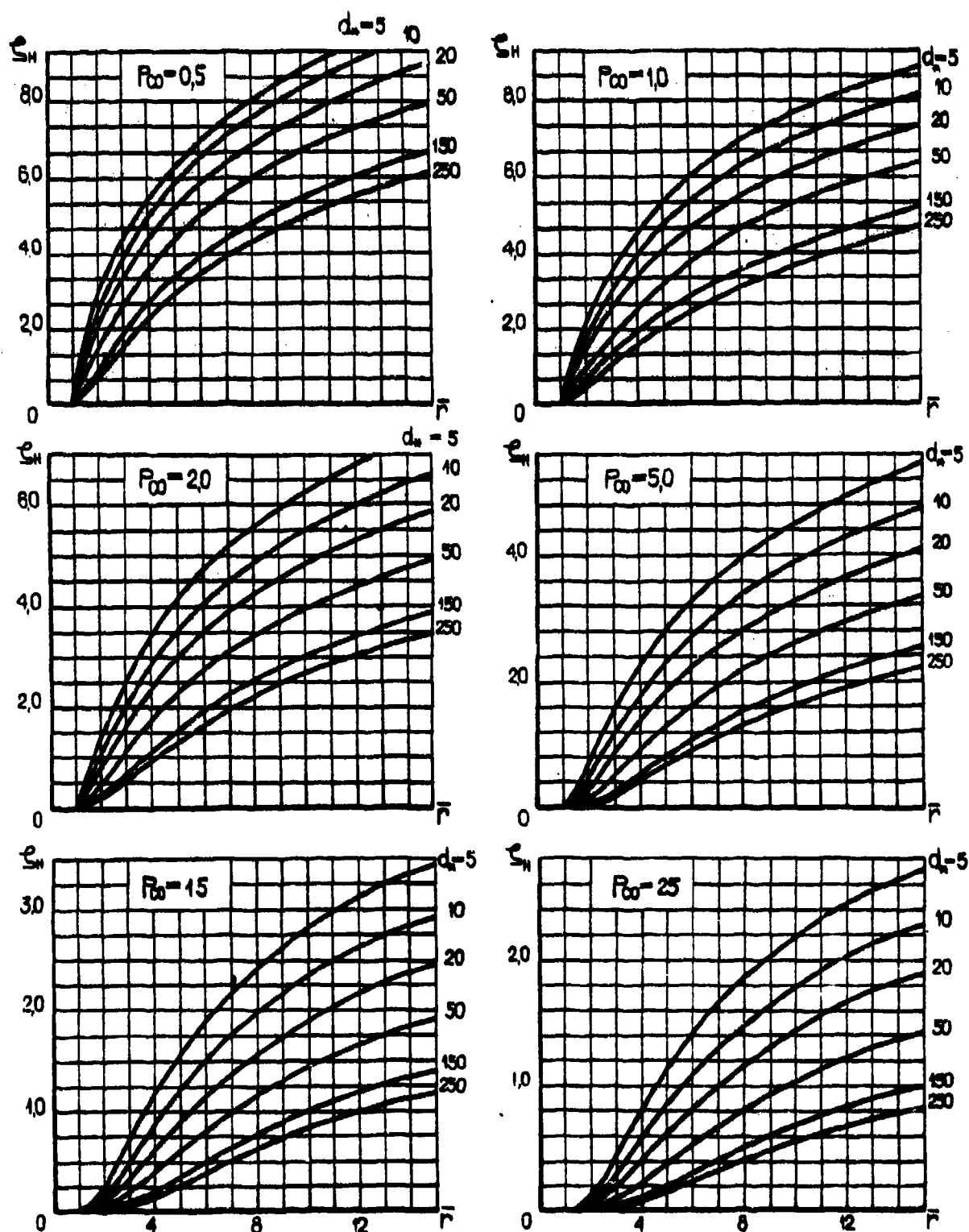
$$\alpha_{0N} = 0.8$$

Fig. 5.18.



$$\alpha_{0K} = 1.0$$

Fig. 5.19.



$\alpha_{0K} = 1, 2$

Fig. 5.20.

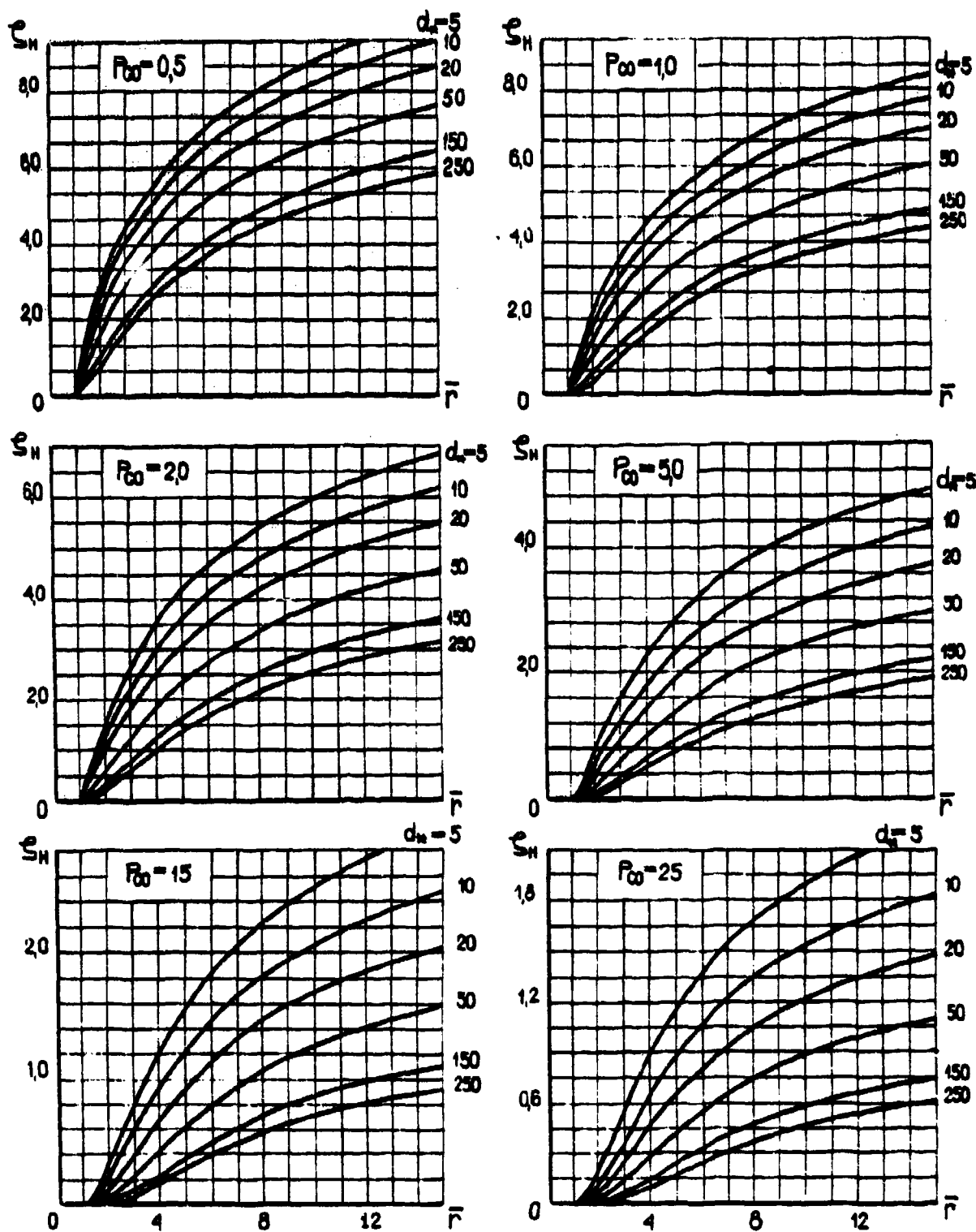


Fig. 5.21. $\alpha_{0K} = 1.4$

FUEL - OXYGEN + ASYMMETRICAL
DIMETHYLHYDRAZINE ($O_2 + (CH_3)_2NNH_2$)

