AD-756 597

THERMODYNAMIC AND TRANSPORT PROPERTIES OF CHEMICALLY REACTING GASEOUS SYSTEMS. PART II

A. Krasin

Foreign Technology Division
Wright-Patterson Air Force Base, Ohio

17 November 1972

FTD-HC-23-0768-72

FOREIGN TECHNOLOGY DIVISION

AIR FORCE SYSTEMS COMMAND

THERMODYNAMIC AND TRANSPORT PROPERTIES OF CHEMICALLY REACTING GASEOUS SYSTEMS
PART II

by

A. Krasin

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FTD-HC-23-768-72

EDITED TRANSLATION

FTD-HC-23-0768-72

THERMODYNAMIC AND TRANSPORT PROPERTIES OF CHEMICALLY REACTING GASEOUS SYSTEMS
PART II

By: A. Krasin

English pages: 218

Source: Termodinamicheskiye I Perenosnye
Svoystva Khimicheski Reagiruyushchikh
Gazovykh Sistem, 1971, pp. 1-237.

Translated Under: F33657-72-D-0854

Requester: FTD/PDTN

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FTD-HC-23-768-72 **Date** 17 Nov. **19** 72

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DOCUMENT CONTROL DATA - R & D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY (Corporate author) Foreign Technology Division Air Force Systems Command U. S. Air Force	2a. REPORT SECURITY CLASSIFICATION UNCLASSIFIED 2b. GROUP

3. REPORT TITLE

THERMODYNAMIC AND TRANSPORT PROPERTIES OF CHEMICALLY REACTING GASEOUS SYSTEMS. PART II

4. DESCRIPTIVE NOTES (Type of report and inclusive dates)
Translation

5. AUTHOR(S) (First name, middle initial, last name)

Krasin, A.

6. REPORT DATE 1971	7a. TOTAL NO. OF PAGES ~~218~~ 231	7b. NO. OF REFS 227
8a. CONTRACT OR GRANT NO. b. PROJECT NO. c. d. T69-04-9	9a. ORIGINATOR'S REPORT NUMBER(S) FTD-HC-23-768-72 9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report)	

10. DISTRIBUTION STATEMENT
Approved for public release; distribution unlimited.

11. SUPPLEMENTARY NOTES	12. SPONSORING MILITARY ACTIVITY Foreign Technology Division Wright-Patterson AFB, Ohio

13. ABSTRACT

The theory and method of calculating thermodynamic and transport properties of a real chemically reacting system $N_2O_4 \rightleftarrows 2NO_2 \rightleftarrows 2NO+O_2$ are explained in this book. The problem of the mechanism of thermal dissociation and radiation-thermal stability of dissociating nitrogen tetroxide is considered. The results of theoretical and experimental investigations on the corrosion resistance of materials in a medium of N_2O_4 are presented. A survey of Soviet and foreign literature on the study of the thermophysical characteristics of the system mentioned is given. Analytical dependences, tabular and graphic materials on heat content, enthalpy, density, viscosity, thermal conductivity, and other properties are presented. The book is intended for scientists, engineers, and technicians, and also for students of higher educational institutions specializing in thermophysics and heat technology.

UNCLASSIFIED
Security Classification

14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Thermodynamic Property						
Radiation Stability						
Nitrogen Tetroride						

UNCLASSIFIED
Security Classification

UDC 621.039.534

Collective of authors. Thermodynamic and Transport Properties of Chemically Reacting Gaseous Systems, Part II, Minsk, "Nauka i Tekhnika", 1971, 240 pages.

The theory and method of calculating thermodynamic and transport properties of a real chemically reacting system $N_2O_4 \rightleftarrows 2NO_2 \rightleftarrows 2NO+O_2$ are explained in this book. The problem of the mechanism of thermal dissociation and radiation-thermal stability of dissociating nitrogen tetroxide is considered. The results of theoretical and experimental investigations on the corrosion resistance of materials in a medium of N_2O_4 are presented. A survey of Soviet and foreign literature on the study of the thermophysical characteristics of the system mentioned is given.

Analytical dependences, tabular and graphic materials on heat content, enthalpy, density, viscosity, thermal conductivity, and other properties are presented.

Thirty tables, 48 drawings, 276 bibliographic entries.

The book is intended for scientists, engineers, and technicians, and also for students of higher educational institutions specializing in thermophysics and heat technology.

PREFACE

In 1967 the first part of the book Thermodynamic and Transport Properties of Chemically Reacting Gaseous Systems was issued at the "Nauka i Tekhnika" Publishing House (Minsk), in which the results of the study of the thermophysical properties of dissociating systems of N_2O_4, Al_2Cl_6 and Al_2Br_6 in an ideal gaseous state were explained. In 1965-1970 at the Institute of Nuclear Power Engineering (IYaE) of the AN BSSR (Belorussian SSR Academy of Sciences), the Institute of High Temperatures of the AN SSR (USSR Academy of Sciences), the State Institute of Applied Chemistry, the Odessa Institute for Engineers of the Maritime Fleet, the Siberian Power Engineering Institute, and others, a complex theoretical and experimental study of the properties of dissociating systems of $N_2O_4 \rightleftarrows 2NO_2$, 149 kilocalories per kg, and $2NO_2 \rightleftarrows 2NO + O_2$, 249 kcal per kg, was performed. In these years in the IYaE AN BSSR single-circuit schemes of AES (atomic electric-power stations) with a gas-liquid cycle operating on N_2O_4 were proposed, the possibilities of the development of gas-cooled fast reactors with intensities of 400-600 kW/kg at maximum gas parameters of 130-170 atmospheres absolute, 480-540° C, and temperatures of the jackets of the TVEL (fuel elements) of 700-750° C. In recent years, proposals for the development of the experiment BRG-30 AES with a gas-cooled fast reactor operating on N_2O_4 were developed and accepted. These circumstances caused the necessity of an experimental study of the thermophysical properties of N_2O_4 in the liquid phase, and the development of methods for calculation and experimental checking of the characteristics of a dissociating gas with consideration of its imperfect nature. Many years of research at the GIPKh (State Institute of Applied Chemistry) made it possible to ascertain an extensive class of construction materials which demonstrated a high corrosion resistance and are to be subjected to further dynamic tests in a medium of N_2O_4 at gas parameters of up to 200 atm. abs. and 700-750° C.

This book is devoted to a more detailed and deeper study of the thermophysical and corrosion characteristics of dissociating nitrogen tetroxide on the basis of the latest experimental investigations. Engineering methods of calculating the most important properties of chemically reacting systems in a dense gaseous state have been developed and are presented.

Tables of thermophysical properties, results of an investigation on radiation-thermal resistance, and recommendations with respect to corrosion-resistant materials in a medium of dissociating nitrogen tetroxide are presented.

The calculated thermophysical characteristics of N_2O_4 presented and their experimental validation make it possible to perform a thermodynamic analysis of cycles, thermal and gasodynamic calculations for a nuclear reactor, turbomachines, heat-exchange apparatus of power plants, and to determine the technical and economic indices of an AES operating on a dissociating coolant.

The study of the mechanism of radiation-thermal and thermal dissociation and recombination of N_2O_4 made it possible to refine the constants of the rates of the reactions, and to develop methods for calculating the parameters of the cycle and the characteristics of the units with a consideration of the kinetics of the chemical reactions.

At the present time, a primary check of the methods developed has been performed and the importance of the consideration of the kinetics of the chemical reactions in N_2O_4 in the development of highly economical AES has been demonstrated. Probably these results will constitute the basis of a third book on thermodynamic and transport properties of dissociating gases.

The book was prepared by a collective of authors of the Institute of Nuclear Power Engineering of the AN BSSR and the State Institute of Applied Chemistry. The Preface and Introduction were written by A. K. Krasin and V. B. Nesterenko; Chapter I by V. B. Nesterenko, M. V. Mal'ko, and G. V. Nichipor; Chapter II by M. A. Bazhin and V. B. Nesterenko; Chapter III by B. G. Maksimov, Yu. G. Kotelevskiy and G. Z. Serebryanyy; Chapter IV by I. K. Dmitriyeva, L. V. Mishina, and I. I. Paleyev; Chapter V by B. G. Maksimov; and Chapter VI by A. M. Sukhotin and N. Ya. Lantratova.

The authors consider it a pleasant duty to express their gratitude to mathematical programmers V. N. Pisarchik and V. D. Sviridova for calculations performed on the Minsk-22 ETsVM (electronic digital computer).

CONVENTIONAL SYMBOLS

P, V, and T are pressure, volume, and temperature, ρ and Z are density and compressibility factors; R is the universal gas constant; M and m are molecular weight and molecular mass; U, H, and S are internal energy, enthalpy, and entropy; C_p is heat content at constant pressure; C_v is heat content at constant volume; K_c, K_p, and K_γ are constants of equilibrium via concentration, partial pressure, and volatility of the components, respectively; f, a, and γ are volatility, activity, and activity factor; α and ξ are degree of dissociation and degree of development of the reaction; x and n are the molar fraction and the number of moles; ν_i represents stoichiometric coefficients; I_k is the rate of the k-th chemical reaction; q is the specific heat flux; $\vec{j}$ and $\vec{g}$ are the flux of moles; r is the latent heat of evaporation; r/k and σ are the parameters of intermolecular reactions; μ is the coefficient of dynamic viscosity; λ is the coefficient of thermal conductivity; D_{ij} is the coefficient of binary diffusion; ω is the acentric Pitzer factor; and χ is the Riedel factor.

The subscripts i, j represent the i-th and the j-th components of the mixture; k is the value of the quantity for a pure gas; i is the value for this gas in the mixture; e is the equilibrium value of the quantity; c is the value of the quantity for a pure gas having a volume and temperature of the mixture and the same number of moles as the gas has in a mixture* represents reduced quantities taken at very low pressures; m means molar [м = m]; s represents saturation; pl represents melting [пл = pl]; kip represents boiling [кип = kip]; isp represents evaporation [исп = isp]; cr indicates a critical state [кр = cr]; tr.t represents the triple point [тр.т = tr.t]; eff represents the effective properties; f is the "frozen" component; r, the "reaction" component; o represents standard conditions; T = 298.15° K and P = 1 atmosphere; O, T represent an ideal gaseous state.

INTRODUCTION

The development of steady-state and transport power engineering, including nuclear engineering, is essentially based on the application of water vapor (steam) as a working fluid. Technical and economic investigations of recent years have demonstrated that in thermodynamic cycles operating on steam economically optimum parameters and limiting values of efficiency have been achieved. Thermodynamic characteristics of cycles and the physical-chemical properties of steam are such that considerable limitations exist with respect to the unit capacity of single-shaft turbo units [1].

At the present time, the problem of the search for new coolants for nuclear reactors operating on fast neutrons, which would make it possible to accomplish simpler schemes for heat conversion than in nuclear reactors with sodium cooling, and to have better physical characteristics than in fast reactors with steam cooling [2, 3], has become extraordinarily urgent.

The Institute of Nuclear Power Engineering of the AN BSSR has been assigned the problem of searching for new gaseous coolants and working fluids making it possible to obtain better thermodynamic characteristics of cycles, a greater unit capacity of single-shaft turbo units than in use of steam, and to develop gas-cooled nuclear reactors operating on fast neutrons with high physical and thermophysical characteristics at the level of temperatures and pressures developed in reactor building and power-machine building [3-7].

As one of such working fluids and coolants, chemically reacting systems have been proposed, in which reversible chemical reactions occur, accompanied by thermal effects of chemical reactions and a variation in the number of moles [8-12]. The increase in the number of moles during heating and the decrease in it during cooling leads to an increase in the efficiency of the thermodynamic cycle, and the presence of a thermal effect in a chemically reacting system provides for high thermal properties for it because of the transfer of a considerable quantity of heat by means of concentration diffusion [5-7].

Out of a large class of chemically reacting systems [5], in which reactions occur with an increase in the number of moles and absorption of heat in the dissociation of the gas, the best-studied is the system $N_2O_4 \rightleftarrows 2NO_2 \rightleftarrows 2NO + O_2$. In 1963-1969 in the IYaE AN BSSR, IVT (Institute of Water Transport) of the AN SSSR, the GIPKh, and other organizations, a large complex of theoretical and experimental works on the study of the thermophysical and physical-chemical properties of N_2O_4 was performed [7]. This made it possible to determine the prospects of the application of dissociating gases as working fluids for power plants and coolants for nuclear reactors and led to the possibility of the development of gas-cooled fast nuclear reactors of 1000-1200 megawatt (electrical) capacity operating on N_2O_4 with the same specific heat intensities as in sodium reactors and with better phsyical characteristics, AES with single-shaft gas turbines operating on N_2O_4 with unit power of 1200-2400 megawatts and a metal content is only a fourth or fifth as much as a plant operating on steam, demonstrated the high thermodynamic efficiency of the gas and gas-liquid cycles on N_2O_4 at the level of temperatures and pressures developed in power engineering by means of a higher regeneration of heat than when operating on steam, as a consequence of the chemical reactions occuring in the coolant.

In this monograph a survey is given of the experimental studies of N_2O_4 and certain results of further works are expounded in the study of the thermodynamic and the transport properties of a chemically reacting system $N_2O_4 \rightleftarrows 2NO_2 \rightleftarrows 2NO + O_2$.

Chapter I

GENERAL PHYSICAL-CHEMICAL PROPERTIES OF NITROGEN TETROXIDE

1. On Experimental Studies of the Thermophysical Properties of N_2O_4

At the present time the chemically reacting system $N_2O_4 \rightleftarrows 2NO_2 \rightleftarrows 2NO + O_2$ has been experimentally studied in adequate detail to perform a primary check of calculation methods and, with certain assumptions, to calculate the properties of the system $N_2O_4 \rightleftarrows 2NO_2 \rightleftarrows 2NO + O_2$ in a wide range of temperatures and pressures, which may be used in thermodynamic investigations of cycles and engineering calculations of the heat-transfer equipment of atomic power plants [13].

We must note that the basic experimental material was obtained at subcritical gas parameters (60-80 ata); as yet experimental data on convective heat transfer of N_2O_4 at supercritical gas parameters are lacking. The accuracy of available experimental data on the thermophysical properties and on heat transfer is lower than that for water and inert gases (He, CO_2, N_2, and others).

The basic parameters of the dissociating N_2O_4 system are presented in Table 1.1.

In the works of the IYaE AN BSSR [5, 6] it was demonstrated that the possible temperature range of the working parameters of thermodynamic cycles operating on N_2O_4 embraces 20-750° C, and 1.1-260 ata with respect to pressure.

At the beginning of works in the IYaE AN BSSR, in spite of the wide field of application of N_2O_4 in the nitrogen industry and in rocket engineering, the N_2O_4 system was inadequately studied in the experimental plan (1-2 ata, 20-150° C). For validation and refinement of calculated data on the thermophysical properties of N_2O_4 in a wide range of temperatures and pressures, the IYaE AN BSSR, together with the CIPKh IVP AN SSSR, ITF SO AN SSSR (Institute of Theoretical Physics of the Siberian Branch of the USSR Academy of Sciences) and the OIIMF (Odessa Institute for Engineers of the Maritime Fleet) performed much work on their experimental investigation.

Table 1.1 Physical-Chemical Properties of N_2O_4

Indices	Values
Molecular weight M_0, g/mole	92.02
Normal boiling temperature, $T_{normal\ boiling}$, °K	294.3
Critical pressure, P_{cr}, ata	103.3
Critical temperature, T_{cr}, °K	431.35
Critical volume V_{cr}, cm^3/mole	165.3
Heat of evaporation $r_{294.3}$, kcal/kg	99.4
Melting temperature (melting point), T_{pl}, °K	262
Heat of chemical reaction	
$N_2O_4 \rightleftarrows 2NO_2$ (I) - $Q_{\chi p1}$, kcal/kg	149
$2NO_2 \rightleftarrows 2NO + O_2$ (II) - $Q_{\chi p2}$, kcal/kg	293
Temperature range of reaction:	
at 1 ata ΔT_1, °K	300-1200
at 100 ata ΔT_2, °K	450-1500

The physical-chemical properties and the state of the experimental investigation of the thermophysical properties of N_2O_4 are prsented in most detail in the works of the IYaE AN BSSR [2, 5, 7]. At the present time this material has been supplemented by new and more accurate data.

The P-V-T dependence of a dissociating system of N_2O_4 in the liquid phase was studied by Reamer and Sage [14] at 294-444° K up to 400 ata; in the gaseous phase by Schlinger and Sage [15] at 294-444° K and 1-130 ata; at higher parameters by Tsymarnyy at the OIIMF [16] at 373-575° K and 60-600 ata. In the IYaE AN BSSR an investigation of the P-V-T of N_2O_4 was accomplished at 373-830° K and 8-125 ata in the new experimental plant by the ballast-free piezometer method with a hot membrane and a hot valve [17]. The error of the experimental data obtained at the IYaE AN BSSR with respect to the P-V-T dependence of N_2O_4 is estimated as being ≤0.5%. With respect to the results of experimental work

[14-17] at the IYaE AN BSSR tables of the properties of N_2O_4 were complilea, which are recommended for engineering calculations [18].

Investigations of the enthalpy heat content, thermal conductivity, and viscosity of N_2O_4 were performed by the IYaE AN BSSR jointly with the IVT AN SSSR.

At the IYaE AN BSSR investigations were made of the enthalpy of liquid N_2O_4 at the isobars of 85, 103, and 115 ata [19], and of heat content in the liquid [7] and gaseous phases [21].

At the IVT AN SSSR the enthalpy of N_2O_4 in the liquid phase was studied by the method of a continuous-flow calorimeter at pressures of 60-300 atmospheres and temperatures up to 158.3° C; part of the experiments were performed in the gaseous phase up to 170° C, and also the heat content of N_2O_4 was measured in the liquid phase at atmospheric pressure.

At the OIIMF and the IYaE AN BSSR with the use of experimental data [11, 17], calculated tables of the thermodynamic functions of an N_2O_4 system in the liquid phase were compiled [22]. The satisfactory agreement of the calculated and experimental data obtained with respect to the enthalpy of N_2O_4 in the liquid phase shows the reliability of the calculated values of the enthalpy, which are recommended for engineering calculations.

The thermal conductivity of N_2O_4 at atmospheric pressures was studied in a wide range of temperatures [25-28]. At the IYaE AN BSSR the thermal conductivity of N_2O_4 was studied in the plant by the method of coaxial cylinders in a temperature range of 300-800° K and a pressure range of 1-50 ata [29]. The experimental data obtained at the IYaE AN BSSR on the thermal conductivity of N_2O_4 agrees satisfactorily with the calculated data only in the temperature range of the first stage of the reaction, $N_2O_4 \rightleftarrows 2NO_2$. In the region of the second stage of the dissociation reaction $2NO_2 \rightleftarrows 2NO + O_2$, experimental data obtained with respect to thermal conductivity agree better with the calculated data with a consideration of the kinetics of the chemical reaction. At the

IYaE AN BSSR a method has been developed for calculating the heat transfer of the system with consideration of the geometry of the heat-conducting clearance and the rates of the chemical reactions of dissociation and recombination [30]. An investigation of the thermal conductivity of N_2O_4 by the heated filament method is being conducted at the IVT AN SSSR.

At first the coefficient of dynamic viscosity of N_2O_4 was experimentally studied at pressures close to atmospheric pressure, in the temperature range of 290-440° K, i.e., only in the range of the first stage of the reaction N_2O_4 $2NO_2$ [31, 32]. At the IYaE AN BSSR an experimental study of the viscosity of N_2O_4 in the temperature range of 300 to 800° K and a pressure range of 1 to 50 ata was conducted by the falling load method in the power plant [33]. The experimental data on the viscosity of N_2O_4 obtained agree well with the most reliable data of Petker and Mason [31] with the calculated data of the IYaE AN BSSR and the OIIMF within limits of error of the experiments, 3.5% at atmospheric pressure, and up to 8% at a pressure of 50 ata. At the IVT AN BSSR the investigation of the viscosity of the N_2O_4 system is being conducted by the oscillating disc method. Preliminary experimental data from the IVT AN SSSR with respect to the viscoscity of N_2O_4 have a degree of accuracy and confirm the reliability of the results obtained earlier by other methods [33].* An experimental investigation of the viscosity of a dissociating system in the liquid phase, including the saturation line, was conducted by the authors of [34] in a temperature range of 273-428° K and a pressure range of 1-400 ata in the plant by the rolling ball method. This experimental work is as yet the only one of its type available and it is desirable to obtain data on the viscosity of N_2O_4 in the liquid phase by another method, since the rolling ball method does not always give satisfactory results on the viscosity of liquids.

The curve of the vapor tension of N_2O_4 was experimentally studied in adequate detail from the temperature of the triple point to the critical point. At the IYaE AN BSSR work was done on the analysis of experimental data of the

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*At the present time experimental data have been obtained on viscosity in the temperature range of 253.8-415.1° K and a pressure range of 25-760 ml Hg with a maximum relative error of 0.9% [46].

curve of the vapor tension of N_2O_4 for the construction of $P_s - T_s(dP_s/dT_s)$ - - T_s-dependences [35]. For the construction of an interpolation generalizing dependence $P_s - T_s$ in reference [35] the most reliable experimental results were used [14, 15, 36-39]. The maximum deviation of the calculated data with respect to pressure P_s from the experimental results does not exceed 2% [35].

On the basis of the curve of the vapor tension of N_2O_4 proposed in reference [35], obtained according to experimental data [14] at the IYaE AN BSSR, the heat of evaporation of N_2O_4 [40] was calculated with the use of the Clausius-Clapeyron equation. The calculated value of the heat of evaporation of N_2O_4 at 1 ata agrees with the experimental results.

The dependence of the constant of equilibrium of the dissociating system $N_2O_4 \rightleftarrows 2NO_2 \rightleftarrows 2NO + O_2$ was experimentally studied by a number of authors [41-45] in a wide range of temperatures. The majority of the works includes the range of pressures below atmospheric. At the IYaE AN BSSR experimental data on the composition of $N_2O_4 \rightleftarrows 2NO_2 \rightleftarrows 2NO + O_2$ were generalized, the thermal effects were refined with respect to the first and second stages of the reaction. In the experimental plan the composition of the dissociating system of N_2O_4 was studied by the spectrophotometric method at the IYaE AN BSSR at P = 1 ata in the temperature range of 130-600° C [45]. At the present time experiments are being conducted with respect to the study of the composition of the N_2O_4 system at increased pressures by the same method at the IYaE AN BSSR.

At the present time available experimental data on a dissociating N_2O_4 system are adequate for engineering calculations of heat-transfer apparatusses (heat exchangers) of AES in the temperature range of 20 to 550° C at 1 to 80 ata. A small amount of experimental data at supercritical pressures made it possible to refine the calculation methodologies of the thermophysical properties of N_2O_4 in the preliminary plan.

A further increase in the accuracy of experimental data is necessary, and also an expansion of the range of experimental investigation of N_2O_4 with respect to temperature up to 750° C and with respect to pressure up to 260 ata.

Experiments of increased accuracy with respect to the enthalpy of N_2O_4 in the liquid and gaseous phases at 20-170 ata and 20-200° C must be designated as the most important experiments.

2. Investigation of the Radiation-Thermal Stability of N_2O_4

Mathematical model of the mechanism of radiation-thermal dissociation of N_2O_4. The radiation decomposition of the system $N_2O_4 \rightleftarrows 2NO_2 \rightleftarrows 2NO + O_2$ was considered at the following conditions: temperature range $440 < T < 800°$ K, power of dose $\delta = 10^{17}$ electron-volts/cm^3/s, mass flow rate $G = 1$ kg/s, cross-section of reactor channel $S_r = 0.0017$ m^2, pressure $P = 47$ ata, stay time of the gaseous mixture in the reactor channel $t_n = 0.04$ s, which are optimum for its application as the coolant of a nuclear reactor. Nitrogen dioxide is present as a basic component in a mixture in a state of chemical equilibrium. At the entry to the reactor channel $[N_2O_4]/[NO_2] = 20\%$ at $T = 440°$ K and $P = 47$ atmospheres, and at the outlet from it $[N_2O_4]/[NO_2] = 0.01\%$ at $T = 800°$ K and at the same pressure.

The most probable means of radiation decomposition of nitrogen tetroxide is the decay of the excited molecules of N_2O_4 along the least bond $N_2O_4 \sim\sim\rightarrow N_2O_4$. In this case the process of radialysis of nitrogen tetroxide is reversible. Its contribution to the decomposition of N_2O_4 may be ignored because of the high rate of thermal dissociation of N_2O_4.

Experimental investigations of the radiation decomposition of nitrogen dioxide [47-49] make it possible to propose the following radical mechanism:

1) $NO_2 \sim\sim\rightarrow NO + O - 72;$
2) $NO_2 \sim\sim\rightarrow N + 2O - 222;$
3) $NO_2 + O \rightarrow NO + O_2 + 45 \quad k_3;$
4) $NO_2 + N \rightarrow 2NO + 78 \quad k_4;$
5) $NO_2 + N \rightarrow N_2O + O + 43 \quad k_5;$
6) $NO_2 + N \rightarrow N_2 + 2O + 3 \quad k_6;$
6a) $NO_2 + N \rightarrow N_2 + O_2 + 120 \quad k_{6a};$

7) $O_2 + N \rightarrow NO + O + 33 \quad k_7$;

8) $NO + N \rightarrow N_2 + O + 75 \quad k_8$;

9) $2NO_2 \rightarrow 2NO + O_2 - 27 \quad k_9,\ k_{-9}$;

10) $N + O + M \rightarrow NO + M + 150 \quad k_{10}$;

11) $NO + O + M \rightarrow NO_2 + M + 72 \quad k_{11}$;

12) $NO + N + M \rightarrow N_2O + M + 114 \quad k_{12}$;

13) $O + O + M \rightarrow O_2 + M + 117 \quad k_{13}$;

14) $N + N + M \rightarrow N_2 + M + 225 \quad k_{14}$;

15) $N_2O_4 \rightarrow 2NO_2 - 13{,}9 \quad k_{15},\ k_{-15}$.

If the process under consideration were determined by reactions 3, 4 and the reaction $2NO + O_2 \quad 2NO_2$, then the nitrogen dioxide would be quantitatively reduced. The irreversible decomposition effect observed in the experiment [47, 49] apparently occurs as a consequence of the reactions of nitrogen atoms 5, 6, and 8, and also as a result of the recombination of the radicals of one type in the volume and at the wall.

At rates of chemical reaction comparable with the velocities of the flow of the gas, the distribution of the concentrations of the components in a unidimensional nonisothermal flow in conditions when these assumptions are valid:

1) diffusion transfer of the matter has no essential effect on the distribution of the parameters of the reacting mixture in the direction of the motion of the flow;

2) the density of the axial thermal flow caused by thermal conductivity, diffusion and turbulent transfer, is small in comparison with the density of the radial thermal flow; is determined by the correlation of these velocities and is described by the following equations [50-53]:

$$C_m \frac{D \dfrac{C_k m_k}{C_m}}{d\tau} = I_k; \tag{1.1}$$

$$C_m C_p \frac{DT}{d\tau} = q_v - \sum_{(k)} h_k I_k,$$

where $D/d\tau = (\delta/\delta\tau) + \overline{W}(\delta/\delta z)$ is a sub-steady-state derivative; $\overline{W}$ is the average velocity of the flow; q is the volumetric density of the thermal flow (heat flux); C_k, m_k, h_k represent the concentration, molecular weight, and specific enthalpy of the k-th component; T_p is the specific heat content of the mixture; $C_m = \sum_{(k)} C_k m_k$.

The quantity of the mass of the k-th component determined by the chemical reactions is equal to $I_k = \sum_{j=1}^{r} \nu_{kj} I_j$, where ν_{kj} is the product of the molecular weight of the k-th component multiplied by the stoichiometric coefficient in the equation of the j-chemical reaction, and I_j is the rate of the chemical reaction.

The terms I_k and $\sum_{(k)} h_k I_k$ in equations (1.1) with a consideration of the chemical reactions (1-15) have the form

$$I_{N_2O_4} = m_{N_2O_4}[k_{-15}(NO_2)^2 - k_{15}(N_2O_4)];$$

$$I_{NO_2} = m_{NO_2}[-W_{NO_2} - k_3(NO_2)(O) -$$
$$-(k_4 + k_5 + k_6 + k_{6a})(NO_2)(N) - 2k_9(NO_2)^2 +$$
$$+ 2k_{-9}(NO)^2(O_2)^2 + k_{11}(NO)(O)M +$$
$$+ 2k_{15}(N_2O_4) - 2k_{-15}(NO_2)^2];$$

$$I_{NO} = m_{NO}[W_{NO} + k_3(NO_2)(O) + 2k_4(NO_2)(N) +$$
$$+ k_7(O_2)(N) + 2k_9(NO_2)^2 + k_{10}(N)(O)M - k_8(NO)(N) -$$
$$-2k_{-9}(NO)^2(O_2) - k_{11}(NO)(O)M - k_{12}(NO)(N)M];$$

$$I_{O_2} = m_{O_2}[k_3(NO_2)(O) + k_{6a}(NO_2)(N) + k_9(NO_2)^2 -$$
$$-k_7(O_2)(N) - k_{-9}(NO)^2(O_2) + k_{13}(O)^2M];$$

$$I_{N_2} = m_{N_2}[k_6(NO_2)(N) + k_{6a}(NO_2)(N) +$$
$$+ k_8(NO)(N) + k_{14}(N)^2M];$$

$$I_{N_2O} = m_{N_2O}[k_5(NO_2)(N) + k_{12}(NO)(N)M];$$

$$I_N = m_N[W_N - (k_5 + k_6 + k_{6a} + k_4)(NO_2)(N) -$$
$$- k_7(O_2)(N) - k_8(NO)(N) -$$
$$- k_{10}(N)(O)M - k_{12}(NO)(N)M - 2k_{14}(N)^2M];$$

$$I_O = m_O[W_O - k_3(NO_2)(O) - k_{11}(NO)(O)M -$$
$$- k_{10}(N)(O)M - 2k_{13}(O)^2M + k_5(NO_2)(N) +$$
$$+2k_5(NO_2)(N) + k_7(O_2)(N) + k_8(NO)(N)];$$

$$\sum_{(k)} h_k I_k = -\{q_{15}[k_{15}(N_2O_4) - k_{-15}(NO_2)^2] +$$

$$\begin{aligned}&+q_9\left[k_9(NO_2)^2-k_9(NO)^2(O_2)\right]+q_3k_3(NO_2)(O)+\\&+\left[q_4k_4+q_5k_5+q_6k_6+q_{6a}k_{6a}\right](NO_2)(N)+q_7k_7(O_2)(N)+\\&+q_8k_8(NO)(N)+q_{10}k_{10}(N)(O)M+q_{11}k_{11}(NO)(O)M+\\&+q_{12}k_{12}(NO)(N)M+q_{13}k_{13}(O)^2M+q_{14}k_{14}(N)^2M\}.\end{aligned}\qquad(1.2)$$

Having substituted expressions (1.2) into equation (1.1), we find that the time distribution of the components of the mixture in a unidimensional flow caused by the occurrence of the chemical reactions (1-15) and by the effect of these reactions on grad T along the flow, is described by a system of 9 nonlinear first-order differential equations:

$$C_m\frac{D\dfrac{(N_2O_4)}{C_m}}{d\tau}=k_{-15}(NO_2)^2-k_{15}(N_2O_4);$$

$$\begin{aligned}C_m\frac{D\dfrac{(NO_2)}{C_m}}{d\tau}&=-W_{NO_2}-k_3(NO_2)(O)-\\&-(k_4+k_5+k_6+k_{6a})(NO_2)(N)-2k_9(NO_2)^2+\\&+2k_{-9}(NO)^2(O_2)+k_{11}(NO)(O)M+\\&+2k_{15}(N_2O_4)-2k_{-15}(NO_2)^2;\end{aligned}$$

$$\begin{aligned}C_m\frac{D\dfrac{(NO)}{C_m}}{d\tau}&=W_{NO}+k_3(NO_2)(O)+2k_4(NO_2)(N)+\\&+k_7(O_2)(N)+2k_9(NO_2)^2+k_{10}(N)(O)M-k_8(NO)(N)-\\&-2k_{-9}(NO)^2(O_2)-k_{11}(NO)(O)M-k_{12}(NO)(N)M;\end{aligned}$$

$$\begin{aligned}C_m\frac{D\dfrac{(O_2)}{C_m}}{d\tau}&=k_3(NO_2)(O)+k_{6a}(NO_2)(N)+\\&+k_9(NO_2)^2-k_7(O_2)(N)-k_{-9}(NO)^2(O_2)+k_{13}(O)^2M;\end{aligned}$$

$$\begin{aligned}C_m\frac{D\dfrac{(N_2)}{C_m}}{d\tau}&=k_6(NO_2)(N)+k_{6a}(NO_2)(N)+\\&+k_8(NO)(N)+k_{14}(N)^2M;\end{aligned}$$

$$C_m\frac{D\dfrac{(N_2O)}{C_m}}{d\tau}=k_5(N_2O)(N)+k_{12}(NO)(N)M;$$

$$
\begin{aligned}
C_m \frac{D\dfrac{(\mathrm{N})}{C_m}}{d\tau} &= W_{\mathrm{N}} - (k_4 + k_5 + k_6 + k_{6a})(\mathrm{NO_2})(\mathrm{N}) - \\
&- k_7(\mathrm{O_2})(\mathrm{N}) - k_8(\mathrm{NO})(\mathrm{N}) - k_{10}(\mathrm{N})(\mathrm{O})M - \\
&- k_{12}(\mathrm{NO})(\mathrm{N})M - 2k_{14}(\mathrm{N})^2 M; \\
C_m \frac{D\dfrac{(\mathrm{O})}{C_m}}{d\tau} &= W_{\mathrm{O}} - k_3(\mathrm{NO_2})(\mathrm{O}) - k_{11}(\mathrm{NO})(\mathrm{O})M - \\
&- k_{10}(\mathrm{N})(\mathrm{O})M - 2k_{13}(\mathrm{O})^2 M + k_5(\mathrm{NO_2})(\mathrm{N}) + \\
&+ 2k_6(\mathrm{NO_2})(\mathrm{N}) + k_7(\mathrm{O_2})(\mathrm{N}) + k_8(\mathrm{NO})(\mathrm{N}); \\
C_p C_m \frac{DT}{d\tau} &= q_v + q_{15}\left[k_{15}(\mathrm{N_2O_4}) - k_{-15}(\mathrm{NO_2})^2\right] + \\
&+ q_9\left[k_9(\mathrm{NO_2})^2 - k_{-9}(\mathrm{NO})^2(\mathrm{O_2})\right] + q_3k_3(\mathrm{NO_2})(\mathrm{O}) + \\
&+ \left[q_4k_4 + q_5k_5 + q_6k_6 + q_{6a}k_{6a}\right](\mathrm{NO_2})(\mathrm{N}) + \\
&+ q_7k_7(\mathrm{O_2})(\mathrm{N}) + q_8k_8(\mathrm{NO})(\mathrm{N}) + q_{10}k_{10}(\mathrm{N})(\mathrm{O})M + \\
&+ q_{11}k_{11}(\mathrm{NO})(\mathrm{O})M + q_{12}k_{12}(\mathrm{NO})(\mathrm{N})M + \\
&+ q_{13}k_{13}(\mathrm{O})^2 M + q_{14}k_{14}(\mathrm{N})^2 M,
\end{aligned}
\tag{1.3}
$$

where (N_2O_4), (NO_2), (NO), (O_2), (N_2), (N_2O), (N) and (O) are the current concentrations of the oxides of nitrogen, oxygen, nitrogen, and the atoms of nitrogen and oxygen; k_j is the constant of the rate of the j-th chemical reaction; q_j is the thermal effect of the j-th chemical reaction; $M = \sum_{(k)} C_k$; W_{NO_2} is the primary rate of the radiolysis of nitrogen dioxide with respect to reactions 1 and 2; W_N, W_O, W_{NO} are the rates of the formation of the atoms of nitrogen, oxygen, and nitric oxide according to the same reactions.

Relative to the energy fields G_1 and G_2 of the decomposition of NO_2 with respect to reactions 1 and 2, on the basis of the calculation given in the survey, the following assumptions were made: at $P \geq 1$ atmosphere, $G_1 = 10$ moles/100, $G_2 = 1$ mole/100. In the range of pressures exceeding atmospheric pressure, the values of G_1 and G_2 vary inversely proportional to P. Experimental values of the specific rates of reactions 3-15 are given in Table 1.2.

Table 1.2 Values of the specific rates of chemical reactions used in the calculations.

i	k_j	T, °K	Reference
3	$k_3 = 1{,}5 \cdot 10^9$ g/mole·sec	300	[54]
4	$k_4 = 0{,}366 \cdot 10^{10}$ g/mole·sec	300	[55]
5	$k_5 = 0{,}476 \cdot 10^{10}$ g/mole·sec	300	[55]
6	$k_6 = 0{,}144 \cdot 10^{10}$ g/mole·sec	300	[55]
6a	$k_{6a} = 0{,}111 \cdot 10^{10}$ g/mole·sec	300	[55]
7	$k_7 = 5 \cdot 10^{10} \exp(-7100/RT)$ g/mole·sec	412—755	[56]
8	$k_8 = 3 \cdot 10^{10} \exp(-200 \pm 700/RT)$ g/mole·sec	476—755	[56]
	$k_9 = 4{,}7 \cdot 10^9 \exp(-26860/RT)$ g/mole·sec	592—656	[57, 58]
9	$k_9 = 4{,}0 \cdot 10^9 \exp(-26900/RT)$ g/mole·sec	630—1020	[59]
10	$k_{10} = 5{,}4 \cdot 10^9$ g²/mole²sec	300	[60]
11	$k_{11} = 1{,}85 \cdot 10^{10}$ g²/mole²sec	293	[61]
12	$k_{12} = 0{,}36 \cdot 10^7$ g²/mole²sec	300	[47]
13	$k_{13} = 0{,}97 \cdot 10^9$ g²/mole²sec	300	[62]
14	$k_{14} = 0{,}62 \cdot 10^{10}$ g²/mole²sec	300	[63]
15	$k_{15} = 10^{16} \exp(-13000/RT)$ 1/sec	253—301	[64]

In the steady-state case, system of differential equations (1.3) has the form

$$\frac{d\frac{(N_2O_4)}{C_m}}{dZ} = \frac{1}{C_m}\,\frac{1}{W}\left[k_{-15}(NO_2)^2 - k_{15}(N_2O_4)\right];$$

$$\frac{d\frac{(NO_2)}{C_m}}{dZ} = \frac{1}{C_m}\,\frac{1}{W}\Big[-W_{NO_2} - k_3(NO_2)(O) -$$

$$-(k_4 + k_5 + k_6 + k_{6a})(NO_2)(N) - 2k_9(NO_2)^2 +$$

$$+ 2k_{-9}(NO)^2(O_2) + k_{11}(NO)(O)M +$$

$$+ 2k_{15}(N_2O_4) - 2k_{-15}(NO_2)^2\Big];$$

$$\frac{d\frac{(NO)}{C_m}}{dZ} = \frac{1}{C_m}\,\frac{1}{W}\Big[W_{NO} + k_3(NO_2)(O) +$$

$$+ 2k_4(NO_2)(N) + k_7(O_2)(N) + 2k_9(NO_2)^2 -$$

$$- 2k_{-9}(NO)^2(O_2) - k_8(NO)(N) + k_{10}(N)(O)M -$$

$$- k_{11}(NO)(O)M - k_{12}(NO)(N)M\Big];$$

$$\frac{d\frac{(O_2)}{C_m}}{dZ} = \frac{1}{C_m W}\Big[k_3(NO_2)(O) - k_7(O_2)(N) +$$

$$+ k_9(NO_2)^2 - k_{-9}(NO)^2(O_2) + k_{13}(O)^2M + k_{6a}(NO_2)(N)\Big];$$

$$\begin{aligned}
\frac{d\,\dfrac{(N_2)}{C_m}}{dZ} &= \frac{1}{C_m W}\left[k_6(NO_2)(N) + k_{6a}(NO_2)(N) + \right.\\
&\quad \left. + k_8(NO)(N) + k_{14}(N)^2 M\right];\\
\frac{d\,\dfrac{(N_2O)}{C_m}}{dZ} &= \frac{1}{C_m W}\left[k_5(NO_2)(N) + k_{12}(NO)(N)M\right];\\
\frac{d\,\dfrac{(N)}{C_m}}{dZ} &= \frac{1}{C_m W}\left[W_N - (k_4 + k_5 + k_6 + k_{6a}) \times \right.\\
&\quad \times (NO_2)(N) - k_7(O_2)(N) - k_8(NO)(N) - k_{10}(N)(O)M -\\
&\quad \left. - k_{12}(NO)(N)M - 2k_{14}(N)^2 M\right];\\
\frac{d\,\dfrac{(O)}{C_m}}{dZ} &= \frac{1}{C_m W}\left[W_O - k_3(NO_2)(O) + k_5(NO_2)(N) + \right.\\
&\quad + 2k_6(NO_2)(N) + k_7(O_2)(N) + k_8(NO)(N) -\\
&\quad \left. - k_{10}(N)(O)M - k_{11}(NO)(O)M - 2k_{13}(O)^2 M\right];\\
C_m W C_p \frac{dT}{dZ} &= q_v + q_{15}\left[k_{15}(N_2O_4) - k_{-15}(NO_2)^2\right] +\\
&\quad + q_9\left[k_9(NO_2)^2 - k_{-9}(NO)^2(O_2)\right] + q_3k_3(NO_2)(O) +\\
&\quad + (q_4k_4 + q_5k_5 + q_6k_6 + q_{6a}k_{6a})(NO_2)(N) +\\
&\quad + q_7k_7(N)(O_2) + q_8k_8(NO)(N) + q_{10}k_{10}(N)(O)M +\\
&\quad + q_{11}k_{11}(NO)(O)M + q_{12}k_{12}(NO)(N)M +\\
&\quad + q_{13}k_{13}(O)^2 M + q_{14}k_{14}(N)^2 M.
\end{aligned} \qquad (1.4)$$

In the last equation the thermal effects of the chemical reactions are taken with their own sign: positive if the reaction is exothermic; negative if it is endothermic. The velocity of the flow of gas is determined as $W = G/C_mS_g$, where G is the mass flow rate, S_g is the cross-section of the reactor channel with respect to the gas. The volumetric heat flux $q_v = q_e(Z)/S_g$.

The times of occurrence of the chemical reaction (15), (-15), (9), (-9) as a function of T are given, calculated for an equilibrium gas mixture at P = 47 atmospheres. As we approach chemical equilibrium, at an unchanged temperature, the probability of a direct reaction decreases, i.e., its time increases, and the probability of a reverse reaction increases, and accordingly the time of the reverse reaction is decreased.

For the molecular reaction $\tau = 1/k$, i.e., its time, at the moment of equilibrium is the same as at moments of time preceeding it.

From a comparison of the characteristics of the times of the chemical reactions with the characteristic stay time of the gas in the reaction channel ($\tau_n \simeq 0.04$ s) we may reach a conclusion concerning the equilibrium occurrence of reaction 15. Therefore the variation of the concentration of nitroben tetroxide along the flow is determined by the variation of the concentration of NO_2 and the content of equilibrium of reactions (15) and (-15):

$$(N_2O_4) = \frac{k_{-15}}{k_{15}} (NO_2)^2, \tag{1.5}$$

and the distortion of grad T along the flow caused in this case is described by the product $q_{15} d \frac{(N_2O_4)}{C_m}/dZ$.

Table 1.3 Time of occurrence of reactions in an equilibrium mixture $N_2O_4 \rightleftarrows 2NO_2 \rightleftarrows 2NO + O_2$ at P = 47 as a function of T.

T, °K	$N_2O_4 \to 2NO_2$	$2NO_2 \to N_2O_4$	$2NO_2 \to 2NO + O_2$	$2NO + O_2 \to 2NO_2$
	τ, сек			
400	$1,3 \cdot 10^{-9}$	$2 \cdot 10^{-9}$	—	—
500	$0,5 \cdot 10^{-10}$	$1 \cdot 10^{-9}$	130,00	500,000
600	$1,0 \cdot 10^{-11}$	$1 \cdot 10^{-10}$	1,68	21,400
700	$1,0 \cdot 10^{-12}$	$1 \cdot 10^{-10}$	0,08	0,164
800	$0,3 \cdot 10^{-12}$	$1 \cdot 10^{-10}$	0,01	0,010

The derivative $d \frac{(N_2O_4)}{CC_m}/dZ$ is expressed via the derivatives $d \frac{(NO_2)}{C_m}/dZ$, dT/dZ and dC_m/dZ:

$$\begin{aligned} d \frac{(N_2O_4)}{C_m} \Big/ dZ = 2 \frac{k_{-15}}{k_{15}} (NO_2) d \frac{(NO_2)}{C_m} \Big/ dZ + \\ + \frac{(NO_2)^2}{C_m^2} \frac{k_{-15}}{k_{15}} \frac{dC_m}{dZ} + \\ + C_m \frac{(NO_2)^2}{C_m^2} \frac{k_{-15}}{k_{15}} \left(\frac{1}{T} + \frac{q_{15}}{RT^2} \right) \frac{dT}{dZ}. \end{aligned} \tag{1.6}$$

For dC_m/dZ the equation has the form

$$\frac{dC_m}{dZ} = -\frac{C_m}{T}\frac{dT}{dZ} - \frac{C_m^2 RT}{P}\sum_{\kappa=1}^{8} d\frac{C_\kappa}{C_m}\Big/ dZ, \tag{1.7}$$

where

$$\sum_{\kappa=1}^{8} d\frac{C_\kappa}{C_m}\Big/dZ = d\frac{(N_2O_4)}{C_m}\Big/dZ + d\frac{(NO_2)}{C_m}\Big/dZ + $$
$$+ d\frac{(NO)}{C_m}\Big/dZ + d\frac{(O_2)}{C_m}\Big/dZ + d\frac{(N_2)}{C_m}\Big/dZ + $$
$$+ d\frac{(N_2O)}{C_m}\Big/dZ + d\frac{(N)}{C_m}\Big/dZ + d\frac{(O)}{C_m}\Big/dZ.$$

Having solved equations (1.6) and (1.7) jointly with the second equation of system (1.4) relative to $d\frac{(N2O4)}{C_m}/dZ$, dC_m/dZ and $d\frac{(NO2)}{C_m}/dZ$, we find that

$$\frac{d\frac{(N_2O_4)}{C_m}}{dZ} = \frac{1}{1 + \frac{4k_{-15}}{k_{15}}(NO_2) - \frac{k_{-15}}{k_{15}}(NO_2)^2} \times$$
$$\times \left\{ \frac{k_{-15}}{k_{15}} \frac{q_{15}}{RT^2} \frac{(NO_2)^2}{C_m} \frac{dT}{dZ} - \frac{k_{-15}}{k_{15}}(NO_2)^2 \frac{RT}{P} \times \right.$$
$$\sum_{\kappa=3}^{8} \frac{d\frac{C_\kappa}{C_m}}{dZ} + \left[2\frac{k_{-15}}{k_{15}}(NO_2) - \frac{k_{-15}}{k_{15}}(NO_2)^2 \frac{RT}{P} \right] \times \tag{1.8}$$
$$\times \frac{S_r}{G} \left[-W_{NO_2} - k_3(NO_2)(O) - \right.$$
$$+ (k_4 + k_5 + k_6 + k_{6a})(NO_2)(N) - 2k_9(NO_2)^2 +$$
$$\left. + 2k_{-9}(NO)^2(O_2) + k_{11}(NO)(O)M \right\}.$$

Having substituted equation (1.8) into the temperature equation and having made the appropriate transformation, we obtain

$$\frac{dT}{dZ} = \frac{S_r}{G} \frac{1}{C_p + \frac{q_{15}^2/RT^2}{\frac{C_m}{(N_2O_4)} + \frac{4C_m}{(NO_2)} - \frac{C_m}{P/RT}}} \times$$

$$
\begin{aligned}
&\times\left\{\frac{q_{e(z)}}{S_r}+\left[\frac{\dfrac{4}{(NO_2)}+\dfrac{RT}{P}}{\dfrac{1}{(N_2O_4)}+\dfrac{4}{(NO_2)}-\dfrac{RT}{P}}\,q_{15}+q_9\right]\times\right.\\
&\quad\times\left[k_9(NO_2)^2-k_{-9}(NO)^2(O_2)\right]+\\
&+\frac{q_{15}}{\dfrac{1}{(N_2O_4)}+\dfrac{4}{(NO_2)}-\dfrac{RT}{P}}\left[\frac{2}{(NO_2)}\left[W_{NO_2}+\right.\right.\\
&\quad+k_3(NO_2)(O)+(k_4+k_5+k_6+k_{6a})(NO_2)(N)-\\
&\quad-k_{11}(NO)(O)M\Big]+\frac{RT}{P}\Big[W_O+k_4(NO_2)(N)-\\
&\quad-k_{10}(N)(O)M-k_{11}(NO)(O)M-k_{12}(NO)(N)M-\\
&\quad\left.\left.-k_{13}(O)^2M-k_{14}(N)^2M\right]\right]+q_3k_3(NO_2)(O)+\\
&+(q_4k_4+q_5k_5+q_6k_6+q_{6a}k_{6a})(NO_2)(N)+q_7k_7(O_2)(N)+\\
&\quad+q_8k_8(NO)(N)+q_{10}k_{10}(N)(O)M+\\
&\quad+q_{11}k_{11}(NO)(O)M+q_{12}k_{12}(NO)(N)M+\\
&\quad\left.+q_{13}k_{13}(O)^2M+q_{14}k_{14}(N)^2M\right\}.
\end{aligned}
\tag{1.9}
$$

The second and third terms in the braces of equation (1.5) describe the heat absorption caused by the effect of the radiation-thermal decomposition of nitrogen dioxide (nitrous oxide) on the equilibrium occurrence of reactions (15), (-15), $(q_{15}^2/RT^2)/[(C_m/N_2O_4) + (4C_m/NO_2) - (C_m/P/RT)]$--an addition to the heat content originating because of the equilibrium occurrence of reactions (15) and (-15) in the gaseous mixture.

Taking into consideration the fact that $C = \sum\limits_{(k)} C_k$, we will assign the variation of the concentration of nitrous oxide by the algebraic equation

$$(NO_2)=C-\sum_{\substack{\kappa=1\\ \kappa\neq 2}}^{8}C_\kappa,$$

where C = P/RT.

We will consider the recombination of the atoms of nitrogen and oxygen at the wall and in the volume. The constant of heterogeneous recombination was approximately estimated under the assumption of axial symmetry of the active particles

$$k_r = \left(\frac{S^2}{8D} + \frac{2S}{\varepsilon \bar{u}}\right)^{-1}.$$

Here S is the diameter of the cylinder; D is the diffusion factor; $\bar{u}$ is the mean square velocity of the recombining particles; is the probability of recombination, depending upon the material of the wall. The probability of the recombination of nitrogen atoms on a metallic wall is 0.1-1. The initial data, accordingly, are equal to: $P \cong 47$ atmospheres, T = 600° K, S = 0.14 cm, and then the relative velocity of the collision of atoms of nitrogen with N_2O_4 $\bar{u}_1 = 1.45 \cdot 10^5$ cm/s, with NO_2 $\bar{u}_2 = 1.11 \cdot 10^5$, with NO $\bar{u}_3 = 1.17 \cdot 10^5$, with O_2 $\bar{u}_4 = 1.16 \cdot 10^5$ cm/s; the velocity of atoms of nitrogen $\bar{u} = 9.45 \cdot 10^4$ cm/s, and the diffusion factor $D = \frac{1}{3}\bar{u}^2 / \sum_{(i)} \sigma_i u_i n_i \cong 0.02$ cm^2/s, and consequently, $S^2/2D = 0.1$, $2S/\varepsilon u = 3 \cdot 10^{-5}$, i.e., a diffusion region of recombination with a recombination constant $k_g = 10$ sec^{-1} occurs. The constant of heterogeneous recombination of the atoms of oxygen is comparable with the constant of heterogenous recombination of the atoms of nitrogen, since the masses of these atoms are close to each other.

The concentrations of the atoms of nitrogen and oxygen are determined from the equations

$$\begin{aligned}\frac{d(N)}{d\tau} = {} & W_N - (k_4 + k_5 + k_6 + k_{ca})(NO_2)(N) - \\ & - k_7(O_2)(N) - k_8(NO)(N) - k_{10}(N)(O)M - \\ & - k_{12}(NO)(N)M - 2k_{11}(N)^2 M;\\ \frac{d(O)}{d\tau} = {} & W_O - k_3(NO_2)(O) + k_5(NO_2)(N) + \\ & + 2k_6(NO_2)(N) + k_7(O_2)(N) + k_8(NO)(N) - \\ & - k_{10}(N)(O)M - k_{11}(NO)(O)M - 2k_{13}(O)^2 M.\end{aligned}$$

Considering the concentrations of the atoms of N and O as steady-state, we arrive at the quadratic equation for their determination

$$[N]^2 + b[N] - c = 0;$$
$$[O]^2 + b_1[O] - c_1 = 0,$$

where

$$b = \frac{1}{2k_{14}M}\left[(k_4 + k_5 + k_6 + k_{6a})(NO_2) + \right.$$
$$\left. + k_7(O_2) + (k_8 + k_{13}M)(NO) + k_{10}(O)M\right];$$
$$c = G_2\delta\cdot 10^{-2}/2k_{14}M;$$
$$b_1 = \frac{1}{2k_{13}M}\left[k_3(NO_2) + k_{10}(N)M + k_{11}(NO)M\right];$$

$$c_1 = \frac{1}{2k_{13}M}\left[W_O + (k_5 + 2k_4)(NO_2)(N) + \right.$$
$$\left. + k_7(O_2)(N) + k_8(NO)(N)\right];$$
$$W_O = (G_1 + 2G_2)\delta\cdot 10^{-2}.$$

At values of the constants given in Table 1.2, the concentrations of atoms of N and O are equal: $[N] = 10^4$ moles/cm^3, $[O] = 10^4$ moles/cm^3.

Considering that $k[N]^2M = 1.7\cdot 10^{-32}$, if $M = N_2$ [63], we obtain $V_{het.}/V_{hom.} = 10/1.7\cdot 10^{-32}\ 6\cdot 10^{20}\cdot 10^4 \approx 10^8$. The rate of heterogeneous recombination of the atoms of oxygen also exceeds the rate of volumetric recombination, but since the time of diffusion of the radicals to the wall is 0.1 sec and the stay time of the gaseous mixture in the reaction volume is 0.04 sec, we may ignore both heterogeneous and homogeneous recombination of the radicals, especially in comparison with processes (3)-(8):

$$\frac{k_{14}(N)^2M}{(k_6 + k_{6a})(NO_2)(N)} \sim 10^{-16};\quad \frac{k_{13}(O)^2M}{k_3(NO_2)(O)} \sim 10^{-15};$$
$$\frac{k_{10}(N)(O)M}{k_3(NO_2)(O) + 2k_4(NO_2)(N)} \sim 10^{-16}.$$

Thus, in conditions when reaction 15 is at equilibrium and we may ignore recombination of the radicals, system (1.4) has the form

$$(N_2O_4)=\frac{k_{-15}}{k_{15}}(NO_2)^2;$$

$$(NO_2)=\frac{P}{RT}-\sum_{\substack{\kappa=1\\ \kappa\neq 2}}^{8}C_\kappa;$$

$$\frac{d\,\frac{(NO)}{C_m}}{dZ}=\frac{S_r}{G}\left[W_{NO}+k_3(NO_2)(O)+\right.$$
$$+2k_4(NO_2)(N)+k_7(O_2)(N)-k_8(NO)(N)+$$
$$+2k_9(NO_2)^2-2k_{-9}(NO)^2(O_2)-$$
$$\left.-k_{11}(NO)(O)M-k_{12}(NO)(N)M\right];$$

$$\frac{d\,\frac{(O_2)}{C_m}}{dZ}=\frac{S_r}{G}\left[k_3(NO_2)(O)+k_{6a}(NO_2)(N)-\right.$$
$$\left.-k_7(O_2)(N)+k_9(NO_2)^2-k_{-9}(NO)^2(O_2)\right];$$

$$\frac{d\,\frac{(N_2)}{C_m}}{dZ}=\frac{S_r}{G}\left[k_6(NO_2)(N)+k_{6a}(NO_2)(N)+k_8(NO)(N)\right];$$

$$\frac{d\,\frac{(N_2O)}{C_m}}{dZ}=\frac{S_r}{G}\left[k_5(NO_2)(N)+k_{12}(NO)(N)M\right];$$

$$\frac{d\,\frac{(N)}{C_m}}{dZ}=\frac{S_r}{G}\left[W_N-(k_4+k_5+k_6+k_{6a})(NO_2)(N)-\right.$$
$$\left.-k_7(O_2)(N)-k_8(NO)(N)-k_{12}(NO)(N)M\right];$$

$$\frac{d\,\frac{(O)}{C_m}}{dZ}=\frac{S_r}{G}\left[W_O-k_3(NO_2)(O)+k_5(NO_2)(N)+\right.$$
$$+2k_6(NO_2)(N)+k_7(O_2)(N)+$$
$$\left.+k_8(NO)(N)-k_{11}(NO)(O)M\right];$$

$$\frac{dT}{dZ}=\frac{S_r}{G}\,\frac{1}{C_p+\dfrac{q_{15}^2/RT^2}{\dfrac{C_m}{(N_2O_4)}+\dfrac{4C_m}{(NO_2)}-\dfrac{C_m}{P/RT}}}\times$$

$$\times\left\{\frac{q_e(Z)}{S_r}+\left[\frac{\dfrac{4}{(NO_2)}+\dfrac{RT}{P}}{\dfrac{1}{(N_2O_4)}+\dfrac{4}{(NO_2)}-\dfrac{RT}{P}}\,q_{15}+\right.\right.$$

$$+ q_9\big]\left[k_9(NO_2)^2 - k_{-9}(NO)^2(O_2)\right] +$$

$$+ \frac{q_{15}}{\frac{1}{(N_2O_4)} + \frac{4}{(NO_2)} - \frac{RT}{P}} \; \frac{2}{(NO_2)} \times$$

$$\times \big[W_{NO_2} + k_3(NO_2)(O) + (k_4 + k_5 + k_6 + k_{6a}) \times$$

$$\times (NO_2)(N) - k_{11}(NO)(O)M\big] +$$

$$+ \frac{RT}{P}\,\big[W_O + k_5(NO_2)(N) - k_{11}(NO)(O)M -$$

$$- k_{12}(NO)(N)M\big] + q_3k_3(NO_2)(O) +$$

$$+ \left[q_4k_4 + q_5k_5 + q_6k_6 + q_{6a}k_{6a}\right](NO_2)(N) + \qquad (1.10)$$

$$+ q_7k_7(N)(O_2) + q_8k_8(NO)(N) +$$

$$\left. + q_{11}k_{11}(NO)(O)M + q_{12}k_{12}(NO)(N)M \right\} .$$

The specific isobaric heat content of the mixture C_p is determined as $C_p = \sum_{k=1}^{8} C_{pk}(C_k m_k/C_m$; $C_{p1} = C_{p(N_2O_4)}$; $C_{p2} = C_{p(NO_2)}$ etc.

