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# THERMODYNAMIC PROPERTIES OF THE GASEOUS DISSOCIATING SYSTEM A12C16 = 2A1C13 (SELECTED ARTICLES)

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Foreign Technology Division
Wright-Patterson Air Force Base, Ohio

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# FOREIGN TECHNOLOGY DIVISION

AIR FORCE SYSTEMS COMMAND

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(SELECTED ARTICLES)

By

V. B. Nesterenko, A. V. Zinov'yev
and M. A. Bazhin, et. al.

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# EDITED TRANSLATION

THERMODYNAMIC PROPERTIES OF THE GASEOUS DISSOCIATING SYSTEM $Al_2Cl_6 \rightleftarrows 2AlCl_3$ (SELECTED ARTICLES)

By: V. B. Nesterenko, A. V. Zinov'yev, M. A. Bazhin
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**ABSTRACT**

(U) This is a continuation of earlier work (Vesti AN BSSR,ser. fiz. tekhnauk no. 1, 1966 and elsewhere) where it was shown that the use of a dissociating gas system as the working medium in a closed gas-turbine cycle increases the gas constant in the turbine and decreases it in the compressor, thus increasing the efficiency, compared with cycles using inert gases, by reducing the irreversible losses in the cycle. The ~~present~~ article deals with the Al(subscript 2)Cl(subscript 6) forms and is formed from 2AlCl(subscript 3) system, for which there are not many published data. The available specific-heat data were approximated by means of a computer in the form of a fifth degree polynomial and the coefficients of this polynomial for Al(subscript 2)Cl(subscript 6) and AlCl(subscript 3) were calculated. From them they calculated the thermodynamic properties of gaseous aluminum chloride under a number of assumptions. Equations are derived on this basis for effective enthalpy and entroy of the dissociating system, for the effective specific heat, at pressures 1-150 atmospheres and 460-2000K. Some of the results are presented in the form of tables and plots. The authors thank . S. Zakharova for the computations with the "Minsk-2" computer nd Academician AN BSSR A. K. Krasin for interest in the work. rig. art. has: 3 figures, 27 formulas, and 3 tables.

## DATA HANDLING PAGE

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**TITLE** HEAT TRANSFER IN THE CHEMICALLY-REACTING EQUILBRIUM SYSTEM $N_2O_4 \rightleftarrows 2NO_2$

**39-TOPIC TAGS**
heat transfer coefficient, reynolds number, prandtl number, gas flow, fluid flow, turbulent flow, pipe flow, flow rate

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**ABSTRACT**

(U) (2)Experimental studies of heat transfer in a chemically reactive gas flow have been carried out at the Institute of Nuclear Power Engineering of the BSSR. As suggested by M. A. Mikheyev and S. S. Kutateladze, the Nusselt number was used as a function of the Reynolds and Prandtl criteria in a forced turbulent flow in a tube. The investigated temperature range was 30-300 degrees C, pressure from 1-60 atm and Reynolds numbers from 10(superscript 4)to 3 times 10 (superscript 5). The experimental unit consisted of a closed loop using a pump for the circulation of N(subscript 2)0(subscript 4). The flow rate was controlled by the pump rpm and a by-pass valve. The test section was a U-tube type made of stainless steel. Experimental and calculated values of the heat transfer coefficient showed close correlation. The derived empirical formulas can be recommended for the description of the heat transfer mechanism in a chemically reactive system. The authors express their appreciation to Academician A.K. Krasin of the AN BSSR for his interest in the study, and to A. N. Kremeshnyy, Yu. I. Bakalin, and V. A. Nikolayev who participated in the study. Orig. art. has: 2 figures., 19 formulas, and 1 table.