	$\epsilon_{ox} = 0,3 - 5,0$	
	$p_{\infty} = 0,1 - 50 \frac{MN}{m^2}$	
	OXIDIZER	FUEL
CHEMICAL FORMULA	O ₂	97,1% (CH ₃) ₂ NNH ₂ + 1,1% (CH ₃) ₂ NH + 1,8% (CH ₃) ₂ NNCH ₃
ENTHALPY $\downarrow \frac{kJ}{kg}$	-398,3	836,5
DENSITY $\rho \frac{g}{cm^3}$	1,135	0,786
ADMIXTURE	LIQUID NITROGEN N ₂	WATER H ₂ O
Range of change in admixture content, by weight	0,008	0,005
Coefficients of extrapolation formulas	A ₂ B ₂ C ₂ D ₂ L ₂	A ₂ B ₂ C ₂ D ₂ L ₂

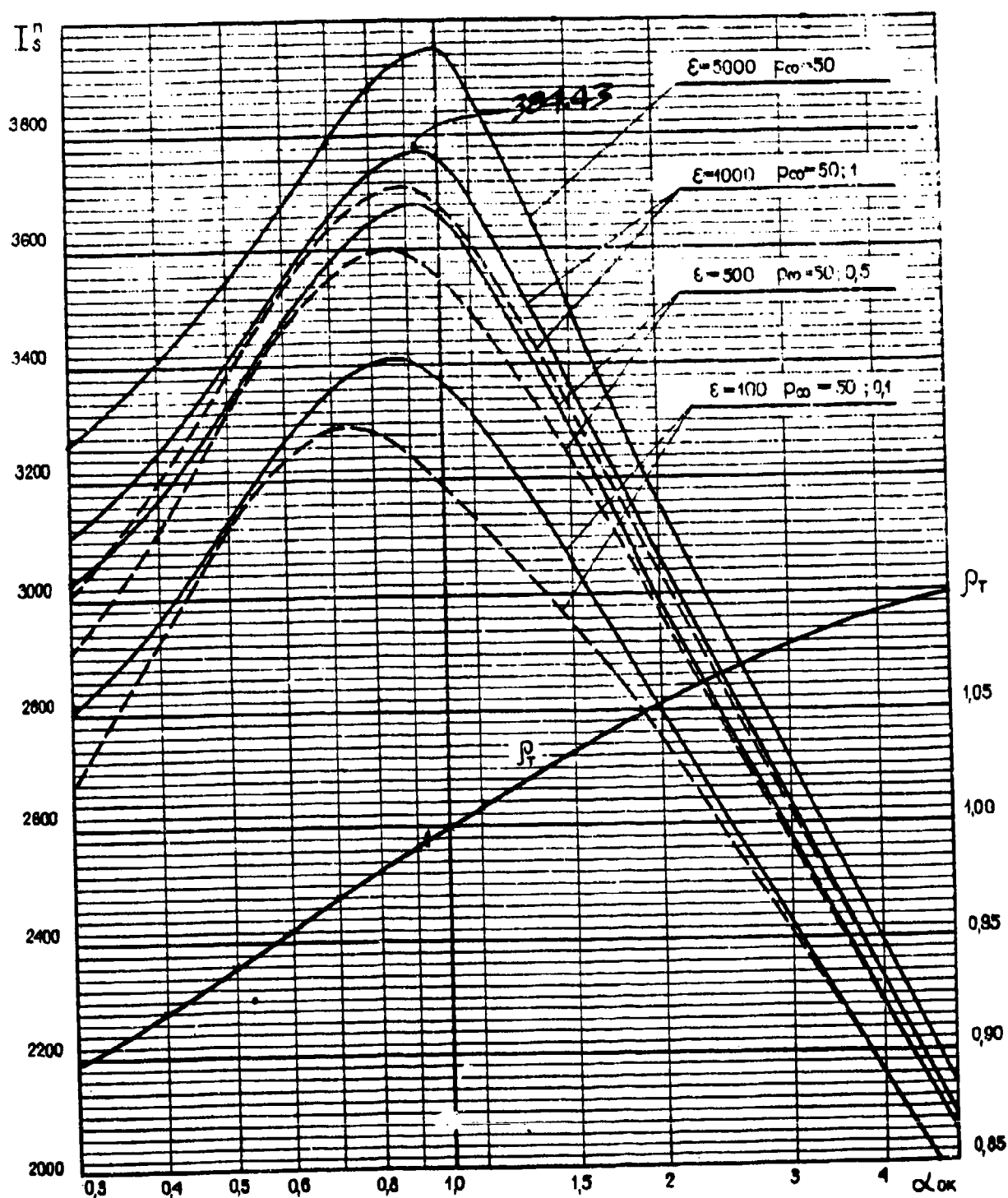


Fig. 5.22.

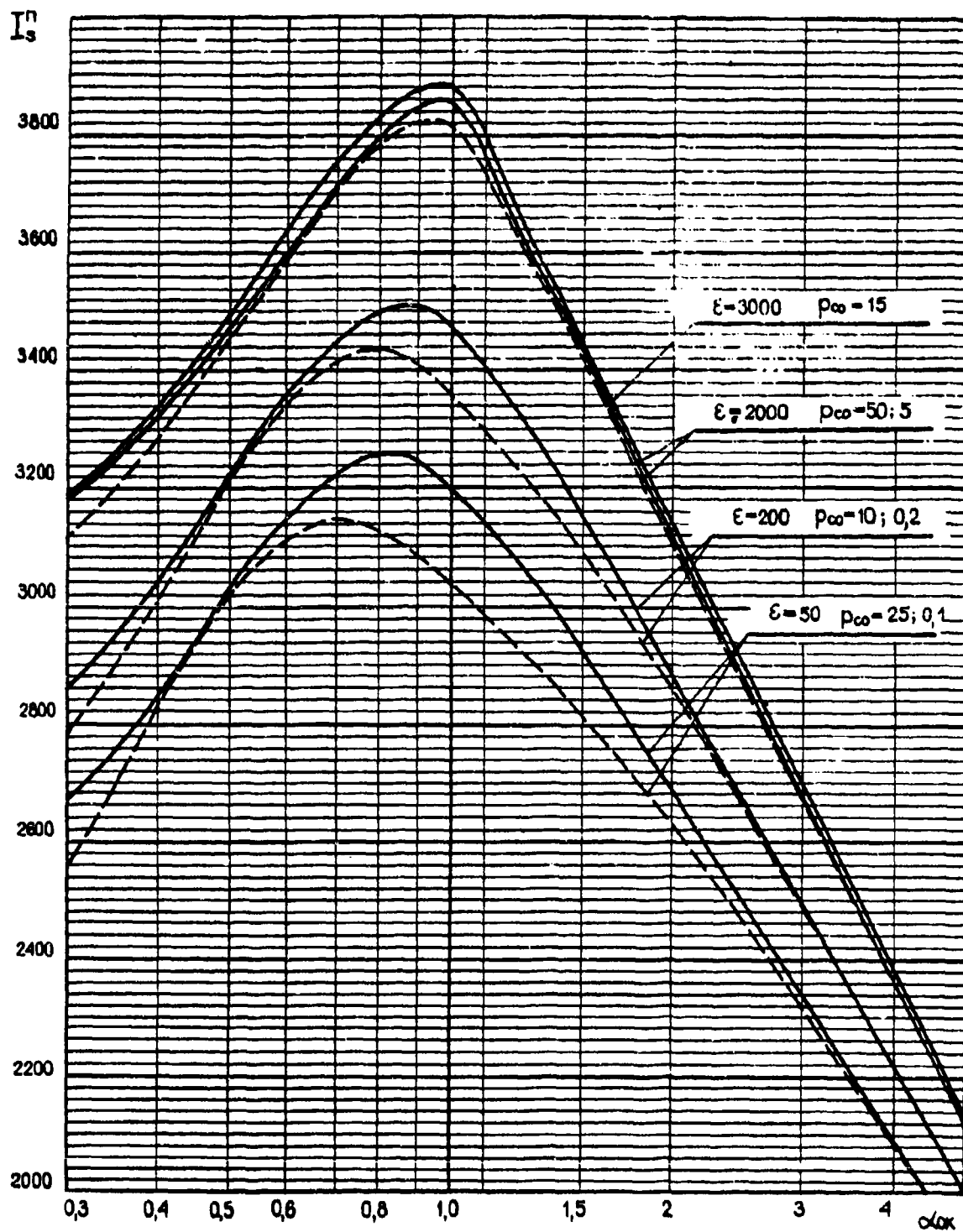


Fig. 5.23.