Since lg of the ratio of the rates of the primary radiation and thermal decomposition of nitrous oxide in the temperature range investigated, 440-800° K, varies from -2.5 to -8 (Fig. 1.1), it is apparent that the numerical solution of system of differential equations (1.10) may be obtained by the method of successive approximations, dividing the system into the two subsystems (1.11) and (1.12):

$$(N_2O_4) = \frac{k_{-15}}{k_{15}}\,(NO_2)^2;$$

$$(NO_2) = \frac{P}{RT} - \sum_{\substack{K=1\\K\neq 2}}^{8} C_K;$$

$$\frac{d\,\frac{(NO)}{C_\Sigma}}{dl} = \frac{S_\Sigma}{G}\,\big[2k_9(NO_2)^2 - 2k_{-9}(NO)^2(O_2) + W_{NO} + \qquad (1.11)$$

$$+ k_3(NO_2)(O) + 2k_5(NO_2)(N) + k_7(O_2)(N) - k_8(NO)(N) -$$

$$- k_{11}(NO)(O)M - k_{12}(NO)(N)M\big];$$

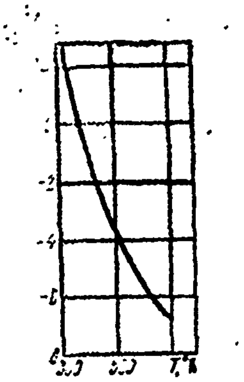


Figure 1.1. Dependence of the ratio of the primary rates of radiation and tnermal decomposition of N$_2$O$_4$as a function of temperature $W_{(NO_2)}=0.187\cdot10^{-5}$ moles/l/s.

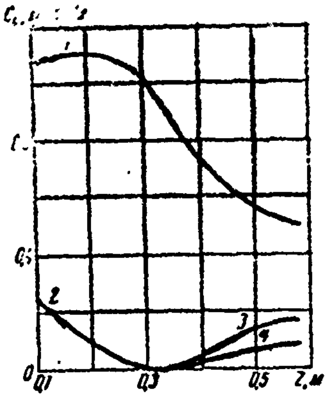


Figure 1.2. Distribution of the concentrations of nitrogen tetroxide, nitric oxide, and oxygen with respect to Z.

1- NO$_2$, 2- N$_2$O$_4$, 3- NO, 4- O$_2$

$$\frac{d\,\dfrac{(O_2)}{C_m}}{dZ} = \frac{S_r}{G}\left[k_9(NO_2)^2 - k_{-9}(NO)^2(O_2) + \right.$$

$$\left. + k_3(NO_2)(O) + k_{6a}(NO_2)(N) - k_7(O_2)(N)\right];$$

$$\frac{dT}{dZ} = \frac{S_r}{G}\,\frac{1}{C_p + \dfrac{q_{15}^2/RT^2}{\dfrac{C_m}{(N_2O_4)} + \dfrac{4C_m}{(NO_2)} - \dfrac{C_m}{P/RT}}} \times$$

$$\times\left\{\frac{q_e(T)}{S_r} + \left[\frac{\dfrac{4}{(NO_2)} + \dfrac{RT}{P}}{\dfrac{1}{(N_2O_4)} + \dfrac{4}{(NO_2)} - \dfrac{RT}{P}}\, q_{15} + q_9\right] \times\right.$$

$$\times\left[k_9(NO_2)^2 - k_{-9}(NO)^2(O_2)\right] +$$

$$+ \frac{q_{15}}{\dfrac{1}{(N_2O_4)} + \dfrac{4}{(NO_2)} - \dfrac{RT}{P}}\left[\frac{2}{(NO_2)} \times\right.$$

$$\times\left[W_{NO_2} + k_3(NO_2)(O) + (k_4 + k_5 + k_6 + k_{6a})(NO_2)(N) - \right.$$

$$\left. - k_{11}(NO)(O)M\right] + \frac{RT}{P}\left[W_O + k_6(NO_2)(N) - \right.$$

$$\left.\left. - k_{11}(NO)(O)M - k_{12}(NO)(N)M\right]\right] + q_3k_3(NO_2)(O) +$$

$$+ (q_4k_4 + q_5k_5 + q_6k_6 + q_{6a}k_{6a})(NO_2)(N) +$$

$$+ q_7k_7(O_2)(N) + q_8k_8(NO)(N) +$$

$$+ q_{11}k_{11}(\mathrm{NO})(\mathrm{O})M + q_{12}k_{12}(\mathrm{NO})(\mathrm{N})M \Big\} .$$

$$\frac{d\,\dfrac{(\mathrm{N_2})}{C_m}}{dZ} = \frac{S_r}{G}\,[k_6(\mathrm{NO_2})(\mathrm{N}) +$$

$$+ k_{6a}(\mathrm{NO_2})(\mathrm{N}) + k_8(\mathrm{NO})(\mathrm{N})];$$

$$\frac{d\,\dfrac{(\mathrm{N_2O})}{C_m}}{dZ} = \frac{S_r}{G}\,[k_5(\mathrm{NO_2})(\mathrm{N}) + k_{12}(\mathrm{NO})(\mathrm{N})M];$$

$$\frac{d\,\dfrac{(\mathrm{N})}{C_m}}{dZ} = \frac{S_r}{G}\,[W_{\mathrm{N}} - k_4 + k_5 + k_6 + k_{6a})\times$$

$$\times(\mathrm{NO_2})(\mathrm{N}) - k_7(\mathrm{O_2})(\mathrm{N}) - k_8(\mathrm{NO})(\mathrm{N}) - k_{12}(\mathrm{NO})(\mathrm{N})M];$$

(1.12)

$$\frac{d\,\dfrac{(\mathrm{O})}{C_m}}{dZ} = \frac{S_r}{G}\,[W_{\mathrm{O}} - k_2(\mathrm{NO_2})(\mathrm{O}) + k_4(\mathrm{NO_2})(\mathrm{N}) +$$

$$+ 2k_3(\mathrm{NO_2})(\mathrm{N}) + k_7(\mathrm{O_2})(\mathrm{N}) +$$

$$+ k_8(\mathrm{NO})(\mathrm{N}) - k_{11}(\mathrm{NO})(\mathrm{O})M].$$

At the corresponding initial conditions, we solve system (1.11) under the assumption that the rate of radiation decomposition of NO_2 is equal to zero. A knowledge of the values of (N_2O_4), (NO_2), (NO), O_2 and T in the zero approximation as a function of Z makes it possible to find the solution of system (1.12).

Solution of the steady-state problem and discussion of the results. A numerical solution to system (1.11) was obtained by the Runge-Kutta method on the Minsk-22 electronic computer under the assumption that at the input to the reactor channel the chemically reacting mixture of gases $N_2O_4 \rightleftarrows 2NO_2 \rightleftarrows 2NO + O_2$ is in equilibrium at T = 440° K and P = 47 atmospheres.

The variation of the heat flow along the reactor channel (with respect to Z) is determined by the equation

$$q_e(Z) = 510 \sin\left(\frac{\pi Z}{l+2h}\right) \frac{\text{kcal}}{\text{m, sec}} .$$

l = 0.5 m, h - 0.08 m. The cross-section of the reactor channel with respect to gas S_g = 0.0017 m^2; the mass flow rate G = 1 kg/s; the primary rates of radiation decomposition are $W = 0.17 \cdot 10^{-5} \sin(\pi Z/l+2h)$; $W_2 = 0.17 \cdot 10^{-6} \cdot \sin(\pi Z/l+2h)$ moles/liter/sec. In the calculation constants of equilibrium of the systems $N_2O_4 \rightleftarrows 2NO_2$ and $2NO_2 \rightleftarrows 2NO + O_2$ were used, as measured by Bodenstein [65]:

$$\lg k_{15} = -\frac{2891}{T} + 1,75 \lg T + 0,0046T - 8,92 \cdot 10^{-6}T^2 + 3,934;$$

$$\lg k_9 = -\frac{5749}{T} + 1,7 \lg T - 0,0005T + 2,839$$

in temperature ranges of 282-404° K and 499-825° K. The dependences of the concentrations of the components of the mixture (N_2O_4), (NO_2), (O_2) and the temperature of the gaseous mixture upon Z are given in Figs. 1.2 and 1.3.

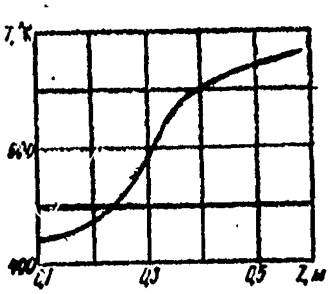


Figure 1.3. Variation of the temperature of a chemically reacting mixture $N_2O_4 \rightleftarrows 2NO_2 \rightleftarrows 2NO + O_2$ with respect to Z.

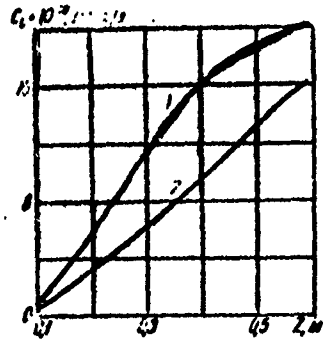


Figure 1.4. Dependence of the concentration of nitrous oxide and nitrogen upon Z.
1- N_2O, 2- N_2

The thermal decomposition of nitrogen tetroxide and nitrogen dioxide occurs very rapidly, and at T ≥ 600° K $(N_2O_4) \leq 0.0029$ moles/l. The dissociation of nitrogen dioxide at temperatures T ≤ 600° K is practically lacking because of the low specific rate of the reaction, but, however, with an increase in temperature the rate constant increases, the reaction time accordingly is decreased, and when T = 700° K the concentration of NO_2 becomes equilibrium.

The solution of system (1.11) obtained makes it possible to find the distribution of the radicals N and O, nitrogen, and nitrous oxide along the reactor channel (Table 1.4, Fig. 1.4).

Table 1.4 Distribution of radicals N and O along the reactor channel

Z, m	0,1	0,16	0,2	0,26	0,3	0,36	0,4	0,46	0,5	0,58
$(N)\cdot10^{17}$, молек/г	0,63	0,92	1,03	1,29	1,51	1,77	1,70	1,44	1,23	0,73
$(O)\cdot10^{15}$, молек/г	0,56	0,83	0,93	1,16	1,37	1,43	1,12	0,75	0,59	0,32

The nature of the dependence of the concentrations of the atoms of oxygen and nitrogen upon Z is determined by the sinusoidal variation of the power of the dose with respect to Z and the dependence of the degree of dissociation of nitrogen dioxide upon Z. In the region where Z < 0.4 m the concentration of the atoms of oxygen is controlled by reaction 3, in the region Z ≥ 0.4 m process 11 plays the determining role (Fig. 1.5).

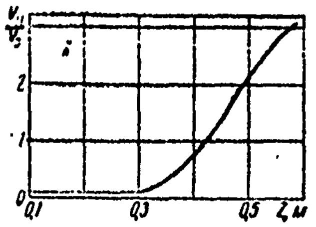


Figure 1.5. Dependence of the ratio of the rates of reactions $NO+O+M \rightarrow NO_2+M$ (11) and $NO_2+O \rightarrow NO+O_2$ (3) upon Z.

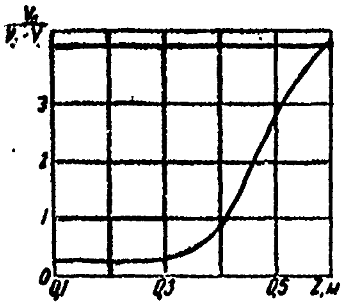


Figure 1.6. Dependence of the ratio of rates of reactions $NO_2+N \rightarrow N_2+2O$ (6), $NO+N \rightarrow N_2+O$ (8), and $NO_2+N \rightarrow N+O_2$ (6a) upon Z.

The formation of nitrous oxide in the system under consideration occurs as a result of the reaction of atomic nitrogen with NO_2: the nitrogen is formed in this same reaction, but with a probability less than a factor of 1.9. This explains the dependence of N_2O and N_2 upon Z in the region $Z < 0.4$ m. When $Z \geq 0.4$ m thermic dissociation of NO_2 becomes perceptible, the concentration of nitric oxide in the reaction volume increases, as a consequence of which the formation of nitrogen begins to be entirely controlled by reaction 8 (Fig. 1.6). Aside from this, the rate of reaction 8 in the region $Z > 0.46$ m is greater than the rate of reaction 5, and therefore with an increase in Z the concentration of nitrogen, with respect to magnitude, approaches the concentration of nitrous oxide.

The nitric oxide, contained in the gaseous mixture, at the outlet from the reactor channel is oxidized by the oxygen as a result of subsequent cooling to a dioxide, and the remaining quantity of oxygen, which corresponds to the irreversible decomposition of nitrogen dioxide under the effect of the radiation, may be calculated by working from the equation of material balance:

$$\varkappa NO_2 \rightsquigarrow \varkappa_1 O_2 + aN_2O + bN_2,$$

where κ is the quantity of nitrogen dioxide, decomposing irreversibly during the stay time of the gaseous mixture in the reactor channel; κ_1, a, and b are the concentrations of oxygen, nitrous oxide, and nitrogen, which are formed in this case.

At the outlet from the reactor channel $a = 0.2 \cdot 10^{-8}$ moles/l, $b = 0.16 \cdot 10^{-8}$ moles/l, and then $\kappa = 0.72 \cdot 10^{-8}$ moles/l, and $\kappa_1 = 0.62 \cdot 10^{-8}$ moles/l, i.e. the following ratio occurs between the products of irreversible radiolysis: $NO_2:(O_2):(N_2O):(N_2) = 1:0.32:0.258$. It agrees satisfactorily with the experimental data [66]. With a decrease in pressure, if P is of the order of several atmospheres, the rate of both the primary and the initial radiation decomposition of the nitrogen dioxide does not change, but the rate of thermal dissociation decreases, however, even if P = 5 atmospheres the magnitude of the ratio of the primary rate of radiation decomposition to thermal decomposition does not exceed 0.3 when T = 440° K. But with a decrease in pressure a certain change is possible in the ratio of the quantities of nitrous oxide and nitrogen toward an increase in the concentration of the latter, caused by an increase in the degree of thermal dissociation of NO_2. Radiation decomposition of NO_2 causes an additional decomposition of N_2O_4. But the process of the adsorption of energy occurring in this case, as a consequence of the low degree of radiation decomposition of NO_2, cannot play any noticeable part. We also may ignore the effect of the energy liberated in the reaction volume as a result of the exothermic reaction (4)-(8), (11), and (12) initiated by the radiation on the temperature gradient along the flow, because the magnitude of the ratio

$$\left(\sum_{i=4}^{8} q_i V_i + q_{11} V_{11} + q_{12} V_{12}\right) / q_{-9} V_{-9}$$

at temperatures of $440 < T < 800°$ K lies in the region from $0.8 \cdot 10^{-2}$ to 10^{-7}. Therefore, the variation of the temperature of the gaseous mixture with respect to Z is entirely determined by the dependence upon the heat flux and the occurrence of the chemical reactions in the gaseous mixture.

Thus, with an adequate degree of accuracy we may affirm that the chemically reacting system $N_2O_4 \rightleftarrows 2NO_2 \rightleftarrows 2NO + O_2$ has a high degree of radiation resistance as a coolant for a nuclear reactor.

3. Kinetics and Mechanism of the Thermal Reactions Occurring in a System Containing the Oxides of Nitrogen and Oxygen

Thermal decomposition of N_2O_4. The stoichiometric equation of the thermal disoociation reaction of nitrogen tetroxide in the gaseous and liquid phases may be written in the following manner:

$$N_2O_4 \rightleftarrows 2NO_2. \qquad (1.13)$$

The kinetics of this fast reaction were studied in the gaseous phase in experiments with respect to the measurement of the dispersion and absorption of ultrasonic vibrations [184,185,189,195,214] in experiments with expanding [215] and stopped [218] gas jets and also in experiments with shock waves [64, 219].

As was established in these works, in the region of pressures $P \leq 1$ atmosphere and of temperatures of the order of 300° K the decomposition of N_2O_4 is a second-order reaction

$$N_2O_4 + M \underset{k_{-1\cdot 14}}{\overset{k_{1\cdot 14}}{\rightleftharpoons}} 2NO_2 + M, \tag{1.14}$$

where M is any molecule; N_2O_4, NO_2 or a molecule of an inert gas activating the N_2O_4 in the direct reaction (1.14) and deactivating the shock complex $NO_2 \cdot$ $\cdot NO_2$, forming in the reverse reaction.

In the region of pressures of $P > 2$ atmospheres and temperatures of $T >$ $> 300°$ K, according to Carrington and Davidson [64, 219], the decomposition of N_2O_4 is a first-order reaction

$$N_2O_4 \underset{k_{-1\cdot 15}}{\overset{k_{1\cdot 15}}{\rightleftharpoons}} 2NO_2. \tag{1.15}$$

The temperature dependence of the constant of the rate of the direct reaction (1.14) was studied in references [189,195,214,219]. According to the data of Carrington and Davidson [219], the second-order rate constant $k_{1.14}$, corresponding to the rate equation

$$-\frac{d(N_2O_4)}{dt} = k_{1.14}(N_2O_4)(M), \tag{1.16}$$

is determined by the expression

$$k'_{1\cdot 14} = 2\cdot 10^{14}\exp(-11000/RT)\, g/mole\cdot sec, \tag{1.17}$$

where R is a gas constant equal to 1.987 calories/mole/degree.

Blend [214] obtained the following dependence for the rate constant $k_{1.14}$:

$$k''_{1\cdot 14} = 1{,}33\cdot 10^{14}\exp(-10240/RT)\, g/mole\cdot sec. \tag{1.18}$$

At T = 300° K the values of the second-order rate constant, calculated according to expressions (1.17) and (1.18), are equal to $1.93\cdot 10^6$ and

$4.68 \cdot 10^6$ l/mole/s, respectively, i.e., the expression of Carrington and Davidson gives lower values of the rate constant in comparison with Blend's expression.

The basis of the non-coincidence of the values of the second-order rate constant calculated according to expressions (1.17) and (1.18) is apparently the different efficiency of the molecules M in the process of the activation of the nitrogen tetroxide. In the conditions of Carrington and Davidson [64, 219], who studied the decomposition of N_2O_4 at a considerable excess of nitrogen, only the nitrogen molecule may stand out as the M molecule. In the experiments of Blend [214], who investigated the dissociation of the pure tetroxide, at M molecules the molecules of N_2O_4 and NO_2 stand out. It is known, however, that the efficiency of the N_2O_4, NO_2, and N_2 molecules in reaction (1.14) is different. According to the data of Cher [195], the relative efficiencies of the N_2O_4, NO_2, and N_2 molecules in this reaction amount, respectively, to: $N_2O_4 = 1$, $NO_2 = 1$, and $N_2 = 0.5$.

With consideration of the relative efficiency of the M molecules expression (1.17) for a case of thermal dissociation of pure nitrogen tetroxide takes the form

$$k_{1.14}^{N_2O_4} = 4 \cdot 10^{11} \exp(-11000/RT)\ \text{l/mole}\cdot\text{sec}. \qquad (1.19)$$

The temperature dependence of the rate constant of the first-order reaction, according to Carrington and Davidson [219], is described by the expression

$$k_{1.15} = 10^{16} \exp(-13100/RT)\ \text{sec}^{-1}. \qquad (1.20)$$

Dependence (1.20) was obtained on the basis of very rough estimates, and therefore the values of $k_{1.15}$ calculated from this dependence give only the order of magnitude of the rate constant.

The kinetics of the dimerization of NO_2, of the reaction that is the reverse to thermal decomposition of N_2O_4 was studied in the works of Wegener

[220, 222]. In the first reference [220] the recombination of NO_2 was studied in an expanding supersonic gas flow, containing small quantities of NO_2, into N_2. In the second reference [222], the rate of the reaction was determined from the measurement of the relaxation time of the disturbance caused by pellets flying with a high velocity in a vessel with N_2O_4 and N_2.

The experimental value of the rate constant of the first-order reaction

$$2NO_2 + M \xrightarrow{k_{1\cdot14}} N_2O_4 + M,$$

according to Wegener, at a temperature of 296° K is equal to $3 \cdot 10^6$ 1/mole/s.

We may compare this magnitude with the value of the rate constant of recombination $k_{-1.14}$, calculated according to the expression

$$k_{-1.14} = k_{1.14}/K_{c1} = R_1 T k_{1.14}/K_{p1}, \tag{1.21}$$

where R_1 is a gas constant equal to 0.0821 atmospheres/1/m/degree/mole, and K_{c1} and K_{p1} are the constants of equilibrium of reaction (1.13), expressed in units of concentration, moles/liter, and units of pressure, atmospheres, respectively.

The equilibrium of reaction (1.13) has been adequately fully studied [41,44,45,57,193]. Calculation works are also available [76, 224]. For calculation of the constant of equilibrium in an ideally gaseous state, in the temperature range of 300-1000° K, the following polynomial was proposed in [2]:

$$\ln K_{p1} = 5{,}887 + 2{,}77 \ln T - 6{,}626 \cdot 10^{-3} T + \\ + 1{,}851 \cdot 10^{-6} T^2 - \frac{28279}{T^2} - \frac{12725}{RT}. \tag{1.22}$$

The value of K_{p1} at T = 300° K, calculated according to expression (1.22) is equal to 0.166 atmospheres. By substituting this value and the value of $k_{1.14}$, calculated according to expression (1.17) (the experiments of Wegener were accomplished at a considerable excess of N_2), into expression (1.21), we obtain $k_{-1.14} = 2.86 \cdot 10^6$ 1/mole/s, which agrees well with the experimental values established by Wegener.

Table 1.5 Specific rate of the reaction $N_2O_4 \rightarrow 2NO_2$ in the liquid phase

T, °K	k_0, sec^{-1}
313	$1.1 \cdot 10^4$
333	$6.9 \cdot 10^4$
353	$3.6 \cdot 10^5$

The decomposition of N_2O_4 in the liquid phase was experimentally investigated in the work of Bauer and his co-workers [247]. In Table 1.5 experimental values of the first-order rate constant of the dissociation of N_2O_4 in the liquid phase are presented [247].

The temperature dependence of the first-order rate constant of thermal decomposition N_2O_4 in the liquid phase, according to Bauer and his co-workers [247], is described by the expression

$$k_{ж} \cdot 1{,}7 \cdot 10^{17} \exp(-19000/RT) \quad \text{sec}^{-1}. \tag{1.23}$$

In reference [7], the reaction times t_ν were calculated, corresponding to the degree of transformation ν, determined by the ratio

$$\nu = \alpha_{noneq}/\alpha_{eq} \tag{1.24}$$

where α_{noneq} and α_{eq} are the nonequilibrium and equilibrium degrees of dissociation.

The calculations were performed according to the expressions:

1) for the second-order reaction

$$t_{\nu 1} = -\frac{1}{k_{1.ж}} \left\{ \frac{K_{c1}}{x_1^0\left(x_0^1 - \frac{1}{2}K_{c1}\right)} \ln\left| \frac{x_1^0 - \nu\frac{K_{c1}}{8}(1-y)}{x_1^0} \right| + \right.$$
$$\left. + \frac{\ln|1-\nu|}{y\left[x_1^0 - \frac{1}{8}K_{c1}(1-y)\right]} - \frac{\ln|(1-\nu)+y(1+\nu)| - \ln|(1+y)|}{y\left[x_1^0 - \frac{1}{8}k_{c1}(1+y)\right]} \right\}; \tag{1.25}$$

2) for the first-order reaction

$$t_{\nu 2} = \frac{1}{k_{1.15}y} \ln \left| \frac{1 + \frac{1+\nu}{1-\nu} y}{1+y} \right|, \qquad (1.26)$$

where $y = \sqrt{1+16x_1^0/K_{c1}}$, and x_1^0 is the initial concentration of N_2O_4, moles/l.

Expressions (1.25) and (1.26) were obtained as the result of integration of the second-order rate equation

$$-\frac{d(N_2O_4)}{dt} = k_{1.14}(N_2O_4)(M) - k_{-(1.14)}(NO_2)^2(M) \qquad (1.27)$$

and the first-order rate equation

$$-\frac{d(N_2O_4)}{dt} = k_{1.15}(N_2O_4) - k_{-(1.15)}(NO_2)^2 \qquad (1.28)$$

upon condition that the concentration of NO_2 at the initial moment of time is equal to zero.

The values of the reaction time for the degree of completion $\nu = 0.99$, calculated according to expressions (1.25) and (1.26), are given in Table 1.6. The values of the rate constants $k_{1.14}$ and $k_{1.15}$ were calculated according to expressions (1.19) and (1.20).

The data in Table 1.6 demonstrate that the time in which the degree of decomposition of N_2O_4 reaches a value equal to 99% of the equilibrium degree at $T \geq 300°$ K and $P \geq 1$ atmosphere, has an order of magnitude of 1 μs, i.e., in these conditions the decomposition of N_2O_4 occurs in practically a state of equilibrium.

Thermal dissociation of NO_2. The kinetics of thermal dissociation were experimentally studied in the temperature range of 473-2300° K [57-59, 248-252].

According to the data of Bodensten and Ramstetter [57], who measured the rate of the reaction in a temperature range of 592-656° K and a pressure range of $NO_2 \sim$ 10-40 mm Hg by the manometric method, the decomposition of NO_2 is a bimolecular process:

$$2NO_2 \xrightarrow{k_{1.29}} 2NO + O_2 \qquad (1.29)$$

Table 1.6 Dependence of the reaction time $N_2O_4 = 2NO_2$ upon P and T (μs)

T, °K	P, atm								
	0,01	0,05	0,1	0,5	1	3	5	10	40
300	1339,650	182,517	72,924	7,899	2,945	—	—	—	—
320	529,257	87,652	37,781	4,639	1,796	0,055	—	—	—
340	212,995	39,480	18,281	2,616	1,062	0,029	0,023	—	—
360	92,655	18,050	8,756	1,465	0,634	0,017	0,013	0,010	—
380	43,727	8,659	4,278	0,787	0,362	0,009	0,008	0,006	0,004
400	22,250	4,432	2,205	0,424	0,203	0,005	0,004	0,003	0,002

Rosser and Wise [59] investigated this reaction by the spectrophotometric method in the temperature range of 630-1020° K. The concentration of NO_2 in the experiments of these authors varied in the range of 10^{-5}-10^{-4} moles per liter. For the second-order rate constants

$$k_{1.29} = \frac{-\frac{d(NO_2)}{dt}}{(NO_2)^2}. \qquad (1.30)$$

Rosser and Wise give the expression

$$k_{1.29} = 10^{[illegible]}\exp(-26600/RT)\ g/mole \cdot sec. \qquad (1.31)$$

According to the experimental data of the authors indicated, the inert gases (N_2, He, CO_2) do not have any essential effect on the kinetics of reaction (1.29) at a pressure up to 1 atmosphere, nor do the walls of the reaction vessel have any such effect.

Ashmore and his co-workers [58, 248], in studying the decomposition of NO_2 by the spectrophotometric method in the temperature range of 473-707° K and the pressure range of NO_2 of the order of several tens of millimeters Hg, found that the rate of the reaction at the early stages is more than twice as great as the magnitude expected in accordance with the data of previous authors [59]. In this case, it was established that the rate of the reaction takes a normal value after the decomposition of NO_2 by 10% or with the introduction of nitric oxide into the reaction vessel in quantities comparable with the quantity of NO_2.

An additional contribution to the decomposition of nitrogen dioxide at early stages, as the authors indicated established [58, 248], belongs to a mechanism with the participation of an intermediate compound in the nitrate form

$$NO_2 + NO_2 \underset{k_{-(1.32)}}{\overset{k_{1.32}}{\rightleftarrows}} NO + NO_3, \qquad (1.32)$$

$$NO_3 + NO_2 \xrightarrow{k_{1.33}} NO_2 + NO + O_2. \qquad (1.33)$$

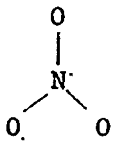
By applying the method of steady-state concentrations to the intermediate compound NO_3, Ashmore and his co-workers [58, 248] obtained the following kinetic equation:

$$-\frac{d(NO_2)}{dt} = k_{eff}\,(NO_2)^2, \qquad (1.34)$$

where

$$k_{eff} = k_{-1.29} + \frac{k_{1.32}k_{1.33}(NO_2)}{k_{-(1.32)}(NO) + k_{1.33}(NO_2)}. \qquad (1.35)$$

At the early stages of the reaction, when $P_{NO_3} >> P_{NO}$, the dissociation of NO_2, as follows from equation (1.35), is a second-order reaction with a rate constant $k'_{eff} = k_{1.29} + k_{1.32}$. At a later stage, when the condition $P_{NO_3} \geq P_{NO}$, the second term in the righthand part of equation (1.35) becomes negligible in comparison with the first and the rate of the reaction takes a normal value. The NO_3 in the nitrate form



is a well-known compound. The absorption spectra of this compound were observed for the first time by Sprenger and Schumacher [253] in the study of the kinetics of the decomposition of ozone in the presence of N_2O_5. At a later time the formation of the nitrate radical was investigated in detail in the works of Davidson and his co-workers [221, 254], who studied the kinetics of the thermal decomposition of N_2O_5 in shock waves. NO_3 is formed at the first stage of the decomposition of nitrogen pentoxide:

$$N_2O_5 \rightarrow NO_3 + NO_2. \qquad (1.36)$$

The NO_3 in the nitrate form is also formed in the reaction

$$O + NO_2 \rightarrow NO_3, \qquad (1.37)$$

which was experimentally demonstrated in the work of Husain and Norrisch [225].

The thermodynamic data of NO_3 were determined by Schott and Davidson [221] and by Ray and Ogg [217]. According to the data of Schott and Davidson $\Delta H_f^0 = 17.1 \pm 1$ kcal/mole, $S^0 = 60 \pm 2$ cal/degree/mole; according to the data of Ray and Ogg, $\Delta H_f^0 = 16.6 \pm 2$ kcal/mole, $S^0 = 61 \pm 2$ cal/degree/mole.

On the basis of the data indicated and the values of the rate of the reaction at early stages of dissociation of NO_2, Ashmore and Barnett [58] determined the following expression for the rate constants $k_{1.32}$, $k_{-1.32}$, $k_{1.33}$:

$$k_{1.32} = 10^{8.89} \exp(-23900/RT) \text{ 1/mole/s} \qquad (1.38)$$

$$k_{-(1.32)} = 10^{9.62} \exp(1700/RT) \text{ 1/mole/s} \qquad (1.39)$$

$$k_{1.33} = 10^{8.07} \exp(-3200/RT) \text{ 1/mole/s} \qquad (1.40)$$

and for the rate constant of the reaction

$$NO + O_2 + NO_2 \xrightarrow{k_{-(1.33)}} NO_3 + NO_2, \qquad (1.41)$$

$$\lg k_{-(1.33)} = 1,32 + \frac{210}{T}. \qquad (1.42)$$

The latter expression was obtained from the condition

$$\frac{k_{1.32}}{k_{-(1.32)}} \cdot \frac{k_{1.33}}{k_{-(1.33)}} = K_{c2}, \qquad (1.43)$$

where K_{c2} is the constant of equilibrium of the summary process

$$2NO_2 = 2NO + O_2.$$

We should note that the rate constant $k_{1.32}$ is determined in accordance with the equation

$$-\frac{d(NO_2)}{dt} = k_{1.32}(NO_2)^2, \qquad (1.44)$$

and the rate constant $k_{-(1.32)}$ is determined in accordance with the equation

$$-\frac{d(NO_3)}{dt} = k_{-(1.32)}(NO_3)(NO).$$

With a consideration of this remark, the equation of the rate of the reversible reaction (1.32) is written

$$-\frac{d(NO_2)}{dt} = k_{1.32}(NO_2)^2 - 2k_{-(1.32)}(NO_3)(NO). \qquad (1.45)$$

The relative contribution of the radical mechanism in the heat composition of NO_2, according to Ashmore and Barnett, is determined by the ratio

$$\frac{\text{radical method}}{\text{bimolecular method}} = \frac{k_{1.32}/k_{1.29}}{1 + \frac{k_{-(1.32)}}{k_{1.33}} \frac{(NO)}{(NO_2)}}. \qquad (1.46)$$

In Table 1.7 the values of the relative contribution of the radical mechanism to the dissociation of NO_2 as a function of the degree of dissociation and the temperature are presented.

Table 1.7 Contribution of the radical mechanism to the decomposition of nitrogen dioxide

$\left(\frac{(NO)}{(NO_2)}\right)$	radical method/bimolecular method		
	$T=473$ °K	$T=573$ °K	$T=673$ °K
0	5,00	2,80	1,90
0,01	1,62	1,11	0,90
0,1	0,27	0,20	0,16
0,3	0,09	0,07	0,06

As follows from Table 1.7, the contribution of the radical mechanism with the participation of NO_3 in the nitrate form has an essential value only in the region of low temperatures and upon fulfillment of the condition $P_{NO_3} \gg$ $\gg P_{NO}$. This is explained by the high rate of the reaction

$$NO_3 + NO \xrightarrow{k_{-(1.32)}} 2NO_2,$$

competing with the reaction

$$NO_3 + NO_2 \xrightarrow{k_{1.32}} NO_2 + NO + O_2.$$

In the range of temperatures T > 1500° K with a considerable excess of inert gas, according to the data of Huffman and Davidson, the following reaction occurs:

$$NO_3 + M \underset{k_{(1.47)}}{\overset{k_{1.47}}{\rightleftharpoons}} NO_2 + O + M. \qquad (1.47)$$

According to their estimates

$$k_{1.47} = 10^{22} T^{-2} \exp(-49600/RT) \text{ 1/mole/s} \qquad (1.48)$$

from whence, when T = 1750° K, $k_{1.47} = 2 \cdot 10^9$, which is comparable with the value of $k_{-(1.32)} = 2.5 \cdot 10^9$, calculated at T = 1750 according to (1.39).

In conditions when $(NO_2) \ll (M)$ and, consequently $(NO) \ll (M)$, reaction (1.47) replaces the reaction $NO + NO_3 \rightarrow (NO_2$, which will correspond kinetically to the decomposition of NO_2 with the second-order rate constant $k'_{eff} = k_{1.29} +$ $+ k_{1.32}$.

The temperature dependence of the rate constant k_{eff} was determined in the work of Huffman and Davidson [249], $k^{g}_{eff} = 2.5\cdot10^{10}\exp(-25{,}000 \pm 5000/RT)$ 1/mole/s (1.49), and Fishburne, Bergbauer, and Edse [251], who studied the dissociation of NO_2 in shock waves in the temperature range of 1500-2100° K in conditions analogous to the conditions of the previous authors ($P_M \gg P_{NO_2}$), give

$$k^{sh.wave}_{eff} = 9\cdot10^{9}\exp(-25700/RT)\ \text{l/mole/s} \qquad (1.50)$$

The values of the rate constants $k_{1.29}$, k^{g}_{eff}, and $k^{sh.wave}_{eff}$, calculated according to expressions (1.31), (1.49), and (1.50) at T = 1750° K, are equal to $k_{1.29} = 1.74\cdot10^{6}$, $k^{g}_{eff} = 18.94\cdot10^{6}$, and $k^{sh.wave}_{eff} = 5.54\cdot10^{6}$, respectively.

On the basis of these quantities and the ratio

$$k_{1.32} = k_{eff} - k_{129} \qquad (1.51)$$

at a temperature of 1750° K we will determine the value of $k'_{1.32} = 17.20\cdot10^{6}$ and $k''_{1.32} = 3.80\cdot10^{6}$ liters/mole/s, which with respect to order to magnitude agrees with the value of $k_{1.32} = 0.81\cdot10^{6}$ 1/mole/s, calculated according to (1.38).

The coincidence of the quantities $k'_{1.32}$, $k''_{1.32}$, and $k_{1.32}$ should be considered as satisfactory, especially if we consider the method of determination of $k'_{1.32}$ and $k''_{1.32}$. Thus, data on the decomposition in shock waves give additional arguments in favor of the mechanism proposed by Ashmore and his coworkers [248].

In the region of high temperatures (T > 1500° K), according to Huffman and Davidson [249], NO_2 decomposes to according to reactions (1.29), (1.32), (1.33), and (1.47), and in parallel according to the mechanism

$$NO_2 + M \xrightarrow{k_{1.52}} NO + O + M, \qquad (1.52)$$

$$O + NO_2 \xrightarrow{k_{1.53}} NO + O_2. \qquad (1.53)$$

The kinetics of the decomposition of NO_2 in reaction (1.52) was investigated in detail in the work of Troe [252]. According to the data of the last author, at a general pressure of the order of 300 atmospheres a transition occurs from the rate equation

$$-\frac{d(NO_2)}{dt} = k_{1.52}^{0}(NO_2)(M) \tag{1.54}$$

to the equation

$$-\frac{d(NO_2)}{dt} = k_{1.52}^{\infty}(NO_2). \tag{1.55}$$

The superscripts "0" and "∞" in equations (1.54) and (1.55) signify, respectively, the rate constant of the reaction in the regions and of high pressures.

For the rate constant $k_{1.52}^{0}$ Huffman and Davidson [249] give the expression

$$k_{1.52}^{0} = 10^{13.17}\exp(-65400/RT)\ 1/\text{mole/s} \tag{1.56}$$

According to Troe's data [252],

$$k_{1.52} = 10^{13.05}\exp(-65000/RT)\ 1/\text{mole/s}. \tag{1.57}$$

The temperature dependence of the rate constant $k_{1.52}^{\infty}$ is described by the following equation [252]:

$$k_{1.52}^{\infty} = 10^{14.3}\exp(-71860/RT)\cdot \text{sec}^{-1} \tag{1.58}$$

The relative contribution of reaction (1.52) into the summary decomposition of NO_2 when $P < 300$ atmospheres in pure nitrogen dioxide is determined by the ratio

$$\frac{k_{1.52}^{0}}{k_{1.29}} = 10^{3.45}\exp(-38100/RT), \tag{1.59}$$

which gives a quantity at a temperature of 1000° K that is equal to $1.2\cdot10^{-5}$, i.e., the contribution of reactions (1.52) and (1.53) to the decomposition of

NO_2 at temperatures $T < 1000°$ K is negligible in comparison with the contribution of reaction (1.29).

Oxidation of NO by oxygen. The reaction of the oxidation of NO with oxygen in the gaseous phase

$$2NO + O_2 \overset{k_{1.60}}{\rightleftarrows} 2NO_2 \qquad (1.60)$$

is of considerable theoretical and practical interest.

The kinetics of the given process were studied for the first time by Bodenstein and his co-workers [186,187,256]. These authors measured the rate of formation of NO_2 by the manometric method in the temperature range 0-389° C at pressures of NO and NO_2 of the order of 10 mm Hg. According to the data of the authors indicated, at stages that are not very close to completion, reaction (1.60) is second order with relationship to NO and first order with relationship to NO_2.

The value of the third-order rate constant, corresponding to the equation of rate

$$\frac{d(NO_2)}{dt} = k_{1.60}(NO)(O_2), \qquad (1.61)$$

according to Bodenstein and Wachenheim [186], at $T = 303°$ K is equal to $13.24 \cdot 10^3$ $l^2/mole^2/s$.

In the work of the authors named it was also established that the third-order rate constant decreases with the growth of the temperature and that during reaction (1.60) the inert gases (SO_2, CO_2) the reaction product ($N_2O_4 = 2NO_2$), water vapor, and the walls of the reaction vessel have no noticeable effect.

After the publication of the results of Bodenstein and his co-workers, a large number of experimental works were performed in which the effect of inert gases was studied [190-193, 207], as well as the composition of the reaction mixture [191,193,199-201,209,258], water vapor [188,194,196-198,202,257], reaction products [200, 201], the wall of the reaction vessel [188,191,196,197, 202,207], and the catalysts [203-206, 220] on the kinetics of the reaction of the oxidation of nitric oxide by oxygen (1.60).

The results obtained in these works have a somewhat contradictory nature.

On one hand, there are data confirming the conclusions of Bodenstein and his co-workers relative to the third-order kinetics. Thus, according to the authors of references [188, 191-193], the inert gases have no effect on the rate of the reaction of NO with O_2. The results of references [191, 198, 207] indicate the absence of a wall effect.

According to the data of the authors of refs. [191,193, 199] the effect of the composition of the reaction mixture was not established. The effect of the water vapor was not observed [194, 199].

On the other hand, results were obtained indicating a deviation from the third-order kinetics. Thus, according to Tracy and Daniels [198], the order of the reaction with relationship to NO is equal to 2.3, and with relationship to O_2, to 0.8 with a degree of oxidation less than 25%, and has a normal value at later stages.

Scholtz [210] established that the kinetics of the oxidation of NO with oxygen depends upon the ratio P_{NO}/P_{O_2}. According to the data of this author, at t = 25° C and P^0_{NO,O_2} = 1-50 mm Hg, the value of the third-order rate constant with a variation of the ratio P_{NO}/P_{O_2} from 30 to 0.06 decreases from $14.80 \cdot 10^3$ $l^2/mole^2/s$ to $8 \cdot 10^3$ $l^2/mole^2/s$.

Hasche [188] demonstrated that the rate of oxidation of NO with oxygen decreases by 20% in a case if the walls of the reactor vessel are coated with paraffin. The latter also observed the favorable effect of water vapor. This effect was also observed in [196, 198].

According to the data of Tipper and Williams [190], the addition of nitrogen to the quantity of 100 mm Hg to the reaction mixture, consisting of 100 mm Hg NO and 50 mm Hg O_2, in the temperature range of 20-570° C decreased the rate of the reaction to half its previous value.

And, finally, in works performed in conditions close to atmospheric conditions ($t \sim 25°$ C, $P_{gen} \sim 1$ atmosphere, $P_{NO} \sim 0.01$ mm Hg, $O_2 \sim 20\%$, $N_2 \sim 80\%$) higher values of the third-order rate constant were obtained [199,207,211,212, 216].

Deviations from the third-order kinetics, established in refs. [188,190, 196,198,199,207,210,211,212,216] were interpreted on the basis of concepts of the complex course of the given reaction. Mechanisms were developed with the participation of intermediate compounds, such as the nitrate radicals NO_3, NO_3 NO, and the dimer of ferric oxide, N_2O_2.

We may demonstrate, however, that such an approach to the explanation of the divergences in the results of different authors is not the only possible one. The data in Table 1.8, in particular, indicate this, in which table for comparison experimental data are given which were obtained by different authors at a temperature close to room temperature.

As follows from this table, the third-order and the values of the rate constant close to a magnitude determined by Bodenstein and Wachenheim were established in the range of variation of pressure from $0.3 \cdot 10^{-2}$ to 340 mm Hg at a variation of the ratio P_{NO}/P_{O_2} from 10^{+2} to 10^{-5}, and in the presence of nitrogen in a quantity varying from several tens to several hundreds of millimeters Hg, and also in the presence and in the absence of water vapor.

From this we may reach the conclusion that the deviations from the third-order kinetics observed in [188,190,196,198,199,207,210] are caused rather by some secondary processes, such as absorption of NO and NO_2 on the wall of the reaction vessel or by reactions of NO and NO_2 with impurities of foreign matter and water vapor.

The data obtained by Greig and Hall [207], in particular, speak in favor of the latter assumption. These authors found that in the study of reaction (1.60) in conditions close to atmospheric conditions, the third-order rate constant depended upon the method of the control of the course of the reaction. In a case when the rate of the formation of NO_2 was controlled by the measurement of the concentration of NO, the value of k at T = 293° K amounted to $20 \cdot 10^3$ $l^2/mole^2/sec$. If they watched the progess of the process by measuring the concentration of NO_2, then with an increase in the pressure of NO within limits from $0.38 \cdot 10^{-2}$ to $3.8 \cdot 10^{-2}$ mm Hg, the value of the rate constant decreased from $20 \cdot 10^3$ $l^2/mole^2/sec$ to $15 \cdot 10^3$ $l^2/mole^2/sec$. The decrease in the value, as the authors' data established, was caused by absorption of NO_2 on the walls of the reaction vessel catalyzed by the nitric oxide.

Smith [197], in studying the reaction

$$2NO + O_2 \rightarrow 2NO_2$$

in experiments with a large quantity of water, demonstrated that the reaction begins with a lesser speed and stops long before completion. In the opinion of Smith, the stopping of the reaction signifies that the rate of discharge of NO_2 with respect to reactions with H_2O becomes comparable with the rate of formation.

Processes of such a type are non-essential for the kinetics of the oxication of NO with oxygen. The given reaction may occur both in the presence and in the absence of these processes. In particular, this conclusion is confirmed by the results of Briner [194], who established the normal occurrence of the reaction at T = 80°C, i.e., in conditions at which the pressure of the wat vapor was negligible. The conclusions of the authors agree with him. On the other hand, the higher values of the third-order rate constant in conditions close to atmospheric conditions obviously are caused by the catalytic effect of the walls of the reaction vessel. The data on the kinetics of catalytic oxidation of NO with oxygen [203, 206, 220] and also the data obtained by Guillory [221] indicate such a possibility. Guillory indicates that the order of reaction (1.60) is equal to two with relationship to NO if $P_{NO} \geq 0.2$

mm Hg, and to one if $P_{NO} < 0.2$ mm Hg. It is known, however, that the decrease in the order of the reaction in the transition to the region of low temperatures and pressures characterizes the transition from a homogeneous reaction to a reaction at the surface. The fact that the contribution of the heterogeneous reaction becomes noticeable only in the region of very low pressures of NO ($P_{NO} < 0.02$ mm Hg) confirms the conclusions of Bodenstein and his coworkers [186, 187, 256], that the oxidation of NO with oxygen is essentially a homogeneous process.

The effect of secondary processes, distorting the kinetics of reaction (1.60), as follows from the data in Table 1.8 and the data in refs. [186, 187,191,192], is less significant in conditions when the pressure of the NO and O_2 is of the order of 10 mm Hg or higher. In these conditions the reaction of the oxidation of NO with oxygen precisely follows the third-order kinetics. The temperature dependence of the rate constant of the third-order reaction, constructed according to the data obtained by authors of refs. [186,187,191, 208], is presented in Fig. 1.7.

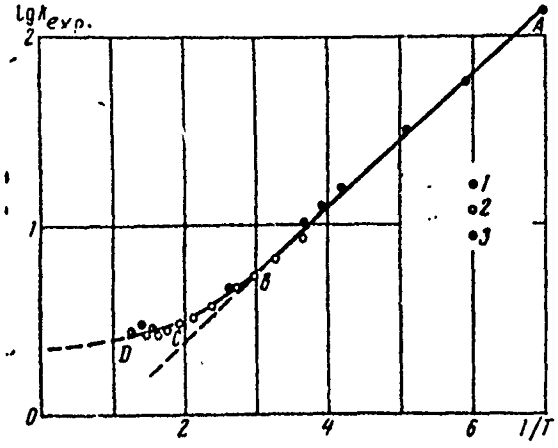


Figure 1.7. Temperature dependence of the rate constant of the reaction $2NO+O_2 \rightarrow 2NO_2$ (1- Matthes' data [38]; 2- Bodenstein's data [57]; 3- data obtained by Ashmore, Barnett, and Tyler [58]).

We may see that the experimental results of different authors lie on the same curve, the slope of which varies with the growth of temperature. We have established the fact that the experimental data of the authors of [186, 187,

Table 1.8 Third-order rate constants of the reaction $2NO + O_2 \rightarrow 2NO_2$

T, °K	P_{NO}, мм Hg	P_{O_2}, мм Hg	P_{NO_2}, мм Hg	P_{N_2}, мм. Hg	P_{H_2O}, мм Hg	$\frac{P_{NO}}{P_{O_2}}$	order of reaction with respect to NO	order of reaction with respect to O_2	$k_{1,60}\cdot10^{-3}$ $\frac{л^2}{моль^2сек}$	ref. no.
303,0	10	10	—	—	—	1	2	1	13,24	[186]
298,0	1	5 - 10	—	—	0,5$^{a)}$	0,2--0,05	2,3	0,8	8,0$^{b)}$	[198]
298,0	10	5 -20	—	—	0,5$^{a)}$	2 -0,5	2,3	0,8	7,50$^{c)}$	[198]
298,0	10	5- 20	—	—	0,5$^{a)}$	2--0,5	2	1	13,0$^{b)}$	[198]
298,0	1,66	3,40	—	—	—	0,487	2	1	12,0	[197]
298,0	1—50	1 --50	—	—	—	0,06	2	1	8,0	[210]
298,0	1—50	1—50	—	—	—	30,0	2	1	14,80	[210]
296,9	243	2,50	—	241	—	97,2	2	1	13,30	[193]
296,9	7,30	696	—	37	—	0,01	2	1	14,80	[193]
298,0	0,109	8,2	—	—	—	1,3 10^{-2}	2	1	15,30	[258]
298,0	0,060	7,9	—	—	—	0,76 10^{-2}	2	1	13,68	[258]
298,0	0,043	8,8	—	—	—	0,49 10^{-2}	2	1	14,78	[258]
298,0	0 0203	10,6	—	—	—	0,19 10^{-2}	2	1	15,60	[258]
298,0	10,6—340	1,06--31	—	—	—	10	2	1	13,92	[209]
298,0	18,4—130	18,4—130	—	—	—	1	2	1	14,84	[209]
298,0	8,1—4,3	81—430	—	—	—	0,1	2	1	14,20	[209]
296,0	0,308 10^{-2}	155	—	605	—	1,99 10^{-5}	2	1	15,90	[200]
296,0	0,304 10^{-2}	155	0,76 10^{-3}	605	—	1,96 10^{-5}	2	1	15,20	[200]
296,0	0,299 10^{-2}	155	1,52 10^{-3}	605	—	1,93 10^{-5}	2	1	15,60	[200]
296,0	0,301 10^{-2}	155	2,28 10^{-3}	605	—	1,96 10^{-4}	2	1	15,10	[200]
293,0	0,118 10^{-1}	210	—	20	—	1,75 10^{-4}	2	1	19,00	[207]
293,0	0,327 10^{-1}	141	—	491	—	2,32 10^{-4}	2	1	20,20	[207]
293,0	0,400 10^{-1}	100	—	530	—	4,00 10^{-4}	2	1	18,20	[207]
293,0	0,350 10^{-1}	54	—	579	—	0,47 10^{-4}	2	1	21,20	[207]
293,0	0,395 10^{-1}	26	—	608	—	1,52 10^{-3}	2	1	20,00	[207]
293,0	0,387 10^{-1}	4	—	623	—	0,97 10^{-2}	2	1	20,00	[207]
293,0	0,380 10^{-1}	0,5	—	608	—	0,77 10^{-4}	2	1	20,00	[207]
293,0	0,380 10^{-1}	135	—	495	2,6	0,37 10^{-4}	2	1	21,00	[207]
293,0	0,380 10^{-1}	135	—	495	4,6	0,37 10^{-1}	2	1	20,80	[207]
298,0	0,02	155	—	605	—	1,29 10^{-4}	2	1	—	[211]
298,0	0,02	155	—	605	—	1,29 10^{-4}	1	1	—	[211]
309,0	0,228 10^{-2}	150	—	610	—	1,50 10^{-5}	2	1	30--40	[216]

a) absence of the effect of water vapor if $P_{H_2O} < 0.5$ mmHg; and catalytic effect of $P_{H_2O} > 0.5$ mm Hg;

b) degree of completion of the reaction exceed 25%;

c) degree of completion of the reaction less than 25%.

191, 208] in coordinates (lg k - lg T) from 1/T lie on a straight line passing through the beginning of the coordinates (see Fig. 1.8).

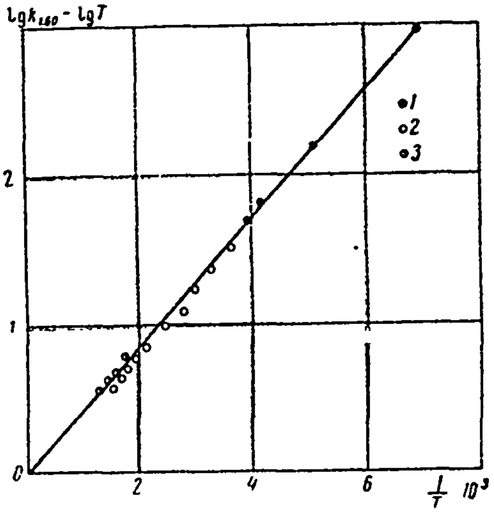


Figure 1.8. Temperature dependence of the third-order rate constant $2NO+O_2 \rightarrow 2NO_2$ (data obtained by: 1- Matthes [208]; 2- Bodenstein and co-workers [186,187]; 3- Ashmore, Barnett, and Tyler [191].

The equation of this straight line has the form

$$k_{1.60}^{emp} = 2T \exp(B/RT), \qquad (1.62)$$

where B = 1.925 kcal/mole, so that

$$k_{1.60}^{emp} = 2T \exp(1.925/RT) \ l^2/mole^2/s. \qquad (1.63)$$

The constant B, entering into the last expression, is determined from the slope of the dependence (lg $k_{1.60}$ - lg T) upon 1/T.

In Table 1.9 for comparison the experimental values of the third-order rate constant established in refs. [186,187,191,208] and the magnitude calculated according to expression (1.63) are presented for comparison.

From Table 1.9 it follows that within the limits of experimental data determined in some conditions, the absolute deviation $\Delta k = k_{1.60}^{exp} - k_{1.60}^{emp}$

preserves one sign. The results of Bodenstein and his co-workers [186, 187] give negative values of Δk, the results of Ashmore and his co-workers [191] and Matthes [208] give positive values of Δk. It is not clear whether such a behavior of the magnitude of Δk is caused by systematic errors of the experimental methods or by the contribution of the walls and impurities of foreign matter manifested differently in the experiments of different authors.

Table 1.9 Temperature dependence of the rate constant of the reaction $2NO + O_2 \rightarrow 2NO_2$.

T	$k^{exp}_{1.60}$	$k^{emp}_{1.60}$	$k^{exp}_{1.60} - k^{emp}_{1.60}$	$\frac{k^{exp}_{1.60} - k^{emp}_{1.60}}{k^{exp}_{1.60}}$	ref. no.
°K	10^{-3} л²моль⁻²сек⁻¹			—	—
143,0	270,00	279,00	−9,00	0,032	[208]
169,0	115,60	101,60	11,80	0,113	[208]
195,0	62,60	56,40	6,20	0,110	[208]
238,0	31,60	27,70	3,90	0,142	[208]
251,0	25,20	23,00	2,20	0,078	[208]
273,0	20,80	16,92	1,88	0,052	[208]
273,0	17,90	18,92	−1,02	0,054	[186]
303,0	14,16	14,76	−0,60	0,041	[186]
333,0	11,03	12,16	−1,08	0,0[illegible]	[185]
363,0	9,00	10,42	−1,42	0,1[illegible]	[186]
377,4	9,90	9,84	0,006	0,006	[191]
414,0	7,94	8,62	−0,70	0,088	[187]
470,0	6,68	7,36	−0,68	0,092	[187]
514,0	6,08	6,76	−0,68	0,010	[187]
564,0	5,68	5,94	−0,56	0,090	[187]
573,0	7,00	6,20	+0,80	0,129	[191]
613,0	5,68	5,94	−0,26	0,440	[187]
633,0	5,82	5,82	0	0	[191]
662,0	5,08	5,72	−064	0,112	[187]
692,0	5,92	5,60	+032	0,057	[191]
779,0	5,70	5,40	+030	0,056	[191]

The maximum value of the relative deviation $k/k_{1.60}$ is of the order of 0.15 and, consequently, the maximum error of the values of the rate constant calculated according to expression (1.63) does not exceed 15%. The mean relative deviation, as follows from the data in Table 1.9, amounts to a magnitude of the order of 10%.

By means of expression (1.63) we will calculate the value of the activation energy of reaction (1.60).

By substituting into the equation

$$E = 4{,}57\,\frac{T_1T_2}{T_2-T_1}(\lg k_2-\lg k_1), \tag{1.64}$$

the values of the rate constant calculated according to (1.63), with k_2 and k_1 indicating the values of the rate constant at temperatures T_2 and T_1 in equation (1.64), we obtain the following ratio:

$$E = 4{,}57\,\frac{T_1T_2}{T_2-T_1}(\lg T_2-\lg T_1)-1925. \tag{1.65}$$

The values of the activation energy $E_{1.60}$, calculated according to the last ratio, are presented in Table 1.10.

Table 1.10 Activation energy of the reaction $2NO + O_2 \rightarrow 2NO_2$

$T_2 - T_1$	$E_{1.60}$	$T_2 - T_1$	$E_{1.60}$
°K	kcal/mole	°K	kcal/mole
150—200	—1,59	500—550	—0,88
200—250	—1,48	550—600	—0,78
250—300	—1,38	600—650	—0,68
300—350	—1,28	650—700	—0,58
350—400	—1,18	700—750	—0,48
400—450	—1,08	750—800	—0,38
450—500	—0,99	—	—

As follows from the data in Table 1. 0, the activation energy of reaction (1.60) in the temperature range of 150-800°K increases from -159 to -0.38 kcal/mole.

We will consider the possible reasons for the negative temperature dependence of the rate constant and the variation of the apparent activation energy calculated according to equation (1.65).

Two opposite points of view are known in the explanation of the negative temperature coefficient of the rate of the given process.