## DATA HANDLING PAGE

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**39-TOPIC TAGS** heat exchange, nitrogen oxide, chemical reaction kinetics, turbulent flow

**09-TITLE** HEAT TRANSFER IN THE CHEMICALLY-REACTING SYSTEM $2NO_2 \rightleftarrows 2NO + O_2$ TAKING THE KINETICS OF THE CHEMICAL REACTION INTO ACCOUNT

**47-SUBJECT AREA** 20

**42-AUTHOR/CO-AUTHORS** NESTERENKO, V. B. ; 16-TVERKOVKIN, B. E.; 16-VERZHINSKAYA, A. B.

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**ABSTRACT**

(U) This a companion to the preceding article ~~in~~ the same source (pp. 42-49) dealing with heat exchange in the presence of chemical reaction, but under equilibrium conditions. The present article deals with the modifications that must be made to the calculations when allowance is made for the kinetics of the chemical reaction. It is shown that although the analysis is made much more complicated by the need for taking into account additional internal sources and sinks of the masses of the individual components, it is possible to obtain sufficiently accurate data by using empirical relations for the calculation of the heat transfer coefficient, by making use of a similarity criterion derived by the method of integral analogs. The equation derived for the heat transfer on this basis was compared with experimental data on heat exchange, carried out for forced turbulent flow in a tube at the Institute of Nuclear Power Engineering AN BSSR at gas temperatures of 140-550C, pressures 10-60 atmospheres, and Reynolds numbers 3 times 10(superscript 4) - 3 times 10(superscript 5). The experimental setup and procedure were the same as in the companion paper. A criterion empirical relation is derived by evaluating the constants of the theoretical equation to fit the experimental data, with plus or minus 15 percent. The authors thank Academician AN BSSR A. K. Krasin for continuous interest in the work.

## Symbol List

| Manuscript page | Symbol | Eng. Equivalent |
|---|---|---|
| 15 | ст | wall |
| 15 | г | g |
| 26 | Д | D |

# THERMODYNAMIC PROPERTIES OF THE GASEOUS DISSOCIATING SYSTEM $Al_2Cl_6 \rightleftarrows 2AlCl_3$

V. B. Nesterenko, A. V. Zinov'yev and M. A. Bazhin

The cycle efficiency of gas turbine power plants can be increased by employing (chemically) reactive systems capable of dissociation upon heating. This results in an increase of the number of moles and, consequently, also of the gas "constant"; upon cooling, a recombination takes place, resulting in a decrease of the number of moles and of the gas "constant".

When such systems are used in a closed gas turbine cycle, the gas in the initial state, with a minimal gas "constant", is compound in the compressor, and is then heated in the regenerator and heater to the maximum temperature of the cycle, this is accompanied by dissociation with heat absorption for the chemical reactions taking place, and an increase of the number of moles and of the gas "constant". After expansion in the turbine, the gas cools in the regenerator and cooler and recombines with evolution of heat of those chemical reactions, a decrease of the mole number and a decrease of the gas "constant" to the minimum cycle value, the cycle is then repeated.

As we noted previously [1], a large gas constant of the working medium in the turbine, as compared to the gas "constant" in the compressor, increases the efficiency and reduces by as much as 30-40% the fraction of the power expended on gas compression in the compressor. The end result is a higher efficiency of the cycle than in inert-gas cycles, due to substantially smaller irreversible losses in the cycle.

There exists a large class of (chemically)reactive systems in which reversible chemical reactions are accompanied by increased number of moles [2, 3].

Thus dissociating aluminum chloride is of great interest as a potential heat carrier and working medium in power plants [1, 4].

Under normal conditions, anhydrous aluminum chloride is a white crystalline substance.

The triple point of $Al_2Cl_6$ is 192.6°C and 2.26 atm. abs. [7, 8].

At atmospheric pressure, aluminum chloride easily sublimates from the crystalline state at 180°C [8].

Its critical temperature and pressure are 355 ± 1.5 °C [19, 20] and 26 ± 1 atm. abs., respectively.

The molecular weight of $Al_2Cl_6$ is 266.70 [13].

The heat of dissociation for the reaction $Al_2Cl_6 \rightleftarrows 2AlCl_3$ is 108.5 kcal/kg [6, 7].

Unfortunately, experimental data on the thermodynamic properties of gaseous aluminum chloride are very scarce and data on its transport properties are not available at all.