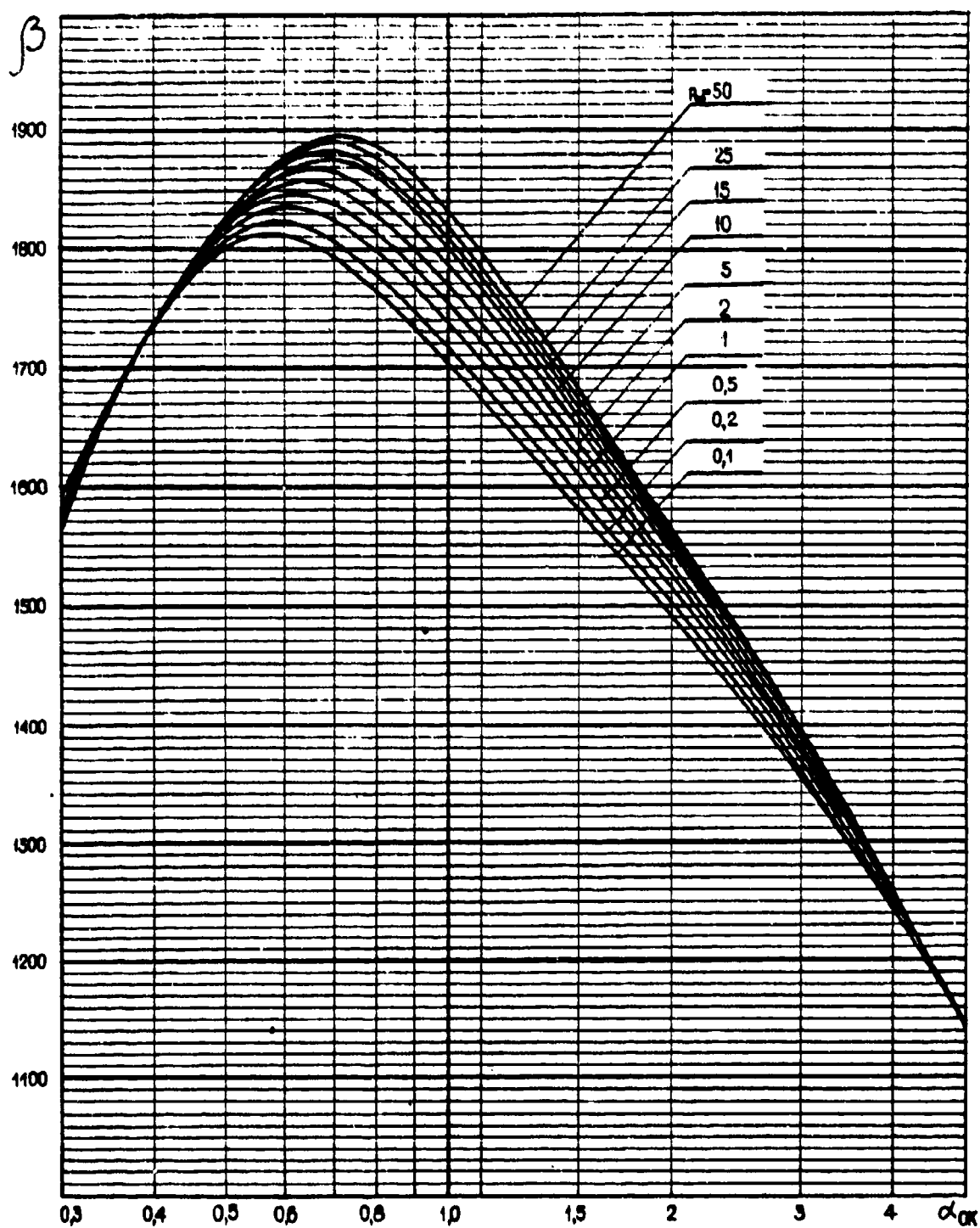


Fig. 5.24.

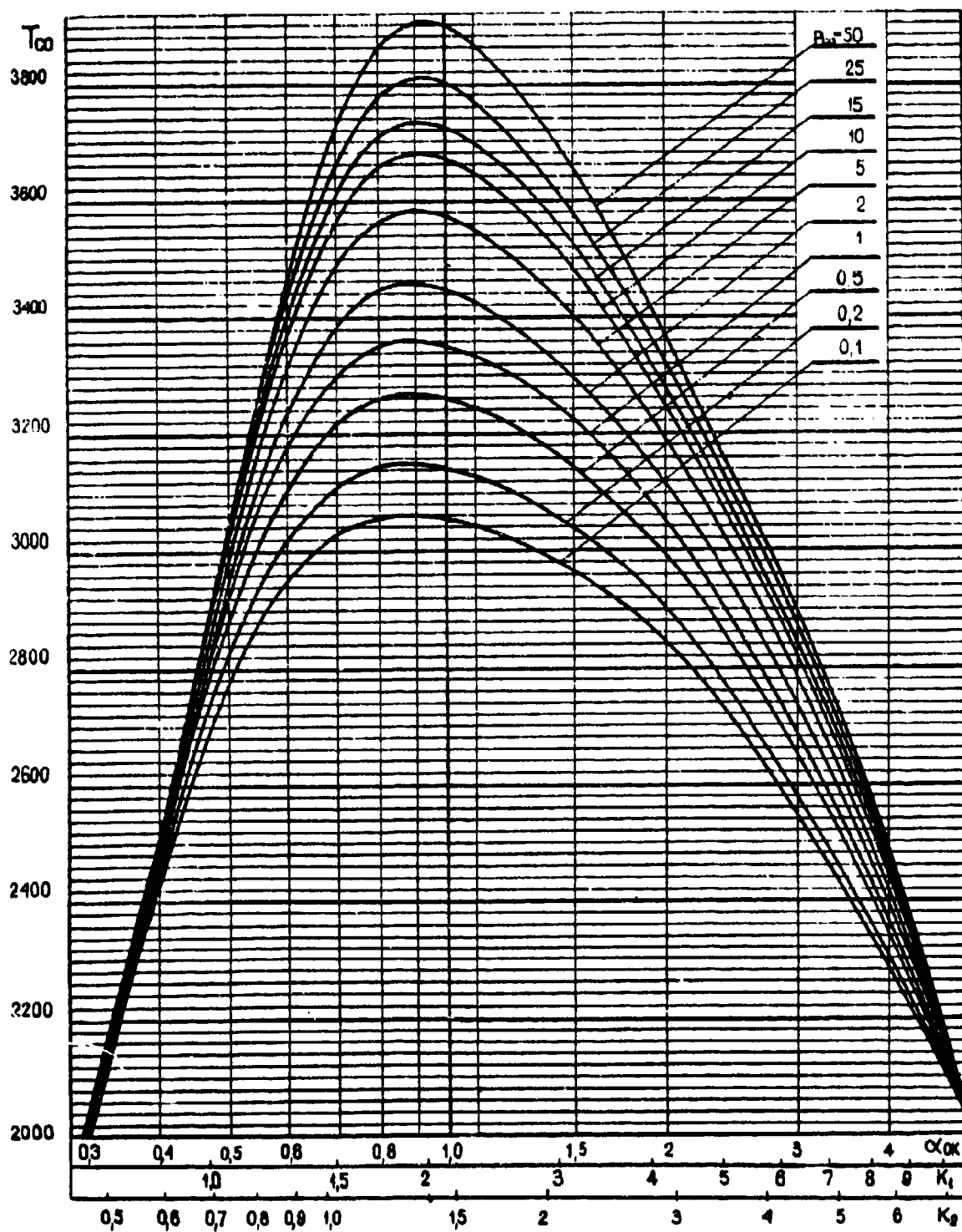


Fig. 5.25.