Bodenstein [187], who assumed that the oxidation of NO by oxygen is an elementary trimolecular reaction, explained the temperature dependence of the rate constant by working from the assumption that with a growth in temperature the number of triple collisions Z_3 decreases.

The erroneousness of this assumption was proved by Tolman [259], who calculated the number of triple collisions Z_3 on the basis of a simple gasokinetic theory. According to Tolman, $Z_3 \sim T$, i.e., it grows slightly with a growth of temperature [207].

Thus, a simple theory of collisions is in no position to explain the kinetics of reaction (1.60) even qualitatively.

Kassel' [260] attempted to improve the conclusions of gasokinetic theory on the basis of consideration of the intermolecular reactions in a real gas. The latter obtained a negative temperature dependence for a number of triple collisions. It is true that there is a serious objection to Kassel's theory. This theory presuppose the effect of the inert gases, which, however, is not confirmed by experimental data [186]. The absence of the effect of the inert gases on the rate of reaction (1.60) makes the conclusions of the author indicated unconvincing.

The given problem has been solved more successfully on the basis of the theory of absolute rates of the reactions. Hershinourts and Eyring [261] calculated the rate constant, assuming that the activated complex has a rectangular configuration

$$\begin{array}{ccccc} O & \cdots & N & \cdots & O \\ & & & & \vdots \\ O & \cdots & N & \cdots & O \end{array}$$

As the oscillatory frequencies of the activated complex, the corresponding frequencies of the N_2O_4 molecules in the gaseous phase were selected. In the calculations it was assumed that the activation energy is equal to zero. The values of the rate constant calculated in these conditions have a negative temperature dependence and agree with the experimental data determined in refs. [186, 187, 208] with respect to order of magnitude.

The result obtained by Hershinourts and Eyring [261] give the opportunity to consider reaction (1.60) as an elementary process with a zero activation energy and a pre-exponential factor decreasing with the growth of temperature. The authors of refs. [262, 263], for example, hold this point of view.

The opposite approach in the explanation of the kinetics of the reaction $2NO + O_2 \rightarrow 2NO_2$ was proposed by Förster and Blich [264].

These authors demonstrated that the negative temperature dependence of the third-order rate constant may be explained on the basis of the following two-stage mechanism:

$$NO + O_2 \rightleftharpoons NO \cdot O_2, \qquad (1.66)$$

$$NO \cdot O_2 + NO \rightarrow 2NO_2, \qquad (1.67)$$

where the first stage occurs in a quasi-equilibrium manner and the second with a measurable rate.

In this case the rate equation is written thus

$$\frac{d(NO_2)}{dt} = k_{1.67}(NO \cdot O_2)(NO). \qquad (1.68)$$

The concentration of the intermediate compound $NO \cdot O_2$ is determined from the condition of equilibrium of reaction (1.61) with respect to the ratio

$$(NO \cdot O_2) = K_{1.66}(NO)(O_2), \qquad (1.69)$$

where $K_{1.66}$ is the constant of equilibrium.

With a consideration of expression (1.69) the rate equation (1.68) takes the form

$$\frac{d(NO_2)}{dt} = k_{eff}(NO)^2(O_2), \qquad (1.70)$$

where

$$k_{eff} = k_{1.67}K_{1.66}. \qquad (1.71)$$

The apparent activation energy in this case is determined by the ratio

$$E_{eff} = \Delta H_{1.66} + E_{1.67}. \qquad (1.72)$$

Here $\Delta H_{1.66}$ is the thermal effect of the formation of the intermediate compound $NO \cdot O_2$, and $E_{1.67}$ is the activation energy of the limiting stage (1.67). If reaction (1.66) occurs with a liberation of heat and the condition $|\Delta H_{1.66}| > E_{1.67}$ is fulfilled, the apparent activation energy E_{eff} will have a negative value.

The effective rate constant in this case will be decreased with a growth of temperature.

Trautz [265] proposed an analogous two-stage mechanism with the participation of the intermediate compound N_2O_2:

$$NO + NO \rightleftharpoons N_2O_2, \qquad (1.73)$$

$$N_2O_2 + O_2 \rightarrow 2NO_2. \qquad (1.74)$$

Trautz's mechanism also leads to third-order kinetics, if reaction (1.73) occurs in a quasi-equilibrium manner, and reaction (1.78) with a measurable rate.

Thus, we may explain, with equal success, the negative temperature dependence of the third-order rate constant on the basis of the proposition of an elementary reaction and also on the basis of the assumption of a complex mechanism.

The variation of the activation energy of reaction (1.60) in the first case, in accordance with the conclusions of Hershinourts and Eyring [261], should be explained by the temperature dependence of the pre-exponential factor.

In the second case the variation of the activation energy of reaction (1.60) may be caused by the temperature dependences of the heat of formation of the intermediate compound and the activation energy of the limiting stage.

However, we may bring serious objections against the interpretation of the data with respect to the kinetics of the oxidation of NO by oxygen.

The essence of this objection lies in the following. We may calculate the third-order rate constant according to the ratio

$$k_{1.60}^{cal} = k_{-(1.60)}/K_{c2} \qquad (1.75)$$

where $k_{-(1.60)}$ is the rate constant of the thermal dissociation of NO_2 when $P_{NO} \leq P_{NO_2}$, K_{c2} is the constant of equilibrium expressed in concentration units.

In a case of an elementary occurrence of reaction (1.60), the fact that the latter ratio can be fulfilled is beyond doubt.

However, it is easy to demonstrate the fact that this ratio can be fulfilled also for a case when reaction (1.60) occurs according to a two-stage mechanism with a pre-equilibrium stage of the formation of an intermediate compound. For an example we will consider a scheme proposed in the work of Förster and Blich [264].

The equation of the rate of the reversible reaction $2NO_2 \rightleftarrows NO\ O_2 + NO$ is written thus:

$$-\frac{d(NO_2)}{dt} = k_{-1.67}(NO_2)^2 - k_{1.67}(NO \cdot O_2)(NO). \qquad (1.76)$$

With a consideration of expressions (1.69) and (1.71), from this we obtain

$$-\frac{d(NO_2)}{dt} = k_{-1.67}(NO_2)^2 - k_{eff}(NO)^2(O_2). \qquad (1.77)$$

At equilibrium $d(NO_2)/dt = 0$, so that

$$\frac{k_{-1.67}}{k_{eff}} = \frac{(NO^2)(O_2)}{(NO_2)} \equiv K_{c2}. \tag{1.78}$$

On the basis of the latter ratio we obtain

$$k_{eff} = k_{-167}/K_{c2}. \tag{1.79}$$

Here $k_{-1.67}$ is the rate constant of the limiting stage of the thermal decomposition of NO_2 according to the two-stage mechanism, i.e., the experimentally established rate constant of the reaction

With a consideration of the latter remark we may write

$$k^{cal}_{1.60} = k_{eff} = (k_{-1.60}/k_{c2}). \tag{1.80}$$

The values of the third-order rate constant calculated according to expression (1.80) are presented in Table 1.11.

In the calculations, as the rate constant $k_{-1.60}$ a rate constant was selected as determined by the expression $k_{-1.60} = k_{1.29} = 10^{9.6} \exp(-26900/RT)$ l/mole/s.

The equilibrium constant K_{c2} was calculated according to the ratio

$$K_{c2} = K_{p2}/R_1T,$$

where K_{p2} is an equilibrium constant expressed in units of pressure (atmospheres).

The temperature dependence of K_{p2} is described by the polynomial

$$\begin{gathered} \times T^{-1} + 17{,}5121 - 0{,}3079\cdot 10^{-4}T - \\ - 1{,}6017\ 10^{-8}T^2 - 0{,}1183\cdot 10^{-12}T^3. \end{gathered} \tag{1.81}$$

Table 1.11 Specific rate of the reaction $2NO + O_2 \rightarrow 2NO_2$ upon condition that $P_{NO} \geq P_{NO_2}$

T	$k^{emp}_{1.60}$	$k^{cal}_{1.60}$	$k^{emp}_{1.60} - k^{cal}_{1.60}$	$\left\| k^{emp}_{1.60} - k^{cal}_{1.60} \right\| \cdot 100$
°K	10^{-3} ℓ^2 mole^{-2} sec^{-1}			%
300	15,18	3,82	11,36	296,0
400	9,02	4,26	4,76	116,0
500	6,80	4,50	2,30	51,0
573	6,22	4,70	1,52	32,0
600	6,02	4,80	1,22	25,0
700	5,58	5,12	0,46	9,0
800	5,36	5,46	—0,10	2,0
900	5,28	5,78	—0,50	9,0
1000	5,28	5,28	—1,00	19,5

This polynomial is suitable for the calculation of the values of K_{p2} in the temperature range of 300-1000°K for an ideally (perfect) gaseous state [2].

As follows from Table 1.11, the values of the rate constant $k^{cal}_{1.60}$, calculated according to expression (1.80), increase as the temperature rises, i.e., even a qualitative agreement with the quantities determined according to expression (1.63) is lacking.

The divergence in the values of the rate constants $k^{cal}_{1.60}$ and $k^{exp}_{1.60}$ cannot be caused by errors in calculation. The following agruments speak in favor of this given affirmation.

Experimental data are available on the oxidation of NO in the temperature range of 143-800°K [186, 187, 191, 208]. Reliable data on the decomposition of NO_2 were obtained in the temperature range 573-1020°K [57-59, 248].

At T = 573°K, according to Ashmore and his co-workers [58],

$$k_{-1.60} = k_{1.59} = 10^{0.60 \pm 0.04} \exp\left(-\frac{26900 \pm 100}{RT}\right) g \cdot mole^{-1} sec^{-1}, \qquad (1.82)$$

which gives an error in the value of $k_{-1.60}$ that is equal to 2%. The error of K_{p2}, obviously, is of the same order of magnitude. The error of values of $k^{exp}_{1.60}$ calculated according to expression (1.63) is no greater than 15%.

Consequently, the permissible divergence between $k_{1.60}^{exp}$ and $k_{1.60}^{cal}$, caused by inaccuracy of the values of $k_{-1.60}$, K_{p2}, and $k_{1.60}^{exp}$ at T = 573°K must not exceed 20%. However, as we may see from Table 1.11, this divergence amounts to 32%.

More significant is the fact that a definite dependence upon temperature exists in the ratio of the rate constants $k_{1.60}^{cal}$ and $k_{1.60}^{exp}$. In the temperature range of 300-1000°K the quantity $k_{\beta} = k_{1.60}^{cal}/k_{1.60}^{exp}$ is determined by the expression

$$k_{\beta} = 10^{0.362}\exp(-320/RT). \tag{1.83}$$

In Table 1.12 for comparison, the values of the factor k_{β} are given, as determined according to this expression, and as calculated according to the ratio

$$k_{\beta} = k_{1.60}^{cal}/k_{1.60}^{exp}.$$

The coincidence of the values of k_{β} calculated in such a manner indicates the validity of expression (1.83).

The explicitly expressed nature of the temperature dependence of the factor k_{β} and the divergence of the values of $k_{1.60}^{cal}$ and $k_{1.60}^{exp}$, obviously, may be explained only by working from the assumption that the reversible reaction

$$2NO + O_2 \underset{k_{-1.60}}{\overset{k_{1.60}}{\rightleftharpoons}} 2NO_2$$

at stages that are not very close to completion occurs simultaneously, along at least two reaction channels.

The channel which gives the basic contribution in the region of high temperatures obviously corresponds to the thermal dissociation of NO_2 with a rate constant determined by expression (1.29). In particular, the coincidence of the values of $k_{1.60}^{cal}$ and $k_{1.60}^{exp}$ at T > 600°K indicates this. With a rise in temperature the rate constant of the high-temperature channel of the oxidation of NO by oxygen increases.

The second reaction channel has a negative temperature dependence of the rate of the reaction. The contribution of this channel has a greater value in the region of low temperatures, so that at T < 300°K the oxidation of NO by oxygen occurs basically along the second reaction channel. This note may be used for estimation of the activation energy $E_{\text{low temp.}}$ and the pre-exponential factor $A_{\text{low temp.}}$ of the low-temperature mechanism of reaction (1.60).

Table 1.12 Temperature dependence of the ratio of the rate constant $k_{1.60}^{\text{emp}}$ and $k_{1.60}^{\text{cal}}$

T, °K	300	400	500	573	600	700	800	900	1000
k'_{β}	0,252	0.463	0.662	0,767	0.800	0,918	1,02	1,09	1,19
k''_{β}	0,252	0,438	0,611	0,715	0;762	0,890	1,01	1,09	1,18

At T = 143°K, according to Matthes [208], the value of $k_{1.60}$ is equal to $1.35\ 10^3\ 1^2\text{mole}^{-2}\text{sec}^{-1}$. At T = 300°K the value of $k_{1.t}$ determined from the ratio

$$k_{\text{low temp.}} = k_{1.60}^{\text{exp}} - k_{1.60}^{\text{cal}} \tag{1.84}$$

is equal to $5.65\ 10^3\ 1^2\text{mole}^{-2}\text{sec}^{-2}$. According to these magnitudes we determine

$$k_{1.t} = 10^{2.53} \exp(1700/RT)\ 1^2\text{mole}^{-2}\text{s}^{-1}. \tag{1.85}$$

We cannot explain the temperature dependence of the rate constant $k_{1.t}$ by working from the assumption that $E_{1.t} = 0$, and $A_{1.t}$ is decreased as the temperature rises, i.e., on the basis of the assumptions of Hershinourts and Eyring [261].

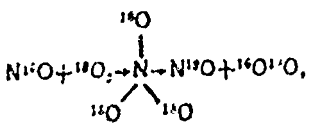
In the latter case we had to assume that the normal temperature dependence of the rate has a complex process, giving the basic contribution in region of high temperatures, since the two reaction channels with positive and negative dependences of the rates of the reaction cannot be elementary simultaneously.

On the other hand, we may assume that both these reaction channels occur complexly or that in the region of high temperatures the reaction occurs in an elementary manner, and in the region of low temperatures in a complex manner.

We will investigate these possibilities in more detail. As follows from a consideration of the mechanisms proposed by Förster and Blich [264], and also by Trautz [265], two-stage mechanisms with pre-equilibrium stages of the formation of intermediate compounds give a negative temperature dependence of the rate constant and the third-order kinetics. We may obtain the third-order kinetics and a positive temperature dependence of the rate of the reaction in a similar manner on the basis of mechanisms (1.66-1.67) and (1.73-1.74).

It is easy to demonstrate that at stages that are not very close to completion only intermediate compounds N_2O_2 and the perioxy radical O_2NO may participate in reaction (1.60).

In the discussion of the thermal dissociation of NO_2 it was noted that the contribution NO_3 in the nitrate structure is negligible at comparable concentrations of NO and NO_2. On the basis of the principle of microscopic reversibility from this it follows that in the reaction $2NO + O_2 \rightarrow 2NO_2$ this intermediate compound does not play an essential part at stages that are not very close to completion. This proposal is confirmed by data on isotope exchange. The results of the work of Sharma and his co-workers [266] indicate the absence of molecules $^{16}O^{18}O$ in the system $N^{16}O$ and $^{18}O_2$ at $T \sim 300°K$, which indicates the absence of the reaction



$$N^{16}O + {}^{18}O_2 \rightarrow N({}^{18}O)({}^{18}O)({}^{16}O) \rightarrow N^{18}O + {}^{16}O^{18}O, \qquad (1.86)$$

i.e., the low probability of the formation of the nitrate radical NO_3.

According to Ray and Ogg [217], the NO_3 in the nitrate form is formed according to the reaction

$$O_2+NO+NO_2 \rightleftharpoons NO_3+NO_2, \quad (1.87)$$

$$NO_3+NO \rightarrow 2NO_2. \quad (1.88)$$

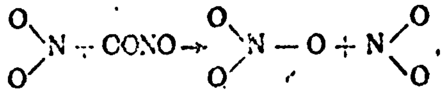
At T ~ 300°K the value of the rate constant $k_{1.87}$ corresponding to the equation

$$\frac{d(NO_3)}{dt} = k_{1.87}(NO)(O_2)(NO_2), \quad (1.89)$$

is equal to $1.36 \cdot 10^2$ $l^2 mole^{-2} s^{-1}$. According to the data of Bodenstein and Wachenheim [186], the third-order rate constant $k_{1.60}$ at T ~ 300°K amounts to $14.16 \cdot 10^3$ $l^2 mole^{-2} s^{-1}$. From a comparison of the values of the rate constant $k_{1.60}$ and $k_{1.87}$ it follows that the channel with the participation of the nitrate radical NO_3 competes with reaction (1.60) only at the concluding stages of the oxidation of NO.

The following fact attracts attention to itself. The NO_3 in the nitrate form is formed according to the reaction $NO + O_2 + M \rightarrow NO_3 + M$ only in a case when the NO_2 molecule is the M molecule. This conclusion may be made on the basis of the data obtained by Sharma and his co-workers [266]. It is clear that the only acceptable explanation of such selectivity of the molecule M may be the explanation based on the assumption that reaction((1.87) is a complex process. A possible mechanism of this reaction, according to Benson [267], is

$$NO + O_2 \rightleftharpoons OONO, \quad (1.90)$$



(1.91)

where OONO is the perioxy radical O_2NO.

We may explain the low efficiency of the direct reaction

qualitatively in the following manner. Obviously the direct reaction of the formation of NO_3 requires the breaking of a very strong bond in the oxygen molecule. The energy barrier in such a reaction must amount to several tens of kilocalories, which makes the occurrence of such a process in the region of low temperatures scarcely probable.

To the contrary, the intermediate compounds N_2O_2 and O_2NO, obviously, are easily formed in the region of low temperatures. We may give a number of experimental data indicating the formation of the dimer N_2O_2 in the gaseous phase. According to the data in refs. [268-270], the heat of the reaction $N_2O_2 \rightleftarrows 2NO$ amounts to about 2 kcal/mole.

Unfortunately there is no direct experimental data relative to the existence of the intermediate compound O_2NO. It is true that there are a number of indirect kinetic data indicating the possibility of the formation of this unstable compound [267].

From the standpoint of the chemical reaction capability the role of the perioxy radical O_2NO in reaction (1.60) is preferable in comparison with the role of the dimer N_2O_2. The limiting stage in the oxidation of NO by oxygen in the first case is

$$O_2\dot{N}O + \dot{N}O \rightarrow \dot{N}O_2, \qquad (*)$$

and in the second case

$$N_2O_2 + O_2 \rightarrow 2NO_2.$$

Here the points over the molecules signify the presence of unpaired electrons.

In a case of the occurrence of the reaction (*) the activation energy may be close to zero, but the heat of the formation of O_2NO amounts obviously to a magnitude of the order of 1-2 kilocalories (as the non-observability of the compound O_2NO requires this). The effective activation energy of reaction (1.60) in this case may have a negative value of 1-2 kcal/mole.

If we accept the fact that reaction (1.60) in the region of low temperatures occurs with the participation of N_2O_2, then considering the fact that the heat of the formation of N_2O_2 is about 2 kcal/mole [268-270], i.e., a magnitude comparable with the effect activation energy of the total process, it is necessary to admit that the activation energy in the reaction between the valently saturated molecule N_2O_2 and the chemically low-active molecule O_2 [271] must have a value that is close to zero, which is scarcely probable.

We note that in the complex mechanism of the type described by Förster and Blick and by Trautz a negative temperature dependence may be obtained only from stabilized intermediate compounds, formed according to the reactions

$$O_2 + NO \rightleftharpoons O_2NO^{I},$$

$$O_2NO^{I} + M \rightleftharpoons O_2NO + M$$

and

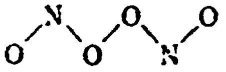
$$NO + NO \rightleftharpoons N_2O_2^{II},$$

$$N_2O_2^{II} + M \rightleftharpoons N_2O_2 + M,$$

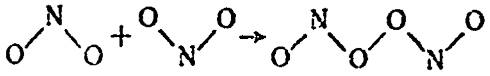
where O_2NO^{I} and $N_2O_2^{II}$ are unstablized quasi-molecules.

Only in this case is the intermediate compound in equilibrium with the reagent, and, consequently, the effective third-order rate constant determined by ratio (1.71) may have a negative temperature dependence.

On the contrary, unstabilized compounds O_2NO^{I} and $N_2O_2^{II}$ may participate in the high-temperature reaction channel of the oxidation of oxygen. The work of Hershbach and his co-workers [272], in which the rate constant for bimolecular composition of NO_2 is calculated, gives some information relative to the high-temperature channel. The latter authors found that the decomposition of NO_2 with an activation energy equal to 26,900 kcal/mole and a pre-exponent equal to $10^{9.6}$ l/mole/s occurs via an activated complex of the following type:



This complex is formed if in the collision the molecules of NO_2 are so oriented that two atoms of oxygen of different molecules are located at the minimum distance, and the two others at the maximum distance, with relationship to each other, i.e.,



The reaction of the oxidation of NO by oxygen in the region of high temperatures, as follows from the principle of microscopic reversibility, must occur via an activated complex of type A. This complex may be formed in the following cases. In the first place, as a result of the simultaneous collision of two molecules of NO and a molecule of O_2; in the second place, in the collision of a molecule of NO with molecules of NO and O_2, located in collision; and in the third place, in the collision of a molecule of NO with an unstabilized quasi-molecule O_2NO.

An activated complex of type A, however, cannot be formed in the collision of a molecule of O_2 with an unstabilized quasi-molecule of $N_2O_2^{II}$, and also in the collision of a molecule of oxygen with two molecules of nitric oxide located in a double collision.

The data from ref. [272] indicate, consequently, the low probability of the occurrence of reaction (1.60) with the participation of an unstabilized quasi-molecule of $N_2O_2^{II}$ also in the region of high temperatures. From this we conclude that the most probable intermediate compound in the reaction of the oxidation of NO by oxygen at stages that are not very close to completion is a compound of NO_3 in the perioxide form.

Chapter II

CALCULATION OF THE THERMODYNAMIC PROPERTIES OF REAL CHEMICALLY REACTING SYSTEMS

It is well known that the thermodynamic properties of real pure gases may be calculated relative to a selected standard state from ordinary differential equations of thermodynamics if the heat content of the gas is known at a very low pressure and its P-V-T data are assigned or in the form of an equation of state or in the form of tables. The thermodynamic properties of gaseous mixtures of constant composition may be calculated relative to the standard state of the mixture according to the same ratios, if the thermal data of the components of the mixture are known, as well as the composition and the data on the compressibility of the mixture. The derivation of these ratios by means of a general limit method for pure gases [67] is given below in order to consider further the possibility of the application of them for calculation of the thermodynamic properties of real chemically reacting systems, for which data on compressibility or the equation of state of the systems as a whole are known.

In this chapter, the partial pressure of the gas in the mixture is the product of its molar fraction in the mixture multiplied by the general pressure of the mixture regardless of whether or not a real or an ideal (perfect) mixture of gases is being considered. The equilibrium pressure of the gas in the mixture is the pressure of this gas in isothermal equilibrium with the mixture through the membrane, penetrable only for this gas alone [232].

In order to distinguish a pure from the same gas in a mixture, the pure gas is designated by the subscript k, and this same gas in a mixture by the subscript i. A pure gas having a common volume, temperature, and chemical potential as in the mixture is designated by the subscript e. Obviously, such a gas is in thermodynamic equilibrium with the mixture through the membrane penetrable only for this gas, and the quantities characteristic for the given gas are "equilibrium quantities." The subscript P denotes the values of the thermodynamic quantities of the pure gas having a general pressure, temperature, and number of moles as in the mixture.

In the derivation, the basic attention is paid to the formulas for the calculation of enthalpy and entropy.

1. The General Limit Method of the Transition for Pure Gases

The procedure called the general limit method by Gillespie [233] assumes that with a decrease in the pressure of a real gas or a mixture of gases at a constant temperature and number of moles, definite thermodynamic properties of a system of real gases approach the ideal gaseous state in a definite manner. By an ideally (perfect) gaseous state of the mixture, we mean such a state of it that the equilibrium pressure of the gas in the mixture is equal to its partial pressure, and the equation of state of the mixture is as follows:

$$PV = \sum_{i=1}^{n} n_i RT,$$

where n_i is the number of moles of the i-th component in the mixture. We will consider two regions of pressures: low pressures, at which the terms of the order of P^2 are negligible in comparison with terms of the order P or one; very low pressures, at which terms of the order of P are negligible in comparison with one.

We will assume: 1) at all temperatures the product of the volume multiplied by the pressure for a fixed mass of a real gas may be presented at a constant temperature in the region of low pressures by the following expression:

$$PV = F(T, m) + A(T, m)P + O(P^2), \tag{2.1}$$

where F(T, m) and A(T, m) for the given gas depend only upon the temperature and the mass, and A(T, m) and its derivatives with respect to temperature are limited, $O(P^2)$ are terms of the order of P^2; and 2) at all temperatures the enthalpy of the fixed mass of the real gas may be presented at a constant temperature in the region of low pressures by the following expression:

$$H = f(T, m) + B(T, m)P + O(P^2), \tag{2.2}$$

where f(T, m) and B(T, m) for the given gas depend only upon the temperature and the mass, and B(T, m) and its derivatives with respect to temperature are limited.

By substituting equations (2.1) and (2.2) into the well-known differential ratio of thermodynamics

$$\left(\frac{\partial H}{\partial P}\right)_T = V - T\left(\frac{\partial V}{\partial T}\right)_P, \tag{2.3}$$

we obtain

$$B + O(P) = \frac{1}{P}\left[F - T\left(\frac{\partial F}{\partial T}\right)_m\right] + \left[A - T\left(\frac{\partial A}{\partial T}\right)_m\right] + O(P).$$

This equation is correct if

$$F - T\left(\frac{\partial F}{\partial T}\right)_m = 0.$$

The integration of this ratio at a constant mass gives

$$F = r(m)T, \tag{2.4}$$

where r(m) depends only upon the mass of the given gas.

Considering this, we obtain from equation (2.1)

$$PV = r(m)\,T + A(T, m) + O(P^2), \tag{2.5}$$

and for the region of very low pressures

$$P^*V^*/rT = 1. \tag{2.6}$$

Since the volume is an extensive quantity, then if in equation (2.6) we replace V by V/m, r becomes a quantity characteristic for each gas. If we express the mass of the given gas in moles, then r will not depend upon the type of gas and we will designate it as R.

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[*] The superscript * everywhere signifies that the quantity is considered at a very low pressure.

Then

$$PV = nRT + \frac{n\beta P}{RT} + O(P^2), \tag{2.7}$$

where n is the number of moles in the volume V and β is a purely temperature function.

In the integration of the differential ratios for the enthalpy and entropy

$$dH = \left(\frac{\partial H}{\partial T}\right)_P dT + \left(\frac{\partial H}{\partial P}\right)_T dP = C_p dT + \left[V - T\left(\frac{\partial V}{\partial T}\right)_P\right] dP,$$

$$dS = \left(\frac{\partial S}{\partial T}\right)_P dT + \left(\frac{\partial S}{\partial P}\right)_T dP = \frac{C_p}{T} dT - \left(\frac{\partial V}{\partial T}\right)_P dP$$

we select the following channel from the point of the standard state (P_0, T_0) to an arbitrary point (P, T): we change the pressure from P_0 to P* at a temperature that is constant and equal to T_0; we change the temperature from T_0 to T at a pressure that is constant and equal to P*; we change the pressure from P* to P at a temperature that is constant and equal to T.

We obtain the following:

$$H(P, T) - H(P_0, T_0) = \int_{T_0 P_0}^{P^*} \left[V - T\left(\frac{\partial V}{\partial T}\right)_P\right] dP + \int_{T_0}^{T} nC_p^* dT + \int_{TP^*}^{P} \left[V - T\left(\frac{\partial V}{\partial T}\right)_P\right] dP, \tag{2.8}$$

$$S(P, T) - S(P_0, T_0) = -\int_{T_0 P_0}^{P^*} \left(\frac{\partial V}{\partial T}\right)_P dP + \int_{T_0}^{T} \frac{nC_p^*}{T} dT - \int_{TP^*}^{P} \left(\frac{\partial V}{\partial T}\right)_P dP. \tag{2.9}$$

In order to ensure that the definite integrals with respect to pressure in formula (2.9) do not diverge when the limit P* tends toward zero, we add the term nR ln(P/P_0) to the integrand expressions and accordingly subtract ln P/P_0 from all the terms. We obtain

$$S(P,\ T)-S(P_0,\ T_0)=\int\limits_{T_0P_0}^{P^*}\left[\frac{nR}{P}-\right.$$

$$\left.-\left(\frac{\partial V}{\partial T}\right)_P\right]dP+\int\limits_{T_0}^{T}\frac{nC_p^*}{T}\,dT+$$

$$+\int\limits_{TP_0}^{P}\left[\frac{nR}{P}-\left(\frac{\partial V}{\partial T}\right)_P\right]dP-nR\ln P/P_0. \qquad (2.10)$$

Let us assume that

$$h^0=h_0^0+\int\limits_{T_0}^{T}C_p^*dT;\ nh_0^0=H(P_0,\ T_0)+$$

$$+\int\limits_{T_0P_0}^{P^*}\left[V-T\left(\frac{\partial V}{\partial T}\right)_P\right]dP; \qquad (2.11)$$

$$S^0=S_0^0+\int\limits_{T_0}^{T}\frac{C_p^*}{T}\,dT;\ nS_0^0=S(P_0,\ T_0)+nR\ln P_0+$$

$$+\int\limits_{T_0P_0}^{P}\left[\frac{nR}{P}-\left(\frac{\partial V}{\partial T}\right)_P\right]dP. \qquad (2.12)$$

From equation (2.2) and ratio $C_p(\delta H/\delta T)_p$ we find that

$$C_p^*=\left(\frac{\partial f}{\partial T}\right)_m+O(P), \qquad (2.13)$$

and, consequently C_p^* is a function of temperature alone.

From equation (2.7) we find that

$$\lim_{P^*\to 0}\int\limits_{P^*}^{0}\left[V-T\left(\frac{\partial V}{\partial T}\right)_P\right]dP=\lim_{P^*\to 0}\int\limits_{P^*}^{0}\left[\frac{nR}{P}-\right.$$

$$\left.-\left(\frac{\partial V}{\partial T}\right)_P\right]dP=0. \qquad (2.14)$$

Definite intetrals with respect to pressure in expressions (2.11) and (2.12) for a standard pressure of 1 atmosphere are small in comparison with

$H(P_0, T_0)$ and $S(P_0, T_0)$ and usually they are ignored.

Considering expressions (2.11)-(2.14), from equations (2.8) and (2.10) we obtain the following:

$$H(P, T) = nh^{\circ} + \int_{0}^{P} \left[V - T\left(\frac{\partial V}{\partial T}\right)_P\right] dP, \tag{2.15}$$

$$S(P, T) = nS^{\circ} + \int_{0}^{P} \left[\frac{nR}{P} - \left(\frac{\partial V}{\partial T}\right)_P\right] dP - nR \ln P, \tag{2.16}$$

where

$$nh^{\circ} = H(P_0, T_0) + n\int_{T_0}^{T} C_p^{\circ} dT,$$

$$nS^{\circ} = S(P_0, T_0) + n\int_{T_0}^{T} \frac{C_p^{\circ}}{T} dT + nR \ln P_0.$$

The equations for the calculation of enthalpy and entropy in coordinate T, V look like the following:

$$H(T, V) = \int_{V} \left[P - T\left(\frac{\partial P}{\partial T}\right)_V\right] dV + PV + ne^{\circ}, \tag{2.17}$$

$$S(T, V) = \int_{V}^{\infty} \left[\frac{nR}{V} - \left(\frac{\partial P}{\partial T}\right)_V\right] dV + nR \ln \frac{V}{nRT} + nS^{\circ}, \tag{2.18}$$

where

$$e^{\circ} = e_0^0 + \int_{T_0}^{T} C_V^{\circ} dT;\quad e_0^0 = h_0^0 - RT_0;\quad S^{\circ} = S_0^0 + \int_{T_0}^{T} \frac{C_V^{\circ}}{T} dT + R \ln \frac{T}{T_0}.$$

2. Calculation of the Thermodynamic Properties of Real Chemically Reacting Systems According to P-V-T Data

The behavior of real chemically reacting systems does not correspond to the assumptions made in the derivation of formulas for calculation of the thermodynamic properties of real pure gases and real mixtures of a constant composition and therefore these formulas cannot be extended to the calculation of the thermodynamic properties of equilibrium real chemically reacting gaseous systems. This affirmation may also be proved by a method that is formal, but clearer. For example, we differentiate formula (2.16) with respect to pressure considering that for an equilibrium chemically reacting system $n = \sum_{(i)} n_i$ depends upon pressure via the constant of equilibrium of the chemical reaction. We obtain the following expression:

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P - \left(\frac{\partial n}{\partial P}\right)_T R \ln P/P_0 .$$

And since

$$\left(\frac{\partial n}{\partial P}\right)_T \neq 0,$$

then one of the general differential ratios of thermodynamics is violated

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P,$$

which also proves the affirmation.

We will derive ratios for calculation of the thermodynamic properties of a real gaseous mixture in which an equilibrium chemical reaction occurs as follows: $\nu_1 R_1 + \nu_2 R_2 + \ldots + \nu\nu_k R_k \rightleftarrows \nu_{k+1} R_{k+1} + \ldots + \nu_e R_e$, working from the following assumption: in the region of very low pressures from zero to P* the pressure of the i-th gas in the mixture is equal to its partial pressure; the equation of state of the i-th component in the region of very low pressures is as follows: $P_i^* V^* = n_i^* RT$. For definiteness, we will consider the dissociation reaction (the direct reaction occurs with an increase in the number of moles), and we will limit our derivation to formulas for calculation of the enthalpy and entropy of the thermodynamic under consideration in T, P-coordinates.

In the integration of the differential ratios for the enthalpy and entropy we select the same channel from the point of the standard state of the mixture (P_{om}, T) to an arbitrary point (P, T) as in a case of pure gases. We obtain the following:

$$H(P,T)-H(P_{om},T)=\int\limits_{T_0,\,P_{om}}^{P^*}\left[V-T\left(\frac{\partial V}{\partial T}\right)_P\right]dP+$$

$$+\int\limits_{T_0}^{T}C^*_{pm}dT+\int\limits_{T\,P^*}^{P}\left[V-T\left(\frac{\partial V}{\partial T}\right)_P\right]dP; \qquad (2.19)$$

$$S(P,T)-S(P_{om},T)=-\int\limits_{T_0\,P_{om}}^{P^*}\left(\frac{\partial V}{\partial T}\right)_P dP+$$

$$+\int\limits_{T_0}^{T}\frac{C^*_{pm}}{T}dT-\int\limits_{T\,P^*}^{P}\left(\frac{\partial V}{\partial T}\right)_P\partial P, \qquad (2.20)$$

where C^*_{pm} is the heat content of a chemically reacting system at a constant, very low pressure P^*.

We will determine C^*_{pm} when P^* tends toward zero.

It is well known that the volume, enthalpy, and entropy are extensive properties. For the homogeneous thermodynamic system under consideration, as a consequence of this, they are first-order homogeneous functions of the number of moles of the components. According to the Euler theorem concerning homogeneous functions

$$S=\sum_{(i)}n_i\left(\frac{\partial S}{\partial n_i}\right)_{P,T,n}=\sum_{(i)}n_iS_i; \qquad (2.21)$$

$$H=\sum_{(i)}n_i\left(\frac{\partial H}{\partial n_i}\right)_{P,T,n}=\sum_{(i)}n_iH_i; \qquad (2.22)$$

$$V=\sum_{(i)}n_i\left(\frac{\partial V}{\partial n_i}\right)_{P,T,n}=\sum_{(i)}n_iV_i, \qquad (2.23)$$

where V_i, H_i, and S_i are the partial molar volume, enthalpy, and entropy, respectively, of the i-th component in the mixture.

In the region of very low pressures, according to the assumptions, the partial molar quantities are equal to the corresponding perfect quantities at a temperature of the mixture and at the partial pressures of the components. Therefore,

$$S(P^*, T) = S^* = \sum_{(i)} n_i^\circ S_i^\circ ; \tag{2.24}$$

$$H(P^*, T) = H^* = \sum_{(i)} n_i^\circ H_i^\circ ; \tag{2.25}$$

$$V(P^*, T) = V^* = \sum_{(i)} n_i^\circ V_i^\circ = \sum_{(i)} n_i^\circ \frac{RT}{P_i^\circ}, \tag{2.26}$$

where

$$H_i^\circ = H_i^0 + \int_{T_0}^{T} C_{pi}^\circ dT, \tag{2.27}$$

$$S_i^\circ = S_{i}^0 + \int_{T_0}^{T} \frac{C_{pi}^\circ}{T} dT - R \ln \frac{x_i^\circ P^*}{P_0}, \tag{2.28}$$

and H_i^0, S_i^0 are the standard enthalpy and entropy of the formation of the i-th component, respectively, x_i is the molar fraction of the i-th component in the mixture, P_0 is the standard pressure of the pure gas.

For convince of subsequent formal transformations, we will express n_i and x_i via ξ, the degree of completeness of the reaction:

$$n_i = n_i^0 + \nu_i \xi \text{ для } i = 1, 2, \ldots, к; \tag{2.29}$$

$$x_i = \frac{n_i}{n} = \frac{n_i^0 + \nu_i \xi}{n^0 + \nu \xi}; \tag{2.30}$$

$$n_i = \nu_i \xi \text{ для } i = к + 1, \ldots, c; \tag{2.31}$$

$$x_i = \frac{\nu_i \xi}{n^0 + \nu \xi}, \tag{2.32}$$

where n_i^0 is the initial number of moles of the i-th component, ν_i represents the stoichiometric coefficients of the reaction, which are positive for the reaction products, negative for the initial substances, and $n_0 = \sum_{i=1}^{к} n_i^0$, $\nu = \sum_{i=1}^{c} \nu_i$.

From the condition of conservation of the stoichiometric ratios

$$n_i^0/\nu_i = -1 \quad (i = 1, 2, \ldots, \kappa). \tag{2.33}$$

By considering expressions (2.25), (2.27), (2.29), and (2.31), we obtain

$$\begin{aligned} C^*_{pn} = \left(\frac{\partial H^*}{\partial T}\right)_P = \sum_{i=1}^{c} n^*_i \left(\frac{\partial H^*_i}{\partial T}\right)_P + \sum_{i=1}^{c} H^*_i \left(\frac{\partial n^*_i}{\partial T}\right)_P = \\ = \sum_{i=1}^{\kappa} (n_i^0 + \nu_i \xi) C^*_{pi} + \sum_{i=\kappa+1}^{c} \nu_i \xi C^*_{pi} + \\ + \sum_{i=1}^{c} \nu_i H^*_i \left(\frac{\partial \xi}{\partial T}\right)_P. \end{aligned} \tag{2.34}$$

The equation of the constant of equilibrium of the chemical reaction under consideration is as follows:

$$\begin{aligned} K_P(T) = \prod_{i=1}^{c} (P_i)^{\nu_i} = \prod_{i=1}^{c} (x_i P)^{\nu_i} = P^{\nu} \prod_{i=1}^{c} (x_i)^{\nu_i} = \\ = P^{\nu} \prod_{i=1}^{\kappa} \left(\frac{n_i^0 + \nu_i \xi}{n^0 + \nu \xi}\right)^{\nu_i} \prod_{i=\kappa+1}^{c} \left(\frac{\nu_i \xi}{n^0 + \nu \xi}\right)^{\nu_i}. \end{aligned} \tag{2.35}$$

Having reduced it to logarithms, we obtain

$$\begin{aligned} \ln K_P(T) = \nu \ln P + \sum_{i=1}^{\kappa} \nu_i \ln (n_i^0 + \nu_i \xi) + \\ + \sum_{i=\kappa+1}^{c} \nu_i \ln \nu_i \xi - \nu \ln (n^0 + \nu \xi). \end{aligned} \tag{2.36}$$

Having differentiated equation (2.36) with respect to temperature, after certain transformations we obtain the following expression for $(\delta\xi/\delta T)_P$:

$$\left(\frac{\partial \xi}{\partial T}\right)_P = \frac{\left(\frac{\partial \ln K_P}{\partial T}\right)_P}{\sum_{i=1}^{c} \frac{\nu_i^2}{n_i} - \frac{\nu^2}{n}}. \tag{2.37}$$

But according to the iosbar equation of van't Hoff

$$\left(\frac{\partial \ln K_p}{\partial T}\right)_P = \frac{\Delta H}{RT^2}, \tag{2.38}$$

where $\Delta H = \sum_{i=1}^{c} \nu_i H_i^*$ is the thermal effect of the reaction. From thence,

$$\left(\frac{\partial \xi}{\partial T}\right)_P = \frac{\Delta H}{RT^2} \Big/ \left(\sum_{i=1}^{c} \frac{\nu_i^2}{n_i} - \frac{\nu^2}{n}\right). \tag{2.39}$$

With the tendency of P* towards zero, from equation (2.35) we may obtain the following expression, considering ratio (2.33) and the fact that $\nu > 0$ (the dissociation reaction):

$$\lim_{P^*\to 0} \xi^* = -\frac{n_1^0}{\nu_1} = 1. \tag{2.40}$$

From thence, with consideration of expression (2.[illegible])

$$\lim_{P^*\to 0} \left(\frac{\partial \xi^*}{\partial T}\right)_P = 0. \tag{2.41}$$

From equation (2.34), with consideration of formulas (2.40), (2.33), and (2.41), we obtain

$$\lim_{P^*\to 0} C_{pm}^* = \sum_{i=K+1}^{c} \nu_i C_{pi}^*. \tag{2.42}$$

We will now demonstrate that when P* tends toward zero, the definite integrals with respect to pressure in formula (2.20), as in a case of pure gases, diverge at the limit P*.

We will consider a perfect chemically reacting system, i.e., a chemically reacting system for which equations (2.24)-(2.28) are fulfilled in the entire region of the variation of the pressure. For such a system, considering equalities (2.26), (2.29), and (2.31), we obtain

$$\left(\frac{\partial V}{\partial T}\right)_P^{u^*} = \frac{1}{P}\sum_{i=1}^{c} n_i R + \frac{RT}{P}\sum_{i=1}^{c}\left(\frac{\partial n_i}{\partial T}\right)_P = \frac{nR}{P} + \frac{\nu RT}{P}\left(\frac{\partial \xi}{\partial T}\right)_P. \tag{2.43}$$

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*The subscript u signifies a quantity for a perfect chemically reacting system.

If we consider equation (2.39), expression (2.43) is rewritten thus:

$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{nR}{P} + \frac{\nu \Delta H}{PT\left(\sum_{i=1}^{c} \frac{\nu_i^2}{n_i} - \frac{\nu^2}{n}\right)}. \tag{2.44}$$

We will consider the partial derivative with respect to pressure from the following quantity:

$$S_m = R \sum_{i=1}^{c} n_i \ln x_i P. \tag{2.45}$$

With a consideration of formulas (2.29) and (2.31)

$$\left(\frac{\partial S_m}{\partial P}\right)_T = R \sum_{i=1}^{c} \frac{n_i}{x_i} \left(\frac{\partial x_i}{\partial P}\right)_T + R \sum_{i=1}^{c} \nu_i \left(\frac{\partial \xi}{\partial P}\right)_T \ln x_i P + \frac{nR}{P}. \tag{2.46}$$

From equations (2.30) and (2.32) we obtain

$$\left(\frac{\partial x_i}{\partial P}\right)_T = \frac{\nu_i n^0 - \nu n_i^0}{n^2} \left(\frac{\partial \xi}{\partial P}\right)_T \quad (i = 1,\ 2,\ \dots,\ \kappa); \tag{2.47}$$

$$\left(\frac{\partial x_i}{\partial P}\right)_T = \frac{\nu_i n^0}{n^2} \left(\frac{\partial \xi}{\partial P}\right)_T \quad (i = \kappa + 1,\ \dots,\ c). \tag{2.48}$$

Having substituted equalities (2.47) and (2.48) into formula (2.46), and considering that $x_i = n_i/n$,

$$\left(\frac{\partial S_m}{\partial P}\right)_T = R \sum_{i=1}^{\kappa} \frac{(\nu_i n^0 - n_i^0 \nu)}{n} \left(\frac{\partial \xi}{\partial P}\right)_T + R \sum_{i=\kappa+1}^{c} \frac{\nu_i n^0}{n} \left(\frac{\partial \xi}{\partial P}\right)_T + R \left(\frac{\partial \xi}{\partial P}\right)_T \sum_{i=1}^{c} \nu_i \ln x_i P + \frac{nR}{P}. \tag{2.49}$$

By carrying $(R/n)(\delta\xi/\delta P)_T$ from the first two terms we obtain

$$\sum_{i=1}^{\kappa} (\nu_i n^0 - n_i^0 \nu) + \sum_{i=\kappa+1}^{c} \nu_i n^0 \quad \nu n^0 - \nu n^0 = 0. \tag{2.50}$$

The third term of (2.49), with consideration of expression (2.35), looks like the following:

$$R\left(\frac{\partial\xi}{\partial P}\right)_T \sum_{i=1}^{c} \nu_i \ln x_i P = R\left(\frac{\partial\xi}{\partial P}\right)_T \ln K_p(T). \tag{2.51}$$

and from thence, by using the well-known ratio

$$\ln K_p(T) = \frac{\Delta S}{R} - \frac{\Delta H}{RT}, \tag{2.52}$$

where $S = \sum_{i=1}^{c} {}_i[S_i^0 + \int_{T_0}^{T} C^*_{pi}(dT/T)]$, the variation of the entropy of the progress of the reaction, we obtain the following

$$R\left(\frac{\partial\xi}{\partial P}\right)_T \sum_{i=1}^{c} \nu_i \ln x_i P = \Delta S\left(\frac{\partial\xi}{\partial P}\right)_T - \frac{\Delta H}{T}\left(\frac{\partial\xi}{\partial P}\right)_T. \tag{2.53}$$

Having substituted equation (1.53) into formula (2.49), and considering identity (2.50), we obtain

$$\left(\frac{\partial S_m}{\partial P}\right)_T = \Delta S\left(\frac{\partial\xi}{\partial P}\right)_T + \frac{nR}{P} - \frac{\Delta H}{T}\left(\frac{\partial\xi}{\partial P}\right)_T. \tag{2.54}$$

Having differentiated equation (2.36) with respect to pressure, after certain transformations we obtain the following expression for $(\delta\xi/\delta P)_T$:

$$\left(\frac{\partial\xi}{\partial P}\right)_T = -\frac{\nu}{P\left(\sum_{i=1}^{c}\frac{\nu_i^2}{n_i} - \frac{\nu^2}{n}\right)}. \tag{2.55}$$

Having substituted equality (2.55) into the last term of equation (2.54), we obtain

$$\left(\frac{\partial S_m}{\partial P}\right)_T = \Delta S\left(\frac{\partial\xi}{\partial P}\right)_T + \frac{nR}{P} + \\ + \frac{\nu\Delta H}{PT\left(\sum_{i=1}^{c}\frac{\nu_i^2}{n_i} - \frac{\nu^2}{n}\right)}. \tag{2.56}$$

By comparing the two last terms of expression (2.56) with equation (2.44), we may obtain the following:

$$\left(\frac{\partial S_m}{\partial P}\right)_T = \Delta S\left(\frac{\partial\xi}{\partial P}\right)_T + \left(\frac{\partial V}{\partial T}\right)_P''. \tag{2.57}$$

From thence

$$\left(\frac{\partial V}{\partial T}\right)^u_P = \left(\frac{\partial S_m}{\partial P}\right)_T - \Delta S\left(\frac{\partial \xi}{\partial P}\right)_T, \tag{2.58}$$

and consequently,

$$\int_{P_1}^{P_2}\left(\frac{\partial V}{\partial T}\right)^u_P dP = [S_m(P, T) - \Delta S\xi(P, T)]|_{P_1}^{P_2}. \tag{2.59}$$

In the region of very low pressures, a real chemically reacting system becomes perfect according to the assumption, and any of the definite integrals with respect to pressure in equation (2.20) at the limit P* may be taken according to formula (2.59).

By considering expression (2.40), we obtain the following from equality (2.45):

$$\lim_{P^*\to 0}[S_m(P^*, T) - \Delta S\xi^*] = \infty.$$

Thus, when P* tends toward zero, the definite integrals with respect to pressure in formula (2.20) diverge. In the first section a method was described which was proposed in ref. [233], by means of which in a case of pure gases and mixtures of constant composition the authors succeeded in avoiding the divergability of the integrals. For this the terms nR/P were added to the integrand expressions so that when P* tends toward zero, when the volume of the real pure gas approaches the volume of the perfect gas, $(\partial V/\partial T)_P$ of a real pure gas approaches nR/P and the integrand expressions tend toward zero, excluding the diversability.

This method in a case of the calculation of the entropy of chemically reacting systems does not lead to a positive result, although it does give the possibility of avoiding the divergability of the integrals. In the region of very low pressures, considering expression (2.43)

$$\frac{nR}{P} - \left(\frac{\partial V}{\partial T}\right)^u_P \approx -\frac{\nu RT}{P}\left(\frac{\partial \xi}{\partial T}\right)_P. \tag{2.60}$$

By comparing equation equations (2.37) and (2.55), we obtain

$$-\frac{nRT}{P}\left(\frac{\partial\xi}{\partial T}\right)_P=\frac{\Delta H}{T}\left(\frac{\partial\xi}{\partial P}\right)_T. \tag{2.61}$$

From thence

$$\int_{P_1}^{P_2}\left[\frac{nR}{P}-\left(\frac{\partial V}{\partial T}\right)_P^u\right]dP=\int_{P_1}^{P_2}\frac{\Delta H}{T}\left(\frac{\partial\xi}{\partial P}\right)_T dP=$$

$$=\frac{\Delta H}{T}\xi(P,T)\Big|_{P_1}^{P_2} \tag{2.62}$$

and, consequently, considering expression (2.40),

$$\lim_{P^*\to 0}\left[\frac{\Delta H}{T}\xi^*\right]=\frac{\Delta H}{T}. \tag{2.63}$$

From this it also follows that at P* tending toward zero, the integrals at this limit in formula (2.20) with the transformed integrand expression tend toward a finite value.

But, having added nR/P to the integrand expression, we must subtract the integrals of nR/T from formula (2.20). If in a case of pure gases and mixtures of gases of constant composition the integral from nR/P is selected elementarily, then in a case of chemically reacting systems, when n depends upon the pressure via the constant of equilibrium (2.35), the integral of nR/P in a general case is impossible to select analytically. Therefore, this method is not applicable in a case of the calculation of the entropy of chemically reacting systems.

In this case, the addition of (V/ T)^u_p directly to the integrand expressions gives a positive result. When P* tends toward zero (δV/δT)$_p$ will tend toward (δV*/δT)$_p$, which coincides in this region of pressures with (δV/δT)^u_p, because of which the integrand expressions will tend toward zero, excluding the divergability of the integrals.

Having added (δV/δT)^u_p to the integrand expressions of formula (2.20) and deducting from it the integrals of (δV/δT)^u_p, we obtain

$$
\begin{aligned}
S(P, T) - S(P_{om}, T_0) = {} & \int\limits_{T_0\, P_{om}}^{P^*} \left[\left(\frac{\partial V}{\partial T} \right)_P^u - \left(\frac{\partial V}{\partial T} \right)_P \right] dP + \\
& + \int\limits_{T_0}^{T} \frac{C_{pm}^*}{T} dT + \int\limits_{T\, P^*}^{P} \left[\left(\frac{\partial V}{\partial T} \right)_P^u - \left(\frac{\partial V}{\partial T} \right)_P \right] dP - \\
& - \int\limits_{T_0\, P_{om}}^{P^*} \left(\frac{\partial V}{\partial T} \right)_P^u dP - \int\limits_{T\, P^*}^{P} \left(\frac{\partial V}{\partial T} \right)_P^u dP.
\end{aligned}
\tag{2.64}
$$

We will determine the magnitude of the last two integrals when P* tends toward zero.

Preliminarily, we will make the following comment concerning the standard state of chemically reacting systems. It is well known that a state of the system, or its component, at which indefinite conditions definite values are awarded to certain thermodynamic parameters is called a standard state. For pure gases, a standard state is a state of a perfect gas, i.e., the limit of a real gas with a decrease in the pressure to zero. Since the entropy of a pure gas does not tend toward a constant value at a P tending toward zero, we cannot select the state of a perfect gas at low pressure as the standard state for the entropy of a pure gas. For the standard state for the entropy of pure gases, the entropy of a hypothetical perfect gas is selected, with the assigned pressure of one physical atmosphere. From these definitions it follows that, in the first place, at the standard state point (P_{om},T_0) a chemically reacting system is perfect (ideal), and ratios (2.24) and (2.25) are fulfilled in it, and, in the second place, at the point of the standard state of a chemically reacting system (as, incidentally, also at the point of the standard state of a mixture of constant composition) we must assign a pressure P_0 = 1 atmosphere as the partial pressure of each component. This leads to the fact that for chemically reacting systems at a standard point we cannot use the conventional ratios between the general pressure of the mixture, the partial pressures of the components, and the degree of completeness of the reaction derived from the condition of thermodynamic equilibrium. If, for example, we consider the general pressure of the mixture as equal to the sum of the partial pressures of the components, determine the degree of completeness of the reaction $\xi(P_{om}$, $T_0)$ according to the general pressure of the mixture P_{om} and the temperature of the mixture T_0 from the equation of the constant of equilibrium (2.35), and then, knowing the molar fractions of the components of the mixture, find anew the partial pressures of the components as the product of the molar fraction of the components multiplied by the general pressure of the mixture, they of course will not be equal to each other or to 1 atmopshere. Therefore, we may also assign a value of $P_{om} = P_0 = 1$ atmosphere to the pressure of a chemically reacting system at the standard point. This does not violate the community of the conclusion, since the thermodynamic functions are determined with an accuracy up to the constant.

Considering the well-known ratio

$$\lim_{p\to 0} P \ln P = 0$$

and equations (2.29), (2.32), (2.40), and (2.45), we obtain

$$\begin{aligned}
&\lim_{P^*\to 0}[S_m(T_0, P^*) - S_m(T, P^*)] = \\
&= \lim_{P^*\to 0} R\left\{\sum_{i=1}^{K} n_i(P^*, T_0)\ln\frac{n_i(P^*, T_0)P^*}{n(P^*, T_0)} - \right. \\
&- \sum_{i=1}^{K} n_i(P^*, T)\ln\frac{n_i(P^*, T)P^*}{n(P^*, T)} + \\
&+ \sum_{i=K+1}^{c} \nu_i\xi(P^*, T_0)\ln\frac{\nu_i\xi(P^*, T_0)}{n(P^*, T_0)} - \\
&- \sum_{i=K+1}^{c} \nu_i\xi(P^*, T)\ln\frac{\nu_i\xi(P^*, T)}{n(P^*, T)} + \\
&\left. + \nu_i[\xi(P^*, T_0) - \xi(P^*, T)]\ln P^*\right\} = 0.
\end{aligned} \tag{2.65}$$

With consideration of expressions (2.65), (2.40), and (2.59)

$$\begin{aligned}
&\lim_{P^*\to 0}\left[\int_{T_0\,P_0}^{P^*}\left(\frac{\partial V}{\partial T}\right)_P'' dP + \int_{T\,P^*}^{P}\left(\frac{\partial V}{\partial T}\right)_P'' \partial P\right] = \\
&= \Delta S^0\left[\xi(P_0, T_0) - 1\right] + \Delta S\left[1 - \xi(P, T)\right] - \\
&- S_m(P_0, T_0) + S_m(P, T),
\end{aligned} \tag{2.66}$$

where

$$\Delta S^0 = \sum_{i=1}^{c} \nu_i S_i^0 .$$

Considering the fact that at the standard point equalities (2.24) and (2.25) are fulfilled, by means of ratio (2.33) we obtain

$$H(P_{\text{ст}},\ T_0)=H(P_0,\ T_0)=\sum_{i=1}^{c} n_i(P_0,\ T_0)\,H_i^0=$$
$$=-\sum_{i=1}^{\kappa} \nu_i H_i^0+\sum_{i=1}^{c} \nu_i H_i^0\,\xi(P_0,T_0), \qquad (2.67)$$

$$S(P_{\text{ст}},\ T_0)=S(P_0,\ T_0)=\sum_{i=1}^{c} n_i(T_0,\ P_0)[S_i^0-$$
$$-R\ln x_i(P_0,\ T_0)\,P_0+R\ln P_0]=-\sum_{i=1}^{\kappa}\nu_i S_i^0+$$
$$+\Delta S^0\xi(T_0,\ P_0)-S_m(P_0,\ T_0). \qquad (2.68)$$

Shifting to the limit when P* tends toward zero in formula (2.64), we substitute expressions (2.42), (2.66), and (2.68) into it, and after a number of simplifications we obtain the final formula for the calculation of the entropy of a real chemically reacting system

$$S(P,\ T_i)=-\sum_{i=1}^{\kappa}\nu_i\ S_i^0+\Delta S\xi(P,\ T)-S_m(T,\ P)-$$
$$-\int_{T_0}^{T}\sum_{i=1}^{\kappa}\nu_i\frac{C_{pi}^{*}}{T}dT+\int_{T_0\ P_0}^{0}\left[\left(\frac{\partial V}{\partial T}\right)_P^{\kappa}-\left(\frac{\partial V}{\partial T}\right)_P\right]dP+$$
$$+\int_{T_0}^{P}\left[\left(\frac{\partial V}{\partial T}\right)_P^{\kappa}-\left(\frac{\partial V}{\partial T}\right)_P\right]dP. \qquad (2.69)$$

Making the transition in formula (2.19) to the limit at P* tending toward zero, we substitute equalities (2.42) and (2.67) into it and obtain the final formula for calculation of the enthalpy of a real chemically reacting system

$$H(P,\ T)=-\sum_{i=1}^{\kappa}\nu_i H_i^0+\sum_{i=1}^{c}\nu_i H_i^0\,\xi(P_0,\ T_0)+$$
$$+\int_{T_0}^{T}\sum_{i=\kappa+1}^{c}\nu_i C_{pi}^{*}\,dT+\int_{T_0\ P_0}^{0}\left[V-T\left(\frac{\partial V}{\partial T}\right)_P\right]dP+$$
$$+\int_{T_0}^{P}\left[V-T\left(\frac{\partial V}{\partial T}\right)_P\right]dP. \qquad (2.70)$$

The degree of completeness of the reaction in these formulas is determined at the corresponding parameters via the dependence of an ideal constant of equilibrium of the chemical reaction upon the temperature.