Dimerization of aluminum chloride in the vapor phase with the formation of $Al_2Cl_6$ molecules was proven by Palmer and Elliot [5] and was confirmed by several other authors. Fischer et al. [6] showed that no noticeable amounts of higher polymers (of the $Al_3Cl_6$ type) are formed in aluminum chloride vapors.

On the basis of the measured densities of saturated vapors, the authors of [6, 7] have calculated the equilibrium constants for the vapor-phase dissociation of $Al_2Cl_6$:

$$Al_2Cl_6 \rightleftarrows 2AlCl_3. \qquad (1)$$

in the temperature ranges of 605-869°K [6] and 669-816°K [7] and the pressure range of 180-475 mm Hg [6].

Very few data are available on the second stage of the dissociation of aluminum chloride. Heise and Willand [9] have studied the absorption spectra of AlCl formed in the homogeneous reaction

$$AlCl_3 \rightleftarrows AlCl + Cl_2, \qquad (2)$$

In the first series of tests they detected absorption lines of the AlCl radical above 1370°K. Repeated tests showed AlCl lines at considerably higher temperature (above 1430°K). As the authors admitted themselves [9], the results of the first test series are doubtful. Tests of the second series also are not very convincing since the AlCl was detected at the very limit of the temperature range accessible to the experimenters and could not be confirmed by a study of the intensity of AlCl lines at higher temperatures.

The possibility that $AlCl_2$ molecules are formed in aluminum chloride vapors at high temperatures cannot be confirmed by experimental data.

Since the nature of the second stage of the vapor-phase decomposition of $Al_2Cl_6$ has not been clarified, while almost no data on the equilibrium constant of the second stage are available; we have made a rough calculation of the isobaric-isothermal potential and of the equilibrium constants of the following equilibrium reactions, which are assumed to be possible in the second-stage dissociation of aluminum chloride at high temperatures:

$$\begin{aligned} 2AlCl_3 &\rightleftarrows 2AlCl_2 + Cl_2, \\ 2AlCl_3 &\rightleftarrows 2AlCl_2 + 2Cl, \\ 2AlCl_3 &\rightleftarrows 2AlCl + 2Cl_2, \\ 2AlCl_3 &\rightleftarrows 2AlCl + 4Cl. \end{aligned} \qquad (3)$$

tion α of the corresponding reactions were estimated. This estimate shows that decomposition of the $AlCl_3$ molecule can be neglected below approximately 1800°K (at 1 atm).

Henceforth, one calculations of thermodynamic properties of gaseous aluminum chloride were carried out by taking into account only the first stage of $Al_2Cl_6$ dissociation [Reaction (1')].

Insofar as the data on the equilibrium constant given in [6, 7] cover a small range of temperatures and pressures, we have calculated the equilibrium dissociation constants of aluminum chloride on the basis of the van't Hoff law, using the heat capacity values of $Al_2Cl_6$ and $AlCl_3$.

The authors of [10], referring to the work of K. Kelley, give an equation for the heat capacity of gaseous $AlCl_3$ in between 298 and 1800°K:

$$c_p = 19.8-2.64\cdot10^5T^{-2} \text{ cal/mol-deg.}$$

The error incurred by the use of this equation is estimated at 4%.

A similar equation is given in [12], but the temperature range is broader (453.3-2500°K).

In our further calculations we used as a basis the heat capacity data calculated in [11] from spectroscopic data, whereby experimentally-determined frequency characteristics were used in the case of $Al_2Cl_6$, while the frequency characteristics for $AlCl_3$ were obtained by comparison with the $AlF_3$ molecule. Unfortunately, it is not possible to estimate the accuracy of these data in view of the absence of any experiments on the determination of the heat capacity of aluminum chloride.

The heat capacity values from [11] were recomputed on a "Minsk-2" electronic digital computer, and the following polynomials were obtained:

$$c_p = a + bT + cT^2 + dT^3 + eT^4 + \ T^5. \qquad (5)$$

The corresponding coefficients for $Al_2Cl_6$ and $AlCl_3$ are listed in Table 1.