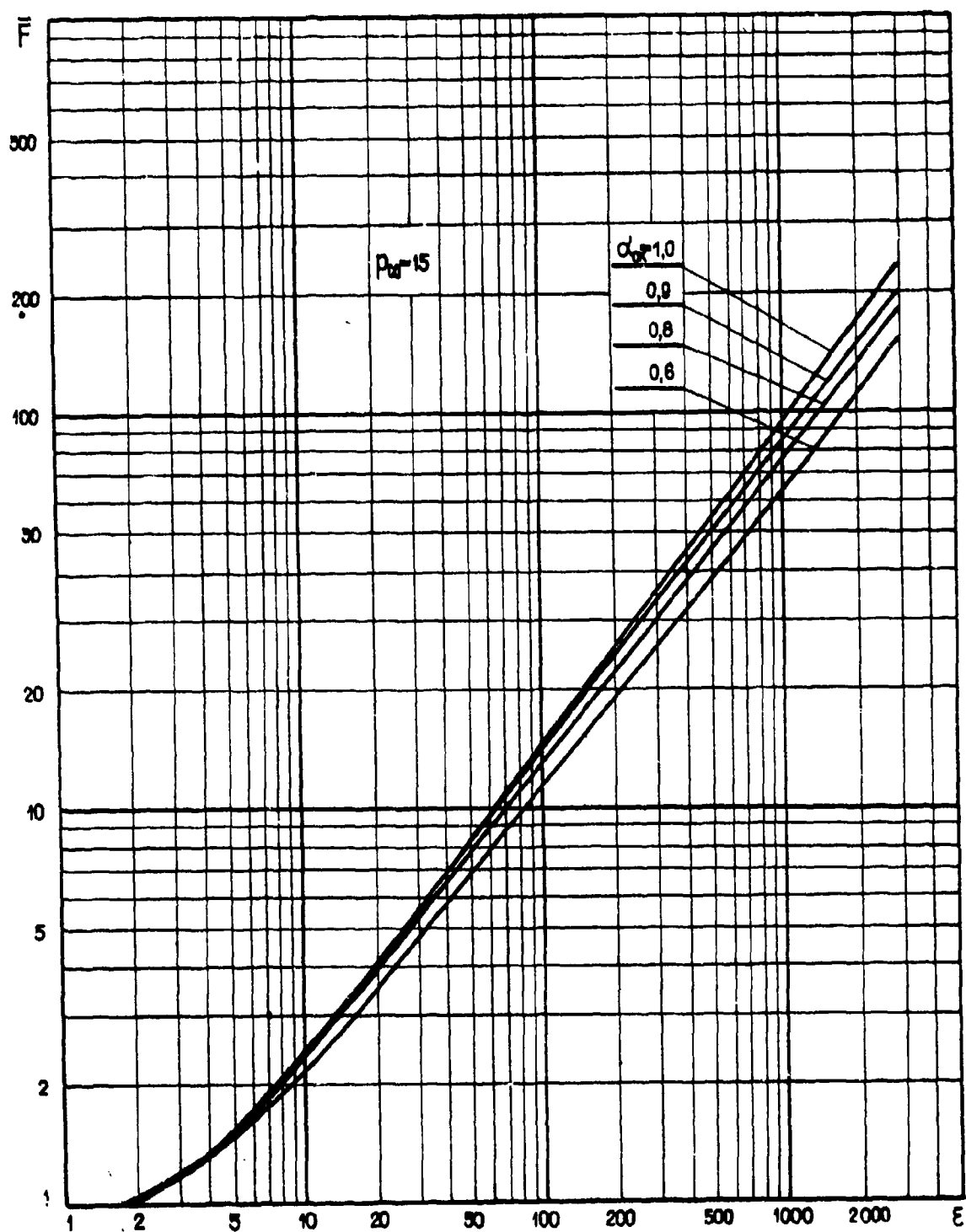


Fig. 5.26.