In a similar manner, by using the well-known differential ratios, we may obtain equations for calculation for the other thermodynamic properties.

The formulas derived have a limited application in the calculation of the thermodynamic properties of real chemically reacting systems in view of the fact that usually the P-V-T data of the systems or the equation of state as a whole are known or are in a very narrow range, or are entirely lacking. Therefore, we must turn to other methods of calculation, based on a knowledge of the behavior of the components of the mixtures for which data with respect to compressibility are known to a greater degree, rather than the behavior of the mixtures as a whole. We will consider further the following, most widely distributed approaches to the calculation of the thermodynamic properties of real mixtures: the Gibbs-Dalton law, the Lewis-Randall rule, and the general limit method for mixtures of gases.

3. The Gibbs-Dalton Law

As the basic principle for the investigation of the thermodynamic properties of gaseous mixtures, Gibbs [234] proposed the following law: the pressure of a mixture of various gases is equal to the sum of the pressures of these gases, each existing in itself at the temperature of the mixture and with those values of the chemical potentials which they have in the mixture. Gillespie [235] called this principle the Gibbs-Dalton law, and indicated that it contained the essential idea of equilibrium necessary for a general thermodynamic investigation of gaseous mixtures. It is apparent that various gases, "each existing in itself at the temperature of the mixture and with the same values of chemical potentials which they have in the mixture," are in equilibrium with the gaseous mixture through the membrane penetrable only for the gas under consideration alone. The pressure of each such gas is the equilibrium pressure.

Thus, the law affirms that when

1) T (of each pure gas) = T (of the mixture),
2) V (of each pure gas) = V (of the mixture)
3) $\mu_k = \mu_i$ (2.71)

the pressure of the mixture of gases is

$$P = \sum_{(\kappa)} P_{\text{ск}}. \tag{2.72}$$

The second condition is required only to fix the values of the extensive properties of pure gases.

We will consider a number of systems: a mixture of gases and each individual pure gas composing the mixture. For the mixture of gases

$$dP = \frac{S}{V}dT + \sum_{(i)} \frac{n_i}{V} d\mu_i$$

and for each individual gas

From thence

$$\left(\frac{\partial P}{\partial \mu_i}\right)_{T,\mu} = \frac{n_i}{V} = C_i; \quad \left(\frac{\partial P_{\text{ск}}}{\partial \mu_\kappa}\right)_T = \frac{n_{\text{ск}}}{V} = C_{\text{ск}}; \tag{2.73}$$

$$\left(\frac{\partial P}{\partial T}\right)_\mu = \frac{S}{V}; \quad \left(\frac{\partial P_{\text{ск}}}{\partial T}\right)_{\mu_\kappa} = \frac{S_{\text{ск}}}{V}. \tag{2.74}$$

From equation (2.72)

$$\left(\frac{\partial P}{\partial \mu_i}\right)_{T,\mu} = \left(\frac{\partial P_{\text{ск}}}{\partial \mu_\kappa}\right)_T;$$

$$\left(\frac{\partial P}{\partial T}\right)_\mu = \sum_{(\kappa)} \left(\frac{\partial P_{\text{ск}}}{\partial T}\right)_{\mu_\kappa}.$$

From this, with a consideration of ratios (2.73) and (2.74),

$$n_i = n_{\text{ск}}, \quad C_i = C_{\text{ск}}, \tag{2.75}$$

$$S = \sum_{(\kappa)} S_{\text{ск}}. \tag{2.76}$$

From the equalities

$$H = TS + \sum_{(i)} \mu_i n_i ,$$

$$H_{\text{ск}} = TS_{\text{ск}} + \sum_{(\kappa)} \mu_{\kappa} n_{\text{ск}}$$

with a consideration of expressions (2.71), (2.75), and (2.76),

$$H = \sum_{(\kappa)} H_{\text{ск}} . \qquad (2.77)$$

In the same manner, by using the well-known ratios of thermodynamics and equations (2.71), (2.75), and (2.76), we may obtain the following equality for the isobaric-isothermic potential G of the mixture:

$$G = \sum_{(\kappa)} G_{\text{ск}}. \qquad (2.78)$$

From the Gibbs-Dalton law, it follows obviously that when

1) T (of each pure gas) = T (of the mixture),
2) V (of each pure gas) = V (of the mixture),

$$n_k = n_i \text{ or } C_k = C_i. \qquad (2.79)$$

From thence, with consideration of equality (2.71), it follows that:

$$p = \sum_{(\kappa)} P_{\text{ск}}, \qquad (2.80)$$

$$\mu_i = \mu_{\text{ск}}, \qquad (2.81)$$

$$S = \sum_{(\kappa)} S_{\text{ск}}, \qquad (2.82)$$

$$H = \sum_{(\kappa)} H_{\text{ск}}, \qquad (2.83)$$

$$G = \sum_{(\kappa)} G_{\text{ск}}. \qquad (2.84)$$

Equation (2.20) constitutes the content of the conventional formulation of Dalton's law. Dalton's law is a consequence of the Gibbs-Dalton law, but the reverse is not correct, since in Dalton's law the idea of equilibrium is lacking.

The Gibbs-Dalton law leads to a complete solution of the problem of the determination of the thermodynamic properties of mixtures of gases according to information concerning the behavior of the pure gases constituting the

the mixture. By using equations (2.17), (2.18), derived by the general limit method for pure gases, from equations (2.82) and (2.83), we obtain the following final expressions for the enthalpy and entropy of the mixture of gases subordinate to the Gibbs-Dalton law:

$$H = \sum_{(\kappa)} \left\{ \int_V^\infty \left[P_\kappa - T\left(\frac{\partial P_\kappa}{\partial T}\right)_V \right] dV_\kappa + n_\kappa e_\kappa^0 \right\}. \tag{2.85}$$

$$S = \sum_{(\kappa)} \left\{ \int_V^\infty \left[\frac{n_\kappa R}{V_\kappa} - \left(\frac{\partial P_\kappa}{\partial T}\right)_V \right] dV_\kappa + n_\kappa R \ln \frac{V}{n_\kappa RT} + n_\kappa S_\kappa^0 \right\}. \tag{2.86}$$

The general limit method gives the following expression for G and T, V-coordinates:

$$G(T, V) = \int_V^\infty \left[P - \frac{nRT}{V} \right] dV - nRT \ln \frac{V}{nRT} + PV + n(e^0 - TS^0).$$

From thence for a mixture of gases, considering expression (2.84), we obtain

$$G = \sum_{(\kappa)} \left\{ \int_V^\infty \left[P_\kappa - \frac{n_\kappa RT}{V_\kappa} \right] dV_\kappa - n_\kappa RT \ln \frac{V}{n_\kappa RT} + P_\kappa V + n_\kappa \left(e_\kappa^0 - TS_\kappa^0 \right) \right\}. \tag{2.87}$$

From equation (2.80), considering expression (2.79), we find that

$$\left(\frac{\partial P}{\partial n_i}\right)_{T,V,n} = \left(\frac{\partial P_{\kappa}}{\partial n_\kappa}\right)_{T,V}. \tag{2.88}$$

From equality (2.87), considering equation (2.88), we obtain an expression for the chemical potential of the i-th component

$$\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{T,P} = \int_V^\infty \left[\left(\frac{\partial P_\kappa}{\partial n_\kappa}\right)_{V_\kappa,T} - \frac{RT}{V_\kappa} \right] dV_\kappa - RT \ln \frac{V}{n_\kappa RT} + RT + \left(e_\kappa^0 - TS_\kappa^0 \right). \tag{2.89}$$

From thence, for the law of existing masses, from the condition of equilibrium in the system,

$$\sum_{(i)} \nu_i \mu_i = 0 \tag{2.90}$$

we obtain the following expression:

$$\ln\frac{K_p}{K_p^*} = -\frac{1}{RT}\sum_{\kappa}\left\{\nu_\kappa\left[\int_V^\infty\left[\left(\frac{\partial P_\kappa}{\partial n_\kappa}\right)_{V_\kappa, T} - \frac{RT}{V_\kappa}\right]dV_\kappa + \sum_{(i)}{}' \nu_i \ln\frac{PV}{\sum_{(i)} n_i RT}\right.\right. \tag{2.91}$$

where

$$\ln K_p^* \quad -\frac{1}{RT}\sum_{(\kappa)}\left\{\nu_\kappa\left[h_\kappa^0 - TS_\kappa^0\right]\right\}. \tag{2.92}$$

From equation (2.91) it is apparent that the constant of equilibrium is a function of the composition of the equlibrium mixture and, consequently, is not calculated by the direct path. For the calculation of the constant of equilibrium it is necessary to use the method of successive approximations. Having at first assumed that $K_p = K_p^*$, we determine the composition, and then determine the righthand part of the equation (2.91) and obtain a second approximation for K_r. We repeat the process as long as the composition of the mixture does not become unchanged within the limits of the given accuracy. The process of the calculations converges rapidly.

4. The Lewis-Randall Rule

Lewis and Randall [236] proposed the following rule as the basis for investigation of the thermodynamic properties of mixtures of gases: the fugacity f_i of the gas in the mixture is equal to the product of the molar fraction of the gas in the mixture multiplied by the fugacity f_{P_k} of this pure gas at the general pressure and temperature of the mixture:

$$f_i = f_{P_\kappa} x_i. \tag{2.93}$$

The fugacity of the pure gas is determined via the ratios

$$\mu = RT\ln f + \Psi(T), \tag{2.94}$$

$$\lim_{P \to 0}\frac{f}{P} = 1 \tag{2.95}$$

at all temperatures.

We will consider a pure gas in isothermic equilibrium with the mixture through a membrane permeable only for this gas alone. The chemical potential of the gas in the mixture if μ_i and the chemical potential of this same pure gas is μ_k, where $\mu_i = \mu_k$. According to the Lewis-Randall law, μ_k and, consequently, μ_i may be calculated by substitution of the fugacity of the pure gas at the general pressure and temperature of the mixture multiplied by the molar fraction of this gas in a mixture in equation (2.94):

$$\mu_i = \mu_k = RT \ln f_{P_k} x_i + \Psi_k(T). \tag{2.96}$$

The Lewis-Randall rule also, like the Gibbs-Dalton law, contains the essential idea of equilibrium as the basis of the investigation of the thermodynamic properties of a mixture of gases.

We will substitute f_{P_k} into equation (2.94) and, considering expression (2.96), we obtain

$$\mu_i = \mu_{P_k} + RT \ln x_i. \tag{2.97}$$

We differentiate equation (2.97) with respect to temperature and pressure at a constant composition and, considering the following conditions derived from the Lewis-Randall rule:

T (of each pure gas) = T (of the mixture),
P (of each pure gas) = P (of the mixture),

$$n_k = n_i, \tag{2.98}$$

we obtain

$$\left(\frac{\partial \mu_i}{\partial P}\right)_{T,n} = \left(\frac{\partial \mu_{P_k}}{\partial P}\right)_T, \tag{2.99}$$

$$\left(\frac{\partial \mu_i}{\partial T}\right)_{P,n} = \left(\frac{\partial \mu_{P_k}}{\partial T}\right)_P + R \ln x_i. \tag{2.100}$$

From general thermodynamics it is known that the lefthand part of equations (2.99) and (2.100) are equal, respectively, to the partial molar volume and the partial molar entropy taken with a minus sign of the i-th gas in the mixture, and the righthand parts are equal to the corresponding molar quantities for a pure gas.

Thus,

$$\left(\frac{\partial V}{\partial n_i}\right)_{P,T,n} = \frac{V_{P_\kappa}}{n_\kappa}, \tag{2.101}$$

$$\left(\frac{\partial S}{\partial n_i}\right)_{P,T,n} = \frac{S_{P_\kappa}}{n_\kappa} - R\ln x_i. \tag{2.102}$$

According to the Euler theorem of homogeneous functions

$$V = \sum_{(i)} n_i\left(\frac{\partial V}{\partial n_i}\right)_{P,T,n} = \sum_{(\kappa)} V_{P_\kappa}. \tag{2.103}$$

$$S = \sum_{(i)} n_i\left(\frac{\partial S}{\partial n_i}\right)_{P,T,n} = \sum_{(\kappa)} S_{P_\kappa} - \sum_{(i)} n_i R\ln x_i \tag{2.104}$$

By using the ratios of general thermodynaamics, we obtain

$$H = \sum_{(\kappa)} H_{P_\kappa}. \tag{2.105}$$

$$G = \sum_{(\kappa)} G_{P_\kappa} - \sum_{(i)} n_i RT\ln x_i. \tag{2.106}$$

Having substituted the expression for the corresponding functions of the pure gases, derived by the general limit method, into equations (2.104), (2.105), and (2.106), we finally obtain the following:

$$H = \sum_{(\kappa)}\left\{\int_0^P\left[V_\kappa - T\left(\frac{\partial V_\kappa}{\partial T}\right)_{P_\kappa}\right]dP_\kappa + n_\kappa h_\kappa^0\right\}. \tag{2.107}$$

$$S = \sum_{(\kappa)}\left\{\int_0^P\left[\frac{n_\kappa R}{P_\kappa} - \left(\frac{\partial V_\kappa}{\partial T}\right)_{P_\kappa}\right]dP_\kappa - \right.$$

$$\left. - \sum_{(i)} n_i R\ln Px_i, \right. \tag{2.108}$$

$$G = \sum_{(\kappa)}\left\{\int_0^P\left[V_\kappa - \frac{n_\kappa RT}{P_\kappa}\right]dP_\kappa + n_\kappa(h_\kappa^0 - TS_\kappa^0) + \right.$$

$$\left. + \sum_{(i)} n_i RT\ln Px_i. \right. \tag{2.109}$$

Thus, the Lewis-Randall rule gives a complete solution of the problem of the determination of the thermodyanmic properties of a mixture of gases with respect to information concerning the behavior of the components of the mixture. From equation (2.109) we obtain the following expression for the chemical potential of the i-th component, considering that $\mu_k = \mu_i$:

$$\mu_i = \int_0^P \left[\frac{V_k}{n_k} - \frac{RT}{P_k}\right] dP_k + RT \ln P x_i + h_k^0 - T S_k^0. \qquad (2.110)$$

By substituting equation (2.110) into (2.90), we obtain the following expression for the law of the existing masses:

$$\ln \frac{K_p}{K_p^0} = -\frac{1}{RT} \sum_{(i)} \left\{ \nu_k \left[\int_0^P \left[\frac{V_k}{n_k} - \frac{RT}{P_k}\right] dP_k \right] \right\} \qquad (2.111)$$

Expression (2.111) for the constant of equilibrium of a mixture of gases subordinate to the Lewis-Randall rule is a function only of the temperature and pressure of the mixture, and does not depend upon the composition of the equilibrium mixture.

5. The General Limit Method for Mixtures of Gases

We will make the following assumption: at all temperatures the ratio of the equilibrium pressure of each gas in the mixture to the product of the molar fraction of this gas in the mixture multiplied by the general pressure of the mixture may be represented in the region of low pressures by the expression

$$\frac{P_{ck}}{x_i P} = 1 + D_i(T, x_1, x_2, \ldots) P + O(P^2), \qquad (2.112)$$

where D_i depends only upon the temperature and composition of the mixture, D_i and their derivatives with relationship to T, n_1, n_2, ... are limited. We will consider a system of $\sum_{(i)} n_i$ of the gaseous mixture and the k-systems of each of n_{ek} moles of each of the components of this mixture.

At all variations, let us assume that T (of each pure gas) = T (of the mixture), V (of each pure gas) = V (of the mixture), $_k = {}_i$. From this it follows that each pure gas will be in equilibrium with the mixture through a membrane permeable only for this gas alone, and the properties of this gas are equilibrium properties. Thus the essential idea of equilibrium is also contained in this approach.

Let us assume that T, μ_1, μ_2, ... are independent variables for the gaseous mixture, and T, μ_k are independent variables for each pure gas. We will rewrite equation (2.112) thus:

$$P_{ck} = Px_i(1 + D_iP),$$

from whence

$$\sum_{(\kappa)} P_{c\kappa} = P(1 + D_mP), \tag{2.113}$$

where

$$D_m = \sum_{(i)} x_i D_i.$$

By differentiating equation (2.113) according to one of the values of μ at a constant value of T and with all the other values of μ. constant, we obtain

$$\left(\frac{\partial P_{c\kappa}}{\partial \mu_\kappa}\right)_T = \left(\frac{\partial P}{\partial \mu_i}\right)_{T,\mu}(1 + 2D_mP) + P^2\left(\frac{\partial D_m}{\partial \mu_i}\right)_{T,\mu}.$$

The partial derivative $(\delta D_m/\delta P)_{T,\mu}$ is limited, from whence

$$P^2\left(\frac{dD_m}{d\mu_i}\right)_{T,\mu} = P^2\left(\frac{dP}{d\mu_i}\right)_{T,\mu}\left(\frac{dD_m}{dP}\right)_{T,\mu}$$

is the order of magnitude greater than $2PD_m$, and we ignore it in the region of low pressures being considered. Therefore,

$$\left(\frac{\partial P_{c\kappa}}{\partial \mu_\kappa}\right)_T = \left(\frac{\partial P}{\partial \mu_i}\right)_{T,\mu}(1 + 2D_mP). \tag{2.114}$$

By differentiating equation (2.113) with respect to T at all the μ-constants we obtain, considering the limitation of $(\delta D_m/\delta P)$,

$$\sum_{(\kappa)}\left(\frac{\partial P_{c\kappa}}{\partial T}\right)\mu_\kappa = \left(\frac{\partial P}{\partial T}\right)\mu\,(1 + 2D_mP). \tag{2.115}$$

From equation (2.114) it follows that

$$\frac{n_{c\kappa}}{V} = \frac{n_i}{V}(1 + 2D_mP), \tag{2.116}$$

and from equation (2.115)

$$\sum_{(\kappa)} S_{c\kappa} = S(1 + 2D_mP). \tag{2.117}$$

Having divided P_{ck} into equation (2.116), with consideration of equality (2.112), we obtain

$$\frac{P_{\text{ск}} V}{n_{\text{ск}}} = \frac{PV}{\sum\limits_{(i)} n_i} [1 + (D_i - 2D_m) P]. \tag{2.118}$$

The lefthand part of this equation refers to a gas existing by itself, and, consequently, for it equation (2.7) is correct.

This gives the following

$$PV = \sum_{(i)} n_i RT + \frac{P}{RT} \sum_{(i)} n_i \beta_m, \tag{2.119}$$

where β_m is a limited function of the temperature and composition of the gaseous mixture.

By using the well-known thermodynamic ratios, we obtain

$$\sum_{(\kappa)} H_{\text{ск}} = H(1 + 2D_m P), \tag{2.120}$$

$$\sum_{(\kappa)} G_{\text{ск}} = G(1 + 2D_m P). \tag{2.121}$$

If we decrease the pressure of the mixture at a constant temperature and composition of the mixture, then, as is appraent from equations (2.117), (2.119)-(2.121), PV and H approach a constant value, while S and G decrease or increase similar to ±ln P.

From ratios (2.117), (2.119)-(2.121), with consideration of equation (2.64), it follows that in the region of very low pressures

$$\left(\frac{P_{\text{ск}}}{P x_i}\right)^* = 1, \quad \left(\frac{n_{\text{ск}}}{n_i}\right)^* = 1; \tag{2.122}$$

$$\left(\frac{\sum\limits_{(\kappa)} P_{\text{ск}}}{P}\right)^* = 1; \tag{2.123}$$

$$S^* = \sum_{(\kappa)} S^*_{\text{ск}}; \tag{2.124}$$

$$H^* = \sum_{(\kappa)} H^*_{\text{ск}}; \tag{2.125}$$

$$G^* = \sum_{(\kappa)} G^*_{\text{ск}} \tag{2.126}$$

and the equation of state

$$(PV)^* = \sum_{(i)} n_i RT. \tag{2.127}$$

From equation (2.125)

$$C_p^* = \sum_{(k)} C_{pk}^*. \tag{2.128}$$

In accordance with equations (2.15) and (2.16) for the enthalpy and entropy of the pure gas we have for the number of moles $\sum\limits_{(i)} n_i$ of a gaseous mixture of constant composition

$$\begin{aligned} H(P,T) - H(P_0,T_0) = & \int\limits_{T_0\;P_0}^{P^*} \left[V - T\left(\frac{\partial V}{\partial T}\right)_{P,n} \right] dP + \\ & + \int\limits_{T_0}^{T} C_p^* dT + \int\limits_{T\;P^*}^{P} \left[V - T\left(\frac{\partial V}{\partial T}\right)_{P,n} \right] dP, \end{aligned} \tag{2.129}$$

$$\begin{aligned} S(P,T) - S(P_0,T_0) = & \int\limits_{T_0\;P_0}^{P^*} \left[\sum_{(i)} n_i R/P - \left(\frac{\partial V}{\partial T}\right)_{P,n} \right] dP + \\ & + \int\limits_{T_0}^{T} C_P^* \frac{dT}{T} + \int\limits_{T\;P^*}^{P} \left[\frac{\sum\limits_{(i)} n_i R}{P} - \left(\frac{dV}{dT}\right)_{P,n} \right] dP - \\ & - \sum_{(i)} n_i R \ln \frac{P}{P_0}. \end{aligned} \tag{2.130}$$

By considering equations (2.125), (2.122), and (2.15), we obtain

$$\begin{aligned} H(P^*,T_0) = \sum_{(k)} H_k(P^*,T_0) = \sum_{(k)} n_{0k} h_{0k}^0 = \\ = \sum_{(i)} n_i h_{0i}^0. \end{aligned} \tag{2.131}$$

From equations (2.124), (2.16), and (2.122),

$$\begin{aligned} S(P^*,T_0) = \sum_{(k)} S_{0k}(P_k^*, T_0) = \sum_{(k)} n_{0k} S_{0k}^0 - \\ - \sum_{(k)} n_{0k} R \ln P_k^* = \sum_{(i)} n_i S_{0i}^0 - \sum_{(i)} n_i R \ln P^* x_i. \end{aligned} \tag{2.132}$$

From equations (2.122) and (2.128)

$$C_p^{\bullet} - \sum_{(\kappa)} C_{p\kappa}^{\bullet} = \sum_{(\kappa)} n_{c\kappa} C_{p\kappa}^{\bullet} - \sum_{(i)} n_i C_{pi}^{\bullet}. \tag{2.133}$$

Thus, from equations (2.129) and (2.131)

$$H(P_0, T_0) + {}_{T_0}\int_{P_0}^{P^*} \left[V - T\left(\frac{dV}{dT}\right)_{P,n}\right] dP = H(P^*, T_0) =$$

$$= \sum_{(i)} n_i h_{0i}^0, \tag{2.134}$$

and from equations (2.130) and (2.132)

$$S(P_0, T_0) + {}_{T_0}\int_{P_0}^{P^*} \left[\frac{\sum\limits_{(i)} n_i R}{P} - \left(\frac{dV}{dT}\right)_{P,n}\right] dP +$$

$$+ \sum_{(i)} n_i R \ln P_0 = S(P^*, T_0) + \sum_{(i)} n_i R \ln P^* =$$

$$= \sum_{(i)} n_i S_{0i}^0 - \sum_{(i)} n_i P \ln x_i. \tag{2.135}$$

We will substitute equations (2.133)-(2.135) into equations (2.129), (2.130), in this case having replaced the limit P* by 0, considering equation (2.119); we obtain the following expressions finally for the enthalpy and entropy of the gaseous mixture:

$$H(P, T) = \int_0^P \left[V - T\left(\frac{dV}{dT}\right)_{P,n}\right] dP + \sum_{(i)} n_i h_i^0, \tag{2.136}$$

$$S(P, T) = \int_0^P \left[\frac{\sum\limits_{(i)} n_i R}{P} - \left(\frac{dV}{dT}\right)_{P,n}\right] dP - \sum_{(i)} n_i R \ln P x_i +$$

$$+ \sum_{(i)} n_i S_i^0. \tag{2.137}$$

The expression for G may be obtained by the same means:

$$G = \int_0^P \left[V - \frac{\sum\limits_{(i)} n_i RT}{P}\right] dP + \sum_{(i)} n_i RT \ln P x_i +$$

$$+ \sum_{(i)} n_i (h_i^0 - TS_i^0). \tag{2.138}$$

From whence

$$\mu = \left(\frac{\partial G}{\partial n_i}\right)_{P,T} = \int\limits_0^P \left[\left(\frac{\partial V}{\partial n_i}\right)_{P,T,n} - \frac{RT}{P}\right] dP + {} + R \ln P x_i + h_i^0 - TS_i^j. \tag{2.139}$$

The expression for the law of the existing masses, therefore, is as follows:

$$\ln \frac{K_p}{K_p^*} = -\frac{1}{RT} \sum_{(i)} \left\{ \nu_i \left[\int\limits_0^P \left[\left(\frac{\partial V}{\partial n_i}\right)_{P,T,n} - \frac{RT}{P}\right] dP \right] \right\} = -\frac{1}{RT} \sum_{(i)} \left\{ \nu_i \left[\int\limits_V^\infty \left[\left(\frac{\partial P}{\partial n_i}\right)_{V,T,n} - \frac{RT}{P}\right] dV \right\} + {} + \sum_{(i)} \nu_i \ln \frac{PV}{\sum\limits_{(i)} n_i RT}. \tag{2.140}$$

This is the most common expression for the law of existing masses from which, with definite simplifying assumptions, expressions are obtained for the law of existing masses in a case of the fulfillment of the Gibbs-Dalton law or the Lewis-Randall rule. In view of the fact that the right side of this equation depends upon the composition, its calculation must be performed by the method of successive approximations, as in a case of calculations according to the Gibbs-Dalton law.

In order to calculate the thermodynamic properties of gaseous mixtures by means of the ratios derived by the general limit method, it is necessary to know the equation of state of the mixture in such a form that the number of moles of the components explicitly enters into it. Usually we give the equation of state of a gaseous mixture of constant composition the same form as we give to the equations of state of pure gases, and each parameter of the mixture, such as B_m, let us say, is connected with the corresponding parameters of the components according to the ratio $B_m = \sum\limits_{(i)} \sum\limits_{(j)} x_i x_j B_{ij}$.

The reaction parameters of non-similar molecules B_{ij} are associated with the parameters of the components according to definite combination rules, serving as the object of numerous theoretical investigations.

The general limit method gives the most accurate presentation of the properties of the gaseous mixtures. In distinction from the Gibbs-Dalton law which requires additivity of the pressures in the common volume and temperature of the mixture of the constants, and the Lewis-Randall rule, which requires additivity of the volumes with a common pressure and temperature of the mixture of the constants, the general limit method does not impose such strict limitations on the equation of state of the mixture. It requires only that PV approach $\sum_{(i)} n_i RT$ in a definite manner with a decrease in the pressure of the mixture to zero. All three methods may be used in the calculation of the thermodynamic properties of real chemically reacting systems. But the application of the Lewis-Randall rule in this case gives the greates advantages. This is associated with the following.

The general limit method gives the following expresssion for the fugacity of the pure gas:

$$\ln f = \frac{1}{RT} \int_0^P \left[\frac{V}{n} - \frac{RT}{P} \right] dP + \ln P.$$

We may express the enthalpy and entropy of the pure gas through the fugacity factor, which, according to definition, is equal to $\gamma = f/P$ by means of the following simple dependences:

$$H(P, T) = -RT^2 \left(\frac{\partial \ln \gamma}{\partial T} \right)_P + nh^0, \tag{2.141}$$

$$S(P, T) = -RT \left(\frac{\partial \ln \gamma}{\partial T} \right)_P - R \ln \gamma P + nS^0. \tag{2.142}$$

From this for the enthalpy and entropy for a real chemically reacting system, subordinate to the Lewis-Randall rule, we obtain the equations

$$H(P, T) = -\sum_{(k)} RT^2 \left(\frac{\partial \ln \gamma_k}{\partial T} \right)_P + \sum_{(k)} n_k h_k^0, \tag{2.143}$$

$$S(P, T) = -\sum_{(k)} RT \left(\frac{\partial \ln \gamma_k}{\partial T} \right)_P - \sum_{(k)} R \ln \gamma_k P - $$
$$+ \sum_{(k)} n_k S_k^0. \tag{2.144}$$

The number of moles of each i-th component, n_i, is determined from the equation of the constant of equilibrium (2.111). This equation may also be expressed via the fugacity factors of the components. By substituting equation (2.110) into equation (2.90), with consideration of expression (2.94), we obtain

$$\sum_{(i)} \nu_i (RT \ln f_i + h_i^{\circ} - TS_i^{\circ}) = 0,$$

or, considering equality (2.92),

$$\sum_{(i)} \nu_i \ln f_i = \ln K_p^{\circ}. \qquad (2.145)$$

From this, considering equality (2.93), we obtain

$$\sum_{(i)} \nu_i \ln f_i = \sum_{(i)} \nu_i \ln f r_\kappa x_i = \sum_{(i)} \nu_i \ln \left(\frac{f r_\kappa}{P} \right) P x_i =$$
$$= \sum_{(\kappa)} \nu_\kappa \ln \gamma r_\kappa + \sum_{(i)} \nu_i \ln P x_i = \ln K_p^{\circ}. \qquad (2.146)$$

We finally obtain

$$\ln K_p = \ln \frac{K_p^{\circ}}{K_\gamma}, \qquad (2.147)$$

where

$$\ln K_\gamma = \sum_{(i)} \nu_i \ln \gamma r_\kappa. \qquad (2.148)$$

Thus, both the composition and the thermodynamic properties of the components of a real chemically reacting system subordinate to the Lewis-Randall rule, are determined only via one quantity, the fugacity factor. In this case, the composition is determined by a direct method, and not by the method of successive approximations, as in a case of the calculation of the composition according to the Gibbs-Dalton law or on the basis of the general limit method for the mixture of gases. With all the approaches explained above for the calculation of thermodynamic properties of mixtures of gases, a knowledge of the volumetric behavior of the components of the mixture is necessary. Usually the volumetric behavior of the components is either known in a very narrow range or is not known at all. In this case, for a description of the volumetric behavior of the components, the law of the corresponding states is used.

In many cases it is useful to consider the behavior of the substances in the given independent variables T_{given}, P_g, V_g determined by the equation $T_g = T/T_{cr}$, $P_g = P/P_{cr}$, $V_g = V/V_{cr}$, where T_{cr}, P_{cr}, and V_{cr} are the critical temperature, pressure, and volume of the substance, respectively. The state of two or several substances in which they have the same values of T_g, P_g, and V_g are called the corresponding states. The law of corresponding states affirms that if two of the given parameters for several substances have the same values, the third parameter for all the substances also has the same value. The fugacity factors of many substances are generalized in tables and curves as a function of the given parameters of the substances. This makes it possible, if we know only the critical parameters of the components, on the basis of the Lewis-Randall rule, to calculate the thermocvnamic properties of real mixtures of gases, including real chemically reacting systems.

In the discussion of the law of corresponding states Hougen and Watson [68] established the fact that the maximum error in the prediction of the volumetric behavior of the substances amounts of 15%, while the error in the prediction of other properties lies in the range of 5-35%. This indicates the degree to which the real substances are subordinate to the law of corresponding states.

The law of corresponding states gives better results for groups of similar substances, each of which corresponds to a quite definite form of the law of corresponding states. The classification of these substances into groups which would satisfy the form of the law of corresponding states that is common for each group has only just begun. The principal difficulty lies in the selection of the basic criteria which would determine most accurately the classification of the given substance in one group or another. Pitzer [69] proposed the following semi-empirical modification of the law of corresponding states, which is widely used at the present time, and includes, aside from the critical parameters, an additional criterion of similarity, and gives results that are an order of magnitude more accurate than the ordinary form of the law of corresponding states.

Statistical theory has demonstrated [70] that the group of substances will be subordinate to the principle of corresponding states only when their intermolecular potentials are identical in form, although the depths of the minimum of the potential and the minimum intermolecular distance, associated with the critical temperature and critical volume, respectively, are characteristic for each substance. Intramolecular motions must be classic, i.e., the quantum effect should be ignored. The only group of substances satisfying these requirements, the heavy inert gases Ar, Kr, and Xe, precisely follow the law of corresponding states. These gases are called simple gases. We may expect that different types of the forms of the molecules and molecular dipole moment will lead to different deviations from the macroscopic properties of simple gases. It has been found, however, that the relative second theoretical virial coefficients of a wide class of the molecular type of substances fall on a single family of curves which may be characterized by one parameter. The exception is found in molecules with a large dipole moment. Substances constituting this class are usually called normal gases. According to the principle of corresponding states, all the substances must have one and the same saturation line in relative coordinates. Actually, this is not so. These lines constitute one family of curves differing from each other in slope. This slope was also selected as the characteristic parameter in the description of the family of curves of virial coefficients and as an additional parameter for a more accurate system of the correlation of the imperfect nature of the behavior of the substances. To this we must add the fact that the saturation line is measured with great accuracy.

The third correlation parameter ω is determined via the following ratio:

$$\omega = -\lg\frac{P_s}{P_{\text{кр}}} - 1,$$

where P_s/P_{cr} is taken at a value of $T_s/T_{cr} = 0.7$ at a point which is quite far from the critical point. This formula was selected so that ω was equal to zero for the simple gases Ar, Kr, and Xe with simple spherical molecules. Normal gases have small positive values of ω. The parameter ω is called the acentric factor because of the fact that it demonstrates the measure of deviation of the intramolecular potential function from the potential function of simple spherical molecules. The P-V-T data of the series of substances were interpolated by series at equal values of $P_g - T_g$ and were constructed as a function of ω. Such curves demonstrated that the compressibility factors of the substances are well described by a linear dependence upon ω:

$$Z = Z^{(0)}(P_{\text{пр}}, T_{\text{пр}}) + \omega Z^{(1)}(P_{\text{пр}}, T_{\text{пр}}).$$

The smooth values of $Z^{(0)}$ and $Z^{(1)}$ taken from these curves are given in tables of $Z^{(0)}(P_g, T_g)$, $Z^{(1)}(P_g, T_g)$ in refs. [69, 71, 72]. The fugacity factors and log $^{(0)}$, log $^{(1)}$ were calculated according to these values of the compressibility factor, and also the corrections for the imperfect nature in the enthalpy of the substances $[(H^0-H)/(RT_g)]^{(0)}$, $[(H^0-H)/(RT_g)]^{(1)}$ [71], corresponding to the dependences

$$\log\gamma = \log\gamma^{(0)} + \omega \log\gamma^{(1)},$$

$$\left(\frac{H^0-H}{RT_{\text{кр}}}\right) = \left(\frac{H^0-H}{RT_{\text{кр}}}\right)^{(0)} + \omega\left(\frac{H^0-H}{RT_{\text{кр}}}\right)^{(1)}.$$

6. Calculation of the Thermodynamic Properties of a Real Chemically Reacting System $N_2O_4 \rightleftarrows 2NO_2 \rightleftarrows 2NO + O_2$

The chemically reacting gaseous system $N_2O_4 \rightleftarrows 2NO_2 \rightleftarrows 2NO + O_2$ has a number of features in the behavior of the first stage of the reaction $N_2O_4 \rightleftarrows 2NO_2$, which complicate the calculation of its thermodynamic properties with a consideration of its imperfect nature [71, 237, 238]. (Everything said below about the behavior of the system $N_2O_4 \rightleftarrows 2NO_2$ and its components is also correct for chemically reacting system $Al_2Cl_6 \rightleftarrows 2AlCl_3$ and others, and therefore the behavior of them was not specially considered.

The components N_2O_4 and NO_2 of this system do not exist in the pure form. They always constitute an equilibrium mixture of gases in which it is impossible to distinguish the bonding of NO_2 to N_2O_4 or the dissociation of N_2O_4 into NO_2 from the non-ideal nature in their behavior by experimental means. In view of this, it is impossible to obtain separate experimental data with respect to the volumetric behavior of these components or to compile equations of state for them. It is also known that a chemically reaction system $N_2O_4 \rightleftarrows 2NO_2$ behaves as a single substance, and not as a mixture of two types of molecules having constant melting and boiling points, critical parameters, and a single saturation line. At the same time, the volumetric behavior of the system, and the strong deviation from a perfect gaseous behavior of the pure substances even at insignificant pressures, demonstrates that this is not a single substance, and therefore its thermodynamic properties cannot be distinguished with respect to ratios for simple substances. It also demonstrates that this is not a simple mechanical mixture of gases. If the experimental P-V-T data of such a type of systems as a whole are unknown, at least their thermodynamic properties may be calculated according to the ratios given above. If such data are lacking, we can still work from the assumption of the separateness of the effect of dissociation or associating of molecules and the imperfect nature of their behavior on the common behavior of the mixture. In this case we may apply any of the approaches considered above, based on a knowledge of the behavior of the components in mandatory combination with the law of corresponding states. Thus, a hypothetical volumetric behavior, assigned in a definite manner by the selection of similar substances for these components is ascribed to the components N_2O_4 and NO_2.

A number of works have been devoted to calculation of the thermodynamic properties of an equilibrium chemically reacting gaseous system $N_2O_4 \rightleftarrows 2NO_2 \rightleftarrows 2NO + O_2$. Furguson and Smith [239] calculated the degree of dissociation, enthalpy and effective heat content at a constant pressure of the first stage of the reaction $N_2O_4 \rightleftarrows 2NO_2$ to a temperature of ~380°K at pressures slightly higher than two atmospheres.

In ref. [10] a calculation of the thermodynamic properties of the entire system $N_2O_4 \rightleftarrows 2NO_2 \rightleftarrows 2NO + O_2$ is given in the temperature range of 300-1500°K and the pressure range of 1-150 atmospheres under the assumption of a perfect nature of the dissociating system under consideration.

Stai and his co-workers [240] calculated the thermodynamic properties of dissociating nitrogen tetroxide with consideration of its imperfect nature. Its enthalpy and entropy were calculated by them in the solid, liquid, two-phase, and gaseous regions up to temperatures of ~500°K at pressures at from ~0.00035 to ~700 atmospheres. The imperfect nature of the substance was considered by the introduction of correcting factors into the enthalpy and entropy of the components of the mixture $N_2O_4 \rightleftarrows 2NO_2$, calculated on the basis of the law of corresponding states according to generalized diagrams and tables $Z = Z(T_g, P_g)$ of Hougen and Watson [68]. According to the affirmation of the authors of the work, the error in the calculations of the thermodynamic properties of the system $N_2O_4 \rightleftarrows 2NO_2 \rightleftarrows 2NO + O_2$ did not exceed 2 %.

We must note that the statement of the problem of the magnitude of the error in the calculation of the thermodynamic properties of real chemically reacting systems of type $N_2O_4 \rightleftarrows 2NO_2$ according to methodologies checked in mixtures of constant composition and even in chemically reacting systems with separating variables, in our view, is premature. Experimental data on the thermodynamic properties of such systems in the gaseous phase at high pressures are lacking. The behavior of them that is known is so specific that estimates obtained according to mixtures of constant composition may not be justified. Therefore, in the analysis of works on the calculation of the thermodynamic properties of a chemically reacting system $N_2O_4 \rightleftarrows 2NO_2 \rightleftarrows 2NO + O_2$ with consideration of its imperfect nature, we will dwell only on the qualitative evaluation of the calculation methods applied, on their logic construction and sequence.

In ref. [240] just such an inconsistency was allowed, since, when considering the imperfect nature of the behavior of the components of the mixture, the authors did not consider the effect of this imperfect nature in the calculation of the composition of the mixture. Incidentally, from this work it is not clear what critical parameters were ascribed to the components N_2O_4 and NO_2. In ascribing a definite volumetric behavior to these components, we must also ascribe definite critical parameters to them, in order to make use of the law of corresponding states in a generalized form.

In ref. [241] the enthalpy and entropy of the system $N_2O_4 \rightleftarrows 2NO_2 \rightleftarrows 2NO + O_2$ were calculated in the range of temperatures from 300 to 1500°K and the range of pressures from 1 to 300 atmospheres with consideration of the effect of the imperfect nature of the system, both on the behavior of the components of the mixture and on its composition. The correcting factors were calculated according to generalized parameters $\gamma = \gamma(T_g, P_g)$ of Hougen and Watson [68]. The effect of its imperfect nature on the composition was considered according to the Lewis-Randall rule (ratios (2.147)-(2.148)). In this case, however, the critical parameters of the components N_2O_4 and NO_2 were assumed to be the same and equal to the critical parameters of the mixture $N_2O_4 \rightleftarrows 2NO_2$. This leads to the fact that corrections for imperfect nature in the behavior of the components N_2O_4 and NO_2 and also the effect of their imperfect nature on the composition of the mixture turn out to be the same. The components N_2O_4

and NO_2, of course, are not similar to each other and therefore are still less similar to the mixture $N_2O_4 \rightleftarrows 2NO_2$. The mixture $N_2O_4 \rightleftarrows 2NO_2$ as a single substance with its own critical parameters is not similar to any of the pure substances and is not subordinate at all to the law of corresponding states in the generalized form. Therefore, it is not logical to accept the critical parameters of the components N_2O_4 and NO_2 to be the same as in the work under consideration. But, on the other hand, in the calculation of the thermodynamic properties of chemically reacting systems of type $N_2O_4 \rightleftarrows 2NO_2$, with a consideration of their imperfect nature, according to the law of corresponding states in principle we cannot avoid errors and inconsistencies of such a type. They are caused by the specific behavior of such systems, not as mixtures of two varieties of molecules, but as single substances. As we have already noted above, according to the law of corresponding states all the substances in relative coordinates have one common saturation line. From this, ascribing definite critical parameters to the components N_2O_4 and NO_2, we also ascribe to them definite saturation lines differing from the saturation line of the system. The selected critical parameters of the components may occupy a different position relative to the critical parameters of the system under consideration in P, T-coordinates. We will assume that both the critical temperatures and the critical pressures of both components of the mixture obtained by some method or other of the determination of the critical parameters are higher than the critical parameters of the system. In this case, at definite values of P and T, located in the gaseous phase of the system as a whole, corrections for the imperfect nature of the components are calculated in their liquid phases (the temperature region between the critical temperature of the system and the critical temperature of any of the components at pressures above the critical pressure of this component). Such a type of situation also originates in all other cases of the mutual arrangement of three critical points (saturation line lines).

We have made an attempt to calculate the thermodynamic properties of the chemically reacting system $N_2O_4 \rightleftarrows 2NO_2 \rightleftarrows 2NO + O_2$ with a consideration of its imperfect nature according to the law of corresponding states in Pitzer's modification when the components N_2O_4 and NO_2 have been ascribed their own pseudocritical parameters, differing from each other and the critical parameters of the system $N_2O_4 \rightleftarrows 2NO_2$. The correction factors for the imperfect nature of the system were calculated according to the Lewis-Randall rule and were introduced both into the behavior of the components of the mixture and into its composition. As a result of the calculation, the H-S diagram of the N_2O_4 system around the line of its saturation was so distorted because of the circumstances mentioned above that we were obliged to dispense with this method and shift to the following one.

In the calculation of the thermodynamic properties of mixtures of a constant composition, the concept of a mixture of a homogeneous substance with pseudocritical parameters, calculated according to definite combination rules, turned out to be very useful. Kay's rule [73] is the simplest and most frequently used, when the pseudocritical parameters of the mixture are considered to be equal to a linear combination of the critical parameters of the components of the mixture and their molar fractions in the mixture. The pseudocritical parameters of the mixture found in such a manner make it possible, according to the law of corresponding states, to then determine the correcting factor for the imperfect nature of the mixture as a single substance. Pitzer and Hultgren [74] have extended Kay's rule to a case of mixtures of substances subordinate to the law of corresponding states as modified by Pitzer. With the variation of the pressure and temperature, a chemically reacting system may be presented in the form of a set of mixtures of a constant composition at each fixed point of P and T, the composition being determined via the constant of chemical equilibrium of the system under consideration. Such a set may be considered as a single substance with variable pseudocritical parameters. The molecular weight of such a substance at various points of P and T will differ, depending upon the composition of the mixture. In ref. [242] the thermodynamic properties of the system $N_2O_4 \rightleftarrows 2NO_2 \rightleftarrows 2NO + O_2$ as a single substance with variable pseudocritical parameters and a variable molecular weight were also calculated. The law of corresponding states was applied in Pitzer's modification. With such an approach to the calculation of the thermodynamic properties of the chemically reacting system $N_2O_4 \rightleftarrows 2NO_2$ the correcting factor for the imperfect nature of the mixture at all pressures and temperatures turned out to be arranged in the purely gaseous region of the system $N_2O_4 \rightleftarrows$ $\rightleftarrows 2NO_2$, although in consideration of the imperfect nature of the composition of the mixture, the distortions indicated above occur as before. Such a calculation scheme, generally speaking, is identical to the assumption that corrections for the imperfect nature of the behavior of all components of the mixture are the same, but in this case the corrections are sought according to the current pseudocritical parameters of the mixture. With a total lack of experimental P-V-T data this methodology for considering the effect of the imperfect nature of the mixture in the calculation of the thermodynamic properties of real chemically reacting gaseous systems gives the most acceptable results. It was used by us in the calculation of the thermodynamic properties of chemically reacting systems $Al_2Cl_6 \rightleftarrows 2Al_2Cl_3$, $Al_2Br_6 \rightleftarrows 2AlBr_3$ [40, 49].

In ref. [243] the thermodynamic properties of the system $N_2O_4 \rightleftarrows 2NO_2 \rightleftarrows 2NO + O_2$ were calculated according to the equation of state or, more accurately, to the approximation equation describing the known experimental data according to the volumetric behavior of the system as a whole in the gaseous phase in the temperature range from the saturation line to 480°K and in the pressure range from 1 to 500 kg/cm^2. In this case the authors of the work do not give the ratios according to which the enthalpy and entropy of this system were calculated. We may only assume that these ratios consist of an ideal part, the sum of the products of the molar fractions of the components multiplied by the values of the corresponding thermodynamic functions of the components at the current temperature and pressure at 1 atmosphere, and the integrals with respect to pressure with a lower limit equal to 1. Conventional ratios, as was demonstrated by us above, are not applicable for the calculation of the thermodynamic properties of chemically reacting systems, but strict ratios derived by us have not yet been published. The latest work devoted to the calculation of the thermodynamic properties of a chemically reacting system $N_2O_4 \rightleftarrows 2NO_2 \rightleftarrows 2NO + O_2$ with consideration of its imperfect nature is ref. [244]. The thermodynamic properties of this system were calculated in this work in the temperature range of 480-2000°K and the pressure range of 1-500 kg/cm^2. The calculations were performed according to the equation of state in the form

$$Z = \sum_{(i)} \sum_{(j)} x_i x_j Z_{ij},$$

where the composition was corrected for its imperfect nature according to the Lewis-Randall rule. The volatility factors were determined on the basis of the law of corresponding states according to generalized dependences derived by Hougen and Watson [68]. The critical parameters of the components N_2O_4 and NO_2 were determined in the following manner. In the first approximation the critical parameters were determined from data concerning the properties of the liquid phaseof N_2O_4 according to the well-known ratios [24], and the critical parameters of NO_2 on the basis of the power constants of the Lennard-Johns potential (6-12). According to the accepted critical parameters from the dependence,

$$Z = x^2 Z_{N_2O_4} + (1-x)^2 Z_{NO_2} + 2x(1-x) Z_{N_2O_4-NO_2}, \qquad (2.149)$$

where x is the molar content of N_2O_4 in the mixture, $Z_{N_2O_4-NO_2}$ represents the compressibility factor, considering the reaction of N_2O_4 with NO_2. The values of Z_{NO_2} were defined, on the isotherms corresponding to the experimental values of Z of the mixture $N_2O_4 \rightleftarrows 2NO_2$, substituted into the lefthand part of the equation. $Z_{N_2O_4}$ and $Z_{N_2O_4-NO_2}$ were determined from the generalized dependences [68] according to the critical parameters $Z_{N_2O_4}$ according to those accepted for N_2O_4, $Z_{N_2O_4-NO_2}$ according to the critical parameters calculated as the arithmetical mean of the critical parameters N_2O_4 and NO_2 [245]. The values obtained for Z_{NO_2} made it possible to refine the critical parameters of NO_2 by means of comparison of Z_{NO_2} with $Z = Z(P_g, T_g)\ CO_2$, accepted as an analog for NO_2 with respect to the first approximation critical parameters. The values of the critical parameters of NO_2 refined in such a manner made it possible to refine the critical parameters of N_2O_4 also by means of separating $Z_{N_2O_4}$ from formula (2.142) and the comparison of these values with the generalized values $Z = Z(P_g, T_g)$ [68]. We note the following illogicality made in this case by the authors of the work under consideration. The form of the initial equation of state was accepted by them, in view of its successful appliapplication in the calculation of the thermodynamic properties of mixtures of constant composition also in the assumption that the chemically reacting system under consideration in each state coincides with the properties of an unreacting mixture of the same real composition. From this also comes the term Z $Z_{N_2O_4-NO_2}$ in equation (2.149), considering the effect of the imperfect nature of the reaction of N_2O_4 with NO_2 on the compressibility factor of the mixture. But the correction for the imperfect nature of the reaction of N_2O_4 with NO_2 is not considered and cannot be considered in the calculation of the composition of the mixture according to the Lewis-Randall rule. In this lies the logical ambiguity of the calculation scheme accepted by the authors.

Thus finding the critical parameters of N_2O_4 and NO_2, the authors calculated that the critical parameters of NO_2 were more reliably determined than the critical parameters of N_2O_4, although they had determined everything only so that the equation of state in the previously selected form satisfactorily described the experimental data with respect to the system $N_2O_4 \rightleftarrows 2NO_2$. Arriving at such an opinion, the authors decided to calculate the thermodynamic properties only in the temperature range of 800-2000°K, where at all pressures in the mixture, according to their estimate, the component N_2O_4 is lacking. Here, as in a previous work [244] of these same authors, in the calculation according to the equation of state (P-V-T) nothing was said of the form of the formulas with respect to which the enthalpy and entropy of the mixture were calculated. In the temperature 480-800°K data on enthalpy and entropy were obtained by means of graphic interpolation between the data calculated in ref. [244] and the data obtained in the work under consideration. Although the interpolation was conducted in deviations from the ideal properties simultaneously with respect to the isobars and isotherms, and the quantities obtained were checked by means of the identity $(i-i_{id}) - T(S-S_{id}) = \int(V-V_{id})dP$, this did not exclude, in principle, arbitrariness in interpolation. With a precisely determined righthand part the identities $(i-i_{id})$ and $(S-S_{id})$ may be determined with such an error that they mutually compensate each other in the fulfillment of the identity as a whole. Such a type of calculations, of course, cannot be carried over to other chemically reacting systems and are of no value, generally speaking, from the methodological standpoint.

For a chemically reacting system $N_2O_4 \rightleftarrows 2NO_2 \rightleftarrows 2NO + O_2$ in a quite wide range of temperatures and pressures, experimental data with respect to the volumetric behavior of the system as a whole in the gaseous phase are known. The equation of state given in ref. [244] describes them in the region of temperatures up to 480°K. But it is so compiled that it cannot be realized on the Minsk-22 ETsVM (electronic digital computer), which is at our disposal. Therefore, in the calculation of the thermodynamic properties we used the P-V-T data in the form of tables. They include P-V-T data processed and matched for a system up to 580 K in the entire range of pressures of interest to us.

The calculation method developed and expounded by us for the thermodynamic properties of chemically reacting systems with respect to P-V-T data as a whole gives the opportunity to calculate the thermodynamic properties of the system $N_2O_4 \rightleftarrows 2NO_2 \rightleftarrows 2NO + O_2$ also, according to its P-V-T data. It is true that the derivation of the formulas for it is somewhat complicated in view of the fact that in the system under consideration two reactions occur in sequence.

The equation of state of the chemically reacting system $N_2O_4 \rightleftarrows 2NO_2 \rightleftarrows 2NO + O_2$ which is perfect in the sense of the assumptions, is as follows:

$$V^u = \frac{RT(1 + \alpha_{10} + \alpha_{10}\alpha_{20})}{MP}, \tag{2.150}$$

where α_{10} is the ideal (perfect) degree of dissociation of the first stage of the reaction, α_{20} is the ideal degree of dissociation of the second stage of the reaction, M is the molecular weight of 1 mole of initially nondissociated N_2O_4, and M = 92 g/mole.

The degrees of dissociation of α_{10} and α_{20} are determined from the joint solution of the equations of the ideal constants of chemical equilibrium of the first and second stages of the reaction as a function of the temperature, with a consideration of their occurrence in sequence:

$$K_{p10}(T) = \frac{4\alpha_{10}^2(1 - \alpha_{20})^2 P}{(1 - \alpha_{10})(1 + \alpha_{10} + \alpha_{10}\alpha_{20})}, \tag{2.151}$$

$$K_{p20}(T) = \frac{\alpha_{10}\alpha_{20}^3 P}{(1 - \alpha_{10})(1 + \alpha_{10} + \alpha_{10}\alpha_{20})}. \tag{2.152}$$

By considering equations (2.150), (2.152), and (2.38), we obtain

$$\left(\frac{\partial V}{\partial T}\right)_P^u = \frac{R}{MP}(1 + \alpha_{10} + \alpha_{10}\alpha_{20}) +$$

$$+ \frac{RT}{MP}\left[\left(\frac{\partial \alpha_{10}}{\partial T}\right)_P + \alpha_{10}\left(\frac{\partial \alpha_{20}}{\partial T}\right)_P + \alpha_{20}\left(\frac{\partial \alpha_{10}}{\partial T}\right)_P\right], \tag{2.153}$$

where

$$\left(\frac{\partial \alpha_{10}}{\partial T}\right)_P = \frac{\alpha_{10}(1-\alpha_{20})}{6RT^2}[\Delta H_1(3+3\alpha_{10}-\alpha_{20}+\alpha_{10}\alpha_{20}) + \\ - \Delta H_2\alpha_{20}(2+3\alpha_{10}+\alpha_{10}\alpha_{20})], \tag{2.154}$$

$$\left(\frac{\partial \alpha_{20}}{\partial T}\right)_P = \frac{\alpha_{20}(1-\alpha_{20})}{6RT^2}[\Delta H_2(2+\alpha_{10}\alpha_{20}) - \\ - \Delta H_1(1-\alpha_{10})], \tag{2.155}$$

ΔH_1 is the thermal effect of the first stage of the reaction, ΔH_2 is the thermal effect of the second stage of the reaction.

From equations (2.151) and (2.152) we obtain

$$\left(\frac{\partial \alpha_{10}}{\partial P}\right)_T = \\ = -\frac{\alpha_{10}(1-\alpha_{10})(3+\alpha_{20})(1+\alpha_{10}+\alpha_{10}\alpha_{20})}{6P}, \tag{2.156}$$

$$\left(\frac{\partial \alpha_{20}}{\partial P}\right)_T = -\frac{\alpha_{20}(1-\alpha_{20})(1+\alpha_{10}+\alpha_{10}\alpha_{20})}{6P}. \tag{2.157}$$

By considering equalities (2.153), (2.156), and equation (1.52), for the system under consideration we obtain the following connection of S_m with $(\delta V/\delta T)_p^u$:

$$\left(\frac{\partial S_m}{\partial P}\right)_T = M\left(\frac{\partial V}{\partial T}\right)_P^u + \Delta S_1\left(\frac{\partial \alpha_{10}}{\partial P}\right)_T + \\ + \Delta S_2\left(\frac{\partial \alpha_{10}\alpha_{20}}{\partial P}\right)_T,$$

where ΔS_1 is the variation of the entropy in the course of the first stage of the reaction, ΔS_2 is the variation of the entropy in the course of the second stage of the reaction. From this

$$M\int_{P_1}^{P_2}\left(\frac{\partial V}{\partial T}\right)_P^u dP = [S_m(P, T) - \Delta S_1\alpha_{10} - \\ - \Delta S_2\alpha_{10}\alpha_{20}]\Big|_{P_1}^{P_2}. \tag{2.158}$$

Since, considering expression (2.151) and (2.152),

$$\lim_{P\to 0}\alpha_{10} = 1, \quad \lim_{P\to 0}\alpha_{20} = 1,$$

For C^*_{pm} of the system under consideration we obtain the following expression (the subscript i here and later on signifies the components N_2O_4, NO_2, NO, and O_2 of the mixture under consideration with respect to sequence):

$$C^{\bullet}_{pm} = \sum_{i=1}^{4} \nu_i C^{\bullet}_{pi} = 2C^{\bullet}_{p3} + C^{\bullet}_{p4}.$$

Ignoring the constants,

$$\int\limits_{T_0\,P_0}^{0} \left[V - T\left(\frac{\partial V}{\partial T}\right)_P\right] dP = \int\limits_{T_0\,P_0}^{0} \left[\left(\frac{\partial V}{\partial T}\right)^{u}_{P} - \left(\frac{\partial V}{\partial T}\right)_P\right] dP,$$

after a number of transformations we obtain the following final expressions for calculation of the entropy and enthalpy of the chemically reacting system $N_2O_4 \rightleftarrows 2NO_2 \rightleftarrows 2NO + O_2$ in the region of known experimental values of P-V-T data of the system as a whole:

$$S(P,\ T) = \frac{1}{92}\Big\{S_1^0 + S_1(T) + \alpha_{10}\Delta S_1 + \alpha_{10}\alpha_{20}\Delta S_2 -$$

$$- R\Big[(1-\alpha_{10})\ln(1-\alpha_{10}) + 2\alpha_{10}(1-\alpha_{20})\ln 2\alpha_{10}(1-\alpha_{20}) +$$

$$+ \alpha_{10}\alpha_{20}\ln\alpha_{10}\alpha_{20} - (1+\alpha_{10}+\alpha_{10}\alpha_{20})\ln\frac{(1+\alpha_{10}+\alpha_{10}\alpha_{20})}{P}\Big]\Big\} +$$

$$+ \frac{1}{A}\int\limits_{0}^{P}\left[\left(\frac{\partial V}{\partial T}\right)^{u}_{P} - \left(\frac{\partial V}{\partial T}\right)_P\right] dP, \qquad (2.159)$$

$$H(P,\ T) = \frac{1}{92}\,[2H_3 + H_4] +$$

$$+ \frac{1}{A}\int\limits_{0}^{P}\left[V - T\left(\frac{\partial V}{\partial T}\right)_P\right] dP. \qquad (2.160)$$

Here S_1^0, $S_1(T)$ are the standard entropy of N_2O_4 and the entropy of N_2O_4 as a function of temperature, respectively; H_3 and H_4 are the enthalpy of NO and O_2 as a function of temperature, respectively; A is the mechanical equivalent of the heat.