Table 1. Coefficients of Formula (5)

| Molecule | $a$ | $b\cdot10^2$ | $c\cdot10^5$ | $d\cdot10^8$ | $e\cdot10^{11}$ | $f\cdot10^{15}$ |
|---|---|---|---|---|---|---|
| $Al_2Cl_6$ | 24,807929 | +7,014366 | −10,977460 | +8,589349 | −3,299125 | +4,947072 |
| $AlCl_3$ | 10,810480 | +3,302241 | − 5,109850 | +3,968190 | −1,515227 | +2,265114 |

The values calculated from polynomials (5) differ by less than 0.5% from the results given in [11] and by less than 1% from the results given in [10, 12].

A review of experimental data on the standard heat of formation of gaseous $AlCl_3$ is given in [13], where the magnitude of the standard entropy for gaseous $AlCl_3$ is also calculated (Table 2).

Table 2. Standard Thermodynamic Parameters of Aluminum Chloride

| 1) Величины | 2) $Al_2Cl_6$ (газ) | 3) Литературный источник | 2) $AlCl_3$ (газ) | 3) Литературный источник |
|---|---|---|---|---|
| 4) Теплота образования при 298°K $\Delta H^{\circ}_{298}$, *кал/моль* | —304600±<br>±2500 | [10] | —142593 | [13] |
| 5) Энтропия при стандартной температуре $S^{\circ}_{298}$, $\frac{кал}{моль \cdot град}$ | 113,769 | [11] | 75,564 | [13[ |

KEY: 1) Parameters; 2) $Al_2Cl_6$ (gas); 3) Literature sources; 4) Heat of formation at $298^{O}K\ \Delta H^{O}_{298}$, cal/mole; 5) Entropy at Standard temperature $S^{O}_{298}$, cal/mole-deg.

Among the values for the heat of formation of gaseous $Al_2Cl_6$ listed in [10, 14, 15], we prefer the value given by Kubaschewski and Evans [10].

The standard entropy of gaseous $Al_2Cl_6$ used in our computation has been calculated by the authors of [11]. By comparing the values of $S^{O}_{298}$ [18] of octatomic molecules (Fig. 1), we obtained a similar value of 111.0 cal/mole-deg, which confirms the correctness of the computations given in [11].

In view of the fact that the dissociation of $Al_2Cl_6$ via Reaction (1) has not been investigated to a sufficient extent, and also in view of the absence (according to our calculations) of a high-temperature dissociation of $AlCl_3$, the thermodynamic properties of gaseous aluminum chloride were calculated under the following assumptions:

1) the equilibrium constant does not depend on the pressure;

2) the second stage of the reaction can be neglected;

3) the dissociating gas is an ideal gas and its equation of state is

$$Pv = \frac{RT}{M_2}(1 + \alpha); \tag{6}$$

4) the reaction follows an equilibrium path.

The thermodynamic properties of dissociating aluminum chloride were determined via a modified method for computing the "effective" properties of a gas undergoing equilibrium dissociation [3].

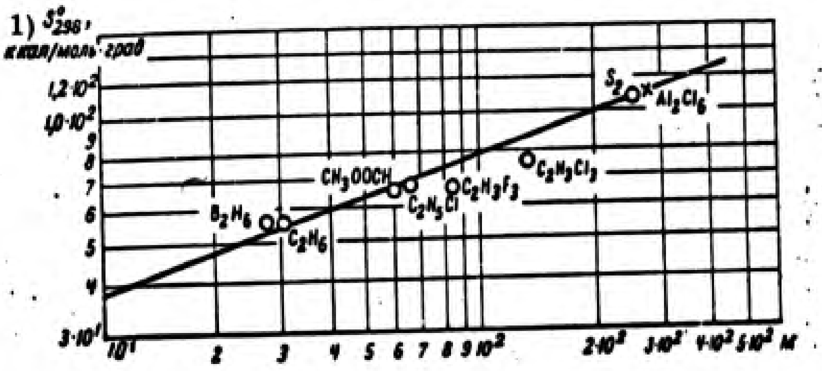

Fig. 1. Standard entropy of gaseous octatomic molecules:

$$\lg S^0_{298} = 0{,}328 \lg M + 1{,}249; \quad M_{Al_2Cl_6} = 266{,}7;$$

$$\lg S^0_{298} = 2{,}045; \quad S^0_{298} \approx 111 \text{ kcal/mole-deg}$$

KEY: 1) kcal/mole-deg.