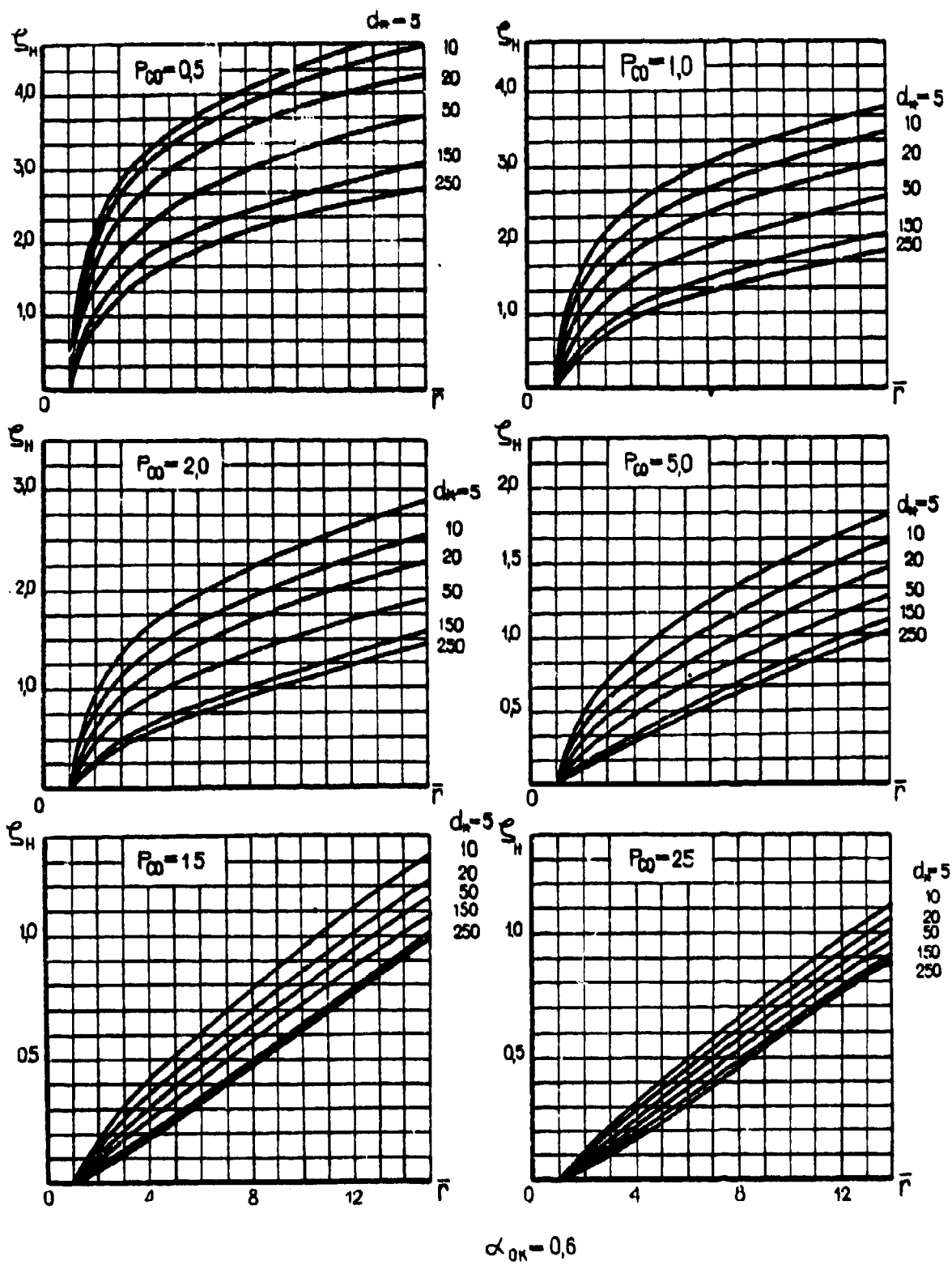
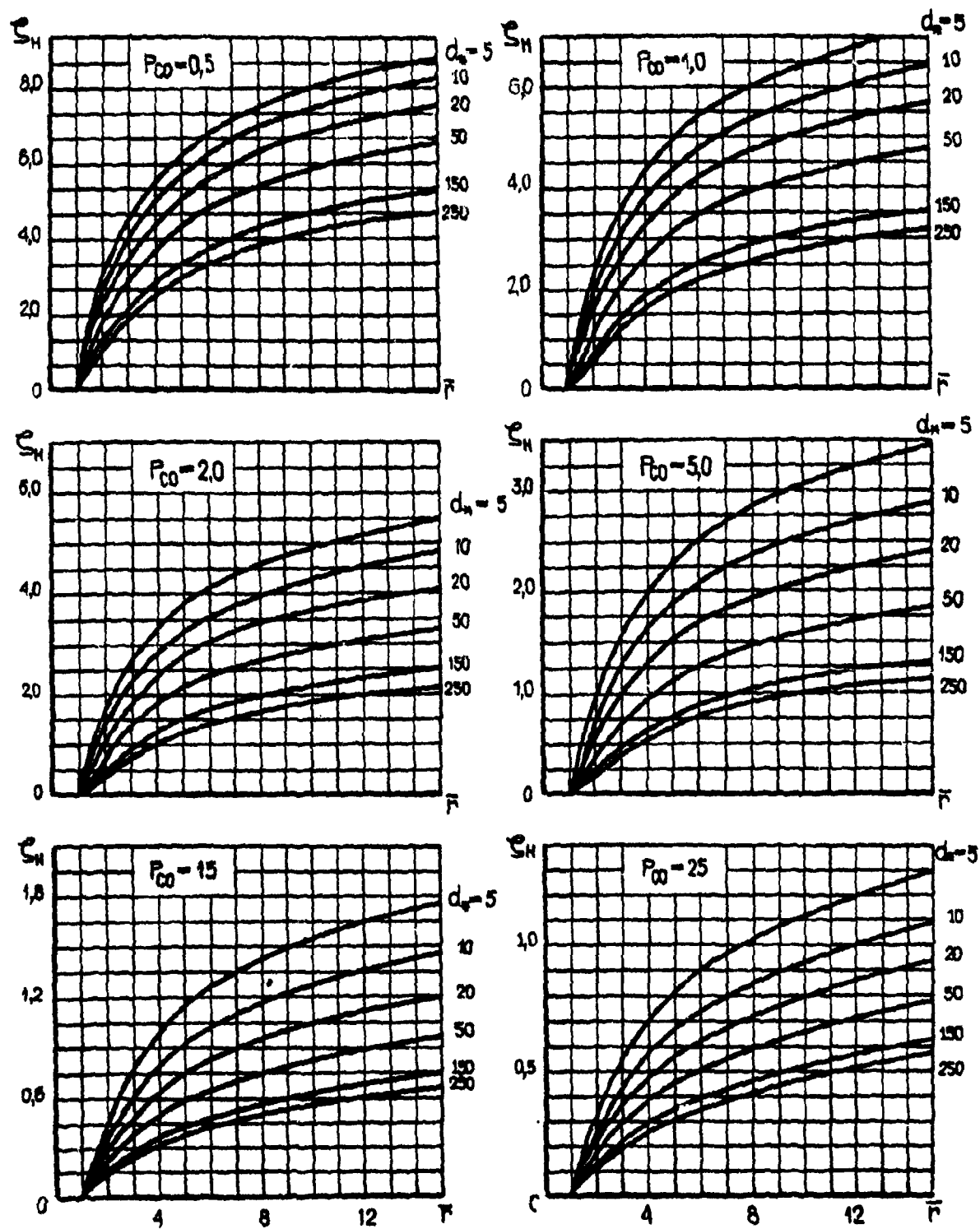
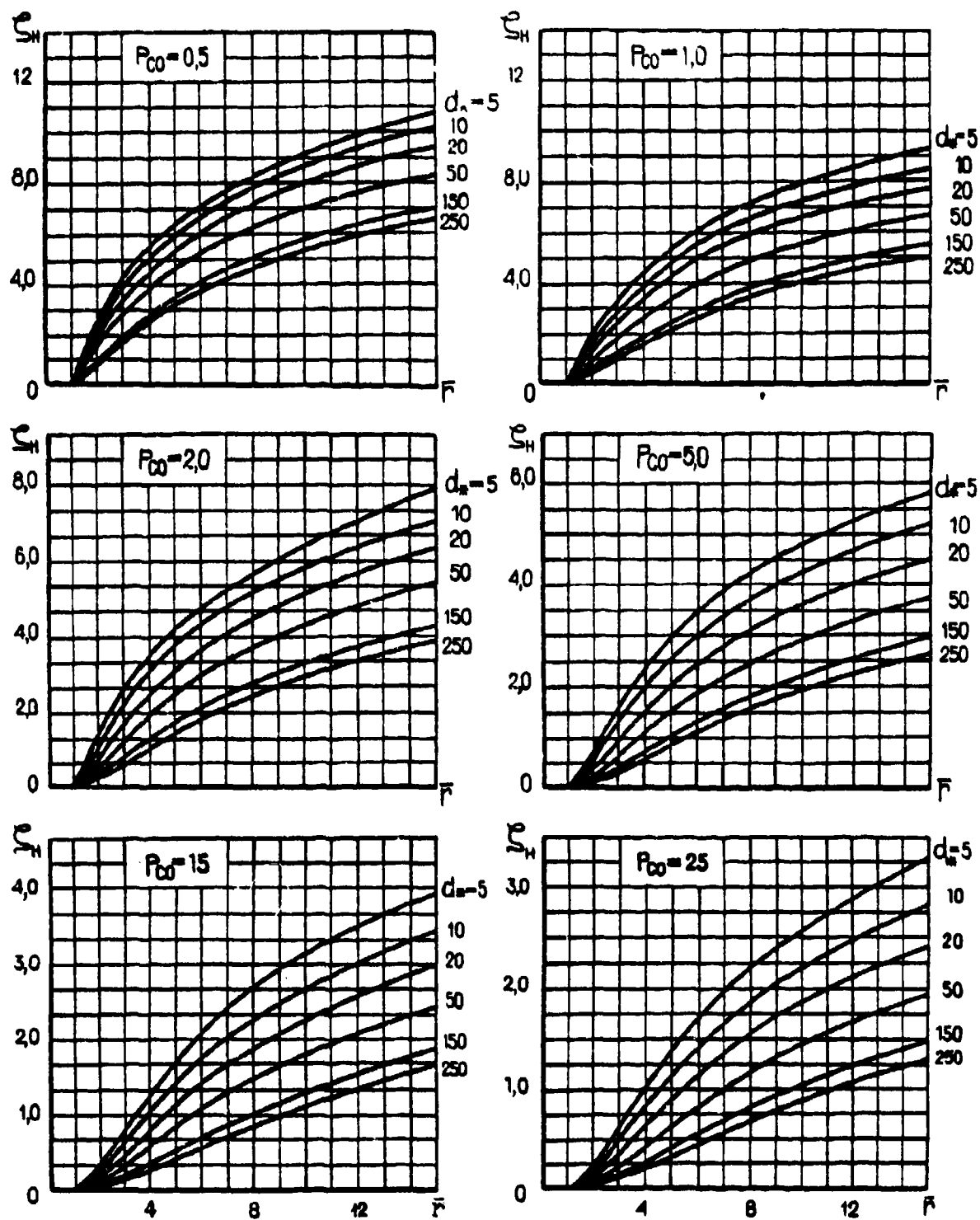


Fig. 5.27.



$\alpha_{0n} = 0.8$

Fig. 5.28.



$$\alpha_{OK} = 1.0$$

Fig. 5.29.