In the region where the P-V-T data of the system $N_2O_4 \rightleftarrows 2NO_2 \rightleftarrows 2NO + O_2$ are lacking, the thermodynamic properties of it were calculated according to the methodology already explained for the representation of a chemically reacting system by a homogeneous substance with a variable molecular weight, with the application of the law of corresponding states in Pitzer's modification with pseudocritical parameters sought according to Kay's rule. The dependence of the ideal constant of equilibrium of the first stage of the reaction $N_2O_4 \rightleftarrows 2NO_2$ upon the temperature was accepted according to ref. [76], and that of the second stage $2NO_2 \rightleftarrows 2NO + O_2$ according to ref. [77]. In accordance with these dependences, the heat of the first stage of the reaction at the point of the standard state is equal to $\Delta H^0_{1298.15} = 13{,}680$ calories/mole. The variation of the entropy in the progess of this reaction at the point of the standard state is equal to $\Delta S^0_{1298.15} = 42.06$ cal/mole/g. For the second stage of the reaction, accordingly, $\Delta H^0_{2298.15} = 17{,}200$ cal/mole, $\Delta S^0_{2298.15} = 34.86$ cal/M/g. The dependence of the enthalpy and entropy of the component N_2O_4 upon the temperature was obtained according to the dependence of the heat content of the component upon the temperature, given in ref. [2]. Analogous dependences for the enthalpy and entropy of the component NO_2, NO, and O_2 were accepted according to ref. [79]. The critical parameters of NO and O_2 are in accordance with ref. [246]. The acentric factors of these components were determined from data according to their saturation lines, as given in ref. [216].

The critical parameters and the acentric factors of the components N_2O_4 and NO_2 were determined in the following manner. From the methodology for a homogeneous substance with a variable molecular weight, explained above, the density of the mixture $N_2O_4 \rightleftarrows 2NO_2$ was calculated with the application of Pitzer's tables with respect to the compressibility factor on fixed isobars (100-150 atmospheres) from the saturation line of the mixture to a temperature of 580°K, i.e., in the range of the experimental P-V-T data of the mixture known on these isobars. In the first approximation, the critical parameters and the acentric factors were accepted for the components of N_2O_4 and NO_2 as the same and as equal to the parameters of the mixture $N_2O_4 \rightleftarrows 2NO_2$. Then by variation of one of the parameters with the others constant, we achieved a great coincidence of the calculated and experimental data. Thus, in sequence, all the parameters were sorted to the best coincidence of the quantities being compared. The critical parameters found for N_2O_4 and NO_2 do not, of course, correspond to any physical sense, but are simply a set of quantities most accurately describing the experimental P-V-T data of the mixture under consideration determined in accordance with the accepted calculation methodology (in this case the composition of the mixture determined with a consideration of its imperfect nature according to the accepted critical parameters may differ strongly from the actual composition because of the inconsistencies indicated above, which are internally proper to the methodology). It is clear that even this set of parameters may lead to large errors in the description of the P-V-T behavior of the mixture in a region where experimental data are lacking.

Chapter III

TRANSPORT PROPERTIES OF N_2O_4

1. Viscosity of Dissociating Nitrogen Tetroxide

The chemical reaction has only an insignificant effect on the transport of an impulse in intermolecular reactions [20]. The effect of the chemical reaction on viscosity is manifested basically in the fact that the composition of the chemically reacting mixture varies as the external parameters vary.

In a case of fast (equilibrium) reactions, the composition at any point in the cross-section of the channel is in local equilibrium with the given temperature. The variation of the composition follows the variation of the temperature practically instantaneously at a constant pressure. In this case, the rates of the direct and reverse chemical reactions are equal to each other, so that in the consideration of problems of transport the equations of chemical kinetics are omitted.

Therefore, if a mixture of chemically reacting gases is in a state of thermochemical equilibrium (it is assumed that thermodynamic equilibrium in the internal degrees of freedom is established much faster than chemical equilibrium), its composition is unambiguously determined by the parameters of state P and T. In a case of nonequilibrium chemical reactions the composition of the mixture will also depend upon hydrodynamic conditions. In this case, the hydrodynamic equation of the flow must be solved together with the equation of chemical kinetics.

But in any case, such a mixture may be represented for calculation of viscosity in any state by a definite mechanical mixture. Since, so far, no satisfactory theoretical formulas exist for calculation of the viscosity of dense gaseous systems, and the semi-empirical ratios using the theory of thermodynamic similarity of the substances, were obtained for dense homogeneous (individual) gases, a mixture of gases, as a rule, is represented by a hypothetical 'homogeneous' substance.

Historically, such an idea was used on the basis of Kay's postulate [73] that a gaseous mixture follows the behavior of a 'homogeneous' (individual) substance with its 'effective' (pseudocritical) parameters. The pseudocritical parameters of the mixture are associated with the critical parameters of the components by definite combination rules, explained in monograph [118]. For example, according to Joffe's rules,

$$\frac{T_{pscr}}{P_{pscr}^{1/2}} = \sum_{i=1}^{n} x_i \frac{T_{cri}}{P_{cri}^{1/2}},$$

$$\frac{T_{pscr}}{P_{pscr}} = \frac{1}{8} \sum_{i=1}^{n} \sum_{j=1}^{n} x_i x_j \left[\left(\frac{T_{cri}}{P_{cri}} \right)^{1/3} + \left(\frac{T_{crj}}{P_{crj}} \right)^{1/3} \right]^3. \qquad (3.1)$$

With reference to a definite class of chemically reacting mixtures, dissociating systems of type $N_2O_4 \rightleftarrows 2NO_2$, the model of a 'homogeneous' substance with 'effective' parameters of the intermolecular reactions serves somewhat better [141]. This method is good if the microparameters are found from experimental data with respect to viscosity. Besides this, such systems consist of components which, as a rule, it is impossible to separate, no matter what the external P and T parameters are. Therefore, it is not possible to determine the critical parameters of such components by experimental means.

The combination rules for finding the 'effective' parameters of the intermolecular reactions were obtained from combination rules for finding pseudocritical parameters and checked in twelve mechanical mixtures in a dense gaseous state [155]:

$$(\varepsilon/\kappa)_{\text{см}}^{1/2} \sigma_{\text{см}}^{3/2} = \sum_{i=1}^{n} x_i (\varepsilon/\kappa)_i^{1/2} \sigma_i^{3/2},$$

$$\sigma_{\text{см}}^3 = \sum_{i=1}^{n} \sum_{j=1}^{n} x_i x_j \sigma_{ij}^3,$$

$$\sigma_{ij} = \frac{1}{2} (\sigma_i + \sigma_j). \qquad (3.2)$$

A characteristic of both methods of the representation of a chemically reacting mixture by a 'homogeneous' substance is the fact that both the pseudocritical parameters and the 'effective' parameters of the intermolecular reactions will be variables: functions of temperature and pressure (for a mixture in chemical equilibrium) or, in a general case, functions of the composition. With reference to the second method the physical model lies in the fact that intermolecular reactions in such systems will be described by a set of potential curves so that each composition will correspond to its own potential of intermolecular reactions, with its own power parameters. For a mixture of variable composition these potential curves make a smooth transition one to the other, composing a potential reaction surface.

Thus, in principle, any generalized dependence of the viscosity obtained in dense homogeneous gases and checked in dense mechanical mixtures, may be extended to a dense chemically reacting mixture, if we represent it by a 'homogeneous' hypothetical substance with a variable molecular weight $N_2O_4 \rightleftarrows 2NO_2$ or with 'effective' pseudocritical parameters (combination rules (3.1)), or with 'effective' parameters of the intermolecular reactions (combination rules (3.50)) [sic], depending upon the form in which the reduction parameter is used (via the macroparameters or via the microparameters) [146].

The effect of the composition on the viscosity of a chemically reacting mixture in an ideal (perfect) gaseous state $\mu_{0,T}$ is entirely considered either by a formula obtained on the basis of the molecular-kinetic theory for a homogeneous (individual) rarefied gas,

$$\mu_{0,T} = 0{,}26693\cdot 10^{-5}\,\frac{\sqrt{M_{sm}T}}{\sigma_{sm}^{2}\Omega^{(2,2)*}(T_{sm}^{*})}\,f_{\mu}^{(\kappa)}(T_{sm}^{*})\,\frac{n\,sec}{m^{2}}, \quad (3.3)$$

or according to the Dean-Stiel expressions [118]

$$\mu_{0,T} \simeq 0{,}34\cdot 10^{-6}\left(\frac{T}{T_{ps\cdot cr}}\right)^{0{,}94} \text{ when } \frac{T}{T_{ps\cdot cr}} < 1{,}5, \quad (3.4)$$

$$\mu_{0,T} \simeq 0{,}1778\cdot 10^{-5}\left[0{,}1338\left(\frac{T}{T_{\text{пс.кр}}}\right) - 0{,}0932\right]^{5{,}8}$$

$$\text{when } \frac{T}{T_{ps\cdot cr}} > 1{,}5. \quad (3.5)$$

As for the basic effect of the pressure on the viscosity of a chemically reacting mixture, it may be considered by applying one of the following generalized dependences obtained for dense homogeneous gases.

The law of corresponding states, using the method of reduction to a dimensionless form by means of the microparameters ε/k and σ, was developed in refs. [148, 149, 154]:

$$\frac{\mu^*_{P,T}}{\mu^*_{0,T}} = \frac{\mu_{P,T}}{\mu_{0,T}} = \sum_{i=0}^{n} \sum_{j=0}^{n} a_{ij} (\log T^*)^j \rho^{*i}; \tag{3.6}$$

$$\frac{\mu^*_{P,T}}{\mu^*_{0,T}} = \frac{\mu_{P,T}}{\mu_{0,T}} = 1 + \sum_{i=1}^{n} a_i \omega^{*i} + \frac{1}{T^*} \sum_{i=1}^{n} b_i \omega^{*i} + \frac{1}{T^{*2}} \sum_{i=1}^{n} c_i \omega^{*i} + \frac{1}{T^{*3}} \sum_{i=1}^{n} d_i \omega^{*i} + \frac{1}{T^{*4}} \sum_{i=1}^{n} e_i \omega^{*i}; \tag{3.7}$$

$$\Delta\mu^* = \mu^*_{P,T} - \mu^*_{0,T} = \sum_{i=1}^{m} a_i \rho^{*i}, \tag{3.8}$$

where

$$\mu^* = \frac{\sigma^2}{\sqrt{me}} \mu; \quad \rho^* = \frac{\sigma^3}{m} \rho; \quad T^* = \frac{\kappa T}{\varepsilon};$$

$$\omega^* = \frac{b_0}{V}; \quad b_0 = \frac{2}{3} \pi N \sigma^3.$$

The method of reduction to a dimensionless form by means of the macroparameters P_{cr} and T_{cr} was applied in refs. [158, 159]:

$$\frac{\rho^{4/3} T_{кр}^{7/6}}{\Delta\mu P_{кр}^{2/3} M^{5/6}} = 5{,}33 - 0{,}0387 \frac{\rho T_{кр}}{P_{кр} M}; \tag{3.9}$$

$$\Delta\mu\xi = 0{,}108 \cdot 10^{-4} [\exp(1{,}43\omega) - \exp(-1{,}112\omega^{1{,}858})]. \tag{3.10}$$

Here

$$\Delta\mu = \mu_{P,T} - \mu_{0,T}; \quad \omega = \frac{\rho}{\rho_{кр}}; \quad \xi = T_{кр}^{1/6} M^{-1/2} P_{кр}^{-2/3}.$$

We may demonstrate that both methods of the application of the law of corresponding states must lead to one and the same results with a definite degree of accuracy, i.e., we may accomplish the mutual transition of formulas (3.6)-(3.10).

We will consider these dependences in the coordinates Δμ* and ρ*. After some simple transformations, expressions (3.6) and (3.7) take the form

$$\Delta\mu^* = \sum_{i=1}^{n} \sum_{j=0}^{n} a_{ij} \mu^*_{0,T} (\log T^*)^j \rho^{*i} = \sum_{i=1}^{n} \sum_{j=0}^{n} A_{ij} \rho^{*i}; \tag{3.11}$$

$$\Delta\mu^* = \sum_{i=1}^{n}\left(\frac{2}{3}\pi\right)^i\left[a_i + \frac{b_i}{T^*} + \frac{c_i}{T^{*2}} + \right.$$

$$\left. + \frac{d_i}{T^{*3}} + \frac{e_i}{T^{*4}}\right]\rho^{*i} = \sum_{i=1}^{n} B_i\rho^{*i}. \quad (3.12)$$

By using the connection between the critical parameters and the molecular constants [118]

$$\frac{\varepsilon}{\kappa} \cong 0{,}77T_{cr}; \quad \sigma \cong 0{,}841V_{\kappa p}^{1/3}; \quad (\varepsilon/\kappa)\sigma^{-3} \cong 8{,}197P_{cr}, \quad (3.13)$$

we obtain for dependences (3.9) and (3.10), with the accuracy of combination rules (3.13), the following expressions

$$\Delta\mu^* = \frac{2{,}706\cdot 10^{-3}\rho^{*4{,}3}}{5{,}33 - 5{,}02\rho^*}; \quad (3.14)$$

$$\Delta\mu^* = 0{,}03778\,[\exp(4{,}126\rho^*) - \exp(-8{,}202\rho^{*1{,}858})]. \quad (3.15)$$

Dependences (3.8), (3.11), (3.12), (3.14), and (3.15) are presented in Fig. 3.1. The dashed lines bound the region of experimental points of 25 homogeneous dense gases and 12 dense gaseous mixtures, information concerning which was assembled in refs. [154-157]. Dependences (3.11) and (3.12) were taken at values of the given temperature $T^* = 1$. Although the coefficients A_{ij} and B_i are strong functions of the given temperature T^*, the general results with respect to $\Delta\mu^*$ varies only very weakly and in the region of $0.9 \leqslant T^* \leqslant 10$ and $0 \leqslant \rho^* \leqslant 0.6$, which according to the conventional parameters amounts to $0.7 < T/T_{cr} < 8$ and $0 < \rho/\rho_{cr} < 2$; these variations lie within the limits of scattering of the experimental values.

Thus, both methods of the presentation of a chemically reacting mixture for calculation of the viscosity by a 'homogeneous' hypothetical substance lead to one and the same results, with a definite degree of accuracy.

For calculation of the coefficient of dynamic viscosity of the dissociating system $N_2O_4 \rightleftarrows 2NO_2 \rightleftarrows 2NO + O_2$ in a dense gaseous state, the method of presentation of such a mixture by a 'homogeneous' hypothetical substance with a variable molecular weight and with 'effective' parameters of the intermolecular reactions was used [142].

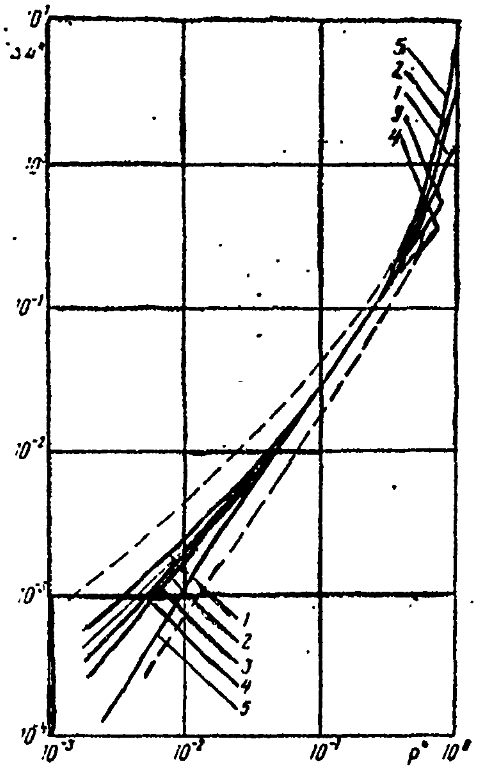

Figure 3.1. Comparison of various generalized dependences of the viscosity of a dense gas in coordinates: given excess viscosity $\Delta\mu^* = (\mu_{P,T} - \mu_{0,T}) \times \sigma^2/\sqrt{m\varepsilon}$ and given density $\rho^* = \rho\,\sigma^3/m$ (generalized dependences: 1- Dean and Stiel [159]; 2- according to this work; 3- Trappeniers and Botzen [148]; 4- Kessel'man and Kamenetskiy [149]; 5- Filippova and Ishkin [158]).

The results of a calculation of the viscosity of dissociating nitrogen tetroxide in an ideal gaseous state according to formula (3.3) are given in Fig. 3.2. The indirect effect of the pressure on the viscosity of the mixture via the variation of the composition is apparent. With an increase in pressure the equilibrium of the reaction $N_2O_4 \rightleftarrows 2NO_2 \rightleftarrows 2NO + O_2$ shifts to the left toward the less viscous component, to the N_2O_4 side according to the first stage of the reaction and to NO_2 according to the second stage (Fig. 3.3).

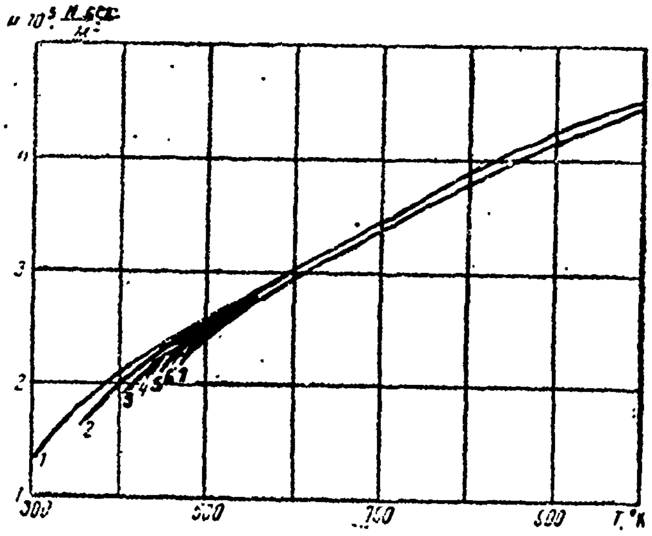

Figure 3.2. Viscosity of dissociating nitrogen tetroxide in an ideal gaseous state:

1- 1 bar; 2- 10 bars; 3- 50 bars; 4- 100 bars; 5- 200 bars; 6- 300 bars; 7- 500 bars.

The basic effect of the pressure on the viscosity was considered by the generalized dependence (3.8). The viscosity of nitrogen tetroxide in a dense gaseous state is presented in Fig. 3.4.

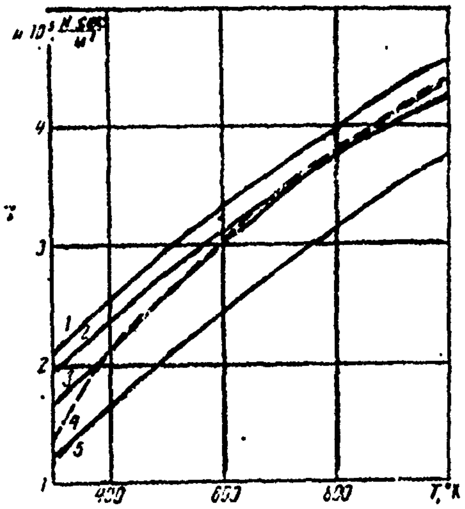

Figure 3.3. Viscosity of the components of the system $N_2O_4 \rightleftarrows 2NO_2 \rightleftarrows 2NO + O_2$ at atmospheric pressure:

1- O_2; 2- NO; 3- NO_2; 4- mixture; 5- N_2O_4.

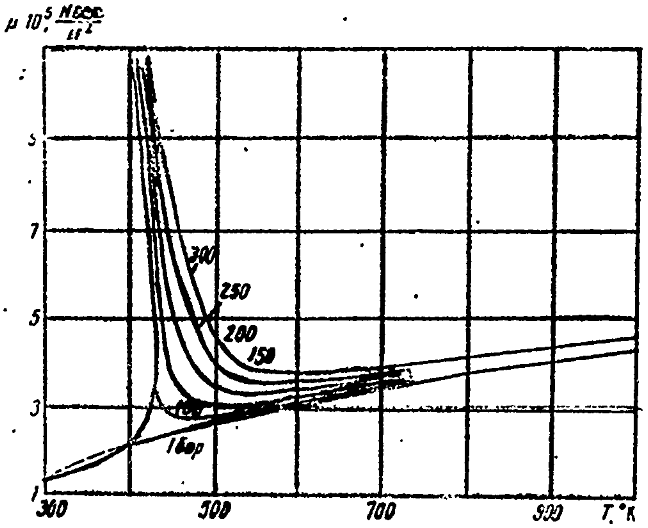

Figure 3.4. Viscosity of the dissociating system $N_2O_4 \rightleftarrows 2NO_2 \rightleftarrows 2NO + O_2$ in a dense gaseous state.

The calculation of the viscosity of the system under consideration was also conducted according to other generalized dependences (3.6), (3.7), (3.9), and (3.10). A satisfactory agreement of all the methods listed is observed within limits of the expected error of 6-8%.

In the calculation of the coefficient of viscosity of a dense chemically reacting mixture, both with respect to the first and with respect to the second methods of representation by a ‘homogeneous’ substance, we may note several nodal moments, which also determine the accuracy of the data obtained.

Both methods claim universality, since the generalizations are applied to homogeneous substances, mechanical mixtures, and mixtures of chemically reacting gases. But they are obtained in individual substances under the assumption that all the gases which were used for the construction of the single dependences are thermodynamically similar. Because of the phase separation of the values of the coefficient of viscosity of individual substances from the averaged curve, and because of the experimental error of the data themselves, the error of generalization amounts on the average to 5-6%. In the extension of the method to mechanical gaseous mixtures the viscosity of the latter is plotted around the generalizing curve by the same scattering.

The application of these generalizations to dense chemically reacting mixtures causes a deterioration in accuracy because of the approximate consideration of the imperfect nature of the components in the calculation of the composition. Since the theoretical estimate is difficult, the non-strict nature of the consideration of the imperfect nature of the components in the composition may be determined in each specific case.

Such a calculation was performed for the system $N_2O_4 \rightleftarrows 2NO_2 \rightleftarrows 2NO + O_2$. As is apparent from Fig. 3.5, the variation of the molar fraction x_i even by 30% introduces an error of about 6% into $\mu_{O,T}$ and an error of the order of 5% into $\mu_{P,T}$. The error in the determination of x_i has a very small effect on the excess viscosity $\Delta\mu$.

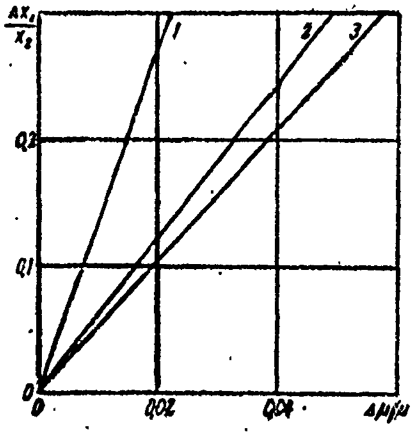

Figure 3.5. The error introduced into the magnitudes of $\Delta\mu$, $\mu_{O,T}$, and $\mu_{P,T}$ because of the possible error in the determination of the composition.

1- $\Delta\mu$; 2- $\mu_{P,T}$; 3- $\mu_{O,T}$

According to preliminary estimates, in the use, for example, of Watson's diagram with respect to volatilities we may err in x by a maximum of 7-8%, which gives a contribution of 1.5-2% to $\mu_{P,T}$. In the use of Pitzer's diagrams [71] this error is decreased. The non-strict nature of the consideration of the imperfect nature of the components in the composition on the viscosity of any chemically reacting system will be felt to a greater degree if the difference in the viscosity of the components of the mixture is greater.

The viscosity of nitrogen tetroxide in a dense gaseous state was experimentally studied in ref. [33]. The data were obtained by the falling weight method in a range of variations of temperature from 300 to 850 K and in a pressure range of 1 to 50 bars with a maximum relative error of 5%. Within the limits of the guaranteed accuracy of the calculation and experimental methods, a satisfactory agreement is observed between the calculated and experimental data, and the maximum divergence does not exceed 8%.

This method of calculating the viscosity of dense chemically reacting mixtures may be extended to any chemically reacting systems. For calculation of the viscosity of dense dissociating systems it is necessary to know the density and the composition, and also the intermolecular constants of the components of the mixture.

2. Thermal Conductivity of Nitrogen Tetroxide

The effective coefficient of thermal conductivity of a reacting mixture of gases is, as is well known [2], the sum of two components describing the two methods of heat transfer in such a mixture: $\lambda_{eff} = \lambda_f + \lambda_r$, where λ_f, the 'frozen' component, describes heat transfer by ordinary molecular thermal conductivity, and λ_r, the reaction component, describes the transfer of enthalpy of the components of the mixture by means of concentration diffusion.

The expanded expression for the effective coefficient of thermal conductivity has the form [132]

$$\lambda_{eff} = \lambda_f + \frac{1}{RT^2} \frac{\Delta H_{p1}^2 A_{22} - 2\Delta H_{p1} \Delta H_{p2} A_{12} - \frac{1}{2} \Delta H_{p2}^2 A_{11}}{A_{11} A_{22} - 2A_{12}^2},$$

$$A_{11} = \frac{1}{\rho_M} \left\{ \frac{(2x_1 + x_2)^2}{x_1 x_2 D_{12}} + \frac{x_3}{x_1 D_{13}} + \frac{x_4}{x_1 D_{14}} + \right.$$

$$\left. + \frac{4x_3}{x_2 D_{23}} + \frac{4x_4}{x_2 D_{24}} \right\},$$

$$A_{12} = \frac{1}{\rho_M} \left\{ \frac{2x_1}{x_1 D_{12}} + \frac{2x_3}{x_2 D_{23}} + \frac{2x_4}{x_2 D_{24}} + \frac{2}{D_{23}} + \right.$$

$$+\frac{1}{D_{24}}+\frac{1}{D_{12}}-\frac{1}{D_{13}}-\frac{1}{9D_{14}}\Big\},$$

$$A_{22}=\frac{1}{\rho_m}\Big\{-\frac{2x_1}{x_3D_{13}}-\frac{x_1}{2x_4D_{14}}-\frac{(2x_4+x_2)^2}{2x_2x_4D_{24}}-$$

$$-\frac{2(x_2+x_3)^2}{x_2x_3D_{23}}-\frac{2x_1}{x_2D_{12}}\Big\}.$$

The quantities entering into these expressions signify the following: ρ_m molar density; x_i molar fraction of the i-th component in the mixture; D_{ij} represents the binary coefficients of the diffusion of the corresponding pairs of components; ΔH_{p1} and ΔH_{p2} are the changes of the total enthalpy of the system as a result of the chemical reaction $\Delta H_{p1} = 2H_2 - H_1$ (stage I), $\Delta H_{p2} = 2H_3 + H_4 - 2H_2$ (stage II). The subscripts 1, 2, 3, 4 correspond to N_2O_4, NO_2, NO, and O_2.

The difficulties of the calculation of the thermal conductivity of a dense reacting mixture lie basically in the absence of a good method of calculating the coefficients of thermal conductivity of ordinary non-reacting dense mixtures and the binary coefficients of diffusion of mixtures of gases in a dense state. Both in one and in the other case up to the present time too little experimental data have been accumulated to permit us to construct any empirical generalizations or formulas making it possible to calculate these coefficients. The theory of transport (transfer) in dense mixtures of gases is still inadequately developed in order to give reliable results in the calculation. Therefore, for the calculations we ordinarily use indirect methods such as, for example, the method of representation of a mixture by a certain homogeneous substance, in the calculation of coefficients of thermal conductivity, and theoretical formulas corrected by means of experimental data in the calculation of diffusion factors.

Calculation of the frozen component of the thermal conductivity of dissociating gases. For the calculation of the frozen component of thermal conductivity at increased pressures, two methods are ordinarily used. The first is calculation according to formulas available for rarefied mixtures, in which data for compressed components are substituted. The second method is based on the representation of the mixture by a certain homogeneous substance with single critical parameters. This makes it possible to use generalizations and formulas that are valid for homogeneous substances for calculation of the thermal conductivity of the mixture. Usually in this case generalizations are used which are constructed on the basis of the law of corresponding states [24, 176].

Both methods give the same errors on the average. In individual cases these errors reach almost 50% [24]. The second method gives greater opportunities for refinement of the calculations, since as new and more reliable experimental data for homogeneous gases appear, new and more accurate generalizations may be constructed. For example, a calculation performed by means of a generalization that recently appeared for homogeneous substances, found by Stiel and Thodos [177], gave a maximum error of approximately 25% in the thermal conductivity of the mixture.

Attempts to decrease the error of calculations have led to the use of a formula somewhat altered by N. B. Vargaftik for homogeneous gases [178]. The formula

$$\lambda_{P,T}-\lambda_{0,T}=B\rho^{n}\left[1+\frac{C\cdot 10^{3}}{Z_{cr}^{3}}\left(\frac{\rho}{\rho_{cr}}-1\right)\right]$$

describes the thermal conductivity of homogeneous gases up to $\rho/\rho_{cr} = 1.8$ with an average error of 5-6%. In this formula $\lambda_{P,T}$ is the thermal conductivity at the pressure P and temperature T; $\lambda_{0,T}$ is thermal conductivity at P = 1 atmosphere and at temperature T.

The quantity B can be calculated according to the formula

$$B=C\left[\frac{\left(\frac{\rho_{cr}}{M}\right)^{2/3}T_{cr}^{1,2}}{M^{1/2}}\right]\frac{1}{\rho_{cr}^{n}Z_{cr}^{3}},$$

$$C=(33,4+0,24M)\,10^{6}.$$

The exponent n is expressed by the dependence n = 1.16 + 0.0024M [179]; ρ_{cr}, T_{cr}, and Z_{cr} are, respectively, the density, temperature, and compressibility at the critical point, and M is the molecular weight of the substance. $\rho/\rho_{cr} = \rho_g$ is the ratio of the density at P and T to the density at the critical point.

As is apparent, in the use of the given formula for calculation of the thermal conductivity of the substance, it is necessary to know its critical parameters and for the mixture its pseudocritical parameters.

Prausnitz and Gunn [118] demonstrated that we may calculate the pseudocritical parameters with a good accuracy according to the formulas

$$V_{\text{м}\,ps.cr}=\sum_{i=1}^{n}x_iV_{\text{м}\,cri},$$

$$Z_{ps.cr}=\sum_{i=1}^{n}x_iZ_{cri},$$

$$T_{ps.cr}=\sum_{i=1}^{n}x_iT_{cri}.$$

Here $V_{m\ ps.cr} = M_{cm}/\rho_{ps.cr}$ is the molar pseudocritical volume; $V_{m\ cr} = M/\rho_{cr}$ is the molar critical volume of the component of the mixture, and $M_{cm} = \sum_{i=1}^{n} x_iM_i$ is the molecular weight of the mixture.

The calculation of the thermal conductivity of the mixture according to the formula gave a maximum deviation from the experimental results that was only approximately half as much as results by means of the generalization of Stiel and Thodos [177].

At present the theory of rarefied gases has been so well developed that the transport properties of the gases and unreacting mixtures may be considered adequately accurately at moderate pressures [160]. Several simplified semi-empirical and empirical formulas have also been proposed [24, 160, 180], with respect to which the thermal conductivity of rarefied mixtures is calculated with an accuracy that is entirely acceptable for engineering purposes.

The thermal conductivity of mixtures consisting of multi-atomic molecules depends both upon the translational and upon the internal degrees of freedom. Brokaw [160] proposes to calculate the thermal conductivity of such mixtures according to the formula $\lambda_{0,T} = \lambda_0^{cm} + \lambda_{in}^{cm}$. A component depending only upon the translational degrees of freedom (or the thermal conductivity of the mixture of monoatomic gases) may be calculated according to the formula

$$\lambda_0^{SM} = \sum_{i=1}^{n} \frac{\lambda_i^0}{1 + \frac{1}{x_i} \sum_{\substack{j=1 \\ j \neq i}}^{n} x_j \Psi_{ij}} .$$

Here

$$\Psi_{ij} = \Phi_{ij} \left[1 + 2{,}41 \frac{(M_i - M_j)(M_i - 0{,}142 M_j)}{(M_i + M_j)^2} \right],$$

$$\Phi_{ij} = \frac{\left[1 + \left(\frac{\mu_i}{\mu_j} \right)^{1/2} \left(\frac{M_j}{M_i} \right)^{1/4} \right]^2}{2\sqrt{2} \left[1 + \frac{M_i}{M_j} \right]^{1/2}} .$$

The coefficient of thermal conductivity of pure monoatomic gases and the coefficients of viscosity of the components are calculated according to the well-known formulas of the kinetic theory

$$\lambda_i^0 = 198{,}91 \cdot 10^{-6} \frac{\sqrt{\frac{T}{M_i}}}{\sigma_i^2 \Omega^{(2,2)*} (T_i^*)} = \frac{15}{4} \cdot 10^{-6} \frac{R}{M_i} \mu_i ,$$

$$\mu_i = 26{,}693 \cdot 10^{-6} \frac{\sqrt{M_i T}}{\sigma_i^2 \Omega^{(2,2)*} (T_i^*)} .$$

Aiken [120] introduced the correction for the monoatomic nature of the gases (consideration of the internal degrees of freedom) for the first time. Later it was refined by Hirschfelder [164]. The thermal conductivity of a pure monoatomic gas is

$$\lambda_i^{in} = \lambda_i^0 \, 0{,}885 \left[\frac{2}{5} \frac{C_{pi}}{R} - 1 \right].$$

Brokaw [160] proposes to consider the contribution of the 'internal' thermal conductivity of the components to the thermal conductivity of a multi-component mixture in the following manner:

$$\lambda_{in}^{SM} = \sum_{i=1}^{n} \frac{\lambda_i^{BH}}{1 + \frac{1}{x_i} \sum_{\substack{j=1 \\ j \neq i}}^{n} x_i \Phi_{ij}} .$$

Calculation of the binary diffusion factors of dense gaseous mixtures. For calculation of the reaction component of the thermal conductivity, it is necessary to know the binary diffusion factors of the pairs of components participating in the reaction. Their calculation presents special difficulties, since there are no generalizations for them based on experimental data. Experimental works are basically concerned with the determination of self-diffusion factors. The only work, by Slettery and Bird [181], generalizing these data makes it possible to calculate the self-diffusion factors of dense gases and that only in a range of given pressures from 0.1 P_g to 4 P_g and given temperatures from 1 T_g to 3 T_g. By means of Slettery's diagram the diffusion factors of certain mixtures were calculated and compared with the experimental data [182]. A satisfactory agreement was obtained. In the construction of the diagram, Slettery and Bird used generalized data on compressibility given by Hougen and Watson [68]. As is well known, they give great errors. It was possible to attempt to improve Slettery's diagram by using the generalized data on compressibility of dense gases given by Pitzer [69], which are an order of magnitude more accurate than the data of Hougen and Watson. However, the introduction of a third correlation parameter, the acentric factor ω leads to great difficulties in the realization of this method. A method for the calculation of the binary diffusion factors of dense gases is explained below, which retains the approach of Slettery, but excludes the numerical differentiation of tables with respect to compressibility.

According to Enskiy's theory for the diffusion factor we have

$$\frac{DP}{(DP)^{\bullet}} \quad b\rho\frac{z}{b\rho\kappa},$$

where

$$b\rho\kappa \quad \frac{V_{M}}{R}\left(\frac{\partial P}{\partial T}\right)_{V} - 1,$$

or in dimensionless coordinates,

$$b\rho\kappa \quad Z\frac{\tau}{\pi}\left(\frac{\partial \pi}{\partial \tau}\right)_{V} - 1.$$

Here

$$\tau \quad \frac{T}{T_{\text{кр}}};\ \pi \quad \frac{P}{P_{\text{кр}}};\ V \quad \frac{\rho_{cr}}{\rho}.$$

In order to avoid differentiation of tables with respect to compressibility, we will determine bρκ from experimental data on the viscosity of dense gases, having used Golubev's equation [183], which describes them with a high degree of accuracy.

In the dimensionless form, Golubev's equation has the following form:

$$\mu_{P,T} - \mu_{0,T} = a\left[\frac{P_{кр}}{T_{кр}}\left(\frac{\partial\pi}{\partial\tau}\right)_V\right]^n.$$

The quantity $(\delta\pi/\delta\tau)_{V=1} = \alpha_{cr}$ in the dimensionless coordinates π and τ characterizes the dip of the buoyancy curve at the critical point. As Pitzer demonstrated [69], α_{cr}, the Riedel factor, is associated with the acentric factor ω in the following manner: $_{cr}$ = 5.808 + 4.93 . After certain transformations, we may obtain the following dependence:

$$\Delta\mu_{P,T} = \frac{\Delta\mu_{кр}}{\alpha^n_{кр}}\left[\frac{\partial\pi}{\partial\tau}\right]^n_V.$$

If we assume, as Golubev does, that n = 1.115, then

$$\left(\frac{\partial\pi}{\partial\tau}\right)_V = \alpha_{кр}\left(\frac{\Delta\mu}{\Delta\mu_{кр}}\right)^{0,89686};$$

$$b\rho\varkappa = Z\frac{\tau}{\pi}\alpha_{кр}\left(\frac{\Delta\mu}{\Delta\mu_{кр}}\right)^{0,89686} - 1.$$

Then for the diffusion factor we obtain

$$\frac{DP}{DP^*} = b\rho - \frac{Z}{Z\frac{\tau}{\pi}\alpha_{кр}\left(\frac{\Delta\mu}{\Delta\mu_{кр}}\right)^{0,89686} - 1}.$$

We calculate the quantity bρ according to the following formula:

$$b\rho = \frac{\mu_{P,T}}{\mu_{0,T}} = \frac{1}{\frac{1}{b\rho\varkappa} + 0,8000 + 0,7614\,b\rho\varkappa}.$$

The quantity (DP)* may be calculated according to the formulas of the kinetic theory of gases or according to Slettery's formula [181]. Finally, for calculation of the mutual diffusion factors of the components of the mixture, we obtain the following expression:

$$PD_{ij} = D^0_{ij} \times \frac{Z_{SM}(b\rho)_{SM}}{Z_{SM}\left(\frac{T_r}{P_r}\right)_{SM}(5,808 + 4,93\omega_{SM})\left(\frac{\Delta\mu}{\Delta\mu_{cr}}\right)^{0,89686} - 1},$$

where D^0_{ij} represents the diffusion factors of a perfect gas at 1 atmosphere:

$$D^0_{ij} = \frac{0{,}002628}{\sigma^2_{ij}\Omega^{(1,1)*}(T^*_{ij})}\sqrt[3]{\frac{T^3(M_i+M_j)}{2M_iM_j}};$$

$$T_{пcм} = T\left[\sum_{i=1}^{n} x_i T_{кpi}\right]^{-1};\quad P'_{пcм} = P\left[\sum_{i=1}^{n} x_i P_{кpi}\right]^{-1};$$

$$\omega_{cм} = \sum_{i=1}^{n} x_i\omega_i.$$

We should bear in mind the fact that the extrapolation of the formulas given above for calculation of the diffusion factor in the region of moderate pressures is incorrect and leads to considerable errors. At moderate pressures (in the given case up to 30 atmospheres) the calculation was performed according to the formulas of the kinetic theory of rarefied gases.

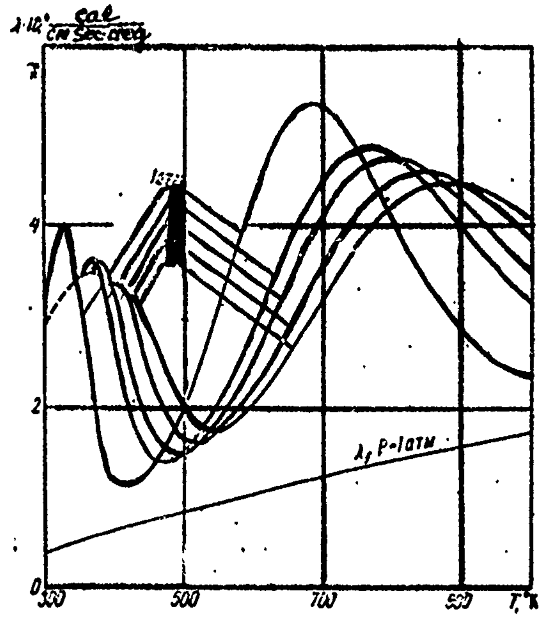

Figure 3.6. 'Effective' thermal conductivity of the system $N_2O_4 \rightleftarrows 2NO_2 \rightleftarrows 2NO + O_2$.

Thus, the quantities causing the basic difficulties in the calculation of the effective thermal conductivity of a compressed reacting mixture (the 'frozen' component and the binary diffusion factors) may be calculated by the methods given above. The other variables (the composition, variation of enthalpy, density, and others), upon which the effect thermal conductivity depends, are calculated by the methods explained in Chapter II.

The results of the calculations are presented in Fig. 3.6.

Chapter IV

THE EFFECT OF THE KINETICS OF THE CHEMICAL REACTION ON HEAT TRANSFER AND MASS TRANSFER IN STATIC STEADY-STATE CONDITIONS (HEAT-CONDUCTING GAS) IN A SYSTEM $N_2O_4 \rightleftarrows 2NO_2 \rightleftarrows 2NO + O_2$

1. The Effect of Chemical Reactions on the Thermal Conductivity of a Mixture of Reacting Gases. The Theory of Local Chemical Equilibrium

A feature of heat transfer in a non-isothermic mixture of chemically reacting gases at rest (a heat-conducting gap) lies in the fact that aside from the ordinary molecular thermal conductivity an additional quantity of heat is transferred (transported) in the form of chemical enthalpy by means of molecular concentration diffusion. Thus, the total 'effective thermal conductivity' of the mixture of reacting gases is determined by the thermal conductivity itself (the 'frozen' component λ_j) and the diffusion component (the 'reaction' component λ_t), which depends upon the thermal effects of the reactions and the gradients of the concentrations of the components.

The contribution of the diffusion transfer to the general heat flux depends upon the ratio of the rate of the chemical transformations in the gas and the rate of the process competing with them -- diffusion equalization of concentrations in the heat-transfer gap.

If the rates of the chemical transformations of the components are much greater than the rate of the latter, the composition of the mixture is in local equilibrium with temperature. Therefore, the total 'thermal conductivity' of an equilibrium mixture is an unambiguous function of the external parameters (it is assumed that in the internal degrees of freedom equilibrium has been established). Such a mixture behaves like a homogeneous (individual) substance with a general thermal conductivity λ_e, the values of which in certain range of the variation of the external parameters (P, T) may exceed the magnitude of the thermal conductivity of an inert mixture of gases by an order of magnitude.

Nernst [161] obtained an expression for the 'effective thermal conductivity' of a binary reacting mixture $A_2 \rightleftarrows 2A$ in a state of thermochemical equilibrium, λ_e, for the first time. But in the notation of the equation of diffusion in the form of Fick's law he used a conventional coefficient of binary diffusion of the unreacting gases, $D = D_{12}$.

However, in distinction from conventional diffusion in the presence of chemical transformations in the mixture the average rate of diffusion of individual components of the mixture in a steady state are not equal to zero, although the average mass velocity is equal to zero. Having taken this into consideration, Haase [132, 162] obtained

$$D_{eff} = \frac{D_{12}}{1+x_{1e}} = \frac{1}{2} D_{12}(1+\alpha_{1e}).$$

We should note that Nernst himself expressed doubts of the correctness of the identity of D with a conventional binary diffusion factor. It was possible to check that $D \neq D_{1e}$ in a mixture with a low degree of dissociation, α_{1e}, where this distinction is noticeable. But the only experimental data available at that time, those of Magnanini and Zunino [143] with respect to $\bar{\lambda}^*$ of the mixture $N_2O_4 \rightleftarrows 2NO_2$ embraced a region of high values of $\alpha_{1e} \geq 0.5$, where $(1/2)(1+\alpha_{1e})$ varies within limits of the 0.75-1. Also, these data were obtained with a great error: the deviation of the experimental values at the same parameters of P and T amounted to up to 30%. Probably the effect of convection as a consequence of a large experimental gap (Fig. 4.1) was felt on the results at low temperatures.

Subsequent experiments confirmed the correctness of Haase's conclusion concerning the 'effective' diffusion factor of a mixture of reacting gases.

Later Butler and Brokaw [132] obtained a general expression for the thermal conductivity of a mixture consisting of any number of reagents and inert components with an arbitrary number of equilibrium chemical reactions. This expression was then simplified [160], which later made it possible for Brokaw [151] to make an excellent transition in the derivation of a ratio for the average 'thermal conductivity' of a nonequilibrium mixture.

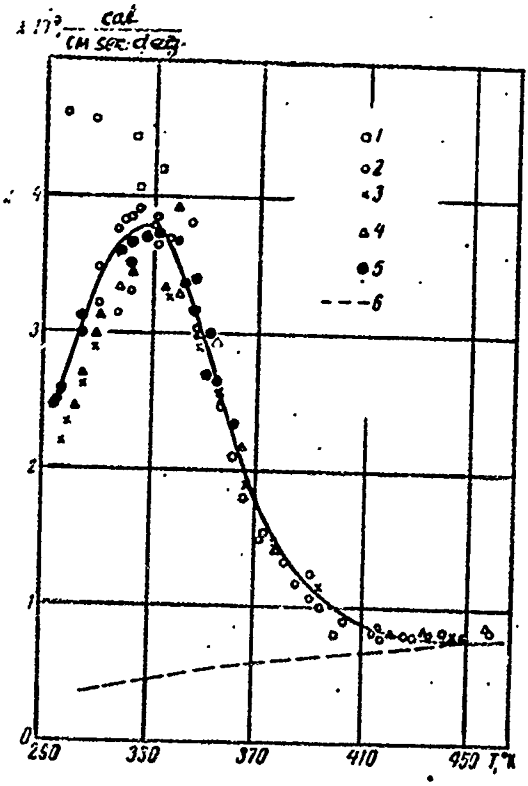

Figure 4.1. Experimental values of the 'thermal conductivity' of the mixture N_2O_4 $2NO_2$ at atmospheric pressure.
1- Magnanini-Zunino [143]; 2- Coffin-O'Neal [25]; 3- Dresvyannikov [145]; 4- IYaE AN BSSR [29]; 5- values from ref. [25], corrected by Brokaw [170, 171]; solid line represents calculated values of λ_{el}; dashed line represents calculated values of λ_{fl} (in this work).

Prigogine and his colleagues [163] and Haase [136] investigated heat transfer and mass transfer in a non-isothermic mixture of reacting gases at rest from the standpoint of the thermodynamics of irreversible processes. The same expression was obtained for the λ_e of the system $A_2 \rightleftarrows 2A$, as by Hirschfelder [164, 165] and by Butler and Brokaw [132] in the assumption of thermochemical equilibrium. In this case Prigogine with his colleagues analyzed the effect of the thermal-diffusion term and arrived at the conclusion that its contribution to equilibrium thermal conductivity is non-essential.

Verba and Portnov [166] obtained an expression for λ_e of a multicomponent mixture by the method of thermodynamics of the irreversible processes.

The theory of local thermochemical equilibrium successfully expalined experimental data with respect to the thermal conductivity of certain mixtures. In particular, the experimental values of the thermal conductivity of hydrogen fluoride with two parallel reactions [2HF $(HF)_2$, ΔH_{p2} = 7400 calories/mole and 6HF $\rightleftarrows$ $(HF)_6$, H_{p6} = 40,500 calories/mole] agree well with the calculated equilibrium values of λ_e [167]. And the latter are 33 times higher than λ_f and almost 3 times as high as λ_{H2}. The experimental data of Chakraborti [169] with respect to the thermal conductivity of the system $PCl_5 \rightleftarrows PCl_3 + Cl_2$ at pressures below 1 atmosphere also agree well with λ_e.

2. Experimental Investigations of the 'Thermal Conductivity' of the System $N_2O_4 \rightleftarrows 2NO_2 \rightleftarrows 2NO + O_2$

Experimental data on the thermal conductivity of dissociating gases are few in number. It is possible that this is connected with methodological difficulties of the investigation of the thermal conductivity of aggressive media at comparatively high temperatures. Probably for this reason those dissociating gases are more thoroughly studied whose thermal decomposition occurs at lower temperatures. As a consequence of the aggressive of the majority of dissociating gases the range of pressures being studied is limited to 1 atmosphere, when glass apparatus may be used.

Nitrogen tetroxide, N_2O_4, is just such a low-boiling substance, the thermal decomposition of which in the gaseous phase begins at comparatively low temperatures.

The investigation of the thermal conductivity of the system $N_2O_4 \rightleftarrows 2NO_2$ was attempted for the first time by Magnanini and Zunino [143, 150] (Table 4.1). We do not have information concerning the details of the experiment or the geometrical dimensions of the apparatus, but the anomalous fluctuation of the curve at P = 1 atmosphere and at low temperatures (see Fig. 4.1) makes it possible to assume that the heat-transfer gap was too great so that in these conditions convection was mixed with true thermal conductivity. The exaggerations of λ_{exp} at T < 330°K speak in favor of this explanation, and also the fact that the anomaly disappears with an increase in temperature at P = 1 atm and with a decrease in pressure.

Feliciani [168], wishing to refine the experimental values of thermal conductivity obtained by Magnanini and Zunino, attempted the investigation of the thermal conductivity of the mixture by the unsteady-state method. He does not give a diagram of his apparatus but, judging by the brief description, the experimental part consisted of a glass flask inside of which the bulb of a thermometer was placed coaxially. The flask, filled with pure N_2O_4, was heated in a thermostat to a temperature exceeding the highest temperature of the range being investigated by 20-30°. Then it was momentarily submerged in another thermostate and an observation was made of the 'time of cooling of the thermometer by steps of 5°'. The pressure was recorded by an aspirator connected with the flask.

The processing of the results of the observations was conducted to an approximate formula of unsteady-state thermal conductivity obtained for the cooling of a solid in the zone of a linear regular regime. The fact sticks out in the description that the average rate of cooling was determined from all the measurements in the selected range of temperatures, while at first the cooling occurs in a disordered unsteady-state regime. In this case, convection continuously originates in the layer of gas, which will facilitate the equalization of the temperatures. Probably partly due to this and partly due to the method of processing we may explain the extraordinarily high values of λ_e obtained by Feliciani (Fig. 4.2). The fact that in an investigation with a large flask large values of λ_e were obtained speaks in favor of the argument of the effect of convection. In Fig. 4.2 for comparison equilibrium values of λ_e at P = 0.4 and 0.7 atm are given.

Later the coefficient of 'thermal conductivity' of the system $N_2O_4 \rightleftarrows 2NO_2$ was investigated by Coffin and O'Neal [25] by the heated filament method. The experimental values [25] are given in refs. [151,167,147,170,171] (see Table 4.1). In this case the error of the experimental data in the range of low pressures P = 0.05-0.2 atm, in the opinion of Coffin [147], reaches 10% because of the effect of thermal accommodation.

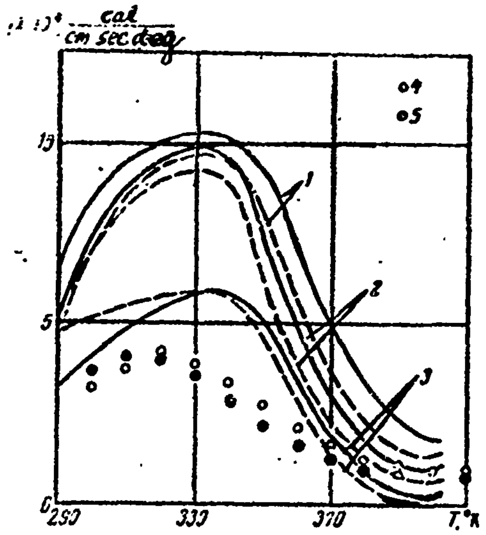

Figure 4.2. Experimental values of the ‘thermal conductivity’ of the mixture $N_2O_4 \rightleftarrows 2NO_2$ obtained by Feliciani [168]. 1- P = 0.733 atm; 2- P = 0.413 atm; 3- P = 0.078 atm; solid lines represent large flask; 4- λ_{el} at P = 1.7 atm; 5- λ_{el} at P = 0.3 atm.

Relative to the values of ‘thermal conductivity’ at P = 1 atm, given in the drawings of Brokaw [170, 171] as experimental values of Coffin and O’Neal, we should note the following. Two corrections were introduced by Brokaw into the experimental values of ref. [25].

The first is associated with the fact that for the calibration of the apparatus in ref. [25] the experimental values obtained by Kannuluik and Karmen with respect to λ_{He} were used, which, according to his opinion, are understated in comparison with the ‘true values’ [173] by 3-4%.

The experimental values of Kannuluik and Karmen actually lie below the values of λ_{He} of Zaytseva [174] (at 500°K by 5.3%, and at 580°K by 6.6%). Probably this is associated with the inaccurate consideration of the effect of radiation: because of the use of a thick heated filament (1.5 mm) in the experiments of Kannuluik and Karmen, the correction for radiation amounted to 20% at 600°K. But the experimental values of λ_{He} of other authors also lie 1-2% below the calculated curve [173] in the region of T = 300-370°K. Thus, although the experimental values of Kannuluik and Karmen at high temperatures are also explicitly understated in comparison with the data of other autors [174, 175] in the region of temperatures investigated by Coffin and O'Neal, they agree satisfactorily with the latter, within the limits of error of the experiment. Thus, in the correction of the values of λ_{exp} [25] with respect to λ_{He} Brokaw somewhat exaggerated λ_{exp}.

Table 4.1 Experimental investigation of the 'effective thermal conductivity' of the system $N_2O_4 \rightleftarrows 2NO_2 \rightleftarrows 2NO + O_2$

Researchers	Year	P,atm	T,°K	Ref. Source	Dimensions of gap, cm
Magnanini-Zunino	Italy 1900	1 0,34	298—472 273—428	[143, 150]	not given
Feliciani	Italy 1905	0,078 0,413 0,763	291—401	[168]	not given
Coffin-O'Neal	USA 1958	0,33—1 0,02—1 1 0,02—1 0,04—1 0,05—1	295—490 295—350 294—388 351,5 296 300	[25, 147] [170, 171] [147] [151, 167]	$R_1=6,48\cdot10^{-3}$ $R_2=0,2405$ $\Delta=R_2-R_1=$ $=0,234$ $R_2/R_1=37,1$
Srivastava-Barua	India 1961	0,135— —0,69	305,318 333,348 363	[26]	$R_1=5\cdot10^{-3}$ $R_2=0,144$ $\Delta=0,139$ $R_2/R_1=28,8$
Barua-Chakraborti	India 1962	0,2—0,87 0,2—0,87	373—393 413,433 453,373	[27]	$R_1=3,75\cdot10^{-3}$ $R_2=0,161$ $\Delta=0,1573$ $R_2/R_1=43$
Dresvyannikov and others	USSR, KAI 1965	0,263; 0,53; 0,78; 0,987	296—871	[144, 145]	$R_1=5,025\cdot10^{-3}$ $R_2=0,162$ $\Delta=0,1567$ $R_2/R_1=32,3$
Bilyk, Timofeyev, and others	USSR IYaE AN BSSR 1967	1; 5; 10, 20, 30; 50	301—780	[29]	$R_1=0,4$ $R_2=0,48$ $R_2/R_1=1,2;$ или $R_2=0,49;$ $R_2/R_1=1,225$
Dastidar-Barua	India 1967	0,061— —0,8	308; 323	[172]	not given

The second correction is associated with the effect of the final rate of the reaction $N_2O_4 \rightleftarrows 2NO_2$ on λ_{exp}. Brokaw corrected the experimental values [25] on the basis of his formula for nonequilibrium 'thermal conductivity'. That is, having excluded the effect of the rate of the reaction, he thus determined the values of equilibrium thermal conductivity, which now are called 'experimental' equilibrium values. Precisely with these 'experimental' data of Coffin and O'Neal are the values of λ_{exp} compared at P = 1 atm in ref. [145].

The difference of the experimental data [25] from the calculated value of the equilibrium 'thermal conductivity' mixture $N_2O_4 \rightleftarrows 2NO_2$, λ_{e1}, observed by Brokaw at $P = 1$ atm, in our view is basically explained by the fact that in the calculation of λ_{e1} he used the parameters of the intermolecular reaction, determined from experimental data μ_{sm} [31]. As later investigations [46] demonstrated, the experimental data of μ_{sm} obtained by Petker and Mason [31] are somewhat exaggerated in the low-temperature region. The experimental data of Coffin and O'Neal agree satisfactorily with the values of λ_{e1} at $P = 1$ atm if in the calculations we use the parameters of the reaction determined from the values of μ_{sm} [46] (Fig. 4.1).

Coffin and O'Neal observed a noticeable decrease of λ_{exp} in comparison with λ_e at low pressures. But since their experimental data at low pressures were obtained with a comparatively large error, Srivastava and Barua [26] decided to repeat the experiment with respect to the determination of the thermal conductivity of the system $N_2O_4 \rightleftarrows 2NO_2$.

The researchers, as in ref. [25], accepted the heated filament method which was well worked out by Kannuluik and Martin. The experimental gap, to avoid natural convection, was reduced in comparison with the one used by Coffin and O'Neal (Table 4.1), and the pressure did not rise above 0.69 atm.

To avoid the chemical reaction of the N_2O_4 with the mercury, the pressure was measured by a glass diaphragm manometer designed by Daniels. The researchers [26] took care to purify the N_2O_4 thoroughly. Srivastava and Barua introduced corrections for radiation, excentricity, temperature difference at the wall, and temperature jump at the wall at low pressures into the experimental values obtained.