The change in the number of moles during dissociation of $Al_2Cl_6$ via Reaction (1) can be written as:

$$(1-\alpha) \rightleftarrows 2\alpha,$$

whence the total number of moles is $n_\alpha = 1 + \alpha$.

Assuming that the components of the mixture are ideal gases, the equations of state for the components and for the mixture (on the basis of 1 mole) are:

$$\begin{gathered} P_2 v = (1-\alpha) RT, \\ P_1 v = 2\alpha RT, \\ P v = (1+\alpha) RT, \end{gathered} \tag{7}$$

whence the partial pressures

$$P_2 = \frac{1-\alpha}{1+\alpha} P, \quad P_1 = \frac{2\alpha}{1+\alpha} P$$

and the equilibrium constant of dissociation of $Al_2Cl_6$ via Reaction (1)

$$K_p = \frac{P_1^2}{P_2} = \frac{4\alpha^2}{1-\alpha^2} P. \tag{8}$$

For convenience, all quantities referring to $Al_2Cl_6$ are henceforth denoted by the subscript 2, and those referring to $AlCl_3$ by the subscript 1.

By virtue of assumption 3) above, concerning the ideal nature of the gas mixture, we have, according to [16]

$$I_{eff} = \Sigma x_j I_j, \tag{9}$$

$$S_{eff} = \Sigma x_j S_j^0 - R x_j \ln x_j - R \ln \frac{P}{P_0}. \tag{10}$$

For the j-th component

$$I_j = I_{0j}^0 + \int_{T_0}^{T} c_p dT, \tag{11}$$

$$S_j = S_{0j}^0 + \int_{T_0}^{T} c_p \frac{dT}{T}. \tag{12}$$

For the equilibrium system (1) with allowance for dissociation

$$\begin{aligned} I_{eff} &= \frac{1}{M_2}\left[I_2 \frac{1-\alpha}{1+\alpha} + I_1 \frac{2\alpha}{1+\alpha}\right] = \\ &= \frac{1}{M_2}[I_2(1-\alpha) + I_1 2\alpha], \end{aligned} \tag{13}$$

$$\begin{aligned} S_{eff} &= \frac{1}{M_2}[S_2(1-\alpha) + S_1 2\alpha] - \\ &- \frac{R}{M_2}[(1-\alpha)\ln(1-\alpha) + 2\alpha \ln 2\alpha - \\ &- (1+\alpha)\ln(1+\alpha) - (1+\alpha)\ln P]. \end{aligned} \tag{14}$$

Here

$$I_2 = \Delta H^0_{298(2)} + i_2, \quad I_1 = \Delta H^0_{298(1)} + i_1; \tag{15}$$

$$S_2 = S^0_{298(2)} + s_2, \quad S_1 = S^0_{298(1)} + s_1. \tag{16}$$

Using the polynomials (5) obtained by us for the heat capacity of gaseous $Al_2Cl_6$ and $AlCl_3$, we find, after integration

$$i_2 = a_2(T-298) + \frac{b_2}{2}(T^2-298^2) + \frac{c_2}{3}(T^3-298^3) + \frac{d_2}{4}(T^4-298^4) + \frac{e_2}{5}(T^5-298^5) + \frac{f_2}{6}(T^6-298^6), \tag{17}$$

$$s_2 = a_2 \ln\frac{T}{298} + b_2(T-298) + \frac{c_2}{2}(T^2-298^2) + \frac{d_2}{3}(T^3-298^3) + \frac{e_2}{4}(T^4-298^4) + \frac{f_2}{5}(T^5-298^5) \tag{18}$$

and analogous expressions for $i_1$ and $S_1$.