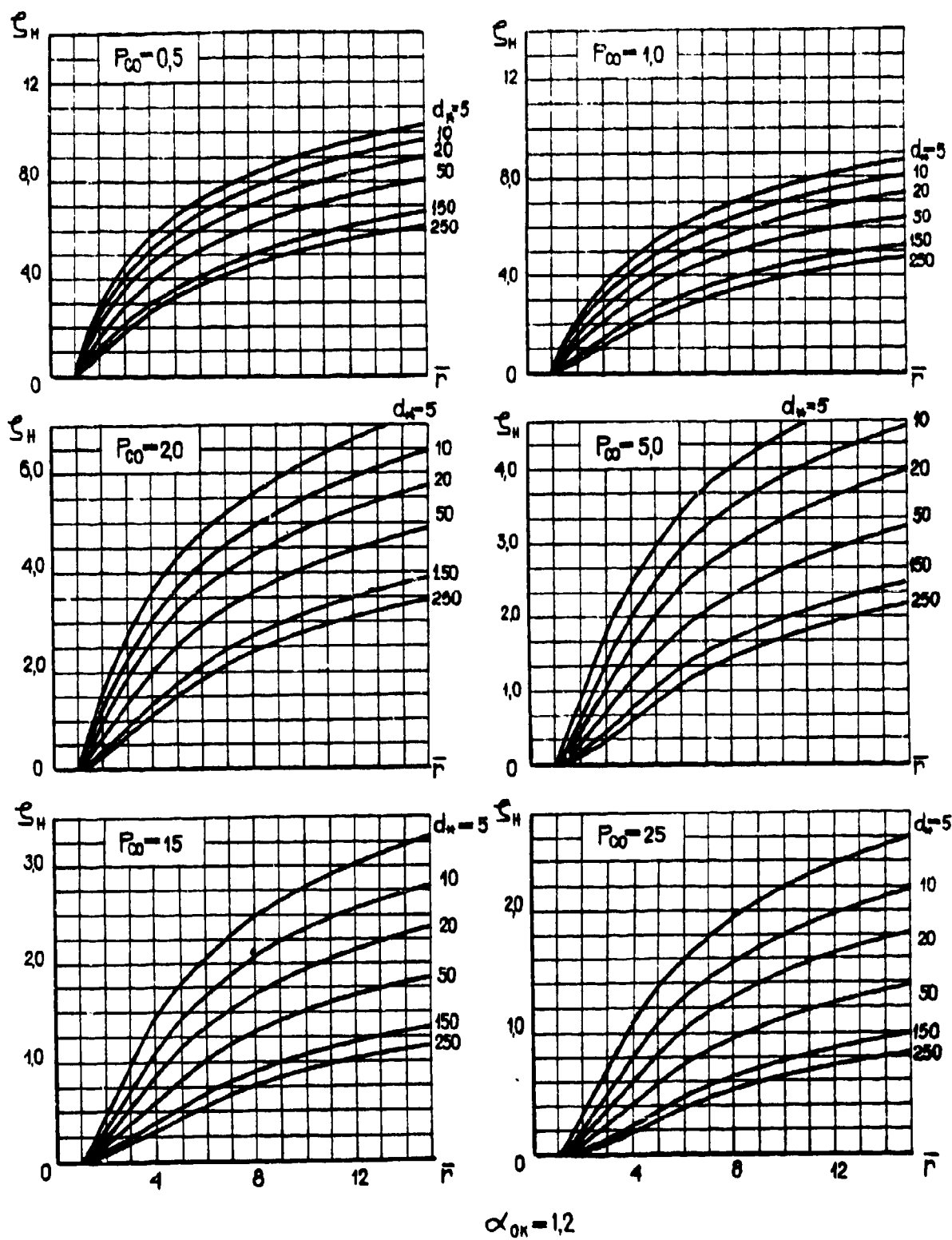
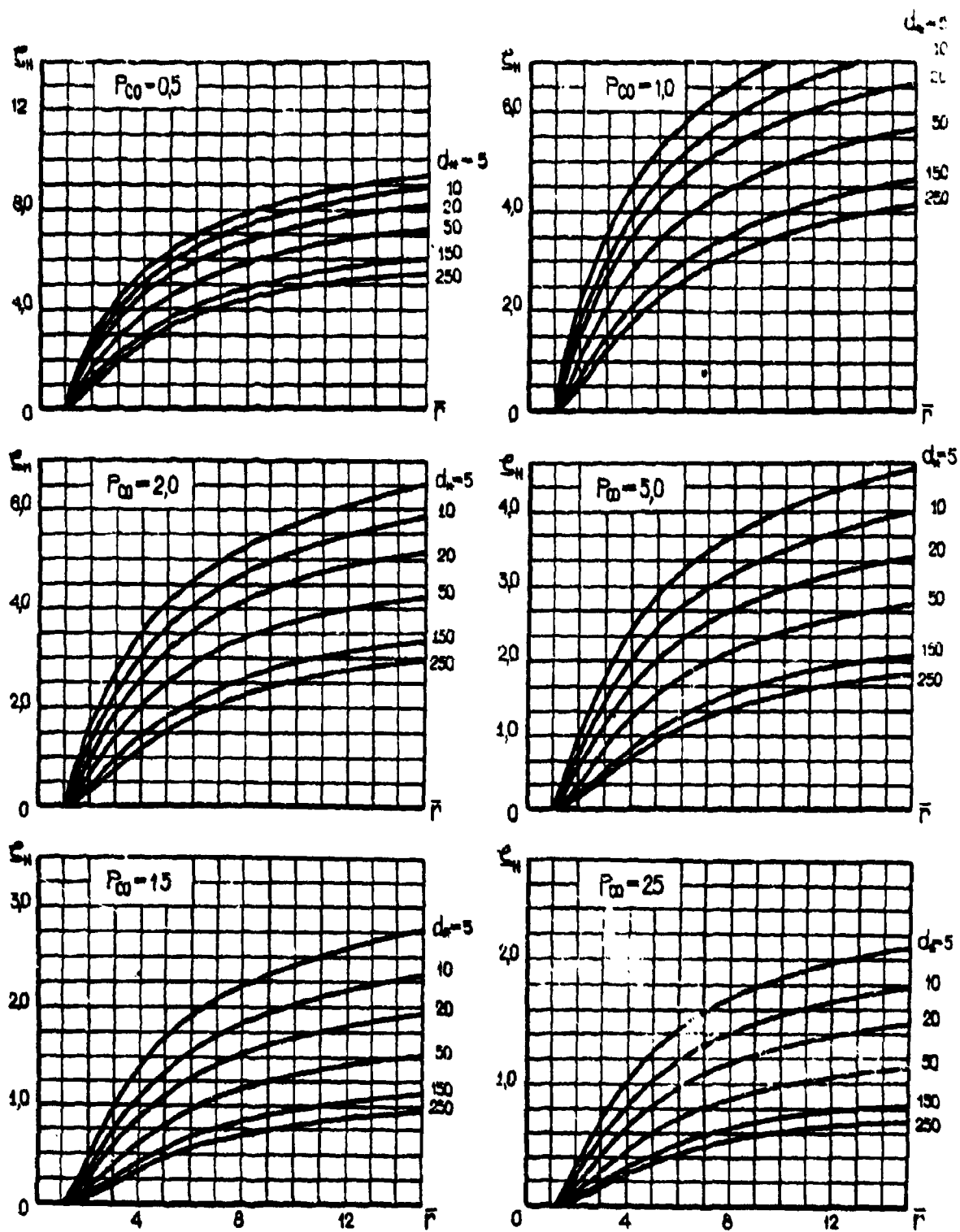


Fig. 5.30.



$$\alpha_{0N} = 1.4$$

Fig. 5.31.