While Coffin and O'Neal did not take the natural experimental data at $P < 1/3$ atm into consideration, assuming that the sharp decrease in λ_{exp} in comparison with λ_e at low pressures was a consequence of the effects of thermal accommodation that were not considered, after the experiments of Srivastava and Barua already no doubts remained that this is to a greater degree a consequence of the relaxation of chemical energy if also after the introduction of the correction for the temperature jump the tendency in the behavior of λ_{exp} with relationship to λ_e at very low pressures remained as before. The problem of the accuracy of the values of λ_{exp} obtained by the authors [26] was not discussed. As calibration values, the values obtained by Kannuluik and Karmen were used.

The work of Barua and Chakraborti [27], where the temperature range was expanded to 200°C, which made it possible to capture the initial region of the thermal dissociation of NO_2 as well, was a continuation of investigation in ref. [26]. It was observed that λ_{exp} in the region of stage II of dissociation is close to the 'frozen' thermal conductivity of the mixture with respect to values. But since in the region of temperatures investigated even equilibrium values of the degree of dissociation did not exceed 0.01-0.02 according to the results obtained it was difficult to make a general conclusion concerning the effect of the kinetics of stage II of dissociation on 'thermal conductivity.'

Dresvyannikov [145] expands the range of temperatures with respect to stage II to 600°C, and performs a quite detailed investigation of 'thermal conductivity' of stage I of the dissociation of N_2O_4 also, as a function of P and T (see Table 4.1). The researcher constructed an experimental apparatus similar to the one described in [26], and accepted approximately the same gap. In the course of the processing of the results corrections were introduced for radiation, heat transfer from the ends, the effect of excentricity, and the temperature difference at the wall. The jump of temperature at the boundary between the wall and the gas was not considered. Gupta and Sachsen established that when $P > 0.1$ atm in the investigation of λ by the heated filament method the effect of the temperature jump need not be considered. It is true that the investigations were concerned with low temperatures ($T = 93.5°C$) and comparatively simple gases (Ne, Ar, H_2, O_2). But since Dresvyannikov conducted his experiments at $P \gtrsim 0.263$ atm, then, probably, the failure to consider the temperature jump in these conditions did not introduce any noticeable error into λ_{exp}.

According to the estimates of the author of ref. [145], the total error of the experimental values of λ_{exp} did not exceed 2.9%. We note that although the control measurements of λ_{NO} [145] did not differ by more than 2% at moderate temperatures from the values obtained by Johnston and Greeley, at high temperatures the values of λ_{NO} [145] are 4-6% above the calculated values obtained with Suyetin's reaction parameters [153].

It is possible that this was caused by the non-strict consideration of the effect of radiation or by failure to consider thermal accommodation at high temperatures.

The experiments of Dresvyannikov confirm the conclusion that at low pressures stage II is a 'slow' reaction.

The work of Dastidar and Barua [172] supplemented the data with respect to thermal conductivity of the system $N_2O_4 \rightleftarrows 2NO_2$. The authors estimated the error in the values obtained as ±2%.

But all the reliable experiments [26, 27, 145, 172] were conducted at pressures $P \lesssim 1$ atm and by one method, with a heated filament. As a heater, a platinum wire was used by everyone. However, according to the reports of the authors of ref. [225], platinum plays the role of a catalyst in the reaction of the oxidation of NO to NO_2. For example, an addition of 0.5% Pt by weight to the glass surface on which the oxidation of NO is conducted increases the yield of NO_2 to 21% at 255 C, and the addition of 0.5% Pt to the surface of Al_2O_3 made it possible to achieve 100% yield of NO_2 from a mixture of NO and NO_2 at t = 315°C. It is true that these works were not conducted with a stoichiometric mixture, but with a mixture with a low content of O_2. Consequently, the quantitative results of this work cannot be applied to the given system. But at low pressures, when the probability of a trimolecular homogeneous reaction is small, we may entirely assume the effect of the catalytic action of Pt.

In any case, in the discussion of experimental data with respect to thermal conductivity obtained by the heated filament method, the problem unavoidably arose as to heterogeneous reactions were not also being mixed with homogeneous reactions, and what the role of the heterogeneous reactions might be.

In order to exclude the possible effect of surface reactions, at the IYaE AN BSSR for investigation of the 'thermal conductivity' of the system $N_2O_4 \rightleftarrows 2NO_2 \rightleftarrows 2NO + O_2$ in a wide range of temperatures (258-773°K) and pressures of 1-50 atm, the coaxial cylinder method was used [29]. The basic design material selected was stainless steel Kh18N10T, which is entirely corrosion-resistant with respect to dried nitrogen tetroxide.

As also in the previous work [144, 145], in the investigations [29] it was established that the 'thermal conductivity' of the mixture $2NO_2 \rightleftarrows 2NO + O_2$ at P = 1 atm in practice does not differ from the 'frozen' component.

The experimental values [29] at a pressure of 50 atm in the region of temperatures corresponding to stage II lies approximately 30-40% above λ_f, corresponding to P = 50 atm. An increase of such an order of magnitude cannot be explained by the effect of the pressure on the thermal conductivity of the individual substances, as follows from an analysis of the values of $\lambda(\pi, \tau)$. At the same time the values of λ_{exp} obtained for the mixture $2NO_2 \rightleftarrows 2NO + O_2$ differed strongly from the asymptotic equilibrium values.

This shows that in practice the condition of thermochemical equilibrium for the mixture under consideration is not always realized, and in the investigation of heat transfer and mass transfer in the heat-transfer gap at different values of P and T we should consider the rate of the chemical transformations of the components of the mixture.

3. The Effect of the Kinetics of Chemical Reactions on the 'Thermal Conductivity' of the Reacting Mixture

The effect of the kinetics of the chemical reactions on the average 'thermal conductivity' $\bar{\lambda}^*$ in the gap was studied by several authors [137,150, 151,225,226].

Meixner [137] obtained an approximate analytical expression for $\bar{\lambda}^*$ of a binary mixture placed in a heat-transfer gap of plane geometry by the method of the thermodynamics of irreversible processes.

Frank and Spalthoff [150] investigated the effect of chemical relaxation ('incomplete estalishment of equilibrium') on the average 'thermal conductivity' of the mixture $A_2 \rightleftarrows 2A$, placed in a gap of cylindrical geometry with a heating filament as the internal cylinder ($R_2/R_1 >> 1$). In this case the authors [150] used a two-temperature scheme accepted by Scheffer-Rating-Aiken in the investigation of the effect of retarded transfer of translational and oscillatory energy on the thermal conductivity of a multiatomic gas. In the construction of the analytical expressions for $\bar{\lambda}^*$ the authors of refs. [137, 150], following Nernst, in the equation of diffusion identified the 'effective' diffusion factor of the components in the reacting mixture with the ordinary binary diffusion factor. Besides this, in the final expression for $\bar{\lambda}^*$ [150], the length of the free path of the molecules is included, the magnitude of which is determined within the limits of the order of magnitude.

The authors of refs. [137, 150] during adjustments used simplifications assuming that the temperature difference in the gap is small and the deviation of the steady-state composition from the equilibrium value is not great.

Spalding [226] in the derivation of an expression for the $\bar{\lambda}^*$ of an ideal dissociating Lighthill gas, placed in a heat conducting gap of plane geometry, aside from these assumptions, assumed a 'frozen' Lewis number Lu_f equal to one. Although Lu_f is actually close to 1 with respect to order of magnitude, for a mixture of reacting gases it may vary strongly with the composition (from 0.8 to 1.2 for the system under consideration).

Brokaw [151] generalized the experience of previous investigations [137, 150]. He obtained a single expression for the average thermal conductivity of a mixture not in chemical equilibrium with one reaction of arbitrary stoichiometry, placed in a gap of any single-parametric geometry (between parallel plates, coaxial cylinders, or concentric spheres).

From a qualitative analysis of the approximate analytical expressions [137, 150, 151, 226] it was established that the 'effective thermal conductivity' of a mixture with finite rates of chemical transformations of the components is not an unambiguous function of the external parameters P, T, but also depends upon the width and geometry of the gap and upon the properties of the surface (thermal accommodation, chemical and catalytic activity).

Below, for brevity, we will call λ^* 'thermal conductivity', including in it the sense of a certain summary characteristic of heat transfer and mass transfer in the reacting mixture in static steady-state conditions, i.e., in a heat-transfer gap.

We will construct a closed system of differential equations and boundary conditions, connecting the basic processes: thermal conductivity, molecular diffusion, and chemical transformations (in the gas and at the surface).

The equation of motion [227] in static steady-state conditions is transformed into P = const.

From the general condition of non-accumulation of mass $\sum_{(f)} g_j M_j = 0$ [227] with reference to the mixture under consideration, we will determine the connection of the molar diffusion flows of the components

$$g_1 + \frac{1}{2} g_2 + \frac{1}{2} g_3 = 0, \tag{4.1}$$

$$g_1 = \frac{1}{2} g_3. \tag{4.2}$$

Stoichiometric ratio (4.2) is valid, since for the given mixture with a good degree of accuracy we may assume that $D_{23} = D_{24}$, $D_{13} = D_{14}$, i.e., in the four-component mixture being investigated we may define two independent components, for example $N_2O_4(g_1)$ and $NO(g_3)$.

The equation of continuity of the j-th component of the mixture in a nonisothermic mixture at rest is written thus

$$\frac{1}{r} \frac{d}{dr} (r g_j) = \sum_{(z)} \nu_{jz} I_z \quad \sum_{(z)} \nu_{jz} (V_{div} - V_{rev}). \tag{4.3}$$

where ν_{jz} is the stoichiometric coefficient of the j-th component in the z-th reaction; I_z is the total rate of the z-th reaction. The rates of the direct and reverse reactions $V_{di(rev)z}$, according to the law of existing masses, is determined as:

$$V_{dir} = k_{dir} \prod_{(j\ initial)} \rho_j^{-\nu_j};\quad V_{rev} = k_{rev} \prod_{(j\ product)} \rho_j^{\nu_j} (\nu_{j\,init} < 0;\ \nu_{j\,prod} > 0), \tag{4.4}$$

where ρ_j is the molar density of the j-th component, which is expressed via the molar density of the mixture and the molar fraction of the component, as

$$\rho_j = \rho x_j. \tag{4.5}$$

The molar fractions of the components of the mixture being studied are connected with each other by the ratio

$$x_2 = 1 - \frac{3}{2} x_3 - x_1;\quad x_4 = \frac{1}{2} x_3. \tag{4.6}$$

Having used expressions (4.4)-(4.6), we write the equation of continuity (4.3) for the independent components:

$$\frac{1}{r}\frac{d}{dr}(rg_1) = -k_{cr1}\rho\left[x_1 - \left(1 - \frac{3}{2}x_3 - x_1\right)^2 \frac{p}{K_{p1}}\right];$$

$$\frac{1}{r}\frac{d}{dr}(rg_3) = k_{cr2}\rho^2\left[\left(1 - \frac{3}{2}x_3 - x_1\right)^2 - \frac{p}{2K_{p2}}x_3^2\right], \tag{4.7}$$

where $k_{dil(2)}$ is the rate constant, and $K_{pl(2)}$ is the constant of equilibrium of stages I and II, respectively.

The equation of multicomponent concentration diffusion for the j-th component of the mixture in the form derived by Stefan and Maxwell [20], obtained by ignoring the effect of thermal diffusion on mass transfer, will be written in the form of Fick's first-order law, using expressions (4.1), (4.2), and (4.6).

$$g_1 = \frac{a_{22}\left(\frac{dx_1}{dr}\right) - a_{12}\left(\frac{dx_3}{dr}\right)}{a_{11}a_{22} - a_{12}a_{21}} =$$

$$= -\rho D_{1I}\frac{dx_1}{dr} - \rho D_{3I}\frac{dx_3}{dr};$$

$$g_3 = \frac{a_{11}\left(\frac{dx_3}{dr}\right) - a_{21}\left(\frac{dx_1}{dr}\right)}{a_{11}a_{22} - a_{12}a_{21}} =$$

$$= -\rho D_{1II}\frac{dx_1}{dr} - \rho D_{3II}\frac{dx_3}{dr},$$

$$a_{11} = \frac{1}{\rho}\left[\frac{1}{D_{12}}\left(\frac{3}{2}x_3 - x_1 - 1\right) - \frac{3}{2D_{13}}\right];$$

$$a_{12} = \frac{x_1}{\rho}\left[-\frac{1}{D_{12}} + \frac{3}{2D_{13}}\right];$$

$$a_{21} = \frac{x_3}{\rho}\left[\frac{1}{D_{13}} - \frac{2}{D_{23}}\right];$$

$$a_{22} = \frac{1}{\rho}\left[-\frac{x_1}{D_{13}} - \frac{1}{D_{23}}\left(1 - x_1 - \frac{1}{2}x_3\right)\right]. \tag{4.8}$$

When $x_3 = x_4 = 0$ (the reaction $N_2O_4 \quad 2NO_2$), as follows from ratios (4.8):

$$g_3 = 0;\ g_1 = -\rho\frac{D_{13}}{1 + x_1}\left(\frac{dx_1}{dr}\right) = -\rho D_1\frac{dx_2}{dr}.$$

When $x_1 = 0$ (the reaction $2NO_2 \quad 2NO + O_2$), we obtain

$$g_1 = 0;\ g_3 = -\rho\frac{2D_{23}}{2 - x_3}\left(\frac{dx_3}{dr}\right) = -\rho D_3\frac{dx_3}{dr}.$$

Here D_1 and D_2 are the 'effective' diffusion factors of the j-th component in a binary reacting mixture, differing from the ordinary ones in an inert mixture because of the appearance of a Stefan flow as a consequence of the variation of the volume in the course of the chemical reaction.

The differential equation of energy [227] in static steady-state conditions is reduced to

$$\frac{1}{r}\frac{d}{dr}(rq) = 0. \tag{4.9}$$

It is supplemented by the phenomenological equation of density of the heat flux q. If we ignore the effect of the diffusion thermal effect and exclude the contribution of radiation, we obtain

$$q = -\lambda_f \frac{dT}{dr} + \sum_{(j)} g_j H_j. \qquad (4.10)$$

Expression (4.10) may be written in the form of a Fourier equation:

$$q = -\lambda^* \frac{dT}{dr}, \qquad (4.11)$$

where the summary 'thermal conductivity' of the mixture under consideration is determined via the thermal effects of the corresponding reactions [274]:

$$\lambda^* = \lambda_f + g_1 \Delta H_{p1} \left(\frac{dT}{dr} \right)^{-1} - \frac{1}{2} g_3 \Delta H_{p2} \left(\frac{dT}{dr} \right)^{-1}. \qquad (4.12)$$

Boundary conditions. The first pair of boundary conditions (first order) are conditions with respect to temperature at the surface:

$$T|_{r=R_1} = T_1; \quad T|_{r=R_2} = T_2. \qquad (4.13)$$

The other conditions are relative to the flows of matter from the surface. In a general case these conditions must consider all the chemical and physical phenomena originating at the surface: thermal accommodation (which has a noticeable effect at low temperatures P<<1 atm); physical and chemical adsorption and chemical reactions, both with participation of the wall material and those of a merely catalytic type.

But no matter in what form these conditions are written, the conditions of the balance of mass at the boundary between the solid surface and the gas are always these: the flow of matter from the surface is compensated by its diffusion removal:

$$I_j^{sur} = g_{j\ \mathrm{dit.sur}} \qquad (4.14)$$

In a general case of an arbitrary reversible reaction, at the surface the boundary conditions (4.14) are nonlinear, since I_j^{sur} is a complex function of the composition, temperature, and properties of the surface.

In a case when the rate of one of the processes (diffusion in the gas or chemical transformations at the surface) is great in comparison with the rate of the other, boundary conditions (4.14) are essentially simplified.

Let us consider, for example, the limiting boundary conditions for the mixture $2NO_2$ $2NO + O_2$. Since there are no factual data concerning the rate of the surface catalytic reaction for the decomposition of NO_2 and, this means, that in a general case I_j^{sur} will be formally constructed, this is convenient to do under the following assumptions. We will assume that the catalytic surface reaction of the decomposition of NO_2 proceeds in accordance with the same bimolecular scheme as in the homogeneous phase. Then I_j^{sur} is determined so that it will satisfy the same condition of equilibrium with respect to x_e as for homogeneous reactions.

Thus, we write the boundary condition in the dimensionless form:

$$-\frac{D_3\rho}{\delta k_{di}^{sur}}\frac{dx_3}{dy}\Big|_{sur} = f(x)\Big|_{sur}, \tag{4.15}$$

where k_{di}^{sur}, naturally, has the dimensionality of the rate constant of the surface reaction (in moles/cm^2/sec), $y = r/\delta$.

The criterion

$$D_3\rho/\delta k_{di}^{sur} = k_x \tag{4.16}$$

characterizes the ratio of the rates of the processes of diffusion in the gas and the chemical transformations at the surface with an accuracy up to the coefficient. If k_{di}^{sur} is great, then $k_x << 1$, $f(x)|_{sur} \rightarrow 0$, so that at the limit

$$x_j|_{sur} = x_e|_{st} \tag{4.17}$$

In this case the rate of the entire process is determined by the rate of diffusion as the slower process. In a very thin layer at the wall $x = x_e$, and outside it x_j is determined by the rate of homogeneous transformations. If k_{di}^{sur} is small, then

$$k_x >> 1, \tag{4.18}$$

so that at the limit

$$\frac{dx_j}{dy}\Big|_{sur} = 0.$$

In the absence of a chemical reaction in the gas this would signify that the composition in the gap x_j = const (if we ignore thermal diffusion). But in the presence of a chemical reaction in the gas the variation of the composition throughout the gap is determined by the rate of homogeneous chemical transformation. Strictly speaking, the definition of the concept of a 'entirely catalytic surface' (4.17) and an 'inert surface' (4.18) in the presence of homogeneous chemical transformations should be given not only with respect to the magnitude of k_x but in comparison of the rates of the chemical reactions at the surface in the gas and the rate of diffusion.

We will construct general boundary conditions for the surface of an arbitrary catalytic activity, relative to an independent component of the mixture, formally up to a certain degree.

Following Brokaw, we will define the concept of catalytic activity as follows: $e_j - (g_{j\ inc} - g_{j\ ref})/(g_{j\ inc} - g_{j\ ref})$ is the number of moles of the j-th component incident per unit of surface in a unit of time and reflected from a unit of surface per unit of time; $g_{j\ ref\ e}$ is the same thing with equilibrium composition at the surface.

Then the flow of moles of the j-th component from the surface of the ε-th activity $g_{j\ sur} = g_{j\ inc} - g_{j\ ref}$, and the equation of the balance of energy at the surface (4.14) is written thus

$$g_{j\ inc} - g_{j\ ref} = -\rho D_j \left|dx_j/dr\right|_{sur} \qquad (4.19)$$

At the limit when $\varepsilon_j = 0$, $g_{j\ inc} = g_{j\ ref}$, $g_{j\ sur} = 0$ or $dx_j/dr|_{sur} = 0$ (the inert surface). When $\varepsilon_j = 1$, $g_{j\ inc} = g_{j\ ref\ e}$, i.e., $x_{j\ sur} = x_{je}$ (a completely catalytic surface).

From the condition of the balance of mass at the surface of the internal and external cylinders, it was established that for the independent component of the mixture, the concentration of which in the progress of the reaction is increased, the 'minus' sign is preserved in equation (4.19) at both surfaces, i.e.,

$$(g_{3\text{inc}} - g_{3\text{ref}})\Big|_{\substack{R_1\\R_2}} = -\rho D_3 |dx_3/dr|_{\substack{R_1\\R_2}}$$

For a component, the concentration of which in the progress of the reaction is decreased, the 'minus' sign is preserved only on the internal surface (Brokaw considered precisely such a case [151]):

$$(g_{1\text{inc}} - g_{1\text{ref}})\Big|_{\substack{R_1\\R_2}} = \pm\rho D_3 |dx_3/dr|_{\substack{R_1\\R_2}}$$

Having expressions for the incident and reflected fluxes, according to the Hertz-Knudsen equation, and introducing the function Ψ_j

$$\Psi_j = \frac{2\varepsilon_j}{2-\varepsilon_j}\,\frac{\bar{V}_j}{4D_j}\left(\bar{V}_j = \sqrt{\frac{8RT}{\pi M_j}}\right), \tag{4.20}$$

we obtain the boundary conditions in the form shown by Brokaw:

$$(x_{3e} - x_3)\Big|_{\substack{R_1\\R_2}} = -\left[\Psi_3^{-1}\frac{dx_3}{dr}\right]\Big|_{\substack{R_1\\R_2}}; \tag{4.21}$$

$$(x_{1e} - x_1)\Big|_{\substack{R_1\\R_2}} = \mp\left[\Psi_1^{-1}\frac{dx_1}{dr}\right]\Big|_{\substack{R_1\\R_2}}. \tag{4.22}$$

Closed system of differential equations (4.7)-(4.9), (4.11), (4.12), and boundary conditions (4.13), (4.21), and (4.22) determines the heat transfer and mass transfer in static steady-state conditions in the mixture $N_2O_4 \rightleftarrows 2NO_2 \rightleftarrows 2NO + O_2$, when both homogeneous reactions proceed with finite rates.

4. Composition and 'Thermal Conductivity' of a Nonequilibrium Reacting Mixture

As follows from the analysis of the experimental data, the effect of the rate of the chemical reaction of stage I is felt on the 'thermal conductivity' only when $P < 1$ atm, so that when $P \geq 1$ atm, the mixture $N_2O_4 \rightleftarrows 2NO_2$, in practice, may be considered as 'equilibrium'. At the same time the rate of the dissociation reaction with respect to stage II is so small that when $P \leq 1$ atm the mixture $2NO_2 \rightleftarrows 2NO + O_2$ may be considered as 'frozen'. Therefore, the effect of the kinetics of the chemical reactions on the 'thermal conductivity' of these mixtures may be investigated individually.

Composition of a nonequilibrium mixture. After substitution of (4.8) into (4.7) and (4.11) into (4.9), we obtain the connected system of nonlinear differential equations following for the mixture $2NO_2$ $2NO + O_2$:

$$\frac{d^2x_3}{dr^2} + \frac{dx_3}{dr}\left(\frac{1}{r} + \frac{d\ln\rho D_{23}}{dr}\right) + \frac{1}{2-x_3}\frac{dx_3}{dr} =$$

$$= -\frac{k_{up2}}{D_{23}}\rho(2-x_3)\left[\left(1-\frac{3}{2}x_3\right)^2 - \frac{P}{2K_{p2}}x_3^3\right];$$

$$\frac{d^2T}{dr^2} + \frac{1}{r}\left(\frac{dT}{dr}\right) + \frac{dT}{dr}\cdot\frac{1}{\lambda^*}\frac{d\lambda^*}{dr} = 0, \qquad (4.23)$$

which may be solved only numerically. With certain simplifying assumptions, the problem permits an analytical solution.

We will use two simplifications: the temperature difference in the gap is small and the deviation of the composition from an equilibrium value is not great.

The first assumption makes it possible, with adequate accuracy, to use thermophysical and chemical constants that are averaged throughout the gap. Aside from this, having assumed, in the first approximation, that * is a weak function of the temperature in the gap, and having integrated the equation of thermal conductivity, we determine that

$$T_0(r) = T_1 - \frac{\Delta T}{\ln(R_2/R_1)}\ln\frac{r}{R_1}. \qquad (4.24)$$

In this approximation we will solve the equation of continuity of the component regardless of the equation of thermal conductivity, i.e., we will open system (4.23).

We will linearize the equation of continuity of the component, using Brokaw's method [151]. By expanding expressions $(2-x_3)^{-1}$ in equation (4.8) and $V_{di(rev)2}$ in equation (4.3) into a Taylor series around the equilibrium value of the composition, and limiting ourselves to the first terms, we obtain

$$\frac{d^2y_3}{dz^2} + \frac{1}{z}\frac{dy_3}{dz} - y_3 = 0, \qquad (4.25)$$

where

$$y_3 = x_{2e} - x_3; \quad z = \varphi_2 r;$$

$$\varphi_2 = \frac{2A_1^{(2)}}{m_2} = \text{const}; \; m_2 = \rho\overline{D}_{3e} = \text{const}; \tag{4.26}$$

$$A_1^{(2)} = 3\rho^2 k_{d,2}\left[\left(1 - \frac{3}{2}x_3\right) + \frac{P}{2K_{p2}}x_{3e}^3\right]. \tag{4.27}$$

The solution of equation (4.25), via the modified first and second order Bessel functions, is written thus:

$$y_3 = C_1 I_0(z) + C_2 K_0(z). \tag{4.28}$$

Boundary conditions (4.21) are rewritten relative to y_3:

$$y_3|_{sur} = \Psi_3^{-1}\left[\frac{B_2}{r} + \varphi_2\frac{dy_3}{dr}\right]\Bigg|_{sur},$$

where

$$B_2 = \lambda_{re2}\, 2\Delta T\left(\rho D_{3e}\Delta H_{p2}\ln\frac{R_2}{R_1}\right)^{-1}. \tag{4.29}$$

The integration constants are determined from the system of linear algebraic equations

$$C_1\left[I_0(z_1) - \frac{\varphi_2}{\Psi_1}I_1(z_1)\right] + C_2\left[K_0(z_1) + \right.$$
$$\left. + \frac{\varphi_2}{\Psi_1}K_1(z)\right] = \frac{B_2}{\Psi_1 R_1}; \quad \Psi_1 = \Psi_{3(1)}\big|_{r=R_1};$$
$$C_1\left[I_0(z_2) - \frac{\varphi_2}{\Psi_2}I_1(z_2)\right] + C_2\left[K_0(z_2) + \right.$$
$$\left. + \frac{\varphi_2}{\Psi_2}K_1(z_2)\right] = \frac{B_2}{\Psi_2 R_2}. \tag{4.30}$$

Performing similar reasonings relative to the mixture $N_2O_4 \rightleftarrows 2NO_2$, from the equations

$$\frac{1}{r}\frac{d}{dr}(rg_1) = -k_{d,1}\rho\left[x_1 - \right.$$
$$\left. - (1 - x_1)^2\frac{P}{K_{p2}}\right], \quad g_1 = -\rho D_1\frac{dx_1}{dr}$$

we obtain the same expression (4.28) for the nonequilibrium composition $y = x_1 - x_{1e}$ with the constants

$$A_1^{(1)} = k_{dj\,1}\rho\left[1 + (1 - x_{1e})\frac{2P}{K_{p1}}\right]; \quad m_1 = \rho\overline{D_{1e}};$$

$$B_1 = \lambda_{re1}\,\Delta T\left[\rho D_{1e}\Delta H_{p1}\ln\frac{R_2}{R_1}\right]^{-1}; \quad \varphi_1^2 = \frac{\overline{A}_1^{(1)}}{m_1}. \tag{4.31}$$

The dimensionless complex $\phi\delta$ characterizes the 'reaction capability' of the gaseous phase. The introduction of the function ϕ by dependences (4.27) and (4.31), differing from Brokaw's method, made it possible, by using the expressions obtained for the time of chemical reaction τ_{chem} [288] and the scale of the time of the diffusion process, τ_{dif} [231] to determine the ratio of the times of the competing processes

$$\varphi\delta = \sqrt{\frac{\tau_{\text{dif}}}{\tau_{\text{chem}}}}, \tag{4.32}$$

where $\delta = R_1 \ln(R_2/R_1)$ is the characteristic linear dimension in cylindrical geometry.

Average and local 'thermal conductivity' of a nonequilibrium mixture. According to definition (4.12), the local 'thermal conductivity' of the mixture is

$$\lambda^* = \lambda_f + \frac{1}{2}\rho D_2\Delta H_{p2}\left(\frac{dx_3}{dr}\right)\left(\frac{dT}{dr}\right)^{-1}. \tag{4.33}$$

From condition (4.9) it follows that $rq = \text{const} = Q$, i.e.,

$$\frac{dT}{dr} = -\frac{Q}{\bar{\lambda}^* r}. \tag{4.34}$$

Having integrated equation (4.34), we obtain

$$Q = \frac{\bar{\lambda}^*\Delta T}{\ln(R_2/R_1)}. \tag{4.35}$$

Having substituted expressions (4.35) and (4.34) into formula (4.33), we obtain an expression for the local 'thermal conductivity'

$$\lambda^* = \lambda_f\left[1 - \frac{\lambda_{re}}{\bar{\lambda}^*}(1 - \gamma r)\right]^{-1}. \tag{4.36}$$

Having integrated equality (4.36) from R_1 to R_2 with a weight r^{-1}, we obtain

$$\bar{\lambda}^* = \lambda_e - \lambda_{re}G. \tag{4.37}$$

In the expressions obtained the functions

$$G = -\frac{\Delta y}{B \ln (R_2/R_1)} \equiv$$

$$\equiv -\frac{1}{B \ln (R_2/R_1)} \{C_1 [I_0(z_2) - I_0(z_1)] +$$

$$+ C_2 [K_0(z_2) - K_0(z_1)]\}, \qquad (4.38)$$

$$\gamma = -\frac{1}{B} \frac{dy}{dr} = -\frac{\varphi}{B} [C_1 I_1(z) - C_2 K_1(z)] \qquad (4.39)$$

depend upon the ratio of the rates of the chemical transformations in the gaseous phase (ϕ) and at the surface (Ψ) upon the geometry of the gap (R_2/R_1) and the characteristic dimension δ.

Having made the limiting transitions ($\Psi \to 0$ or $\Psi \to \infty$) in equations (4.30), (4.38), in particular cases we obtain the function G:

1) both surfaces are chemically and catalytically inert ($\Psi_{1(2)} \to 0$)

$$G = \left\{[I_0(z_2) - I_0(z_1)] \left[K_1(z_1) \frac{R_1}{R_2} - K_1(z_2)\right]\right\} +$$

$$+ \left\{(K_0(z_2) - K_0(z_1)] \left[I_1(z_1) \frac{R_1}{R_2} - I_1(z_1)\right]\right\} \times$$

$$\times \{\varphi\delta \{[I_1(z_2) K_1(z_1) - I_1(z_1) K_1(z_2)]\}^{-1};$$

2) the internal surface is inert, and the external surface is entirely catalytic ($\Psi_1 \to 0$, $\Psi_2 \to \infty$)

$$G = \frac{I_0(z_2) K_0(z_1) - I_0(z_1) K_0(z_2)}{\varphi\delta [I_0(z_2) K_1(z_1) + I_1(z_1) K_1(z_2)]};$$

3) the internal surface is entirely catalytic, and the external surface is inert ($\Psi_1 \to \infty$, $\Psi_2 \to 0$)

$$G = \frac{I_0(z_2) K_0(z_1) - I_0(z_1) K_0(z_2)}{\varphi\delta \frac{R_2}{R_1} [K_0(z_1) I_1(z_2) + K_1(z_2) I_0(z_1)]};$$

4) both surfaces are entirely catalytic ($\Psi_1 \to \infty$, $\Psi_2 \to \infty$) $G \approx 0$.

The Bessel functions for the values of the argument $0.02 < z < 10$ are tabulated in ref. [229]. At values of $z > 10$ in the calculations of G, we should use expansions of the Bessel functions into series [230]. For the heat-transfer gap between the coaxial cylinders (the ratio R_2/R_1 of order 1) when both z_1 and $z_2 \geq 20$, the expressions for the function G are rewritten thus:

$$G_{gen} = -\frac{1}{R_1 \ln (R_2/R_1)} \left\{ 2 \sqrt{\frac{R_1}{R_2}} \frac{\varphi}{\Psi_1 \Psi_2} + \right.$$

$$+ [\mathrm{sh}(z_2 - z_1)] \left[\frac{1}{\Psi_1} - \frac{R_1}{R_2 \Psi_2} \right] - \frac{\varphi}{\Psi_1 \Psi_2} \left(1 + \right.$$

$$\left. + \frac{R_1}{R_2} \right) \mathrm{ch}(z_2 - z_1) \} \{ \mathrm{sh}(z_2 - z_1) \left(\frac{\varphi^2}{\Psi_1 \Psi_2} - 1 \right) +$$

$$\left. + [\mathrm{ch}(z_2 - z_1)] \varphi \left[\frac{1}{\Psi_2} - \frac{1}{\Psi_1} \right] \right\}^{-1};$$

$$G_{\substack{\Psi_1 \to 0 \\ \Psi_2 \to 0}} = \frac{1 + \frac{R_1}{R_2}}{\varphi R_1 \ln \frac{R_2}{R_1}} \left[\frac{1}{\mathrm{th}(z_2 - z_1)} - \right.$$

$$\left. - \frac{2}{\sqrt{\frac{R_2}{R_1}} \left(1 + \frac{R_1}{R_2} \right) \mathrm{sh}(z_2 - z_1)} \right];$$

$$G_{\substack{\Psi_1 \to 0 \\ \Psi_2 \to \infty}} = \frac{1}{\varphi R_1 \ln \frac{R_2}{R_1}} \mathrm{th}(z_2 - z_1);$$

$$G_{\substack{\Psi_1 \to \infty \\ \Psi_2 \to 0}} = \frac{1}{\varphi R_2 \ln \frac{R_2}{R_1}} \mathrm{th}(z_2 - z_1).$$

If z_1 and z_2 are so great (at great values of ϕ or δ) that $z_2 - z_1 \geq 4$, the expressions obtained above are simplified:

$$G_{\Psi_1, \Psi_2} = \frac{1 + \frac{R_1}{R_2}}{\varphi R_1 \ln \frac{R_2}{R_1}} = \frac{1 + \frac{R_1}{R_2}}{\varphi \delta_1};$$

$$G_{\substack{\Psi_1 \to 0 \\ \Psi_2 \to \infty}} = \frac{1}{\varphi \delta_1};$$

$$G_{\substack{\Psi_1 \to \infty \\ \Psi_2 \to 0}} = \frac{1}{\varphi \delta_2}; \quad \delta_2 = R \ln \frac{R_2}{R_1}.$$

In the heat-transfer gap of cylindrical geometry with a heated filament as the internal cylinder ($R_2/R_1 \gg 1$) the function G should be calculated according to the common formulas (4.38) when $z_2 < 4$.

When $z_2 > 4$ the following inequalities are valid: $I_0(z_2) >> I_0(z_1)$; $I_1(z_2) >> I_1(z_1)$; $K_1(z_1)(R_1/R_2) >> K_1(z_2)$; $I_1(z_2) >> I_1(z_1)(R_1/R_2)$; $K_0(z_2) << \, << K_0(z_1)$. In this case expressions (4.38) are simplified:

$$G_{\substack{\Psi_1 \to 0 \\ \Psi_2 \to 0}} = \frac{1}{\varphi R_1 \ln (R_2/R_1)} \left\{ \frac{I_0(z_2)}{I_1(z_2)} \frac{R_1}{R_2} + \frac{K_0(z_1)}{K_1(z_1)} \right\};$$

$$G_{\substack{\Psi_1 \to 0 \\ \Psi_2 \to \infty}} = \frac{1}{\varphi R_1 \ln (R_2/R_1)} \frac{K_0(z_1)}{K_1(z_1)};$$

$$G_{\substack{\Psi_1 \to \infty \\ \Psi_2 \to 0}} = \frac{1}{\varphi R_2 \ln (R_2/R_1)} \frac{I_0(z_2)}{I_1(z_2)};$$

$$\left(\text{when } z > 10 \; \frac{I_0(z_2)}{I_1(z_2)} = 1 \right)$$

The function G varies in the range [0.1] (Fig. 4.3). When $G \to 0$ (a high rate of reaction in the gas or a large width of the gap, $\Delta = R_2 - R_1$) $\bar{\lambda}^*$, according to equation (4.37), tends toward the maximum possible value of λ_e. In the other extreme case, when $G \to 1$ (low rates of the reactions or small values of Δ), $\bar{\lambda}^* \to \lambda_f$.

The width of the heat-transfer gap in the experiment is limited to avoid convection. Therefore, an increase in the average 'thermal conductivity' may be achieved basically by an increase of the 'reaction capability' of the gas as a consequence of an increase in P and T. The limiting values of $\bar{\lambda}^* = \lambda_e$ at a width of the gap of 1 mm is realized for stage II at P = 500 atm and T = 1000 K (Fig. 4.4), while for stage I it is already achieved at $P \leq 1$ atm (Fig. 4.5).

The second limiting case $\bar{\lambda}^* = \lambda_f$ for stage II is realized at P = 1 atm at all temperatures (Fig. 4.4), and for stage I at the same gap, only at very low pressures $P << 1$ atm.

Since with an increase in the width of the gap the characteristics time of the diffusion process is increased, then it is qualitatively clear that with a noticeable increase in Δ, even at rates of the chemical transformations that are not very high, we may achieve an increase in λ^* and even obtain $\bar{\lambda}^* \cong = \lambda_e$ only as a consequence of a perceptible increase in τ_{dif}. Or, by a decrease in Δ, $\bar{\lambda}^* \to \lambda_f$ is achieved. But for this (at high values of τ_{chem}) we must change Δ by orders of magnitude.

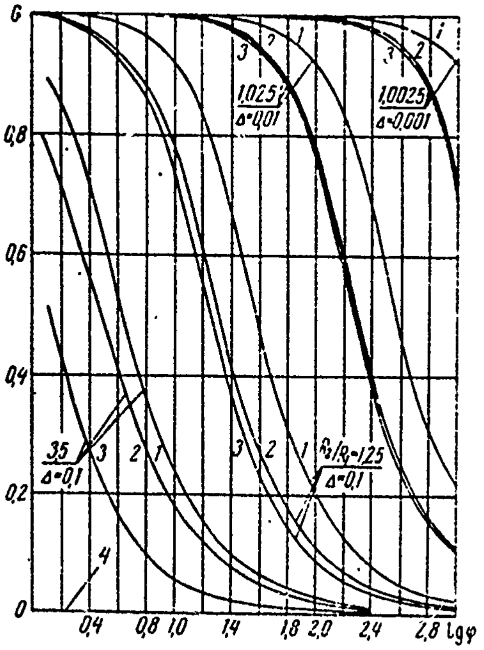

Figure 4.3. Variation of the function G as a function of the 'reaction capability' of the gaseous phase (coaxial cylinders $R_1=0.4$ cm, $\Delta = R_2 - R_1$, I) $R_2/R_1 = 1.0025$, $\Delta=0.001$ cm; II) 1.025, 0.01; III) 1.25, 0.1; IV) 3.5, 1.0. 1) both surfaces inert, $\Psi_1 \to 0$, $\Psi_2 \to 0$; 2) surface of internal cylinder inert, external entirely catalytic, $\Psi_1 \to 0$, $\Psi_2 \to \infty$; 3) $\Psi_1 \to \infty$, $\Psi_2 \to 0$; 4) $\Psi_1 \to \infty$ $\Psi_2 \to \infty$).

It is practically impossible to establish such special experiments with respect to checking the effect of the width of the gap on 'thermal conductivity' since the limiting high values of Δ must nevertheless be such as to exclude the effect of convection in the heat transfer gap, and the lower limit of the width of the gap is dictated by design possibilities. But, other things being equal, we may investigate the effect of Δ on $\overline{\lambda}^*$ by calculation methods. Cases with extreme values of Δ are also of practical interest: 1) at forced convection with a high rate, in the pipe the heat boundary layer, through which the heat is transferred basically by thermal conductivity, is very thin, of the order of tenths or hundredths of a millimeter, Δ_{min}; 2) in natural convection, around pipes of large diameter the boundary layer is very thick (tens of millimeters), Δ_{max}. The effect of the width of the gap on $\overline{\lambda}^*$ is given in Fig. 4.6.

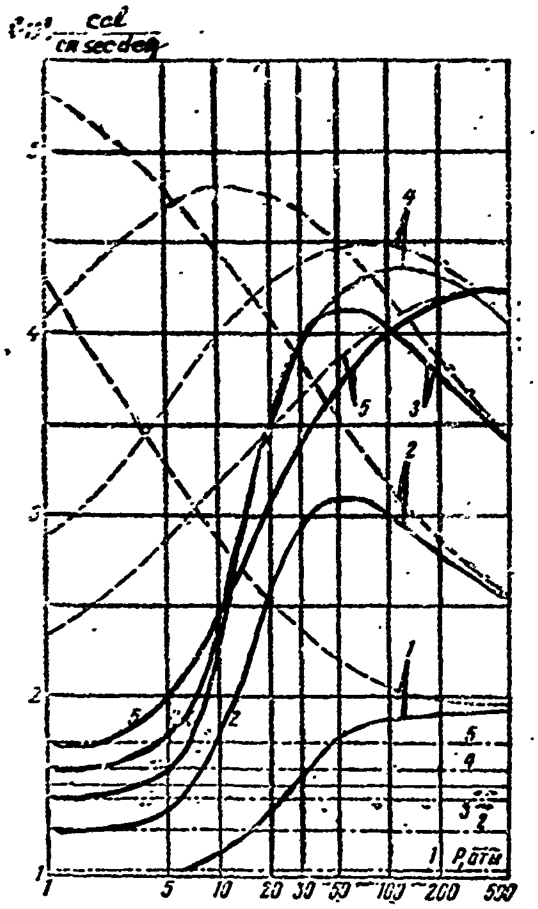

Figure 4.4. Variation of the average 'thermal conductivity' of the mixture $2NO_2 \rightleftarrows 2NO + O_2$ in the gap as a function of the pressure and temperature (R_1=0.4, R_2=0.5 cm, both surfaces inert):

1- T = 600°K, 2- 700°, 3- 800°, 4- 900°, 5- 1000°; dashed line λ_{e2}, dash-dot line λ_{f2}.

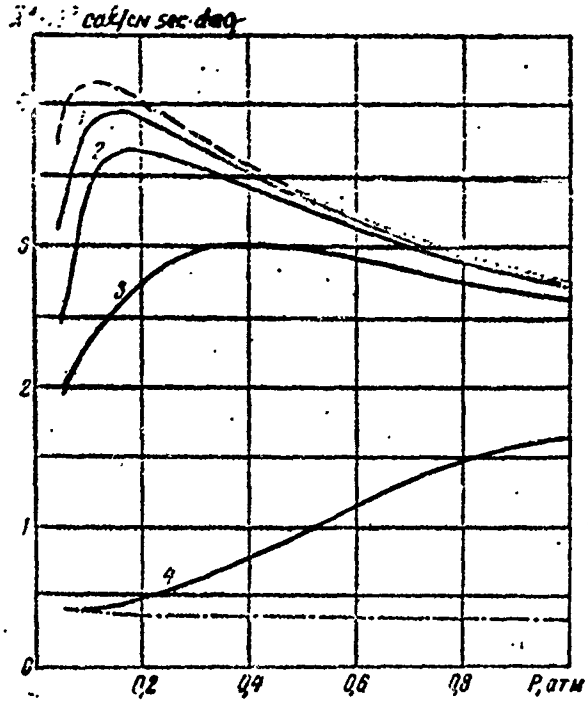

Figure 4.5. Effect of the width of the gap on the 'thermal conductivity' of the mixture $N_2O_4 \rightleftarrows 2NO_2$ ($\overline{T} = 300°$, $R_1 = 5 \cdot 10^{-3}$ cm, inert surfaces):

1- R_2-R_1=1 cm, 2- 0.1 cm, 3- 0.01 cm, 4- 0.001 cm.

We will also direct attention to the fact that λ*, calculated for different geometries (R_2/R_1 = var) at the same values of P, T, and Δ, will differ somewhat (Fig. 4.7). We must rememter this in the comparison of the experimental data obtained by the heated filament method and by the coaxial cylinder method.

If one of the surfaces is catalytically active, this has a noticeable effect on the average 'thermal conductivity'. The effect of limiting activities of the surface ($\Psi \to 0$ or $\Psi \to \infty$) and the finite catalytic activity of each of them on $\overline{\lambda}$* was investigated in detail in ref. [225]. From an analysis of the general expression for G (4.38), (4.30) it was established that if chemical transformations occur in the gas with a finite rate, the definition

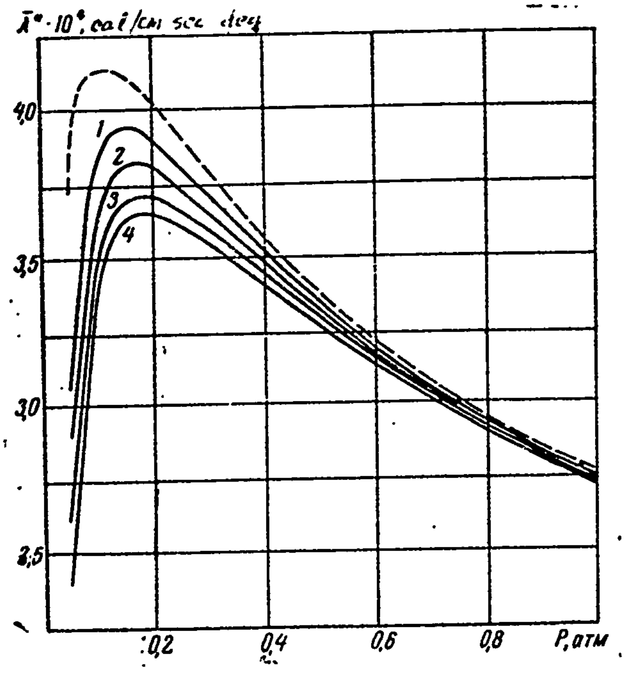

Figure 4.6. Effect of the width of the gap on the 'thermal conductivity' of the mixture $2NO_2 \rightleftarrows 2NO + O$ ($R_1 = 0.4$ cm, $P = 50$ atm).

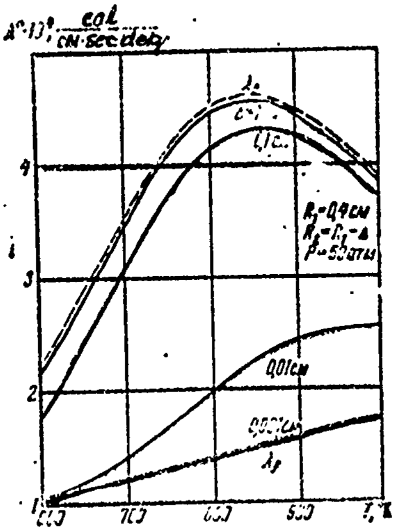

Figure 4.7. Effect of the geometry of the gap on the 'thermal conductivity' of the mixture $N_2O_4 \rightleftarrows 2NO_2$ ($T=300°K$):

1- $R_1=0.4$ cm, $R_2/R_1=1.25$, $\Delta=0.1$cm; 2- $6.48 \cdot 10^{-3}$; 37.1; 0.2339 [25]; 3- $5 \cdot 10^{-3}$, 32.2; 0.162 [145]; 4- $5 \cdot 10^{-3}$, 21; 0.1.

of the concepts of 'inert' and 'entirely catalytic' surface should not be given according to the absolute value of Ψ, but in a comparison of the rates of the chemical transformations in the gas and at the surface, i.e., according to the ratio ϕ/Ψ.

From the estimates of the contribution of individual terms in formulas (4.38), (4.30), it was found that when $\phi/\Psi \geq 30$ the surface may be considered 'inert'. If $\phi/\Psi \leq 0.05$, the surface may be considered as 'entirely catalytic'. Working from this conclusion, we selected the range of variation of ε_j in the investigation of the effect of the finite catalytic activity of the surface on $\overline{\lambda}^*$ (Fig. 4.8).

Investigations similar to those which were performed with G may also be performed with the function λ [231]. In particular cases λ(r) is determined according to the formulas:

$$\gamma_{\substack{\Psi_1\to 0\\ \Psi_2\to 0}} = -\frac{1}{R_1}\times$$

$$\times\frac{\left[K_1(z_2)-K_1(z_1)\frac{R_1}{R_2}\right]I_1(z)-\left[I_1(z_2)-I_1(z_1)\frac{R_1}{R_2}\right]K_1(z)}{I_1(z_2)K_1(z_1)-I_1(z_1)K_1(z_2)};$$

$$\gamma_{\substack{\Psi_1\to 0\\ \Psi_2\to \infty}} = \frac{1}{R_1}\,\frac{K_0(z_2)I_1(z)+I_0(z_2)K_1(z)}{I_1(z_1)K_0(z_2)+I_0(z_2)K_1(z_1)};$$

$$\gamma_{\substack{\Psi_1\to \infty\\ \Psi_2\to 0}} = \frac{1}{R_2}\,\frac{K_0(z_1)I_1(z)+I_0(z_1)K_1(z)}{I_1(z_2)K_0(z_1)+K_1(z_2)I_0(z_1)}.$$

At large values of the argument z > 10, in the coaxial cylinder method the function (r) are determined by the expression:

$$\gamma_{\substack{\Psi_1\to 0\\ \Psi_2\to 0}} = \frac{1}{R_1}\left\{\sqrt{\frac{R_1}{r}}\,\frac{\operatorname{sh}(z_2-z)}{\operatorname{sh}(z_2-z_1)}+\frac{R_1}{R_2}\sqrt{\frac{R_2}{r}}\,\frac{\operatorname{sh}(z-z_1)}{\operatorname{sh}(z_2-z_1)}\right\};$$

$$\gamma_{\substack{\Psi_1\to 0\\ \Psi_2\to \infty}} = \frac{1}{R_1}\sqrt{\frac{R_1}{r}}\,\frac{\operatorname{ch}(z_2-z)}{\operatorname{ch}(z_2-z_1)};$$

$$\gamma_{\substack{\Psi_1\to \infty\\ \Psi_2\to 0}} = \frac{1}{R_2}\sqrt{\frac{R_2}{r}}\,\frac{\operatorname{ch}(z-z_1)}{\operatorname{ch}(z_2-z_1)}.$$

In the heated filament method, with simplifications accepted in the derivation of the expression for G, the following formulas are valid:

$$\gamma_{\psi_1\to 0,\ \psi_2\to 0} = \frac{1}{R_1}\left[\frac{I_1(z)}{I_1(z_2)}\frac{R_1}{R_2} + \frac{K_1(z)}{K_1(z_1)}\right];$$

$$\gamma_{\psi_1\to 0,\ \psi_2\to \infty} = \frac{1}{R_1}\left[\frac{K_0(z_2)}{K_1(z_1)}\frac{I_1(z)}{I_0(z_2)} + \frac{K_1(z)}{K_1(z_1)}\right];$$

$$\gamma_{\psi_1\to \infty,\ \psi_2\to 0} = \frac{1}{R_2}\left[\frac{I_1(z)}{I_1(z_2)} + \frac{I_0(z_1)}{I_1(z_2)}\frac{K_1(z)}{K_0(z_1)}\right].$$

When z, z_1, z_2 10, these latter formulas are simplified:

$$\gamma_{\psi_1\to 0,\ \psi_2\to 0} = \frac{1}{R_1}\sqrt{\frac{R_1}{r}}\left\{\sqrt{\frac{R_1}{R_2}}\exp\left[-(z_2-z)\right] + \right.$$
$$\left. + \exp\left[-(z-z_1)\right]\right\};$$

$$\gamma_{\psi_1\to 0,\ \psi_2\to \infty} = \frac{1}{R_1}\sqrt{\frac{R_1}{r}}\left\{\exp\left[-(z_2-z)\right]\exp\left[(z_2-z_1)\right] + \right.$$
$$\left. + \exp\left[-(z-z_1)\right]\right\};$$

$$\gamma_{\psi_1\to \infty,\ \psi_2\to 0} = \frac{1}{R_2}\sqrt{\frac{R_2}{r}}\left\{\exp\left[-(z-z_1)\right]\exp\left[(z_2-z_1)\right] + \right.$$
$$\left. + \exp\left[-(z_2-z)\right]\right\}.$$

In Fig. 4.9 the variation of the local thermal conductivity *(r) in a gap with inert surfaces is given. It is apparent that the higher the 'reaction capability' of the gas, the less is the region of wall effects.

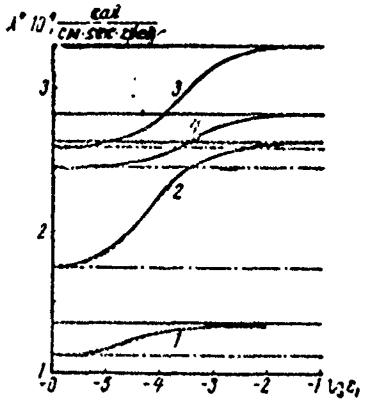

Figure 4.8. Effect of the finite catalytic activity of the surface of the surface of a cylinder on the 'thermal conductivity' of the mixture $2NO_2 \rightleftarrows 2NO + O_2$ (P=100 atm, R_1=0.4 cm, R_2=0.5 cm, the surface of the external cylinder being chemically and catalytically inactive, $\varepsilon_2=10^{-6}$):

1- T=600°K, 2- 700°, 3- 900°, 4- 1000°, solid line represents $\overline{\lambda}^*_{\psi_1\to\infty,\psi_2\to 0}$; dot-dah line represents $\overline{\lambda}^*_{\psi_1\to 0,\psi_2\to 0}$.

At small temperature differences in the gap (of the order of 5°), in the calculation of the local 'thermal conductivity' according to formula (4.36), we may use the value $\phi = \phi(\overline{T}) = \text{const}$ with an adequate degree of accuracy. At values of ΔT of the order of 20° and $\overline{T} = 1000°K$, such an averaging with respect to temperature $\phi(T)$ leads to an error of the order of 7-9% in λ^* by $r=\frac{1}{2}(R_1+R_2)$. This is associated with the fact that the rate constant of the reaction entering into $\phi(T)$ depends exponentially upon the temperature. Consequently in the calculation of $\lambda^*(r)$ at large values of ΔT in a heat-transfer gap (or in a boundary layer) we must use the mean integral magnitude $\overline{\phi(T)}$.

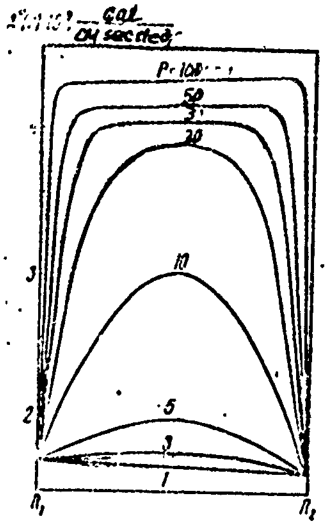

Figure 4.9. Variation of the local 'thermal conductivity' in the gap of the mixture $2NO_2 \rightleftarrows 2NO + O_2$. Both surfaces are inert; $\overline{T} = 950°K$ ($T = 960$, $T = 940°K$); $R_1 = 0.4$ cm, $R_2 = 0.5$ cm.

The results given in the brief communication [277] are surprising. With correct general reasonings, the authors give very strange qualitative results. On the basis of the dependence derived for $\lambda^*(y)$ the authors established the fact that when $P = 1$ atm and $t = 600$ C at a distance $y = 5 \cdot 10^{-3}$ cm from the surface, the 'thermal conductivity' reaches the equilibrium value λ_e. From the results given (the analytical and numerical solution) it follows that even when $\Delta = 0.1$ cm, λ^* and $\overline{\lambda}^*$ at these parameters are equal to the 'frozen' thermal conductivity. This is even more valid in a layer with a thickness of

$5 \cdot 10^{-3}$ cm. Our conclusion is thus confirmed by the experimental values of the average 'thermal conductivity' λ_{exp} [29, 144].

The authors do not give the values of ΔT at which they made these estimates. If the values of ΔT accepted were great (of the order of ΔT in the boundary layer) then the cause of such results may be the incorrect averaging of the coefficients in the equation of continuity.

If we consider the two terms for the equilibrium composition and the average 'thermal conductivity' of the mixture $2NO_2 \rightleftarrows 2NO + O_2$ in expansion $(2 - x_3)^{-1}$ and $V_{di(rev)2}$, we may obtain the analytical expression (approximation II) [274]. In the heat transfer gap, in view of the smallness of the temperature difference ΔT, the contribution of these terms is not great, but it may turn out to be noticeable in the investigation of heat transfer in the boundary layer.

5. Comparison of Nonequilibrium Values of the 'Effective Thermal Conductivity' with the Experimental Data

A validation of the chemical kinetic constants used in the calculations of $\bar{\lambda}^*$ was performed in ref. [228].

The values of $\bar{\lambda}^*$ of the mixture $N_2O_4 \rightleftarrows 2NO_2$ obtained and the experimental data of Coffin and O'Neal, Srivastava and Barua, Barua and Dastidar, and Dresvyannikov at $P < 1$ atm, within the limits of the error of calculation and of the experiment, agree (Fig. 4.10) if we use the parameters of the intermolecular reaction of the components determined from experimental values μ_{sm} in the calculations [46]. The agreement of the calculated equilibrium values of λ_{el} with the experimental data [29] at $P > 1$ atm is also satisfactory, although in the region of the peak of thermal conductivity λ_{exp} is systematically lower (by 10-20%). It is probable that this is associated with the error of measurement by the spring thermocouples of several differences $T \cong 5°$ in this region. At higher temperatures, where $T \cong 10\text{-}20°$ was maintained, this error is decreased and $\lambda_{exp} \cong \lambda_{el}$.

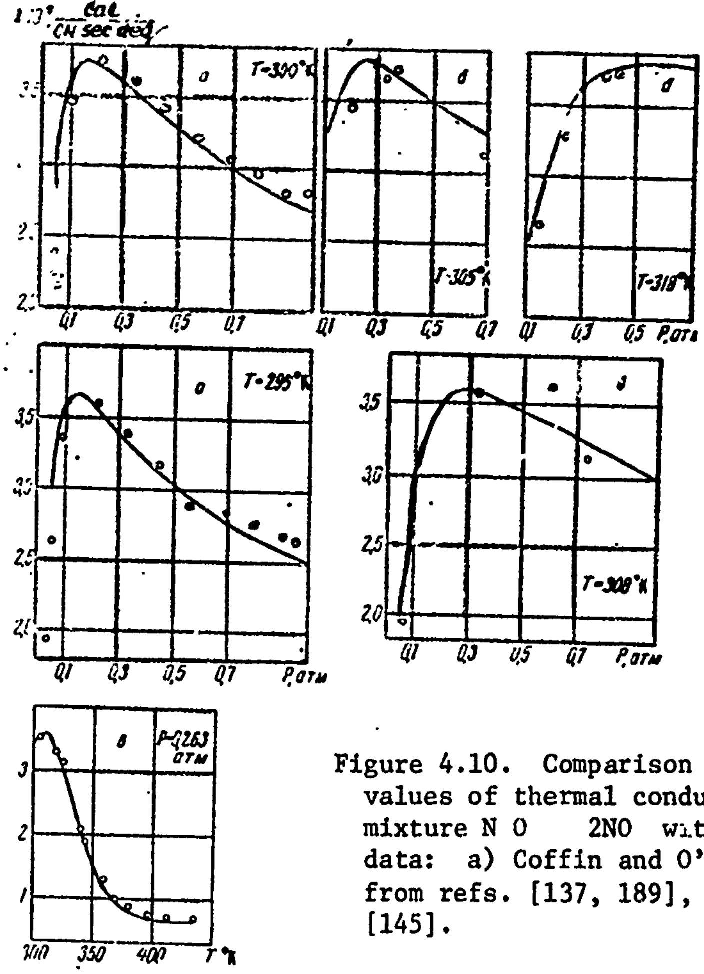

Figure 4.10. Comparison of the calculated values of thermal conductivity of the mixture N 0 2NO with experimental data: a) Coffin and O'Neal [25], b) data from refs. [137, 189], c) Dresvyannikov [145].