Solving equations (13)-(18) simultaneously, we obtain computational formulas for the "effective" enthalpy and entropy of the dissociating system $Al_2Cl_6 \rightleftarrows 2AlCl_3$:

$$I_{eff} = \frac{1}{M_2}\left[(1-\alpha)(\Delta H^0_{298(2)} + i_2) + 2\alpha(\Delta H^0_{298(1)} + i_1)\right], \tag{19}$$

$$S_{eff} = \frac{1}{M_2}\left[(1-\alpha)(S^0_{298(2)} + s_2) + 2\alpha(S^0_{298(1)} + s_1)\right] - \frac{R}{M_2}\left[(1-\alpha)\ln(1-\alpha) + 2\alpha\ln 2\alpha - (1+\alpha)\ln(1+\alpha) + (1+\alpha)\ln p\right]. \tag{20}$$

To calculate the degree of dissociation, $\alpha$, occurring in (19) and (20), the values of the equilibrium constants were determined as follows:

Using the well-known van't Hoff relationship [15]

$$\frac{\partial \ln K_p}{\partial T} = \frac{Q_p}{RT^2}, \tag{21}$$

we obtain, after integration

$$\ln K_p = \frac{1}{R}\int \frac{Q_p}{T^2}\,dT + \text{const}, \tag{22}$$

where

$$Q_p = 2I_1 - I_2 = 2\Delta H^0_{298(1)} - \Delta H^0_{298(2)} + 2i_2 - i_1. \tag{23}$$

Solving (17) and (22) simultaneously and using the relation

$$\ln K_p = -\frac{\Delta z}{RT} \tag{24}$$

at T = 298°K, we can determine the value of the constant in (22). Then (22) will assume the form

$$\begin{aligned}\ln K_p = \frac{1}{R}\Big\{&2S^0_{298(1)} - S^0_{298(2)} - \frac{1}{T}\left(2\Delta H^0_{298(1)} - \Delta H^0_{298(2)}\right) + \\ &+ (2a_2 - a_1)\left[\ln\frac{T}{298} - \left(1 - \frac{298}{T}\right)\right] + \frac{2b_2 - b_1}{2}\,\frac{(T-298)^2}{T} + \\ &+ \frac{2c_2 - c_1}{3}\left[\frac{T^2 - 298^2}{2} - \left(1 - \frac{298}{T}\right)\right] + \\ &+ \frac{2d_2 - d_1}{4}\left[\frac{T^3 - 298^3}{3} - \left(1 - \frac{298}{T}\right)\right] + \\ &+ \frac{2e_2 - e_1}{5}\left[\frac{T^4 - 298^4}{4} - \left(1 - \frac{298}{T}\right)\right] + \\ &+ \frac{2f_2 - f_1}{6}\left[\frac{T^5 - 298^5}{5} - \left(1 - \frac{298}{T}\right)\right]\Big\}.\end{aligned} \tag{25}$$

By differentiation of (19), we can also obtain an expression for calculating the "effective" heat capacity of the dissociating $Al_2Cl_6$

$$\begin{aligned}c_{p\,\mathrm{eff}} = \left(\frac{\partial I_{\mathrm{eff}}}{\partial T}\right)_P = \frac{1}{M_2}\Big[\left(\frac{\partial \alpha}{\partial T}\right)_P &\left(2\Delta H^0_{298(1)} - \right. \\ &\left. - \Delta H^0_{298(2)} + 2i_1 - i_2\right) + c_{p_2}(1-\alpha) + c_{p_1} 2\alpha\Big].\end{aligned} \tag{26}$$

After differentiating (8) and substitution into (21), we obtain

$$\left(\frac{\partial \alpha}{\partial T}\right)_P = \frac{Q_p}{2RT^2}\,\alpha(1-\alpha^2). \tag{27}$$

Using (23) and (27), it is easy to transform (26) into

$$c_{p\,\mathrm{eff}} = \frac{1}{M_2}\left[c_{p_2}(1-\alpha) + c_{p_1} 2\alpha + \frac{\alpha(1-\alpha^2)}{2RT^2}\,Q_p^2\right], \tag{28}$$

where $c_{p2}$ and $c_{p1}$ are calculated from the polynomials (5).