FUEL - OXYGEN + AMMONIA ($O_2 + NH_3$)

	$a_{ox} = 0,6-2,0$	
	$p_{\infty} = 0,2-50 \frac{MN}{m^2}$	
CHEMICAL FORMULA	OXIDIZER	FUEL
	O_2	NH_3
ENTHALPY $\frac{kJ}{kg}$	-398,3	-4184,8
DENSITY $\frac{g}{cm^3}$	1,135	0,6819
	$T = -90,188^\circ K$	$T = -239,73^\circ K$
ADMIXTURES	LIQUID NITROGEN N_2	WATER H_2O
Range of change in admixture content, by weight	0,008	0,004
Coefficients of extrapolation formulas	$A, B, C, D,$	$A, B, C, D,$

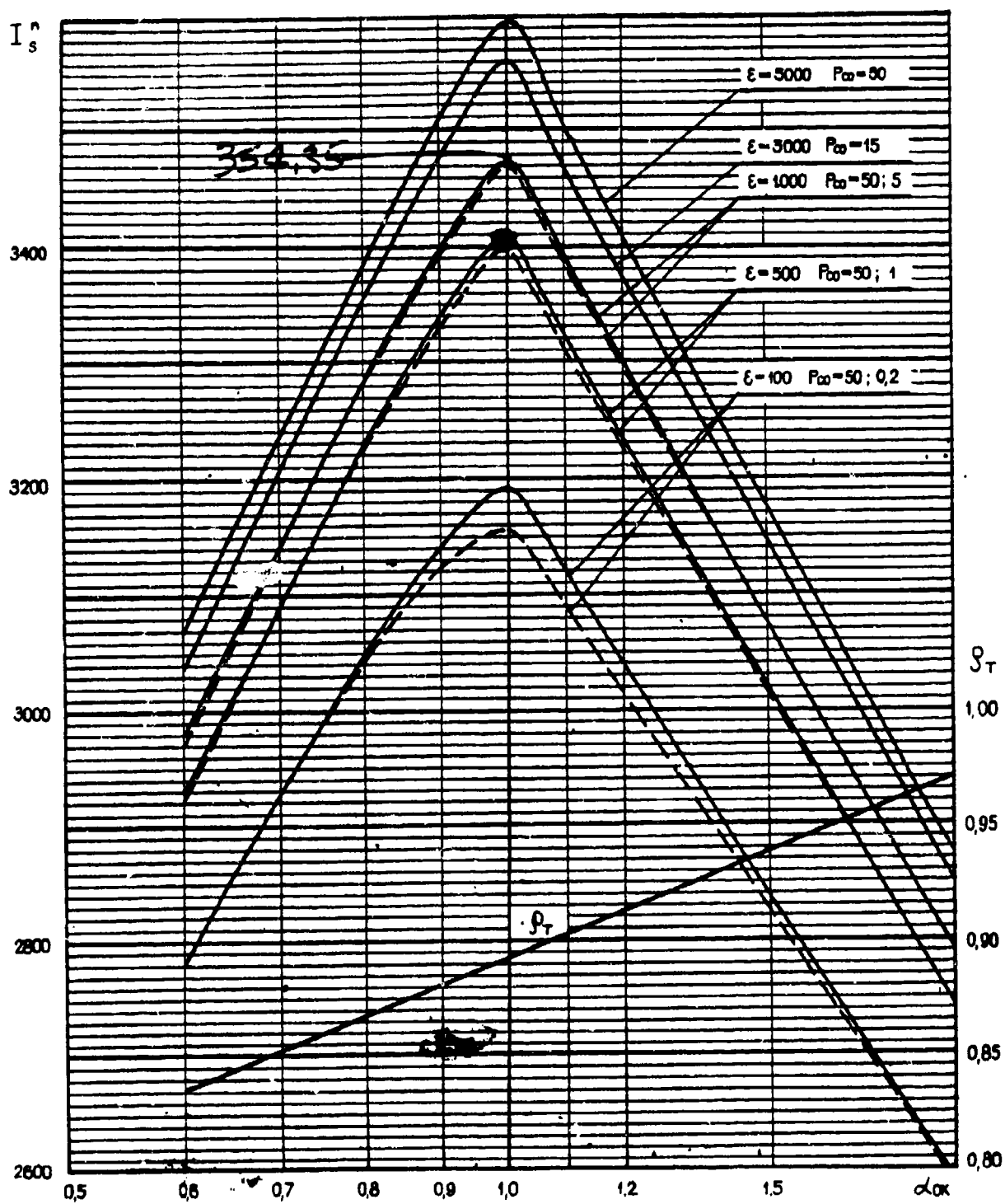


Fig. 5.32.

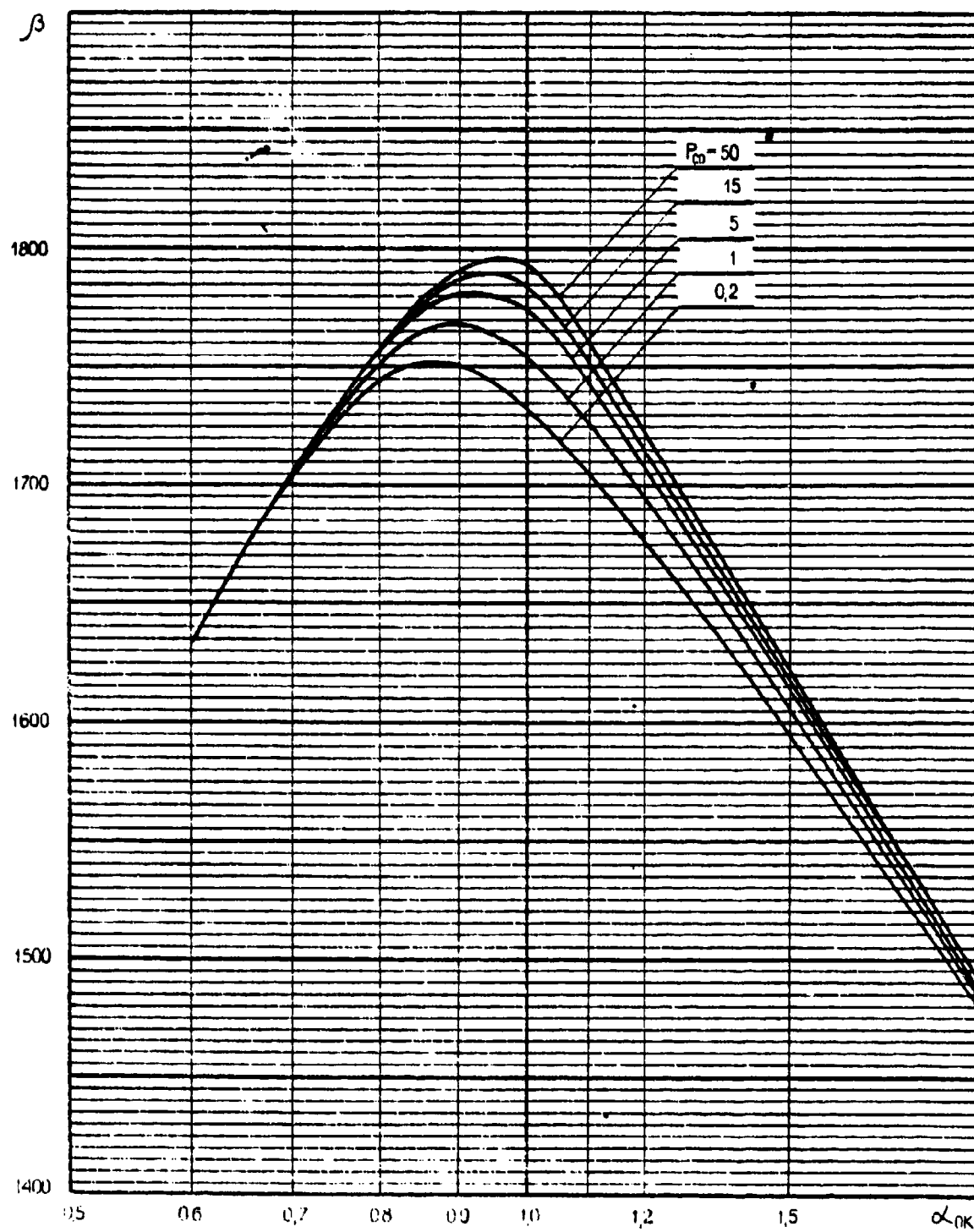


Fig. 5.33.