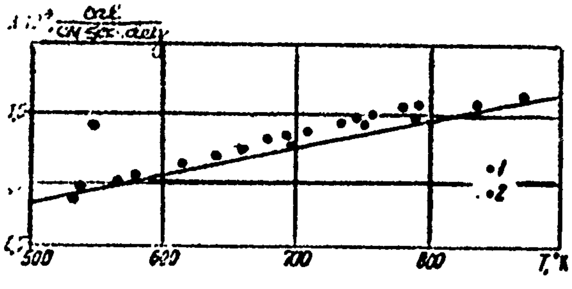

Figure 4.11. Comparison of the calculated and experimental values of the thermal conductivity of the mixture $2NO_2 \rightleftarrows 2NO + O_2$:

1) smoothed values [29]; 2) experimental data [145]; solid line, 'frozen' thermal conductivity.

We will note that the system $N_2O_4 \rightleftarrows 2NO_2$ is not the most fortunate selection from the standpoint of checking the effect of the rate of the chemical reaction on the 'thermal conductivity'. The effect of chemical relaxation on $\bar{\lambda}^*$ of this mixture is felt noticeably when $P << 1$ atm, where accommodation surface effects are manifested. But when $P = 1$ atm the nonequilibrium nature of the chemical reaction $N_2O_4 \rightleftarrows 2NO_2$ decreases the 'thermal conductivity' in comparison with λ_{el} by not more than 1.5-2%. Thus, the range of pressures being investigated is very narrow.

The experimental [29, 144] and the calculated values of $\bar{\lambda}^*$ of the mixture $2NO_2 \rightleftarrows 2NO + O_2$, obtained analytically from formula (4.37) and by numerical solution of system of equations (4.23) on an ETsVM, at $P = 1$ atm, are practically equal to the 'frozen' thermal conductivity (Fig. 4.11).

The experimental values of $\bar{\lambda}^*$ [29] at $P > 1$ atm at the present time are the only ones. Since in the determination of the 'thermal conductivity' [29] the method of coaxial cylinders was used as relative, the dimensions of the heat-transfer gap were not accurately determined. With an external diameter of the internal cylinder of 0.8 cm, the width of the gap amounted hypothetically to 0.6-0.8 cm, if, of course, there was no noticeable excentricity in the apparatus. When $P = 5$ atm and 10 atm the calculated values of $\bar{\lambda}^*$ agree satisfactorily with the experimental data [29] (Fig. 4.12). But when $P = 30$ and 50 atm and $T > 650$ K the difference in the calculated and experimental data exceeds 20% and increases as the temperature rises. At the same time, the behavior of $\lambda_{exp}(\pi, \tau)$ at high pressures is not subordinate to the dependences established for an inert ('frozen') mixture or an individual substance. Usually the effects of the pressure on the thermal conductivity of the latter $(\lambda_{smooth} - \lambda_{id})/\lambda_{id}$ amounts to not more than 5-7% at the same given critical parameters of π, τ. However, the increase in the 'thermal conductivity' of the mixture under consideration when $P = 50$ atm $(\lambda_{exp} - \lambda_f)/\lambda_f$ amounts to approximately 30-40% (Fig. 4.13).

If in the course of the experiments or in the processing of the results [29] no methodological error was committed, a hypothetical explanation of the divergences between the experimental [29] and the calculated values at high values of P may be the variation of the mechanism of the decomposition of NO_2 with an increase in P.

However, in that region of temperatures and pressures where a divergence between the calculated and experimental values of $\bar{\lambda}^*$ is observed, the experimental investigation of the rate constant k_{pr2} was not conducted (Fig. 4.14).

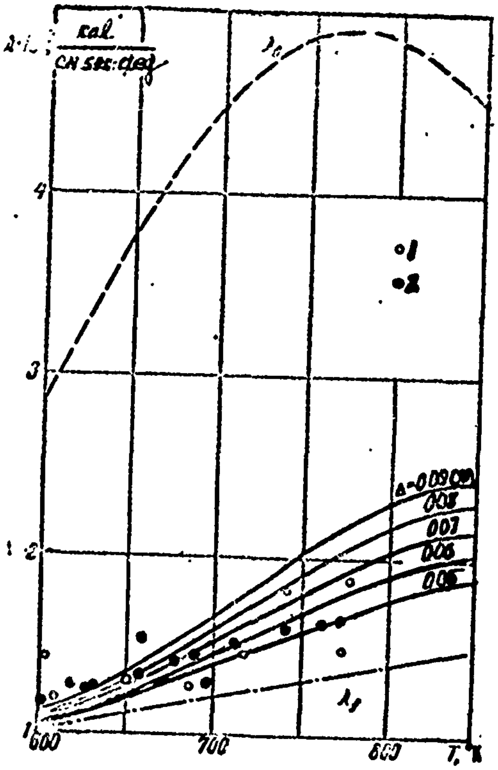

Figure 4.12. Comparison of calculated and experimental values of thermal conductivity of the mixture $2NO_2 \rightleftarrows 2NO + O_2$ at P = 10 atm.

1) experimental data in section 1, 2) in section 2; solid line represents calculated values for gaps of different widths, R_1 = 0.4 cm.

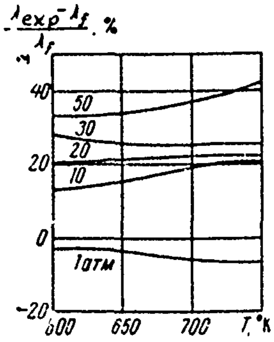

Figure 4.13. Effect of pressure on the 'thermal conductivity' of the mixture $2NO_2 \rightleftarrows 2NO + O_2$, observed in the experiment [29].

The thermal decomposition of NO_2 according to the scheme $2NO_2 \rightleftarrows 2NO + O_2$ is referred by Laidler [275] to the class of elementary gaseous reactions. And this entirely agrees with the investigations of Bodenstein and his coworkers [43] and those of Rosser and Wise [59], at P = 1-2 atm the rate of the reaction varies with the concentration of NO_2 according to the law of a simple second-order reaction. From thence the conclusion is suggested that such a reaction is a simple bimolecular reaction.

Strictly speaking, many complex reactions in limited boundaries of the variation of the parameters P, T are subordinate to simple kinetic laws. But in a wide range of P, T the orders of magnitude of these reactions vary, which speaks of the complex nature of the latter.

Relative to the decomposition of NO_2 it was also established [252] that at high temperatures (T = 1450-2000°K) and at high pressures a change of the order of the reaction from second to first occurs. Troe [252] investigated the decomposition of NO_2 in a medium of Ar (the concentration of NO_2 amounted to 0.05-2%) in a high-pressure shock tube at a general concentration of the diluent of $1.5 \cdot 10^{-5} \leq \rho_{Ar} \leq 2.5\ 10^{-3}$ moles/cm^3, which corresponds to the general pressure $2 \leq P \leq 400$ atm. When P > 300 atm, a deviation of the reaction from the second order was observed, although the decomposition of NO_2 according to the strictly first order scheme may occur at very high pressures (P >>1000 atm), as follows from the arguments given above.

Following the Lindemann-Hinshelwood theory, we assume that the mechanism of the decomposition of NO_2 through the activated complex is as follows:

$$NO_2 + NO_2 \underset{k_{-1}}{\overset{\kappa_1}{\rightleftarrows}} NO_2 + (NO_2)^*,$$

Relative to the activated complex $(NO_2)^*$ the equation of kinetics is written:

$$(NO_2)^* \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} NO + O.$$

On the basis of the method of steady-state [275] ($d\rho_{act}/dt = 0$), we will determine the concentration of the activated complex

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$$(k_{pr2eff})_{P\uparrow} = \frac{k_1 k_2}{k_{-1}} = k'_{pr2}.$$

Here $k'_{pr2} = 10^{14.3}\exp(-71860/RT)\,\text{sec}^{-1}$ is the expression for the first-order rate constant obtained by Troe by extrapolation to high pressures.

At low densities $k_{pr2eff} = k_1 = k''_{pr2}$. And thus,

$$k_{pr2eff} = \frac{k'_2}{\frac{k''_{pr2}}{k'_{pr1}}\rho_{NO_2} + 1}, \tag{*}$$

where $k''_{pr2} = 10^{16.05}\exp(-65000/RT)(\text{cm}^3/\text{mole/sec})$ is the second-order rate constant obtained by Troe in the range T = 1450-2000°K up to pressures P = 80 atm. This latter essentially differs from the constant k_{pr2}, obtained by Rosser and Wise and by Bodenstein [43, 59], since the decomposition of NO_2 at moderate temperatures occurs, although in accordance with a second-order scheme with a somewhat different mechanism.

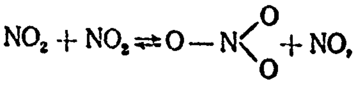
From the ratio (*) it follows that the magnitude of P at which the decomposition will occur according to the second-order scheme is determined by the condition

$$\frac{k''_{pr2}\rho_{NO_2}}{k'_{pr2}} \geqslant 10.$$

At T = 1500°K this condition is fulfilled when P > 1000 atm. At a pressure P = 1, 10, 80, 100, 300, 400, and 1000 atm, the values of $k'_{pr2} = 6.77\ 10^{-3}$/sec and the values of $k''_{pr2}\rho = 26.3;\ 263;\ 2.1\cdot10^3;\ 2.63\cdot10^3;\ 7.88\cdot10^3;\ 1.04\cdot10^3$ and $2.63\cdot10^4$, respectively.

The extrapolation of Troe's formula k''_{pr2} to the region of moderate temperatures (Fig. 4.15) investigated by Rosser and Wise and by Bodenstein, demonstrated that the contribution of this mechanism in the range T = 600-1000°K is negligible.

Mal'ko assumed that thermal decomposition at moderate temperatures occurs with the formation of the intermediate substances NO_3 and N_2O_2:



$$NO_2 + NO_2 \rightleftarrows O{-}N\begin{matrix}O\\ \\O\end{matrix} + NO,$$

$$NO_2 + NO_2 \rightleftarrows OONO + NO,$$
$$NO_2 + NO_3 \rightleftarrows N_2O_2 + O_2,$$
$$NO_2 + NO_2 \rightleftarrows NO + NO + O_2.$$

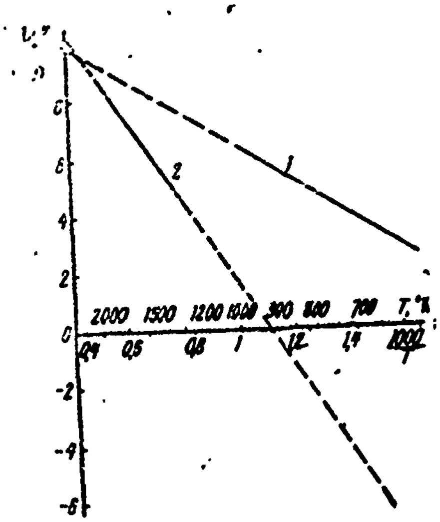


Figure 4.15. Temperature dependence of the second-order rate constant of the reaction of thermal decomposition of NO_2 (1- is the constant determined by Rosser and Wise and by Bodenstein $k_{pr2} = (1/2)10^{12.6}\exp(-26900/RT)$, 2- is Troe's constant $k''_{pr2} = 10^{16.05}\exp(-65000/RT)$ cm^3/mole/sec).

The effective rate constant of the decomposition of NO_2 of the second-order, obtained from such a scheme,

$$k_{pr2M} = 5{,}675\cdot 10^{7}T\exp(-26600/RT),$$
$$k_{\text{эксп}2M} = T\exp(1925/RT)$$

within limits of ±3-4% coincides with the constant k_{pr2}, i.e., on the basis of available information concerning the mechanism of the decomposition of NO_2 in the gaseous phase we cannot make either a qualitative or even a quantitative conclusion conerning the variation of the constant k_{pr2} [43,59] at P = 10-50 atm, and T = 650-800°K. For the final explanation of the divergence of the experimental data [29] from the calculated values of $\bar{\lambda}^*$ of the mixture $2NO_2 \rightleftarrows 2NO + O_2$, at the IYaE AN BSSR a repetition of the experiments was attempted. In the course of the processing of the results of the experiment on calibrated gases it was established that in an apparatus of the type described in ref.

[29] conditions of isothermicity are not observed along the length of the cylinders in the working section. This considerably complicated the processing of the results of the experiment. After consideration of the corrections associated with the overflows of heat along the cylinders, the constants in the working formula were determined on the basis of data with respect to the thermal conductivity of He and N_2, which were then used in the determination of the 'thermal conductivity' of the mixture $N_2O_4 \rightleftarrows 2NO_2 \rightleftarrows 2NO + O_2$. These new experimental values of the 'thermal conductivity' agree, with an error no higher than ±2-3% with the calculated values of $\bar{\lambda}^*$ obtained according to the formulas described above in the entire range of P and T investigated (1-150 atm, and from T_s to 750°K). Only in the region of the peak of the thermal conductivity in the first stage of the reaction do the divergences increase to 5-7%.

6. Generalization of the Values of the Nonequilibrium Composition and the Thermal Conductivity

From an analysis of the functional form of the expressions obtained for the nonequilibrium composition (4.28) and the average 'thermal conductivity' (4.37) it follows that aside from the conditions P = idem; T = idem, for similarity of the processes of heat transfer and mass transfer in the heat-transfer gap in a mixture with finite rates of the chemical transformations it is necessary that the following condition be fulfilled:

$$\frac{\tau_{dif}}{\tau_{chem}} = \text{idem} \quad \text{for} \quad \frac{R_2}{R_1} = \text{idem}.$$

By means of this additional criterion of similarity, the values of the nonequilibrium composition are generalized: $\Delta x/\Delta x_2 = (x_{R_1} - x_{R_2})/(x_{eR_1} - x_{eR_2})$ and also the average 'thermal conductivity' of the mixture $N_2O_4 \rightleftarrows 2NO_2 \rightleftarrows 2NO + O_2$. We note that the generalized curves given in Fig. 4.16 determine the 'thermal conductivity' also of another different nonequilibrium mixture, placed in the heat transfer gap of the geometry under consideration.

At the characteristic time of the chemical transformations, here the chemical relaxation time τ_{chem} is used, which in distinction from the time of the establishment of equilibrium, does not depend upon the initial deviation, but is determined only by the physico-chemical properties of the system and by the external parameters. With reference to the mixtures under consideration the following expressions were obtained for τ_{chem} [228]:

$$\tau_{chem1} = \left\{k_{pR1}\left[1 + \frac{2P}{K_{p1}}(1 - x_{1c})\right]\right\}^{-1};$$

$$\tau_{chem2} = \left\{3\rho k_{pR2}\left[2\left(1 - \frac{3}{2}x_{3c}\right) + \frac{P}{K_{p2}}x_{3c}^2\right]\right\}^{-1}.$$

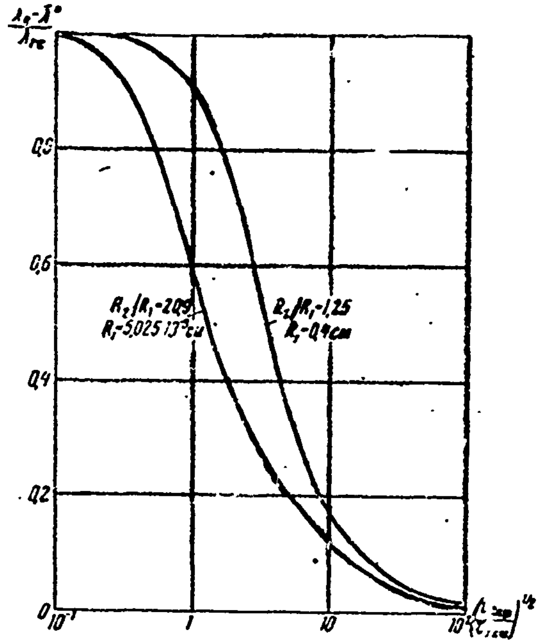


Figure 4.16. Generalized dependence $(\lambda_e-\bar{\lambda}^*)/\lambda_{re} = f(\tau_{dif}/\tau_{chem})$

The time scale of the diffusion process is determined by the method of the theory of similarity from the differential equation of diffusion of the reacting gases, $\tau_{dif} = \delta^2/D_j$, where $D_j = D_{1e}$ for mixture I, and $D_j = D_{3e}$ for mixture II (4.8).

The characteristic dimension in the heat-transfer gap of cylindrical geometry is $\delta = R_1 \ln(R_2/R_1)$. If the gap between the cylinders, $\Delta = R_2 - R_1$ is small in comparison with R_1 and R_2 (in the investigation of the 'thermal conductivity' by the coaxial cylinder method at large values of P), then $\delta \cong R_2 - R_1$.

Chapter V

THERMOPHYSICAL PROPERTIES OF N_2O_4 IN THE LIQUID PHASE

1. Degree of Dissociation of the System $N_2O_4 \rightleftarrows 2NO_2$ in the Liquid Phase

The experimental study of the equilibrium of the reaction $N_2O_4 \rightleftarrows 2NO_2$ in the liquid phase was conducted at atmospheric pressure at temperatures $T \le T_{\text{natural boiling}} = 294.5$ K [109]112]. Duncall [109] studied the dissociation of nitrogen tetroxide only for three temperatures by means of the visual calorimetric method, with a gas flame as the light source. According to Sone [111], from measurements of the magnetic susceptibility of nitrogen tetroxide it follows that in the liquid phase 0.7% NO_2 is contained. However, his work contains an inaccuracy in the determination of the magnetic susceptibility. The most reliable data were obtained by the spectrophotometric method in ref. [112]. The concentration of the NO_2 component in the liquid was determined by means of comparison of data with respect to adsorption in the liquid phase with adsorption of a known concentration in the vapor phase. The results give a linear dependence between lg K_x and 1/T.

Since a knowledge of dissociation is necessary in the solution of many problems, such as, for example, those associated with the variation of the aggregate state of the substance, a calculation was made of the degree of dissociation of nitrogen tetroxide in the region of temperatures from the melting point to the critical point in the vapor phase and the liquid phase at at the saturation line [113].

A feature of the system under consideration is the inseparability of the components N_2O_4 and NO_2, no matter what the external parameters P and T may be. At a liquid-vapor equilibrium, the variation of the system or its number of degrees of freedom, according to the Gibbs phase rule, is equal to

$$W = 2 + c - r - \phi = 2 + 2 - 1 - 2 = 1$$

i.e., only one independent parameter exists, such as P_s, T_s, or α_s, for example, which hampers the opportunity of the application of many ratios obtained in the theory of solutions. In other words, it is impossible to trace the property-composition dependence without variation of P and T.

In considering the dissociation reaction $N_2O_4 \rightleftarrows 2NO_2$ as an equilibrium reaction (actually, at pressures $P \sim 1$ bar the time of the establishement of chemical equilibrium in the system is 10^{-4}-10^{-5} sec in the gaseous phase [114]; in the liquid phase equilibrium is established much more rapidly: the lifetime of NO_2 in a medium of N_2O_4 at a temperature T = 283.2 K and at atmospheric pressure amounts to $0.2\ 10^{-8}$ sec according to the data in ref. [115]), we may demonstrate that to each pair of values of P and T its own composition of the mixture corresponds.

The degree of dissociation of the vapor at the saturation line was determined according to the methodology explained in Chapter II.

The activity factor γ'' of the entire system was found according to the general rule as a measure of the deviation of the real molar volume from the molar volume of an ideal (perfect) gas at the same values of P and T:

$$RT \ln \gamma''_{\text{см}} = -\int_0^P (V_{id} - V_{\text{см}})\, dP.$$

The real molar volume is determined with a knowledge of the degree of dissociation and of the experimental data with respect to the density of the system in the gaseous phase [15, 16] and on the saturation line [116]. The P-V-T data were taken from ref. [35].

In this case the activity factors γ''_i are:

$$\log \gamma''_1 = \log \gamma''_{\text{см}} + x''_2 Y;$$

$$\log \gamma''_2 = \log \gamma''_{\text{см}} - x''_1 Y;$$

$$Y = \left(\frac{\Delta H}{RT_{cr}}\right) \frac{T_{cr2} - T_{cr1} + 2(1 - x''_2)(2T_{cr\tau} - T_{cr1} - T_{cr2})}{2{,}303\, T_{\text{кр}}} + $$

$$+ (Z_{\text{см}} - 1) \frac{P_{cr2} - P_{cr1} + 2(1 - x''_2)(2P_{cr\tau} - P_{cr1} - P_{cr2})}{2{,}303\, P_{\text{кр}}} -$$

$$- \log \gamma^{(1)}_{\text{см}} (\omega_2 - \omega_1).$$

Thus, the composition of the vapor at the saturation line is calculated by the method of successive approximations. For the zero approximation the value of α_0 at $\gamma_i'' = 1$ is selected. Then by calculating γ_{sm}'' and γ_i'' in the first approximation, we find α_j''. Two or three approximations are sufficient.

This method of calculating γ_i'' is very laborious. With a sufficient degree of accuracy we may use the expression $\log \gamma_i'' = \log \gamma_i^{(0)} + \omega_i \log \gamma_i^{(1)}$.

The degree of dissociation at the critical point determined according to the first method amounts to $\alpha_{cr} = 0.321$ and according to the second method, $\alpha_{cr} = 0.30$, which is entirely adequate for engineering calculations.

At equilibrium on the curve of the co-existence of liquid and vapor, because of the equality of chemical potentials of the components in both phases and with the same selection of the standard state of the activity of the i-th component in the equilibrium phases are the same: $a_i' = a_i'' = a_i = x_i'\gamma_i' = x_i''\gamma_i''$. Since $\gamma_i' = P_i/P_{i\ id}$, $P_{i\ id} = x_i'P_i^0$, $a_iP_i^0 = P_i$, and $P_{id} = \sum\limits_{(i)} x_i'P_i^0 = P/Z_{sm}$, by the selection method we may determine the composition in the liquid phase at the saturation line.

At low temperatures the connection between the compositions of the equilibrium phase is described by the following expression [117]:

$$\frac{x_1''}{x_2''} = \frac{P_1}{P_2} = \frac{P_1^0\gamma_1'}{P_2^0\gamma_2'} \cdot \frac{x_1'}{x_2'}.$$

For the calculation of P_i^0 we may use a generalized Riedel formula, establishing the dependence between the given value of the pressure of the saturated vapor of the i-th component $\pi_i^0 = P_i^0/P_{cr1}$ upon the magnitude of the critical parameter χ_{cri} and the given temperature $\tau_i = T/T_{cr1}$: $-\log \pi_i^0 = \phi(\tau_i) + (\chi_{cr1} - 7)\Psi(\tau_i)$.

The values of the functions $\phi(\tau)$ and $\Psi(\tau)$ are given in ref. [118]. The Riedel parameter is associated with the acentric factor ω by the equation $\chi_{cr1} = 5.808 + 4.930\omega_i$, and $\omega_i = (0.291 - Z_{cr1}/0.08)$, where $Z_{cr1} = (P_{cr1}/V_{cr1})/RT_{cr1}$.

For the component N_2O_4, $\omega_1 = 0.350$, and for NO_2 $\omega_2 = 0.375$.

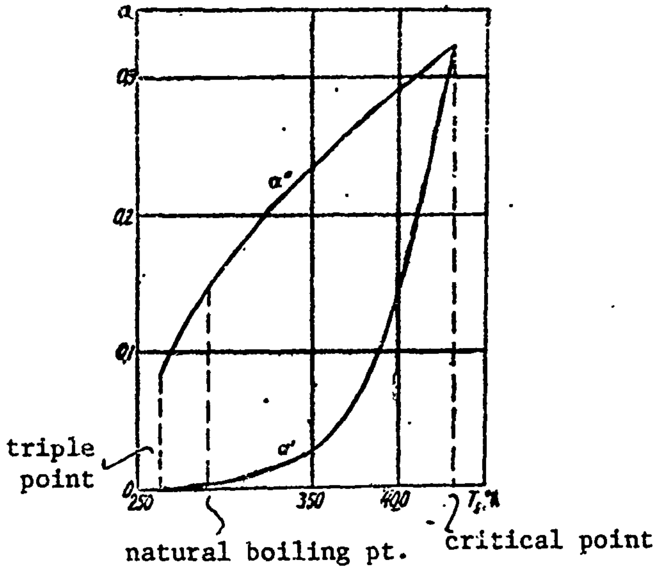


Figure 5.1. Degree of dissociation of the system $N_2O_4 \rightleftarrows 2NO_2$ in liquid and in vapor at the saturation line.

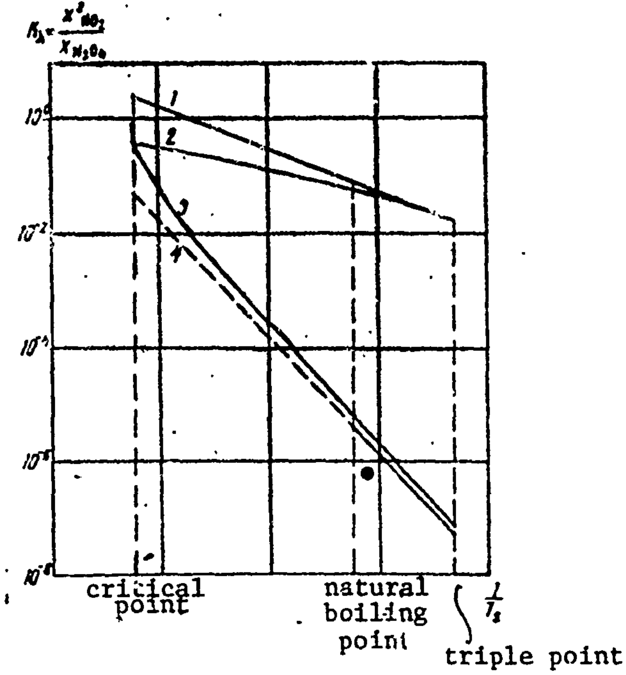


Figure 5.2. Dependence of the constant of equilibrium of the dissociation reaction $N_2O_4 \rightleftarrows 2NO_2$ in the gaseous and in the liquid phases at the saturation line upon the magnitude of the reverse temperature $1/T_s$:

1- $K''_{x\ id}(P,T)$; 2- $K''_x(P,T)$; 3- $K'_x(P,T)$; 4- $K'_x(T)$.

The calculated data concerning the degree of dissociation of the liquid and vapor at the saturation line from the melting point to the critical point are given in Fig. 5.1.

In Fig. 5.2 a curve of the dependence of the constant of equilibrium $K_x = x_2^2/x_1$ is shown in the gaseous and in the liquid phases, respectively; where 1) is $K''_{x\ id}(P,T)$ in an ideally (perfect) gaseous state; and 4) shows the plotting of the experimental values of $K''_x(T)$ [112] from the triple point to the normal boiling point. From the boiling point to the critical point the values shown by the dashed line are extrapolated. The experimental point of $K'_x(T)$ at a temperature T = 293.2 K according to data from ref. [109] is designated by a circle.

Table 5.1 Degree of dissociation of liquid and vapor of the system $N_2O_4 \rightleftarrows 2NO_2$ at the saturation line.

T_s, °K	P_s, bars	α'	α''
261,9	0,192	0,000170	0,066
270,0	0,320	0,000236	0,089
280,0	0,560	0,000512	0,111
290,0	0,854	0,000810	0,133
291,0	1,028	0,00137	0,142
300,0	1,342	0,00382	0,154
310,0	2,037	0,00521	0,170
320,0	3,003	0,00590	0,186
330,0	4,378	0,0142	0,200
340,0	6,329	0,0219	0,213
350,0	9,094	0,0311	0,225
360,0	12,94	0,0493	0,238
370,0	18,13	0,0714	0,252
380,0	24,94	0,0992	0,264
390,0	33,66	0,127	0,275
400,0	44,66	0,161	0,287
410,0	58,48	0,199	0,298
420,0	76,05	0,244	0,310
430,0	98,88	0,303	0,319
431,35	102,49	0,321	0,321

In Table 5.1 the calculated values of the degree of dissociation of liquid and vapor at the saturation line from the melting point to the critical point are given.

2. Curve of the Vapor Tension

In the literature two works are known which generalize numerous experimental data with respect to the curve of the vapor tension [35, 119]. The numerical values of the saturation pressure in both works agree within the limits of accuracy of the experiment, in the range of the variation of the temperature from the triple point.to the critical point. The magnitude of the derivatives $(dP/dT)_s$ calculated according to the polynomial proposed in ref. [119] practically coincide with the data in ref. [35] from the triple point to 410°K. At higher temperatures the derivatives in ref. [119] lie lower and at the critical point the divergences reach 5%. If we use the Planck-Gibbs rule for analysis of the reliability of these data near the critical point, it turns out that from the volumetric behavior of nitrogen tetroxide even a slightly greater value of $(dP/dT)_s^{cr}$ follows than in ref. [35], which shows the preferability of these data.

In Table 5.2 the values of P_s - T_s are given, obtained by a generalization of the data in refs. [14,15,36,37,38,41,55].

3. Curve of Orthobaric Densities

The analysis and processing of experimental data with respect to densities of liquid and vapor at the saturation line were given in ref. [116]. The values of the density of the liquid and vapor obtained by the same means as the values of P_s - T_s according to the data in [14, 36, 37, 38] are given in Table 5.3.

4. Density of N_2O_4

The density of the liquid phase of N_2O_4 was measured by Reamer and Sage [14] and by Tsymarnyy [16]. Tsymarnyy's processed data agree well with the data in ref. [14]. The matched data are given in Table 5.4.

5. Surface Tension

For a description of the dependence of surface tension upon temperature, the Guggenheim equation was used [23]:

$$\sigma = \sigma_0 \left(1 - \frac{T}{T} \right)^{11/9}.$$

Table 5.2 Calculated values of the saturation pressure of N_2O_4 and of the derivative (dP/dT) along the curve of the vapor tension.

T. °K	$\frac{dP}{dT}$, $\frac{bar}{°K}$	P. bar	T. °K	$\frac{dP}{dT}$, $\frac{bar}{°K}$	P. bar
262	0,0151	0,1915	306	0,0716	1,7309
263	0.0153	0.2067	307	0,0740	1,8036
264	0.0155	0,2221	308	0,0765	1,8789
265	0,0157	0,2377	309	0,0791	1,9567
266	0.0160	0,2535	310	0,0818	2,0371
267	0,0162	0,2696	311	0,0845	2,1202
268	0,0166	0,2860	312	0,0874	2,2062
269	0.0170	0,3028	313	0,0904	2,2950
270	0,0174	0,3200	314	0,0934	2,3869
271	0,0180	0,3377	315	0,0966	2,4820
272	0,0185	0,3560	316	0,0999	2,5802
273	0,0192	0.3748	317	0,1034	2,6819
274	0,0199	0,3944	318	0,1069	2,7870
275	0,0207	0,4147	319	0,1106	2,8958
276	0,0216	0.4358	320	0,1145	3,0084
277	0,0225	0,4579	321	0,1185	3,1249
278	0,0235	0,4809	322	0,1227	3,2455
279	0,0246	0,5019	323	0,1270	3,3703
280	0.0257	0,5301	324	0,1315	3,4996
281	0.0269	0.5564	325	0,1362	3,6334
282	0,0282	0,5839	326	0,1411	3,7721
283	0,0295	0,6128	327	0,1461	3,9157
284	0,0308	0,6429	328	0,1514	4,0641
285	0,0322	0,6744	329	0,1568	4,2185
286	0,0337	0,7074	330	0,1625	4,3782
287	0,0352	0,7418	331	0,1684	4,5436
288	0.0367	0.7778	332	0,1745	4,7150
289	0.0383	0.8153	333	0,1808	4,8926
290	0.0399	0.8544	334	0,1873	5,0766
291	0,0416	0,8952	335	0,1941	5,2673
292	0.0433	0.9376	336	0,2011	5,4649
293	0.0450	0,9818	337	0.2084	5,6696
294	0,0468	1,0277	338	0,2158	5,8817
295	0,0486	1,0754	339	0.2236	6,1014
296	0,0505	1,1250	340	0,2316	6,3290
297	0,0524	1,1761	341	0,2398	6,5647
298	0,0543	1,2297	342	0,2483	6,8087
299	0.0563	1,2850	343	0,2571	7,0614
300	0,0583	1,3423	344	0,2661	7,3230
301	0,0604	1,4016	345	0,2754	7,5938
302	0,0625	1,4630	346	0,2850	7,8739
303	0,0647	1,5266	347	0,2948	8,1638
304	0,0669	1,5924	348	0,3049	8,4638
305	0,0692	1,6605	349	0,3152	8,7736

T. °K	$\frac{dP}{dT}$, $\frac{бар}{°K}$	P. бар	T. °K	$\frac{dP}{dT}$, $\frac{бар}{°K}$	P. бар
350	0,3259	9,0942	397	1,1484	41,0944
351	0,3368	9.4255	398	1,1748	42,2560
352	0,3480	9,7678	399	1,2018	43,4443
353	0,3594	10,1215	400	1,2294	44,6598
354	0,3711	10,4868	401	1,2577	45,9033
355	0,3831	10,8639	402	1,2867	47,1755
356	0,3954	11,2531	403	1,3165	48,4771
357	0,4079	11,6548	404	1,3471	49,8088
358	0,4208	12,0691	405	1,3785	51,1715
359	0,4338	12,4964	406	1,4108	52,5661
360	0,4472	12,9369	407	1,4440	53,9935
361	0,4608	13,3909	408	1,4782	55,4545
362	0,4747	13,8586	409	1,5135	56,9503
363	0,4889	14,3404	410	1,5498	58,4819
364	0,5033	14,8365	411	1,5874	60,0504
365	0,5181	15,3472	412	1,6260	61,6569
366	0,5330	15,8728	413	1,6660	63,3028
367	0,5483	16,4131	414	1,7073	64,9894
368	0,5638	16,9694	415	1,7501	66,7180
369	0,5796	17,5411	416	1,7943	68,4900
370	0,5957	18,1287	417	1,8401	70,3071
371	0,6120	18,7325	418	1,8876	72,1708
372	0.6286	19.3528	419	1,9368	74,0828
373	0,6455	19,9898	420	1,9878	76,0450
374	0,6626	20,6435	421	2,0407	78,0590
375	0,6801	21,3152	422	2,0957	80,1271
376	0,6978	22,0011	423	2,1527	82,2511
377	0,7158	22,7108	424	2,2120	84,4333
378	0,7341	23,4358	425	2,2736	8,6759
379	0,7527	24,1791	426	2,3377	88,9814
380	0,7716	24,9112	427	2,4043	91,3522
381	0,7908	25,7223	428	2,4736	93,7909
382	0,8103	26,5228	429	2,5457	96,3004
383	0,8301	27,3129	430	2,6208	98,8834
384	0,8502	28,1831	431	2,6989	101,5429
385	0,8707	29,0436	431,35	2,7270	102,4924
386	0,8916	29,9247			
387	0,9128	30,8227			
388	0,9344	31,7504			
389	0,9564	32,6958			
390	0,9788	33,6634			
391	1,0016	34,6535			
392	1,0248	35,6667			
393	1,0485	36,7033			
394	1,0727	37,7639			
395	1,0974	38,8489			
396	1,1226	39,9589			

Table 5.3 Density of liquid and vapor in a saturation state of the system N_2O_4.

T, °K	ρ_s^{liq}, g/cm^3	ρ_s^{vap}, g/cm^3	T, °K	ρ_s^{liq}, g/cm^3	ρ_s^{vap}, g/cm^3
262	1,5145	0,00066	307	1,4150	0,006115
263	1,5126	0,00072	308	1,4126	0,006694
264	1,5108	0,00078	309	1,4101	0,006974
265	1,5089	0,00084	310	1,4076	0,007252
266	1,5070	0,00090	311	1,4051	0,007529
267	1,5050	0,00096	312	1,4026	0,007805
268	1,5031	0,00102	313	1,4001	0,008080
269	1,5011	0,00108	314	1,3976	0,008354
270	1,4991	0,00115	315	1,3951	0,008629
271	1,4971	0,00122	316	1,3926	0,008902
272	1,4951	0,00129	317	1,3900	0,009177
273	1,4930	0,00136	318	1,3875	0,009453
274	1,4909	0,00143	319	1,3849	0,009731
275	1,4889	0,00150	320	1,3823	0,010012
276	1,4867	0,00157	321	1,3798	0,010296
277	1,4846	0,00165	322	1,3772	0,010584
278	1,4825	0,00173	323	1,3746	0,010878
279	1,4803	0,00181	324	1,3720	0,011178
280	1,4782	0,00189	325	1,3694	0,011484
281	1,4760	0,00197	326	1,3668	0,011798
282	1,4738	0,00206	327	1,3641	0,012121
283	1,4716	0,00215	328	1,3615	0,012453
284	1,4693	0,00224	329	1,3588	0,012794
285	1,4671	0,00234	330	1,3562	0,013146
286	1,4648	0,00244	331	1,3535	0,013510
287	1,4626	0,00254	332	1,3508	0,013885
288	1,4603	0.00265	333	1,3481	0,014273
289	1,4580	0.00277	334	1,3454	0,014674
290	1,4557	0.00289	335	1,3427	0,015089
291	1,4534	0.00301	336	1,3399	0,015518
292	1,4511	0.00315	337	1,3372	0,015961
293	1,4487	0,00329	338	1,3344	0,016420
294	1,4464	0,003430	339	1,3316	0,016893
295	1,4440	0.003568	340	1,3289	0,017381
296	1,4417	0.003711	341	1,3260	0,017890
297	1,4393	0,003881	342	1,3232	0,018412
298	1,4369	0.004082	343	1,3203	0,018951
299	1,4345	0.004300	344	1,3174	0,019508
300	1,4321	0,004536	345	1,3146	0,020082
301	1,4297	0,004785	346	1,3116	0,020673
302	1,4273	0,005043	347	1,3087	0,021283
303	1,4249	0,005310	348	1,3058	0,021911
304	1,4224	0,005582	349	1,3028	0,022558
305	1,4200	0,005858	350	1,2998	0,023224
306	1,4175	0,006136	351	1,2968	0,023910

T, °K	ρ_s^{liq}, g/cm^3	ρ_s^{vap}, g/cm^3	T, °K	ρ_s^{liq}, g/cm^3	ρ_s^{vap}, g/cm^3
352	1,2937	0,024616	397	1,1089	0.098768
353	1,2907	0,025342	398	1,1030	0.102100
354	1,2876	0,026089	399	1,0970	0.105543
355	1,2845	0,026859	400	1,0909	0.109100
356	1,2813	0,027650	401	1,0846	0,112771
357	1,2781	0,028465	402	0,0782	0,116564
358	1,2749	0,029303	403	1,0717	0.120483
359	1,2717	0,030167	404	1,0650	0.124532
360	1,2684	0,031056	405	1,0582	0.128720
361	1,2651	0,031972	406	1,0511	0.133054
362	1,2617	0,032917	407	1,0440	0.137545
363	1,2583	0,033891	408	1,0366	0.142203
364	1,2549	0,034895	409	1,0291	0.147043
365	1,2514	0,035932	410	1,0213	0.152082
366	1,2479	0,037002	411	1,0134	0.157340
367	1,2444	0,038108	412	1,0052	0.162841
368	1,2408	0,039251	413	0,9968	0.168613
369	1,2371	0,040433	414	0,9881	0.174691
370	1,2335	0,041657	415	0,9791	0,181115
371	1,2297	0,042923	416	0,9698	0,187931
372	1,2259	0,044234	417	0,9601	0,195196
373	1,2221	0,045593	418	0,9500	0,202976
374	1,2182	0,047001	419	0,9395	0,211351
375	1,2143	0,048461	420	0,9281	0,220115
376	1,2103	0,049976	421	0,9167	0,230281
377	1,2062	0,051518	422	0,9012	0,241090
378	1,2021	0,053179	423	0,8909	0,253015
379	1,1979	0,054871	424	0,8763	0,266273
380	1,1936	0,056629	425	0,8602	0,281145
381	1,1893	0,058453	426	0,8421	0,297994
382	1,1849	0,060317	427	0,8210	0,317284
383	1,1801	0,062313	428	0,7956	0,339565
384	1,1759	0,064354	429	0,7627	0,365371
385	1,1713	0,066472	430	0,7154	0,396418
386	1,1666	0,068670	431	0,6251	0,447276
387	1,1618	0,070950	431,35	0,5500	0,550
388	1,1569	0,073314			
389	1,1520	0,075765			
390	1,1470	0,078306			
391	1,1418	0,080937			
392	1,1366	0,083663			
393	1,1313	0,086484			
394	1,1258	0,089402			
396	1,1146	0,095542			

Note: $_{s}^{vapor}$, for T < 294°K was obtained according to the straight-line diameter method.

Table 5.4 Density ρ of N_2O_4 in the liquid phase, g/cm^3.

t, °C	P, ama									
	1	5	10	15	20	30	40	50	100	150
—10	1,5050	1,5055	1,5060	1,5065	1,5070	1,5080	—	—	—	—
0	1,4845	1,4815	1,4850	1,4860	1,4870	1,4880	1,4900	1,4920	—	—
10	1,4630	1,4635	1,4640	1,4650	1,4660	1,4680	1,4700	1,4720	—	—
20	1,4415	1,4420	1,4430	1,4440	1,4450	1,4470	1,4490	1,4510	1,4590	1,4650
30	—	1,4190	1,4200	1,4210	1,4220	1,4240	1,4260	1,4280	1,4365	1,4430
40	—	1,3960	1,3970	1,3980	1,3990	1,4010	1,4030	1,4050	1,4125	1,4205
50	—	1,3710	1,3720	1,3730	1,3740	1,3760	1,3780	1,3800	1,3880	1,3970
60	—	—	1,3460	1,3470	1,3480	1,3500	1,3520	1,3540	1,3635	1,3730
70	—	—	—	1,3190	1,3200	1,3220	1,3210	1,3260	1,3370	1,3470
80	—	—	—	—	1,2875	1,2900	1,2925	1,2950	1,3085	1,3200
90	—	—	—	—	—	1,2560	1,2585	1,2615	1,2780	1,2915
100	—	—	—	—	—	1,2180	1,2210	1,2245	1,2450	1,2605
110	—	—	—	—	—	1,1750	1,1780	1,1825	1,2065	1,2255
120	—	—	—	—	—	—	1,1265	1,1305	1,1620	1,1865
130	—	—	—	—	—	—	—	1,0635	1,1080	1,1400
140	—	—	—	—	—	—	—	—	1,0380	1,0840
150	—	—	—	—	—	—	—	—	0,9355	1,0120
160	—	—	—	—	—	—	—	—	—	0,9145

t, °C	P, ama								
	200	250	300	350	400	450	500	550	600
20	1,4705	1,4765	1,4825	1,4890	1,4945	—	—	—	—
30	1,4500	1,4560	1,4620	1,4690	1,4750	—	—	—	—
40	1,4285	1,4355	1,4120	1,4485	1,4550	1,4615	1,4680	1,4740	1,4800
50	1,4050	1,4130	1,4205	1,4270	1,4310	1,4410	1,4470	1,4530	1,4585
60	1,3820	1,3900	1,3980	1,4050	1,4125	1,4200	1,4270	1,4310	1,4395
70	1,3575	1,3660	1,3750	1,3830	1,3910	1,3990	1,4065	1,4130	1,4200
80	1,3320	1,3115	1,3515	1,3600	1,3690	1,3770	1,3860	1,3920	1,3995
90	1,3045	1,3155	1,3265	1,3365	1,3465	1,3555	1,3645	1,3710	1,3785
100	1,2755	1,2875	1,3005	1,3120	1,3220	1,3320	1,3115	1,3495	1,3565
110	1,2430	1,2570	1,2725	1,2815	1,2960	1,3070	1,3170	1,3260	1,3360
120	1,2060	1,2235	1,2100	1,2545	1,2680	1,2800	1,2900	1,3000	1,3100
130	1,1650	1,1855	1,2055	1,2210	1,2370	1,2505	1,2620	1,2750	1,2815
140	1,1160	1,1420	1,1655	1,1815	1,2025	1,2180	1,2320	1,2460	1,2570
150	1,0580	1,0910	1,1180	1,1135	1,1635	1,1820	1,1980	1,2140	1,2265
160	0,9850	1,0315	1,0650	1,0950	1,1200	1,1405	1,1600	1,1780	1,1930

The quantity σ_0 entering into this equation is determined according to experimental data [122] (i = 1.6, 19.8, and 20°C; σ = 29.52, 26.50, or 25.58 dynes per cm and is assumed to be equal to 102.34 dynes/cm.

The value of σ at a temperature of 19.8°C was not assumed in the consideration, since it does not correspond to the fluctuation of the dependence σ = = f(T). The values of the surface tension calculated according to Guggenheim's equation are as follows: at t = 0, 20, 40, 60, 80, 100, 120, 130, 140, 150°C; σ = 30, 25.5, 21, 16, 8, 12.7, 8.8, 5.25, 3.65, 2.15, 0.8 dynes/cm.

6. Heat of Vaporization

The results of the calculation of the heat of vaporization of N_2O_4 are given in refs. [2, 40] and in Table 5.5.

7. Equation of State

The equation of state of liquid $N_2O_4 \rightleftarrows 2NO_2$ up to 431.4°K and 500 atm [22] is as follows:

$$P = A(T)\gamma^2 + B(T)\gamma^4 + C(T)\gamma^6,$$

where

$$A(T) = -0{,}085207 + 1{,}279672\,\Theta^{-1} - 6{,}955565\,\Theta^{-2} +$$
$$+ 16{,}465772\,\Theta^{-3} - 15{,}560336\,\Theta^{-4} + 3{,}870183\,\Theta^{-5};$$
$$B(T)\cdot 10^6 = 0{,}047883 - 0{,}733055\,\Theta^{-1} + 4{,}025217\,\Theta^{-2} -$$
$$- 9{,}380286\,\Theta^{-3} + 7{,}573269\,\Theta^{-4};$$
$$C(T)\cdot 10^{12} = 0{,}003775 - 0{,}020625\,\Theta^{-1} +$$
$$+ 0{,}079741\,\Theta^{-2} - 0{,}038026\,\Theta^{-3}.$$
$$\Theta = T/100\,^\circ K.$$

and γ is the density in kg/m^3.

The mean deviation of the densities calculated according to the equation from the data given by Reamer and Sage amounts to 0.13%.

Table 5.5 Values of the heat of vaporization of liquid N_2O_4 obtained according to the Clausius-Clapeyron equation.

P, am	T, °K	H kcal/kg	P, am	T, °K	H kcal/kg
1,0	294,3	98,1	16.6	366,2	104,7
1,4	299,9	100,5	19,8	372,2	103,5
1,7	305,4	102,7	23,4	377,2	102,1
2,2	311,0	104,1	27,7	383,2	100,0
2,7	316,2	106,4	32,6	389,2	97,4
3,39	322,2	105,6	38,2	394,2	91,2
4,2	327,2	105,9	44,8	400,2	90,0
5,2	333,2	108,4	52,3	405,2	85,3
6,4	339,2	106,1	60,7	411,2	78,9
7,8	344,2	106,2	70,6	416,2	70,8
9,5	350,2	110,2	81,5	422,2	58,7
11,5	355,2	106,0	93,9	427,2	39,9
13,8	361,2	105,4	103,3	431,4	0,0

8. Heat Content

The experimental results of the measurements of the heat content of liquid N_2O_4 at atmospheric pressure [21, 41] agree well with each other. The heat content of liquid N_2O_4 at higher pressures was calculated by graphic differentiation of data with respect to enthalpy calculated according to the equation of state of the liquid phase given above (Table 5.6).

9. Enthalpy

The enthalpy of the liquid phase of N_2O_4 was measured at the IYaE AN BSSR [19]. A satisfactory agreement was demonstrated between the calculated and experimental data.

10. Thermal Conductivity of N_2O_4

In the published literature there is only one work concerning the thermal conductivity of nitrogen tetroxide in the liquid phase [125]. It is devoted to an experimental investigation of λ at pressures up to 340.2 atm and in the temperature range of 4.44-71°C. In order to avoid heat losses from the edges of the flat slab (the method of parallel plates) or end losses from the cylindrical experimental section (the coaxial cylinder method), the authors of this work [125] applied the spherical Baume method. The experimental gap between the two working surfaces amounted to 0.508 mm, which was refined in calibrated experiments with mercury. The maximum temperature difference amounted to 2°F and 4°F, depending upon the volumetric behavior of the nitrogen tetroxide. Free convection was insignificant, since even for the saturation temperatures the product Gr•Pr was less than 1000 [126]. Nitrogen tetroxide of 98% industrial purity was then purified in a laboratory rectification column, and the impurities amounted to less than 0.002 molar fraction. From a measurement of the electrica power fed to the system, the temperature difference, and the heat losses the error of measurement of thermal conductivity was estimated by the authors as 0.0022 kcal/m/hr/degree and the experimental points lay around a smoothed curve with a deviation of 0.00086 kcal/m/hr/degree. The data on thermal conductivity are given in Table 5.7.

Table 5.6 Heat content C_p of liquid nitrogen tetroxide kcal/kg/degree

t, °C	P, am 100	140	180	220	260	300
20	0,354	0,341	0,330	0,318	0,306	0,298
30	0,370	0,359	0,347	0,336	0,324	0,315
40	0,388	0,375	0,365	0,353	0,341	0,335
50	0,405	0,393	0,382	0,370	0,360	0,351
60	0,422	0,410	0,400	0,388	0,378	0,370
70	0,438	0,429	0,419	0,406	0,397	0,389
80	0,455	0,446	0,436	0,424	0,415	0,407
90	0,471	0,465	0,455	0,440	0,434	0,425
100	0,486	0,480	0,471	0,460	0,453	0,445
110	0,532	0,526	0,508	0,500	0,493	0,485
120	0,691	0,612	0,536	0,587	0,578	0,567
130	0,832	0,783	0,746	0,733	0,708	0,699
140	1,185	1,051	0,976	0,934	0,890	0,866
150	2,265	1,056	1,342	1,182	1,115	1,062
155	3,110	2,195	1,665	1,320	1,232	1,162

Table 5.7 Thermal conductivity λ of nitrogen tetroxide in the liquid phase, kcal/m/hr/degree

P, am	t, °C							
	0	10	20	30	40	50	60	70
1	0,1221	0,1185	0,[illegible]44					
5	0,1223	0,1186	0,1146	0,1103	0,1057	0,0997		
10	0,1224	0,1187	0,1146	0,1104	0,1058	0,0999	0,0935	0,0845
15	0,1226	0,1188	0,1147	0,1105	0,1058	0,1000	0,0936	0,0817
20	0,1227	0,1189	0,1148	0,1106	0,1059	0,1002	0,0938	0,0849
30	0,1230	0,1191	0,1151	0,1108	0,1061	0,1005	0,0941	0,0852
40	0,1233	0,1194	0,1154	0,1110	0,1064	0,1008	0,0944	0,0856
50	0,1236	0,1197	0,1157	0,1113	0,1068	0,1011	0,0947	0,0860
75	0,1243	0,1205	0,1165	0,1121	0,1076	0,1019	0,0955	0,0868
100	0,1250	0,1213	0,1173	0,1129	0,1084	0,1027	0,0963	0,0877
150	0,1265	0,1228	0,1189	0,1145	0,1099	0,1043	0,0978	0,0895
200	0,1279	0,1242	0,1203	0,1[illegible]	0,1114	0,1057	0,0994	0,0913
250	0,1294	0,1257	0,1218	0,1177	0,1130	0,1072	0,1009	0,0932
300	0,1309	0,1273	0,1233	0,1192	0,1145	0,1087	0,1025	0,0950
350	0,1324	0,1289	0,1248	0,1207	0,1161	0,1103	0,1042	0,0967
400	0,[illegible]339	0,1304	0,1263	0,1222	0,1176	0,1117	0,1059	0,0984

11. Viscosity of the Liquid Phase of N_2O_4

The values of the viscosity of the liquid phase of N_2O_4 [2] are given in Table 5.8.

Table 5.8 Viscosity of nitrogen tetroxide in the liquid phase $\mu \cdot 10^5$, kcal/sec/m^2.

P, am	t, °C							
	0	10	20	30	40	50	60	70
1	5,321	4,771	4,256					
5	5,331	4,781	4,261	3,828	3,379	2,971		
10	5,341	4,7[illegible]	4,271	3,838	3,394	2,978	2,635	2,309
15	5,357	4,806	4,281	3,848	3,405	2,985	2,640	2,321
20	5,382	4,822	4,292	3,858	3,413	2,992	2,645	2,339
30	5,398	4,842	4,307	3,869	3,425	3,017	2,655	2,357
40	5,423	4,862	4,322	3,879	3,440	3,023	2,676	2,380
50	5,465	4,898	4,363	3,919	3,481	3,053	2,693	2,396
75	5,530	4,939	4,414	3,965	3,516	3,089	2,724	2,[illegible]35
100	5,596	5,007	4,470	4,006	3,552	3,129	2,773	2,477
150	5,717	5,112	4,567	4,077	3,603	3,186	2,836	2,531
200	5,826	5,224	4,674	4,159	3,670	3,242	2,895	2,571
250	5,913	5,331	4,771	4,235	3,726	3,293	2,921	2,610
300	—	5,484	4,893	4,302	3,787	3,333	2,951	2,651
350	—	—	4,966	4,375	3,843	3,384	3,017	2,698
400	—	—	—	—	3,899	3,420	3,053	2,747

Table 5.7 Thermal conductivity λ of nitrogen tetroxide in the liquid phase, kcal/m/hr/degree

P. am	t,°C							
	0	10	20	30	40	50	60	70
1	0,1221	0,1185	0,1144					
5	0,1223	0,1186	0,1146	0,1103	0,1057	0,0997		
10	0,1224	0,1187	0,1146	0,1104	0,1058	0,0999	0,0935	0,0845
15	0,1226	0,1188	0,1147	0,1105	0,1058	0,1000	0,0936	0,0817
20	0,1227	0,1189	0,1148	0,1106	0,1059	0,1002	0,0938	0,0849
30	0,1230	0,1191	0,1151	0,1108	0,1061	0,1005	0,0911	0,0852
40	0,1233	0,1194	0,1154	0,1110	0,1064	0,1008	0,0944	0,0856
50	0,1236	0,1197	0,1157	0,1113	0,1068	0,1011	0,0947	0,0860
75	0,1243	0,1205	0,1165	0,1121	0,1076	0,1019	0,0955	0,0868
100	0,1250	0,1213	0,1173	0,1129	0,1084	0,1027	0,0963	0,0877
150	0,1265	0,1228	0,1189	0,1145	0,1099	0,1043	0,0978	0,0895
200	0,1279	0,1242	0,1203	[illegible]	0,1114	0,1057	0,0994	0,0913
250	0,1294	0,1257	0,1218	0,1177	0,1130	0,1072	0,1009	0,0932
300	0,1309	0,1273	0,1233	0,1192	0,1145	0,1087	0,1025	0,0950
350	0,1324	0,1289	0,1248	0,1207	0,1161	0,1103	0,1042	0,0967
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Table 5.8 Viscosity of nitrogen tetroxide in the liquid phase $\mu \cdot 10^5$, kcal/sec/m^2.

P. am	t, °C							
	0	10	20	30	40	50	60	70
1	5,321	4,771	4,256					
5	5,331	4,781	4,261	3,828	3,379	2,971		
10	5,311	4,786	4,271	3,838	3,394	2,978	2,635	2,309
15	5,357	4,806	4,281	3,848	3,405	2,985	2,640	2,324
20	5,382	4,822	4,292	3,858	3,413	2,992	2,645	2,339
30	5,398	4,842	4,307	3,869	3,425	3,017	2,655	2,357
40	5,423	4,862	4,322	3,879	3,440	3,023	2,676	2,380
50	5,465	4,898	4,363	3,919	3,481	3,053	2,693	2,396
75	5,530	4,939	4,414	3,965	3,516	3,089	2,724	2,435
100	5,596	5,007	4,470	4,006	3,552	3,129	2,773	2,477
150	5,717	5,112	4,567	4,077	3,603	3,186	2,836	2,531
200	5,826	5,224	4,674	4,159	3,670	3,242	2,895	2,571
250	5,913	5,331	4,771	4,235	3,726	3,293	2,921	2,610
300	—	5,484	4,893	4,302	3,787	3,333	2,951	2,651
350	—	—	4,966	4,375	3,843	3,384	3,017	2,698
400	—	—	—	—	3,899	3,420	3,053	2,747

Table 5.8 (continued)

	t, °C								
P, ат	80	90	100	110	120	130	140	150	155
1									
5									
10									
15	2,018								
20	2,039	1,753							
30	2,069	1,796	1,509	1,218					
40	2,098	1,827	1,549	1,266	0,984				
60	2,120	1,860	1,595	1,330	1,035	0,780			
75	2,176	1,927	1,690	1,434	1,180	0,919	0,601		
100	2,227	1,993	1,764	1,524	1,293	1,050	0,775		
150	2,275	2,064	1,853	1,641	1,437	1,223	0,917		
200	2,324	2,120	1,908	1,713	1,511	1,295	1,086	0,872	0,765
250	2,401	2,161	1,947	1,753	1,560	1,366	1,172	0,979	0,887
300	2,426	2,192	1,993	1,789	1,606	1,417	1,233	1,052	0,968
350	2,459	2,217	2,029	1,820	1,631	1,450	1,279	1,111	1,000
400	2,493	2,273	2,074	1,860	1,672	1,498	1,335	1,193	1,091

Chapter VI

THE CORROSION OF CONSTRUCTION MATERIALS IN A MEDIUM OF N_2O_4

In the selection of a coolant, problems of the corrosion resistance of construction materials in the entire range of working temperatures and pressures are essential.