The relations thus found allowed the computation, on the "Minsk-2" electronic digital computer, of the "effective" enthalpy, entropy and heat capacity of dissociating

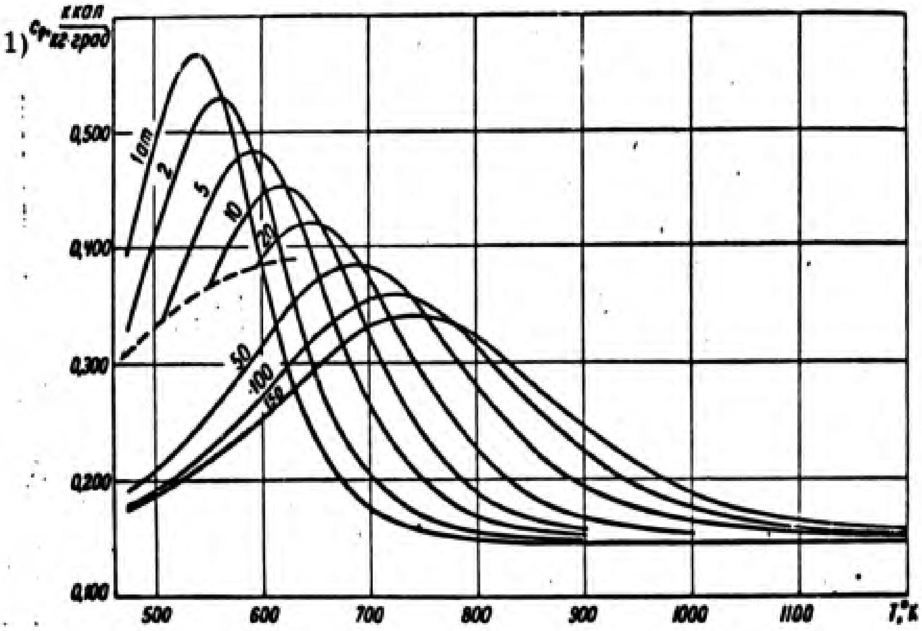

Fig. 2. Effective heat capacity of gaseous, dissociating aluminum chloride.

KEY: 1) $c_p$, kcal/kg-deg.

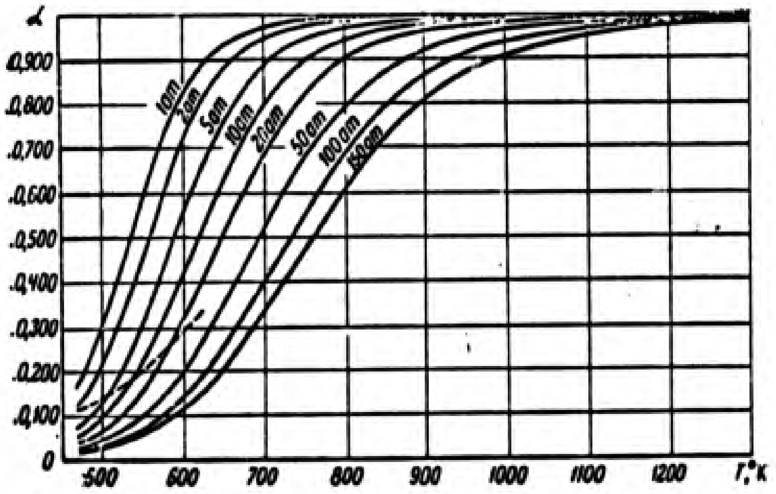

Fig. 3. T-diagram of dissociating gaseous aluminum chloride.

aluminum chloride in the pressure range of 1-150 atm and the temperature range of 460-2000°K (some of the results are given in Table 3).

On the basis of the values so obtained, an I-S diagram was plotted. The plot of $c_{p\ eff} = f(P, T)$ is shown in Fig. 2, and the composition diagram for the system $Al_2Cl_6 \rightleftarrows 2AlCl_3$ at various temperatures is given in Fig. 3. The critical pressure of the $Al_2Cl_6$ system was calculated from approximate relations and the saturation curve is shown on the plots by broken lines.