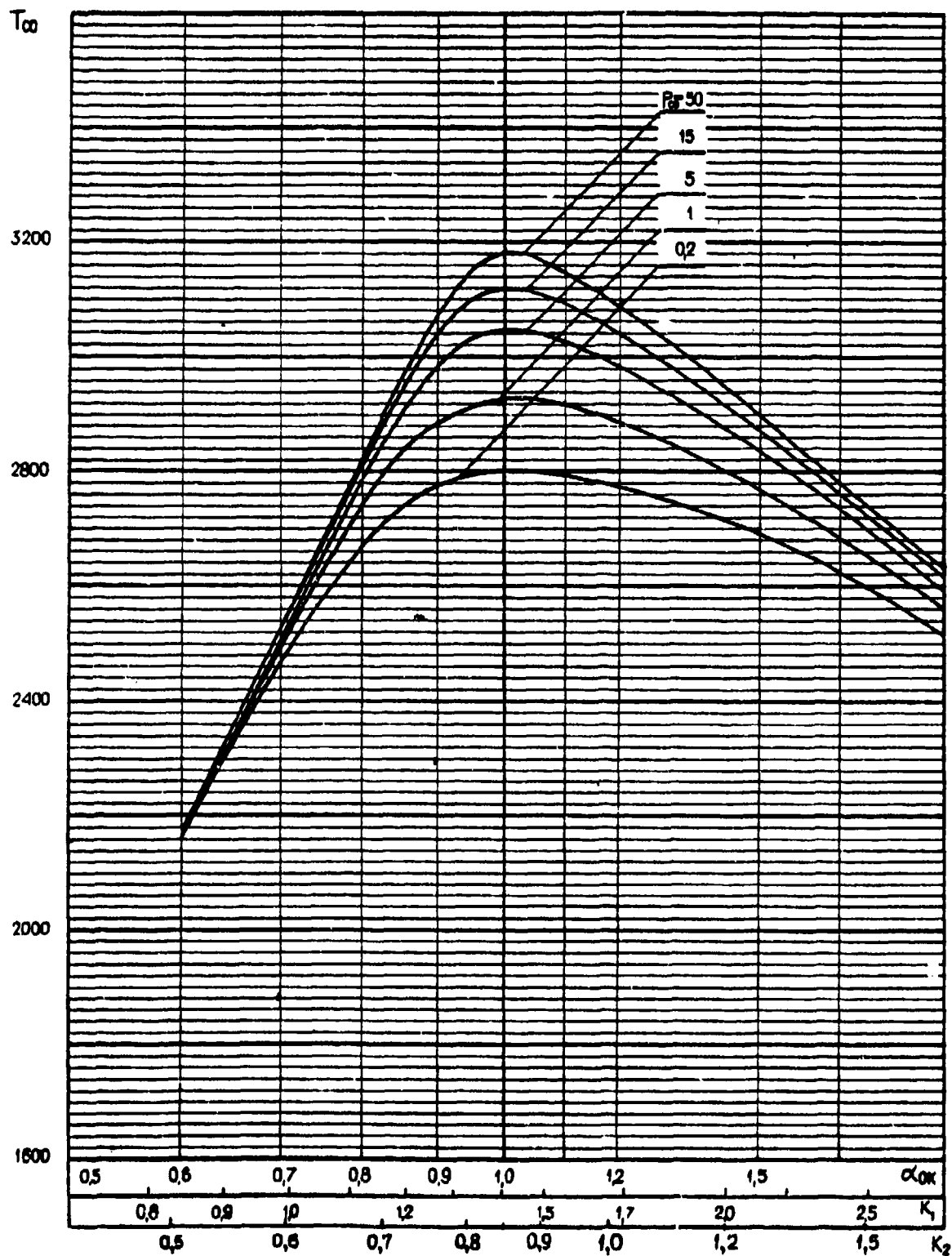


Fig. 5.34.

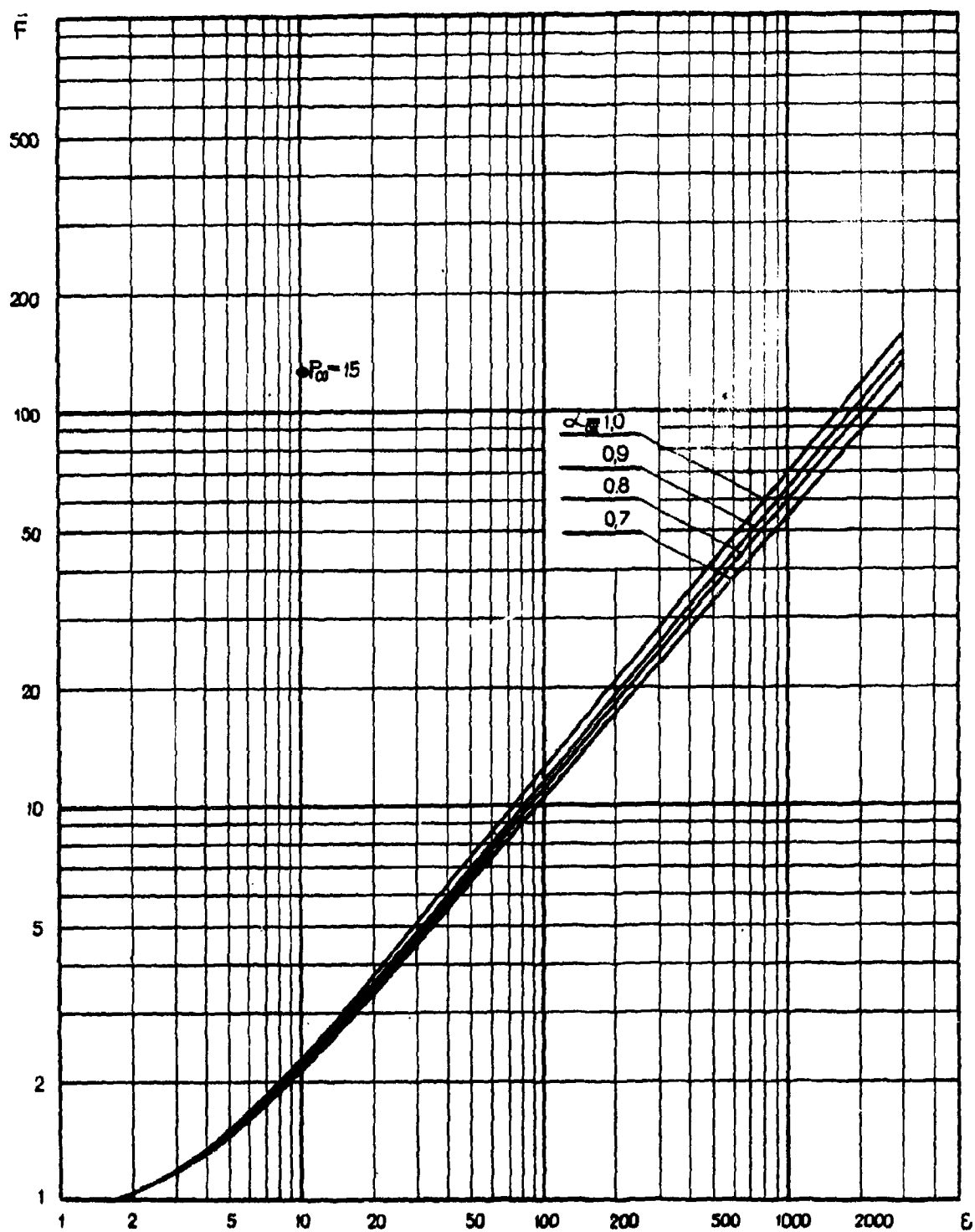


Fig. 5.35.

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