Special requirements from the standpoint of corrosion resistance are imposed upon materials used in reactor building. The most rigid requirements are imposed upon the material of the TVEL jacket, and the permissible level of corrosion is not higher than 0.02-0.05 mm per year [82].

However, even at comparatively low rates of corrosion of 10^{-3}-10^{-4} mm per year, which are not hazardous at all from the standpoint of the strength properties of the material, the problem of the accumulation of the solid phase in the coolant because of corrosion during prolonged operating periods of AES is essential.

The solubility of the salts and oxides of metals in N_2O_4 is negligible [83], and therefore corrosion products are precipitated from the solution in the form of a solid phase and during prolonged operation of the plant are accumulated in the circuit. The solid particles in the circuit may also appear as a result of the separation of films, if the protective films formed on the surface of metals in the process of operation are inadequately thin and are not firmly meshed with the metal.

The accumulation of noticeable quantities of the solid phase is intolerable in AES. The solid particles may create a clogging of the clearances between the TVEL jacket, which in turn leads to local overheatings and to the jackets being burned through, and, consequently, to the breakdown of the reactor. At a high flow velocity, the solid particles may have an erosion effect on individual parts of the plant, and especially on the turbine blades. Besides this, corrosion products may be carriers of radioactivity throughout the circuit.

In connection with this, very rigid requirements are imposed on the corrosion resistance of materials for AES operating on N_2O_4.

1. Experimental Data Concerning the Corrosion Resistance of Construction Materials of Power Plants in a Medium of N_2O_4

At ordinary temperatures, a number of alloys based on aluminum, iron, and nickel exist, having a high degree of resistance with respect to nitrogen oxides, which are used in the storage and transportation of nitrogen tetroxide [83-86].

Such materials include stainless steels, aluminum, and many alloys based on it. Non-ferrous metals, such as silver, copper, zinc, and cadmium are not resistant at these temperatures. Carbon steel and nickel have only a low degree of resistance. In the presence of teflon [86] an intensification of the corrosion of stainless and carbon steels is observed.

Extensive material on the study of the reaction of metals with individual nitrogen oxides at increased temperatures and at atmospheric pressure was collected in refs. [87, 88] and in later works [89, 90].

The investigation of corrosion resistance of construction materials in an equilibrium mixture of nitrogen oxides at temperatures of 100-700°C and a pressure up to 150 atmospheres was conducted in the plants represented in Figs. 6.1-6.3 [91].

Short-term tests with a soaking time of 350 hours were conducted in the plant represented in Fig. 6.1.

In autoclaves 3 fabricated from stainless steel Kh18N10T, the specimens being tested were placed on metal suspensions. The autoclave was hermetically sealed and nitrogen was blown through it, the heating was switched on and the temperature in the autoclave was brought up to the given magnitude. Then to remove the nitrogen, the autoclave was blown through with nitrogen tetroxide and the pressure in it was brought up to the given value. At these parameters, the specimens were kept for a definite time. The tests were conducted in a temperature range of 100-700°C at pressures of 20-150 atmospheres.

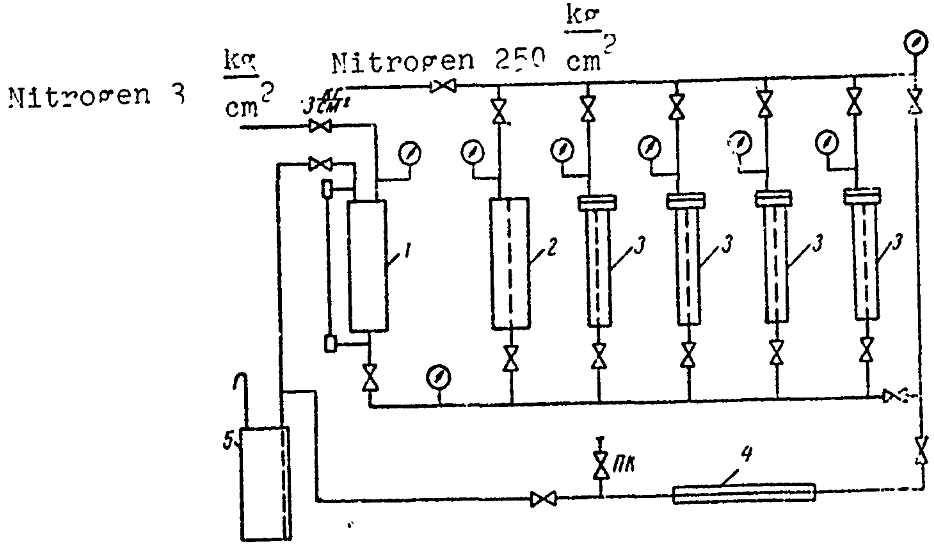


Figure 6.1. Diagram of a plant for performing short-term corrosion tests at high temperatures and pressures:

1- service tank; 2- evaporator; 3- autoclave; 4- refrigerator; 5- neutralizer.

Long-term tests, with a duration up to 11,000 hours, were conducted at a temperature of 500°C and a pressure of 50 atm in the autoclaves represented in Fig. 6.2.

In the lower part of the autoclave was located liquid nitrogen tetroxide, and in the part the specimens being tested. After the loading of the specimens and the nitrogen tetroxide, the autoclave was sealed. Electric furnaces were placed on the upper and lower parts of the autoclave.

For the development of a constant pressure in the autoclave, the temperature in its lower part, for the entire experiment, was maintained at 130±5°C. At this temperature, the tension of the saturated vapors of nitrogen tetroxide was equal to approximately 50 atm.

In the upper part of the autoclave, where the specimens being investigated were placed, a temperature of 500±10°C was maintained. The temperature was automatically regulated by means of an electronic potentiometer.

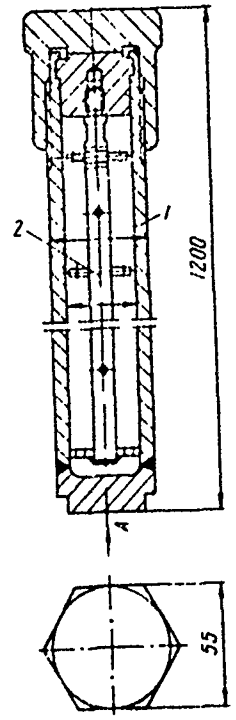


Figure 6.2. Autoclave for the performance of long-term corrosion tests at high temperatures and pressures:

1- autoclave; 2- suspensions for specimens

For corrosion tests in conditions of a throughflow of N_2O_4 an apparatus was developed whose simplified diagram is shown in Fig. 6.3.

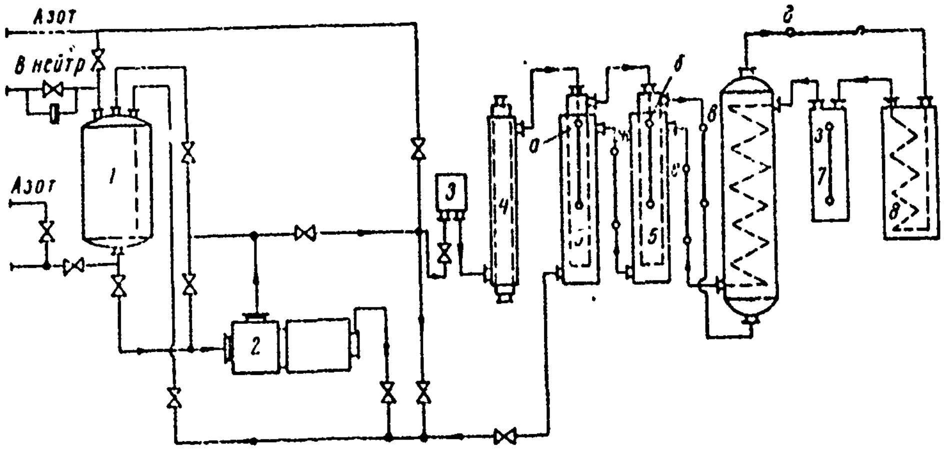


Figure 6.3. Diagram of an apparatus for performing corrosion tests in a flow of N_2O_4 at high temperatures and pressures:

1- service tank; 2- pump; 3- flowmeter; 4- heater; 5- low-temperature regenerator; 6- high-temperature regenerator; 7- high-temperature working section; 8- electric heater; a,b,c- working sections in the zone of temperatures of 80-100°C; d- working section in gaseous phase at temperatures of 300-350°C; e- working section in gaseous phase at temperature of 550°C; f,g- working sections in liquid phase after condensation.

From a barrel, by means of nitrogen with a pressure of 1.5 atm, liquid nitrogen tetroxide was transported to the service tank 1. The filling of the service tank occurred through a connecting piece with open drainage from above.

In the filling of the tank by 90%, the excess liquid was removed via a siphon pipe and passed through a monitoring device, by means of which the filling was visually monitored.

The circulation of the N_2O_4 in the circuit was accomplished by a pump. The nitrogen tetroxide passed, in sequence, into a heater 4 with steam heating, to low-temperature regenerators 5 connected in series, a high-temperature regenerator 6, and an electric heater 8.

Seven working sections were arranged in the path of the motion of the coolant: sections a, b, c in liquid N_2O_4 in the zone of temperatures of 800 to 100°C [sic]; d in the gaseous phase in the zone of temperatures of 300 to 350°C; e in the gaseous phase at a temperature of 500°C; and f, g in the liquid phase after condensation at a temperature of 100-110°C.

If we assume the profile and cross-sections through which the fluid must pass in the working sections, it is possible to test specimens of various types (round and flat) and to provide any velocity of the flow of the coolant.

The necessary pressure in the system was created by means of feeding nitrogen into the service tank 1 from an external additional high-pressure line.

The monitoring of the pressure was accomplished according to a whole series of acid-resistant manometers, installed at various points in the system.

The flow rate of the nitrogen tetroxide entering into the system was monitored by a calorimetric flowmeter.

The investigation of the corrosion resistance of metals in industrial nitrogen tetroxide at high temperatures was performed by the weight method. However, this method does not make it possible to determine the rate of corrosion with an adequate degree of accuracy or to study the kinetics of the corrosion processes at temperatures of 20-50 C. For these purposes, a methodology of the resistometric determination of very small rates of corrosion of wire specimens in nitrogen tetroxide was developed [91, 92].

The resistometric method of determining the rate of corrosion lies in the measurement of the electrical resistance of specimens with a small cross-section, placed in a corrosive medium.

The range in the resistance of a wire specimen as a function of its cross-section is expressed by the formula

$$R=\rho\frac{l}{\pi r^2}, \qquad (6.1)$$

where R is the resistance of the specimen in ohms; ρ is the specific resistance of the metal in ohms/cm/mm^2; l is the length of the specimen, in cm; and r is the radius of the specimen, in mm.

Consequently, corrosion losses of metal in the process of testing may be determined as the difference of the radii before and after testing and thay may be calculated according to the formula

$$\Delta r=r_0\left(1-\sqrt{\frac{R_0}{R_\tau}}\right). \qquad (6.2)$$

Here R_0 and R_τ are the resistance of the specimen at the initial moment and at moment of time τ.

Thus, by measuring the resistance of the specimens located in a corrosion medium, we may, according to the variation of the resistance, determine the magnitude of the variation of the radius of the specimen, i.e., the corrosion losses.

Among the undoubted advantages of this method is the possibility of watching the course of the corrosion process without withdrawing the specimen from the medium being investigated and without removal of the corrosion products in industrial plants.

Among the shortcomings of this method is its limited applicability: it can be applied only for media with low and medium electrical conductivity. Another limitation is associated with the high degree of sensitivity of this method to temperature oscillations.

At the present time measurements of small resistances are technically possible with a high degree of accuracy (0.03-0.05%), which makes it possible to use the resistometric method for studying small rates of corrosion.

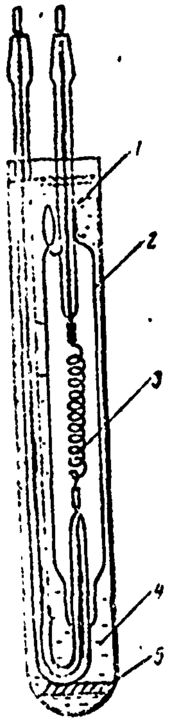


Figure 6.4. Cell for measuring the rate of corrosion:

1- current leads; 2- measuring cell; 3- specimen; 4- casing; 5- packing.

The investigation was conducted on wire specimens with a diameter of 0.1 to 0.2 mm. After degreasing, the wires were twisted into a coil and placed in the cell (Fig. 6.4). The fastening of the specimen to the platinum current leads was accomplished by means of contact welding for stainless steel and with an aluminum intermediate piece in a case of aluminum. The current leads of the cell were connected with the wires of the measuring circuit by means of silver-plated contacts. To decrease the resistance of the connecting wires to the maximum, PShch-6 was used, the resistance of which did not exceed $4 \cdot 10^3$ ohms per meter. For monitoring the effect of temperature on accuracy of measurement of the resistance in the thermostat empty sealed cells with specimens of the material being investigated (standards) were installed in the thermostat. The resistance of these specimens remained practically unchanged in the entire course of the experiments, which testified to the satisfactory accuracy of the measuring system and the thermostat coupling.

A diagram of an apparatus for studying the kinetics of the corrosion process of metals by the resistometric method is given in Fig. 6.5.

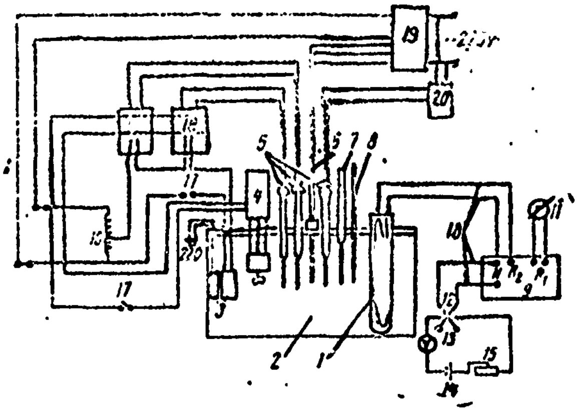


Figure 6.5. Diagram of an apparatus for studying the kinetics of the corrosion of metals by the resistometric method:

1- measuring cell; 2- thermostat; 3- electric heaters; 4- small turbine; 5- contact thermometers.

The specimens being investigated, in cells 1 filled with N_2O_4, were placed in a thermostat 2, the temperature of which was maintained by means of electric heaters 3, contact thermometers 5, electronic relays 18, and solution mixing turbines 4 at a constant level, with an accuracy of ±0.01°C. The resistance of the specimens was measured by means of a direct-current single-double bridge of type R-329 10.

The methodology described made it possible to perform a long-term continuous study of the kinetics of corrosion processes and to measure a rate of corrosion of the order of 10^{-4}-10^{-5} mm per year with an accuracy up to $1 \cdot 10^{-6}$ mm per year. A condition of the achievement of such an accuracy is the adequate uniformity of corrosion and invariability of the specific resistance of the specimens during the experiment.

By means of the methodology developed, the kinetics of the rate of corrosion of stainless steels and aluminum in nitrogen tetroxide at a temperature of 50°C was studied [92]. In Fig. 6.6 the characteristic kinetic curves of the rate of corrosion of stainless steel Kh18N10T in gaseous nitrogen tetroxide at a temperature of 50°C are presented. In all the cases investigated, the kinetic curves have the same nature. The rate of corrosion at first drops sharply and then remains constant.

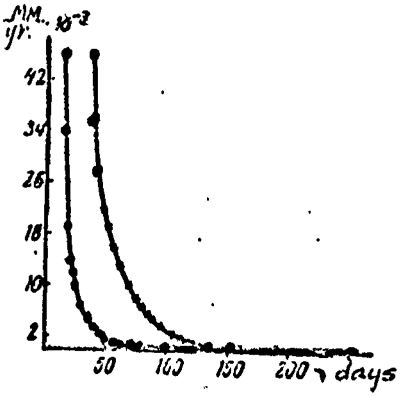


Figure 6.6. Kinetics of the corrosion of steel Kh18N10T in N_2O_4 at a temperature of 50°C.

Such a fluctuation of the kinetic curves testifies to the formation of passivating oxide films on the metal surface, which determine the corrosion resistance of the aluminum and the stainless steel in nitrogen tetroxide.

The kinetic curves may be described by a single empirical equation

$$V = (V_0 - V_{\text{ст}}) \exp(-a\tau) + V_{\text{ст}}, \qquad (6.3)$$

where V is the rate of corrosion at moment of time τ; V_0 is the rate of corrosion at the initial moment; and V_{st} is the steady-state rate of corrosion.

Equation (6.3) demonstrates that

$$\lg(V - V_{\text{ст}}) = \lg(V_0 - V_{\text{ст}}) - \frac{a}{2{,}303}\tau, \qquad (6.4)$$

i.e., the dependence of $\lg(V-V_{st})$ upon τ must have the form of a straight line with a dip at $a/2.303$. A check demonstrated that linearity is observed in almost all the cases investigated.

Films formed at a temperature of 50°C on the surface of stainless steel are quite thin and are not observed visually. Only in solutions containing HNO_3 are dark films, the surface of which is less than 0.5 micron, formed on the surface of the steel after prolonged contact with N_2O_4. Films formed on aluminum and its alloys during prolonged contact of these materials with N_2O_4 at a temperature of 50°C may reach several microns. The thickness of such films may easily be determined under the microscope. For the determination of the thickness of thin oxide films on aluminum and its alloys an impedance method has been developed [93].

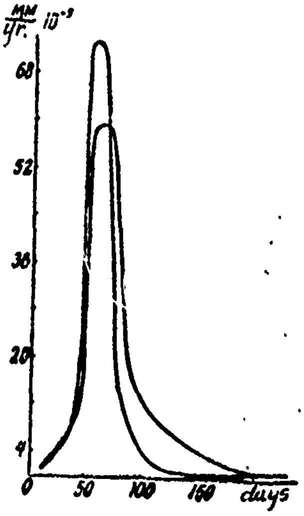


Figure 6.7. Kinetics of the corrosion of steel Kh18N10T in liquid N_2O_4, containing small quantities of HNO_3, at a temperature of 50°C.

In the liquid phase of N_2O_4 containing a small admixture of HNO_3, the kinetic curves of the corrosion of stainless steel Kh18N10T have the form given in Fig. 6.7. The rate of corrosion at first increases, passes through a maximum and decreasing, approaches the steady-state value. Apparently, at the first moment in the contact of the air-oxide surface of the steel with N_2O_4 nitric acid hampers the formation of the protective film [92]. Only after 100-250 days does the formation of an equilibrium protective oxide film in the given conditions end, after which the corrosion process becomes steady-state.

A considerable share of the corrosion losses during the test fall in the pre-steady-state period, the duration of which depends upon the conditions of the fabrication and treatment of the specimens. For the purpose of decreasing the duration of the unsteady-state regime and decreasing corrosion losses in this period, different methods of preliminary passivation, as given in Table 6.1, were tested.

Table 6.1 Conditions of preliminary passivation of specimens of Kh18N10T steel.

Composition of passivating solutions	Passivation temperature °C	Passivation time, hours
30% HNO_3 + 2% $K_2Cr_2O_7$	18-20	4
57% HNO_3	18-20	4
5% HNO_3 + 0.5 $K_2Cr_2O_7$	18-20	4
30% HNO_3	18-20	4
Oxidation in the air	300	240

After the appropriate passivation, kinetic curves of the corrosion of stainless steel in the same conditions were taken.

As is apparent from Fig. 6.8, all forms of preliminary passivation gave the expected effects. The magnitudes of the maximum rate of corrosion in the pre-steady-state period, the duration of this period, and the steady-state rate of corrosion decreased considerably.

Thus, in the process of preliminary treatment, a passive film is formed on the surface of stainless steel, which has good protective properties and makes it possible to decrease corrosion losses in the pre-steady-state period considerably at a temperature of 50°C. Liquid N_2O_4, apparently, not only provides conditions for the stability of this film, and consequently also of the passive state, but also improves its protective properties. The decrease of the steady-state rate of corrosion to a fraction of its former figure is a favorable consequence of passivation.

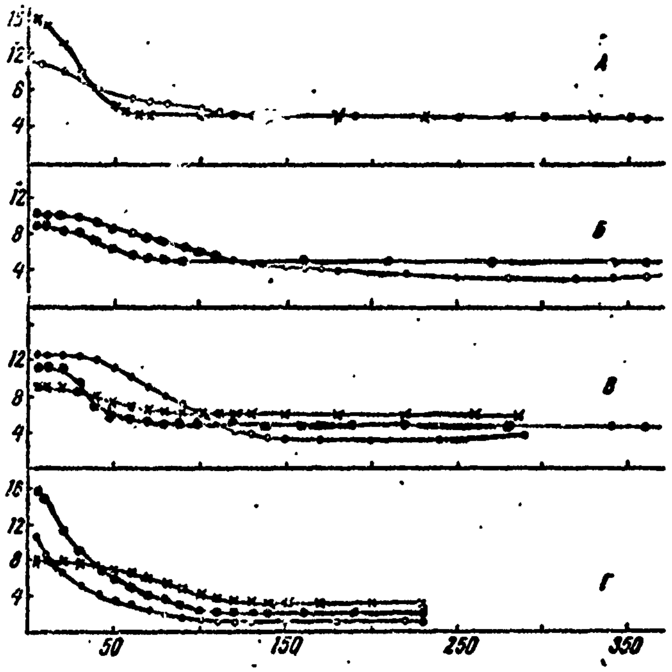


Figure 6.8. Kinetics of the corrosion of preliminarily passivated Kh18N10T steel in liquid N_2O_4 containing HNO_3 at a temperature of 50°C:

along the vertical, rate of corrosion mm/yr$\cdot 10^4$; along the horizontal, duration of tests, days; A- passivation in 57% HNO_3 at 18-20°C, 4 hrs; B- passivation in 30% HNO_3 + 2% $K_2Cr_2O_7$ at 18-20°C, 4 hrs; C- passivation in 5% HNO_3 + 0.5% $K_2Cr_2O_7$ at 18-20°C, 4 hrs; D- passivation in the air at 300°C, 10 days.

With an increase in temperature, the rate of corrosion of stainless steels increases somewhat [94-96]. At a temperature of 100°C a loss of weight within limits of 0.0005-0.003 g/m^2/hr (Table 6.2) is observed. In the transition to higher temperatures, losses of weight are replaced by a gain (Figs. 6.9, 6.10). Above 350°C the corrosion resistance of stainless steels varies but little.

In the region of temperatures 100-700°C a whole number of stainless steels and alloys based on nickel exists, all having high corrosion resistance. The surfaces of these materials, when in contact with nitrogen oxide, are coated with dense oxide films. The corrosion of stainless steels at temperatures of 500-700°C amounts of 0.0002-0.002 g/m^2/hr.

Table 6.2 Corrosion resistance of metallic materials in N_2O_4 at high temperatures and pressures. Duration of tests, 360 hours.

Material	Temperature, °C	Rate of corrosion, $g/m^2/hr$		
		20 atm	50 atm	150 atm
Armco iron	500	—	−0,036	—
Steel St.3	100	−0,22	—	—
	700	+0,18	—	—
Steel 18KhNVL	100	−0,0047	+0,009	—
	350	—	+0,009	—
	500	—	+0,064	—
Steel 20SGL	100	−0,73	—	—
	350	—	−0,29	—
	600	—	+0,51	—
Steel 2Kh13	100	−0,0025	—	—
	350	+0,0005	+0,0015	+0,0040
	500	+0,0005	+0,0012	+0,0013
	600	—	+0,0029	—
	700	+0,0012	+0,0008	—
Steel 3Kh13	350	—	+0,0003	+0,013
	500	+0,0006	—	—
	600	—	—	+0,0084
Steel Kh25	100	−0,0017	—	—
	350	+0,0008	+0,0022	+0,0040
	500	+0,0008	+0,0006	+0,0002
	600	—	+0,0002	—
	700	+0,0008	—	—
Steel Kh28	100	−0,0007	—	—
	350	+0,0006	—	—
	500	+0,0007	—	—
	700	+0,0007	—	—
Steel 1Kh17N2	500	+0,0001	+0,0006	+0,0019
Steel Kh18N12M2	500	+0,0001	—	—
Steel 1Kh12N2VMF	350	—	+0,0014	—
	500	—	+0,0017	—
Steel Kh18N10T	100	−(0,0007—0,0015)	—	—
	350	+0,0006	+0,0017	+0,0055
	500	+0,0003	+0,0013	+0,0008
	600	—	+0,0004	+0,0036
	700	+0,0005	+0,0003	—
Steel Kh16N15MZB	500	−0,0002	+0,0022	+0,0010
Steel Kh18N11B	500	−0,0003	+0,0007	—

Table 6.2 (continued)

Material	Temperature, °C	Rate of corrosion g/m^2/hr		
		20 atm	50 atm	150 atm
Steel Kh18N12MZT	100	−0,0022	—	—
	350	−0,0003	+0,0015	+0,0040
	500	+0,0004	+0,0015	+0,0003
	600	—	+0,0001	—
	700	+0,0007	+0,0002	—
Steel Kh20N14S2	500	−0,0003	+0,0012	—
Steel (KH21N6M2T	350	+0,0011	—	—
	500	+0,0004	—	—
Steel Kh21N5T	500	+0,0010	—	—
Steel Kh23N18	350	−0,0003	+0,0022	+0,0030
	500	+0,0003	+0,0013	+0,0008
Steel Kh23N28MZDZT	100	−0,0012	—	—
	350	−0,0003	−0,0019	+0,0042
	500	+0,0003	−0,0007	—
	600	—	—	+0,0035
	700	+0,0006	—	—
Steel OKh23N28MZDZT	350	—	−0,0001	—
Steel Kh25[illegible]TL	350	—	+0,0001	+0,0045
	600	—	—	−0,0010
Steel Kh32N8	350	—	+0,0006	—
Steel Kh12N20TZR	100	−0,0009	—	—
	350	+0,0016	+0,0016	+0,0055
	500	—	+0,0022	—
Steel KhN35VT	100	−0,0044	—	—
	350	—	+0,0004	+0,0064
	500	—	+0,0004	—
	600	—	—	+0,0042
Steel OKh20N10MZDZS5	500		+0,0074	—
Alloy KhN73T2YUB	350	—	+0,0011	—
	500	—	+0,0016	—
Alloy KhN78T	100	−0,0057	—	—
	350	−0,0036	+0,0020	—
	500	−0,0014	+0,0021	—
Alloy KhN54V15T	350	−0,0006	+0,0019	+0,0040
	500	—	—	+0,0022
Nickel N-1	100	−0,16	—	—
	350	−0,0017	−0,0011	+0,0014
	500	+0,0006	−0,0006	—
	700	+0.0090	+0,0033	—
Pig iron Sch15-32	100	−1,14	—	—
Chrome-nickel cast iron	350	−0,53	—	—
Cobalt	500	—	+0,05	—
Stellite	500	—	+0,04	—
Molybdenum	500	—	+0,18	—

In conditions of a throughflow of nitrogen tetroxide, the rate of corrosion of these steels is somewhat higher than in static conditions, but at 500°C, 25 atm, and a flow velocity of 25 m/sec does not exceed a magnitude of 0.005 g per m^2 per hour (Table 6.3), which is permissible for the materials of TVEL jackets. Also, the fact that oxide films formed on the surface of stainless steels are preserved in flow-through conditions, which testifies to their firm meshing with the surface of the metal, is essential.

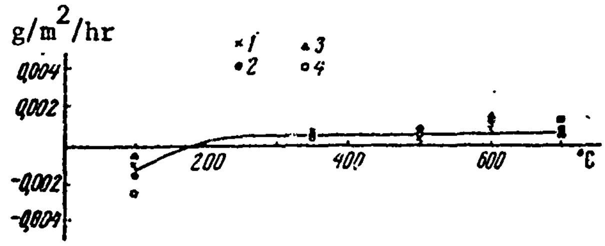


Figure 6.9. Dependence of the rate of corrosion of stainless steels in N_2O_4 upon temperature at a pressure of 20 atm:

1- steel Kh18N10T; 2- Kh25; 3- Kh28; 4- 2Kh13.

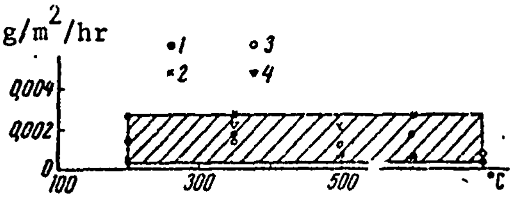


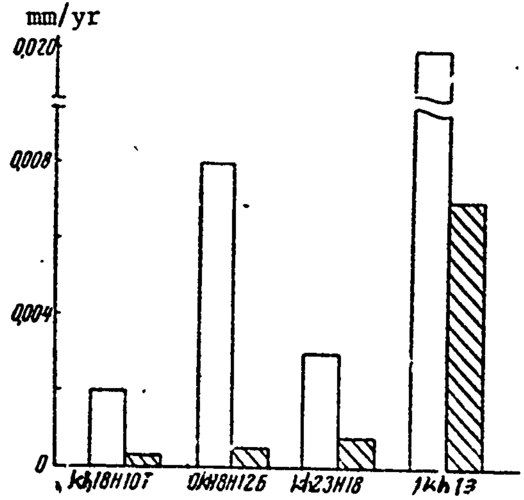
Figure 6.10. Dependence of the rate of corrosion of stainless steels in a medium of N_2O_4 upon the temperature at a pressure of 50 atm:

1- Kh18N10T; 2- Kh16N15MZB; 3- 2Kh13; 4- Kh25.

In Fig. 6.11 the comparative characteristics of the resistance of stainless steels at a temperature of 600°C in N_2O_4 and in air are given [97]. As is apparent from Fig. 6.11, the resistance of stainless steels in N_2O_4 at high temperatures is above the resistance of these materials in the air at the same temperatures.

The high corrosion resistance of stainless steels in N_2O_4, both in static conditions and in conditions of a throughflow of the coolant, is preserved for a long time (Figs. 6.12, 6.13). The nature of the dependence of the corrosion

Table 6.3 Corrosion resistance of metallic materials in a flow of N_2O_4: 500°C, 25 atm, 28 m/sec.



upon time at 500 C remains the same as at 50 C (Fig. 6.6). Such a nature of the dependence testifies to the formation of passive oxide films on the surface of the steel in the reaction with N_2O_4. The steady-state value of the rate of corrosion of steel Kh18N10T at 500 C and 50 atm for static conditions is equal to +0.0008 $g/m^2/hr$. In conditions of a throughflow the steady-state value of the rate of corrosion is equal to +0.002 $g/m^2/hr$.

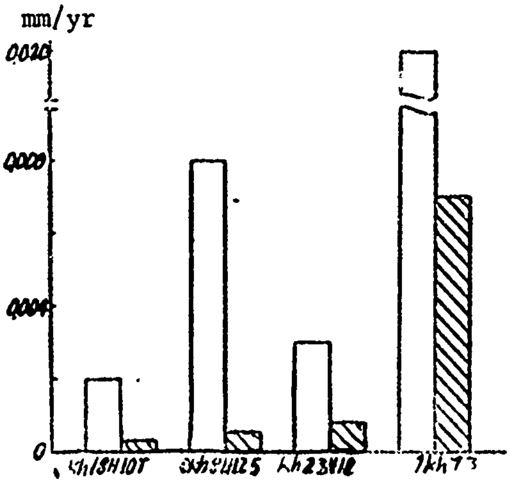


Figure 6.11. Rate of corrosion of stainless steels in the medium of N_2O_4 and in the air at a temperature of 600°C, in a time of 10,000 hours:

1- air, 1 atm; 2- N_2O_4, 50 atm.

With an increase in the velocity of the flow, the corrosion of stainless steels increases somewhat (Fig. 6.14). A similar picture is observed with an increase in pressure (6.15).

Figure 6.12. Dependence of the corrosion resistance of stainless steel Kh18N10T upon the soaking time in N_2O_4 in static conditions at a temperature of 500°C and a pressure of 50 atm.

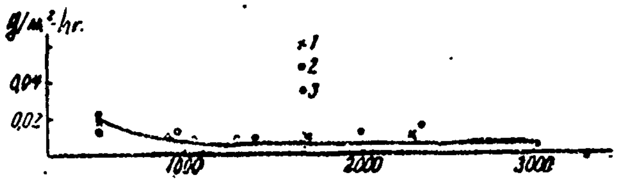


Figure 6.13. Dependence of the corrosion resistance of stainless steels upon soaking time in a flow of N_2O_4 at a temperature of 500°C, a pressure of 25 atm, and a velocity of 25 m/sec.

1- Kh18N10T; 2- Kh16N15MZB; 3- 1Kh14N18V2B

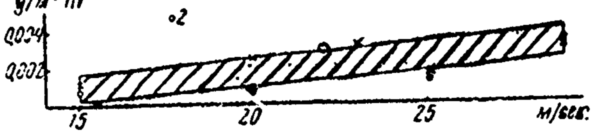


Figure 6.14. Effect of the velocity of the flow on the corrosion of stainless steels in N_2O_4 at 500°C, 25 atm, 400 hrs:

1- Kh18N10T; 2- Kh16N15MZB.

No noticeable variation of the mechanical properties of Kh18N10T and OKh18N10T steels after prolonged soaking of them in nitrogen oxides at 500°C and at 50 atm is observed (Table 6.4).

Figure 6.15. Effect of pressure on the corrosion of stainless steels in N_2O_4 in static conditions at 500 C:
1- Kh18N10T; 2- Kh16N15MZB; 3- 2Kh13; 4- 1Kh17N2.

The satisfactory corrosion resistance of stainless steels in a medium of nitrogen oxides at high temperatures and pressures is confirmed by experience of the operation of a number of plants and test stands. Thus, apparatuses for making corrosion tests in static conditions, fabricated from Kh18N10T steel, operated at temperatures up to 600°C and at pressures up to 150 atm for a number of years without noticeable changes and continue to operate at the present time. An apparatus for the investigation of corrosion resistance in flow-through conditions operates in a medium of nitrogen oxides at a temperature of 500°C and a pressure of up to 28 atm for 5000 hours. A necessary condition of the corrosion resistance of the evaporators and condensers is a high degree of purity of the nitrogen tetroxide.

Table 6.4 Variation of the mechanical properties of steels after tests in N_2O_4 at 500° and 50 atm.

Material	Duration of test, hours	Ultimate strength kg/mm^2	Yield point kg/mm^2	Relative elongation %
Kh18N10T	Initial	63.6	31.2	34.5
the same	5070	62.7	30.8	29.0
the same	6100	64.0	30.3	33.4
OKh18N10T	Initial*	50.2	20.0	40.0
the same	5070	61.3	26.4	36.8
the same	6100	61.3	28.2	42.3

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*Data taken from handbook [98].

A number of other apparatuses and test stands for the investigation of the thermophysical properties of nitrogen tetroxide fabricated of stainless steel Kh18N10T have been operating for 500-1500 hours. During the operating time of the apparatuses no primary corrosion of the welded joints has been observed.

The corrosion of welded connections was checked in special hollow thin-walled welded specimens, filled with helium, in conditions of a flow through them of gaseous nitrogen oxides at 500°C and 25 atm for 2000 hours. After the tests no leaks of helium were observed, which testifies to the complete preservation of hermetic sealing of welded connections in the process of the tests.

In distinction from stainless steels, carbon and low-alloy steels do not have adequate resistance to nitrogen oxides. At a temperature of 100°C a considerable loss of weight is observed in these materials. The rate of corrosion of carbon steel St.3 and low-alloy steel 20SGL reaches a magnitude of 0.21 and 0.73 $g/m^2/hr$, respectively (see Table 6.2). And on the specimens, together with oxide films, friable, powdery, and resin-like sediments form. With an increase in temperature, the loss of weight is replaced by a considerable gain. The surface of these materials is coated by a thin friable layer of corrosion products.

The rate of corrosion at 500°C and 50 atm amounts to +0.03 $g/m^2/hr$ for carbon steel St.3, and for steels 20SGL and 18KhNVL, +0.05 and +0.06 $g/m^2/hr$, respectively.

Carbon and low-alloy steels are not recommended for use in AES using N_2O_4 as a coolant, since their corrosion in the entire range of operating temperatures occurs with the formation of powdery sediments and resin-like substances.

Nickel and alloy KhN78T are also unsuitable for operating in nitrogen tetroxide. The corrosion of these materials at temperatures of 50-100°C occurs with the formation of salts.

Armco iron is even less resistant, as thick, easily-removed layers of oxides of iron are formed on its surface. The rate of corrosion amounts to

-0.036 g/m^2/hr at 500°C and 50 atm. Cobalt and an alloy based on it, stellite, show a considerable gain in weight in these conditions. The rate of corrosion is equal to +0.05 and +0.04 g/m^2/hr, respectively. The surface of the specimens is coated with a black film. The corrosion is irregular.

Molybdenum is subjected to considerable corrosion in N_2O_4 at 500°C and 50 atm. Its rate of corrosion amounts to +0.18 g/m^2/hr. The surface of the specimens is coated with yellowish hummocky sediment.

Grey cast iron, the rate of corrosion of which is equal to 1.2 g/m^2/hr, also has little resistance at 100°C. The corrosion is point-like in nature.

In the region of temperatures of 100-150°C at a pressure of 20 atm, aluminum and alloys based on (Table 6.5) have a high resistance with respect to gaseous oxides of nitrogen. Their rate of corrosion does not exceed 0.002 mm per year. Anodized aluminum D16 is an exception, as its rate of corrosion at 100°C is equal to 0.016 mm/year. The surface of the majority of the alloys, after testing at 100°C, remains unchanged; after tests at 150°C the specimens are coated with bluish films of iridescent colors.

Table 6.5 Corrosion resistance of aluminum and aluminum alloys in N_2O_4 at high temperatures and pressures (test duration, 360 hours, converted to mm/year).

Material	20 atm			50 atm
	100 °C	150 °C	200 °C	200 °C
ADI	—	—	—	$0,9 \cdot 10^{-2}$
AMg	$<2 \cdot 10^{-3}$	$<2 \cdot 10^{-3}$	$<2 \cdot 10^{-3}$	$1,35 \cdot 10^{-2}$
AMg3M	—	$<2 \cdot 10^{-3}$	—	—
AMg6	—	$<2 \cdot 10^{-3}$	$1,9 \cdot 10^{-3}$	—
AMg6M	—	$<2 \cdot 10^{-3}$	—	—
AMg6T	$<2 \cdot 10^{-3}$	—	$2,4 \cdot 10^{-3}$	—
AMg5VM	—	$<2 \cdot 10^{-3}$	—	=
AK6	$<2 \cdot 10^{-3}$	$<2 \cdot 10^{-3}$	$<2 \cdot 10^{-3}$	—
AK8	$<2 \cdot 10^{-3}$	—	$<2 \cdot 10^{-3}$	$4,8 \cdot 10^{-2}$
AL4	$<2 \cdot 10^{-3}$	—	$<2 \cdot 10^{-3}$	—
AV	$<2 \cdot 10^{-3}$	—	$<2 \cdot 10^{-3}$	—
	—	$<2 \cdot 10^{-3}$	$2,3 \cdot 10^{-3}$	—
D16 anodized	$16 \cdot 10^{-3}$	—	$4,2 \cdot 10^{-3}$	—

With an increase of temperature to 200°C the rate of corrosion of certain aluminum alloys increases insignificantly, but on the surface of the specimens grey, friable films, easily washed away, are formed. An increase in pressure from 20 to 50 atm increases the rate of corrosion by tens of times.

Thus, the application of aluminum alloys is possible only up to temperatures of 100-150°C.

Titanium and titanium alloys (Table 6.6) are very resistant in an equilibrium mixture of gaseous oxides of nitrogen at 200°C and 20 atm. The rate of corrosion of all the materials tested is less than $1 \cdot 10^{-3}$ mm/year. The surface of the specimens after testing remains without visible changes. Oxide films are formed on specimens of alloy OT4 and a gain in weight is observed.

Table 6.6 Corrosion resistance of titanium alloys in N_2O_4 at 200°C and 20 atm (test duration, 360 hours)

Material	Rate of corrosion, mm/year
VT1-1	$1.0 \cdot 10^{-3}$
VT1-5	$1.0 \cdot 10^{-3}$
AT6	$1.0 \cdot 10^{-3}$
OT4*	$7.5 \cdot 10^{-3}$

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*The tests were conducted at a temperature of 600 C.

Titanium alloys, in distinction from aluminum alloys, are not sensitive to the water content in nitrogen tetroxide.

As packing and sealing materials, aluminum, fluoroplast (polyfluoroethylene resin) and mica have shown good results.

For friction pairs at temperatures of 50-100°C, steels, ceramics, certain carbon-graphite materials, cytale plastics, and others may be used.

2. Study of the Structure and Composition of the Solid Phase of Corrosion Products of Construction Materials in a Medium of N_2O_4

As was noted above, one of the important problems in the question of selecting construction materials for AES using N_2O_4 as a coolant is the formation of the solid phase of the corrosion products.

While at temperatures of 500-700°C the reaction of the metals with N_2O_4 proceeds with the formation of oxide films, providing high resistance of a large number of stainless steels and alloys based on nickel, in the low temperature part of the circuit this reaction occurs bascially with the formation of salts and resin-like substances, although together with this on the surface of the metals oxide films are also formed. The accumulation of these salts in the course of time may lead to stopping up the pipes of the heat-transfer apparatus (heat exchanger) in the low-temperature region of the circuit.

Aside from this, the salts carried away by the flow of coolant into the zone of high temperatures, decomposing there, are transformed into the corresponding oxides and in the form of solid particles may spread throughout the circuit, causing erosion of the apparatus and increasing the radioactivity of the coolant.

For reliable forecasting of the accumulation of the solid phase in N_2O_4, according to data concerning the kinetics of the corrosion process, it is necessary to know the chemical nature and properties of the substances formed.

The solid products of the corrosion of steel Kh18N10T formed in the N_2O_4 in the process of corrosion tests at a temperature of 50°C, depending upon the ratio of iron and chromium compounds in them, change their color from light brown to emerald green. In a dry atmosphere they are stable, but in the presence of moisture they decompose with the liberation of brown vapors of nitrogen oxides.

For the purpose of identification of the compounds entering into the composition of the products of the corrosion of steel Kh18N10T, their infrared spectra were studied.* The IR spectra of the products of corrosion are characterized by very clear absorption bands at 1018-1030, 1043-1060, 1280-1292, 1300-1310, 1425-1440, 1460-1490, 1510, 1540-1550, 1560-1585, 1610-1614, 1680-2250-2260 cm^{-1}. As a result of the comparison of the spectrum with the characteristic absorption frequencies of a number of molecules and groups of atoms, the presence of which was assumed in the composition of the products of corrosion, the following facts were established.

The corrosion products do not contain absorbed N_2O_4 or absorbed HNO_3 in themselves [99-100]. In the spectrum of the corrosion products the absorption bands which are characteristic for ion nitrates and nitrites, according to the data in refs. [101, 102] are absent.

The absence of nitrite ions in the composition of the specimens investigated is also confirmed by the method of microcrystoloscopic analysis. In the IR spectra the absorption bands of the ions NO_2^+ and NO_2^- are also not observed [101]. The strong absorption observed at 1280-1292 and 1610-1650 cm^{-1} is characteristic for symmetrical (1255-1300 cm^{-1}) and asymmetrical (1610-1655 cm^{-1}) valency oscillations of the group ONO_2 of covalent nitrates [101, 102]. The strong absorption bands in the region of 1460-1600 cm^{-1} are also characteristic for this group [103].

The absorption bands of average intensity at 2250-2260 cm^{-1} deserve special attention, as they are proper to the nitroso ion NO^+ [101, 104].

Thus, the analysis of the infrared absorption spectra of the corrosion products unambiguously testifies to the presence of covalent nitrates of the metals and nitroso ions in their composition.

According to data from emission spectral analysis, iron, chromium, and nickel are present in the corrosion products.

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*The investigations explained below were performed by A. M. Sukhotin, P. P. Samoylyuk, V. P. Istomina, V. P. Istomina, N. Ya. Lantratova, G. A. Rubinchik, and O. G. Antropova.

In the comparison of the absorption frequencies of the corrosion products with available data concerning the IR spectra of individual compounds of these metals, the presence of the tetranitroferrate ion was established [105]. With a consideration of the absorption band at 2250-2260 cm^{-1} of the nitroso ions, which may be proper to complexes of other components of the mixture and not merely to iron complexes, we may assume that the corrosion products of Kh18N10T steel are a mixture of anhydrous nitroso nitrate complexes of metals: $(NO^+) \times$ $\times [Fe(NO_3)_4]^-$; $\{(NO^+)[Cr(NO_3)_4]^-\}N_2O_4$; $(NO^+)_2[Ni(NO_3)_4]^{-2}$.

The corrosion products of nitrogen tetroxide are identical in the liquid and gaseous phases.

For the purpose of confirming the assumptions expressed with respect to the results of the study of the IR spectra, certain properties of the corrosion products were investigated: hygroscopicity, thermal stability, solubility in polar and non-polar solvents, and others. It was established by x-ray structural analysis that the corrosion products have a crystalline structure.

In the absorption of moisture, the crystals are transformed into a resinous mass, to which the amorphous halo of the x-ray photographs of the specimens being flooded with water testifies. In the process of further absorption of moisture, the nitrate complexes are reformed into crystalline hydrates of the ion nitrates.

The thermal stability of the corrosion products was studied by the thermogravimetric method. On the differential thermal analysis curve of anhydrous corrosion products, consisting primarily of iron compounds, three endoeffects are observed which are characteristic for the thermal decomposition of the nitroso tetranitroferrate [105]. The curves of the thermogravimetric analysis testify that the process of decomposition is completed at a temperature of 220° C. In this case, the weight losses of the specimens amount to 83-86%. No 'plateau' is observed on the curves, which is also proper to the decomposition of nitrate complexes of the nitroso ions of iron and chromium.

The existence of corrosion products in the form of nitroso nitrate complexes is also indicated by their solubility.

Corrosion products rapidly dissolve in polar solvents (nitromethane, dioxane, acetonitrol), forming stable yellowish-brown solutions. The stability of the tetranitroferrate and nitroso ions in these solutions, which is a characteristic feature of the solutions of these compounds in polar solvents, is confirmed by the IR spectra. In non-polar solvents (such as carbon tetrachloride, for example), the corrosion products do not dissolve.

The behavior of the compounds with relationship to aromatic hydrocarbons is unique. In the introduction of the corrosion products into benzene, on the bottom of the vessel a thick red oily mass is formed. Later it slowly dissolves in the hydrocarbon, with the formation of a precipitate. A similar picture is observed in the introduction of nitroso tetranitroferrate into benzene [105].

The corrosion products, like the nitrate complexes, react energetically with diethylene ester [105, 106]. In introduction into water, it rapidly dissolves with the liberation of brown vapors of nitrogen oxides. Later the solid phase is separated and precipitated from the solution, which is explained by the hydrolysis of the corrosion products, with the formation of the hydrates of the oxides of the metals.

Thus, the investigations made of the composition and the study of certain properties of the corrosion products give grounds to assume that they consist primarily of nitrate complexes of the basic components of the stainless steel: iron, chromium, and nickel.

Together with the investigation of the chemical nature of the corrosion products, the picture of their formation and the kinetics of their accumulation in the system were studied.

For performing the investigation, hermetically sealed glass vessels were developed, the external shape and diagram of which are presented in Fig. 6.16.

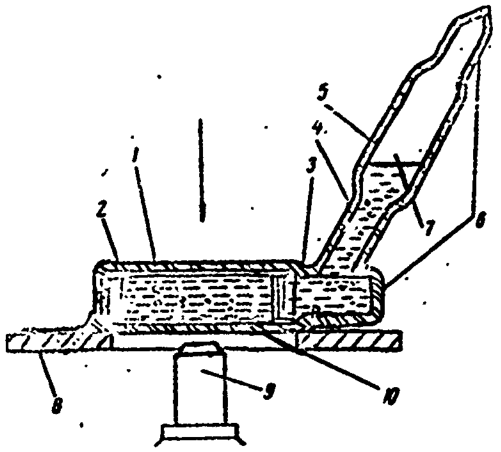

Figure 6.16. Diagram of a vessel for studying the kinetics of the accumulation of the solid phase of corrosion products:

1- body of the vessel; 2- specimen; 3- bleed; 4- tube for filling; 5- volumetric expansion compensator; 6- point of seal; 7- level of solution in vessel; 8- microscope subject stage; 9- objective lens of microscope; 10- particles of solid phase.

The vessel was fabricated from molybdenum glass and consists of a body 1, a bleed 3, and a tube 4, with a volumetric expansion compensator, 5. The body of the vessel (cuvette) is made in the form of a cylinder with a height of 10-12 mm with two plane-parallel optically transparent bottoms, with a thickness of 1-1.5 mm. The bleed (tap), intended for placing a specimen into the cuvette, is sealed into the shell of the body of the vessel. For filling the cuvette with nitrogen tetroxide, a tube 4 is sealed into this tap at an angle of 60°.

Specimens fabricated from sheet steel Kh18N10T, with a thickness of 0.1 mm in the form of corrugated bands with a height of 10 mm and a length of 250 mm. One degreased specimen each was placed into each cuvette, after which the tap 3 was sealed. In the cuvette the specimen was placed spirally along the generatrix of the body, and in this case a view of more than 80% of the surface of the bottom of the cuvette was provided. After pressurizing the vessel with inert gas at a pressure of 4 atm, it was washed with alcohol and dried. The cuvettes prepared for the tests were filled with nitrogen tetroxide containing a small admixture of acid and were sealed.

The accumulation of the corrosion products in the course of the experiment was monitored by the microscopic method of the determination of the granulometric composition of the particles contained in it [107, 108]. The dispersion analysis was performed by means of a biologically inert MBI-12 microscope by means of photographing the bottom of the cuvette, with random selection of the field of view.

After the determination of the granulometric composition of the particles contained in the initial N_2O_4, the cuvettes were placed in a thermostat and were kept there at a temperature of 50±3°C.

The photography was accomplished at a temperature of 18-20°C every 15 days. For a uniform distribution of the particles in the volume, before the cuvettes were photographed, they were shaken for 3 minutes and then allowed to settle on the specimen stage.

The completeness of the precipitation of the particles was monitored by means of visual inspection of the entire layer of N_2O_4 under the microscope. The magnification of the microscope during photographing of the specimen amounted to X27. The quantity of fields to be photographed was determined according to the formula

$$Z = 10/0.785d^2_{\text{field of view}}$$

and at the magnification accepted amounted to 6 fields; d_{fov} is the diameter of the field of view. For the purpose of increasing the accuracy of the results obtained, the quantity of fields photographed was increased to 30-36. The count of the particles in the dispersivity intervals was accomplished by the method of projecting the negatives of the microphotographs onto a screen with a total magnification of X200. The greatest length of the crystal or unit was accepted as the dimension of the particles. The content of the particles in dispersivity intervals of 1 ml of nitrogen tetroxide served as the comparative accumulation characteristic.

The calculation of the quantity of particles in this volume was performed according to the formula

$$N = (A\ 1000)/Z_{ph}F_{fov}h$$

where A is the total quantity of particles of the given interval of dimensions in all the fields of view; F_{fov} is the area of the field of view of mm^2; and h is the height of the layer of liquid in the cuvette in mm.

In the inspection of the precipitates under the microscope it was established that the precipitating solid phase of the corrosion products is a mixture of individual crystals of various dimensions and units (aggregates), partially consisting of a large central crystal overgrown with small crystals.

In the initial stage of the process of corrosion, crystals with a dimension of 5-30 microns accumulate most rapidly in the system. Together with this, the distribution of the particles in the 5-200 micron range beginning at 15 days is described satisfactorily by a single curve, which testifies to the uniform nature of the relative growth of the quantity of particles in each interval of dimensions. After 45-60 days the content of the particles in this range remains approximately constant. However, in connection with the continuing corrosion of the steel, the general mass of the crystals increases continuously because of the growth of the large defect crystals. The increase in the general mass of the crystalline solid phase in the same period of the corrosion process corresponds with respect to order of magnitude to the expected accumulation according to data from corrosion losses.

Thus, the process of the corrosion of Kh18N10T steel at 50°C in a limited volume of nitrogen tetroxide is accompanied by the saturation of the liquid phase by soluble corrosion products and by the precipitation of the crystalline solid phase into a precipitate. The kinetics of the crystallization of the solid phase at the initial stage of the process are characterized by a sharp increase in the total quantity and dimensions of the crystals.

Later a stabilization of the dispersed composition of the particles having dimensions of 5-200 microns is observed. A growth of individual large crystals is also observed. Such a picture, apparently, will be observed in the corrosion of materials in the entire low-temperature part of the circuits of AES.

On the basis of the data obtained with respect to the kinetics of corrosion and the chemical composition of the corrosion products, we may determine the general quantity of the solid phase in the process of prolonged contact of steel with nitrogen tetroxide. Data on the kinetics of the accumulation and the dispersed composition of the corrosion products make it possible to make a rational selection of the filters in the system.

The process of corrosion of stainless steel in this range of temperatures may be represented in the following manner.

In the reaction of the steel with the nitrogen tetroxide, on its surface an oxide film is formed, which also determines the magnitude of the steady-state rate of corrosion. An insignificant part of the metal going into solution enters into the formation of this film. The basic fraction of the metal makes the transition to a solution in the form of a crystalline solid phase of the corrosion products, which consists primarily of a mixture of nitrate complexes of the metals of type $M(NO_3)_nXN_2O_4$ where M is the metal and n is the valency of the metal. In particular, iron, chromium, nickel, and titanium, probably, form the compounds $(NO^+)[Fe(N_3)_4]^-$; $\{(NO^+)[Cr(NO_3)_4]^-\}$; $(NO^+)_2[Ni(NO_3)_4$.

The mechanism of the processes leading to the formation of the solid phase in nitrogen tetroxide, depending upon its composition, may be described by the following equations:

the system $M\text{-}N_2O_4$:

$$M+\left(X+\frac{3}{2}n\right)N_2O_4\rightarrow M(NO_3)_nXN_2O_4+nN_2O_3;$$

the system $M\text{-}N_2O_4\text{-}HNO_3$

$$M+\left(X+\frac{1}{2}n\right)N_2O_4+nHNO_3\rightarrow M(NO_3)_nXN_2O_4+$$

$$+\frac{1}{2}nN_3O+\frac{1}{2}nN_2O_3;\ \frac{1}{2}nH_2O+nN_2O_4\rightarrow$$

$$\rightarrow nHNO_3+\frac{1}{2}nN_2O_4,$$

or, in summary, $M + (X + \frac{3}{2}n)\ N_2O_4 \rightarrow M(NO_3)_nX\ N_2O_4 + nN_2O_3$.

Thus, in the system $M-N_2O_4-HNO_3$ the total reaction of the process is the same as in a case of $M-N_2O_4$.

These equations generally reflect the mechanism of the process of the formation of the corrosion products. Actually, this process occurs via a number of intermediate stages, including, probably, the reaction of the nitrogen tetroxide with the oxide film.

In the region of high temperatures (above 200 C) the formation of the complex compounds of the metals with nitrogen tetroxide is impossible because of their thermal instability. In this range of temperatures, the corrosion of steel occurs with the formation of only the oxides of the metals: either in the form of protective oxide films, firmly meshed with the metal, or in the form of powdery corrosion products. The corrosion of the metals in this case is entirely determined by the protective properties of the oxide films.

3. Discussion of the Results of Corrosion Tests of Construction Materials in a Medium of N_2O_4

Experience in the operation of AES with two-circuit schemes using water, CO_2, and especially single-circuit schemes with a boiling-water reactor, have demonstrated that construction materials may be used if the rate of their corrosion does not exceed 0.02-0.05 mm/year [82].

The investigation of the corrosion resistance of the materials Kh18N10T, EI-847, EI-654, EI-629, EI-432, Kh-25, 3Kh13, aluminum and titanium alloys, graphite AG-1500, high-chrome cast iron, fluoroplast, and others, as used in modern reactor construction, in a medium of N_2O_4, demonstrated that the rate of corrosion of the materials indicated amounts to a magnitude of the order of 0.001-0.01 mm/year.

In the temperature range of 100-700°C a large number of stainless steels and alloys based on nickel exists, having a high degree of corrosion resistance. The surfaces of these materials, in contact with nitrogen oxides, are coated by dense protective oxide films. The fact that the oxide films formed on the surface of the construction materials in a medium of N_2O_4 are preserved in flow conditions (at a velocity of 25-40 m/sec), which testifies to their firm meshing with the surface of the metal, is essential. In the tests of welded joints no intercrystallite or pitting corrosion was established, and their corrosion resistance is the same as that of the basic material; in preliminary strength tests no change in the mechanical properties of steels Kh18N10T or OKh18N10T was ascertained after their prolonged soaking in N_2O_4 at 50 atm and 500°C.

Comparisons made of the corrosion of stainless alloys at 600°C in N_2O_4 in the air also demonstrated that in a medium of N_2O_4 stainless alloys have a greater resistance than in air.

The presence of low-temperature corrosion (up to 150°C) of stainless steel Kh18N10T required the study of the structure and composition of the solid phase of the corrosion products. The experimental data made it possible to give preliminary recommendations with respect to the selection of the type of filters and the purification system for a N_2O_4 coolant. These filters are being tested and have shown positive results in test stands during 1966-1970. As with any other new coolant, a thorough and careful treatment of the technology of dissociating nitrogen tetroxide as a coolant and working fluid for atomic electric-power stations is required.

The investigations made of the corrosion resistance of a large quantity of conventionally used construction materials in reactor and power machine-building demonstrated that for all units of AES operating on N_2O_4 for a temperature level of 200-750°C and at pressures of 1-170 atm.ab. corrosion-resistant construction materials produced by Soviet industry are available, which can provide reliable and long-term operation of power plants using N_2O_4. This conclusion is confirmed also by the results of tests of a model gas turbine operating on N_2O_4 in 1969-1970 on an experimental power test stand with a gas-liquid cycle having a thermal capacity of 1050 kilowatts.

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