## Table 3. "Effective" Enthalpy and Entropy of the System $Al_2Cl_6 \rightleftarrows 2AlCl_3$

| T, °K | P, atm. | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 1 | | 2 | | 4 | | 6 | | 8 | | 10 | |
| | $-I_{eff}$ | $S_{eff}$ | $-I_{eff}$ | $S_{eff}$ | $-I_{eff}$ | $S_{eff}$ | $-I_{eff}$ | $S_{eff}$ | $-I_{eff}$ | $S_{eff}$ | $-I_{eff}$ | $S_{eff}$ |
| 500 | 1091,31 | 0,5494 | 1097,02 | 0,5315 | 1101,25 | 0,5169 | — | — | — | — | — | — |
| 550 | 1063,77 | 0,5545 | 1072,79 | 0,5776 | 1080,73 | 0,5560 | 1084,65 | 0,5449 | 1087,08 | 0,5377 | — | — |
| 600 | 1040,08 | 0,6432 | 1047,42 | 0,6218 | 1056,22 | 0,5986 | 1061,52 | 0,5851 | 1065,15 | 0,5759 | 1067,84 | 0,5690 |
| 650 | 1025,34 | 0,6669 | 1029,05 | 0,6513 | 1034,85 | 0,6329 | 1039,23 | 0,6208 | 1042,68 | 0,6119 | 1045,50 | 0,6048 |
| 700 | 1015,40 | 0,6816 | 1017,03 | 0,6691 | 1019,96 | 0,6550 | 1022,51 | 0,6456 | 1024,77 | 0,6385 | 1026,78 | 0,6326 |
| 750 | 1007,17 | 0,6930 | 1007,91 | 0,6817 | 1009,31 | 0,6697 | 1010,63 | 0,6621 | 1011,86 | 0,6563 | 1013,03 | 0,6516 |
| 800 | 999,52 | 0,7029 | 999,88 | 0,6921 | 1000,58 | 0,6810 | 1001,25 | 0,6742 | 1001,92 | 0,6692 | 1002,55 | 0,6651 |
| 850 | 992,07 | 0,7119 | 992,26 | 0,7014 | 992,63 | 0,6906 | 993,00 | 0,6842 | 993,36 | 0,6795 | 993,72 | 0,6758 |
| 900 | 984,70 | 0,7203 | 984,80 | 0,7099 | 985,02 | 0,6993 | 985,23 | 0,6931 | 985,44 | 0,6886 | 985,64 | 0,6851 |
| 950 | 977,35 | 0,7283 | 977,42 | 0,7179 | 977,55 | 0,7074 | 977,67 | 0,7013 | 977,80 | 0,6963 | 977,93 | 0,6934 |
| 1000 | 970,02 | 0,7358 | 970,05 | 0,7254 | 970,14 | 0,7150 | 970,22 | 0,7089 | 970,30 | 0,7045 | 970,38 | 0,7011 |
| 1100 | 955,34 | 0,7498 | 955,36 | 0,7394 | 955,40 | 0,7291 | 955,43 | 0,7230 | 955,47 | 0,7187 | 955,51 | 0,7153 |
| 1200 | 940,63 | 0,7626 | 940,64 | 0,7522 | 940,66 | 0,7419 | 940,68 | 0,7358 | 940,70 | 0,7315 | 940,72 | 0,7282 |
| 1300 | 925,89 | 0,7744 | 925,90 | 0,7640 | 925,91 | 0,7537 | 925,92 | 0,7476 | 925,94 | 0,7433 | 925,95 | 0,7400 |
| 1400 | 911,13 | 0,7853 | 911,13 | 0,7750 | 911,14 | 0,7646 | 911,14 | 0,7586 | 911,15 | 0,7543 | 911,16 | 0,7509 |
| 1500 | 896,33 | 0,7955 | 896,33 | 0,7852 | 896,34 | 0,7749 | 896,34 | 0,7688 | 896,35 | 0,7645 | 896,35 | 0,7612 |
| 1600 | 881,52 | 0,8051 | 881,52 | 0,7947 | 881,53 | 0,7844 | 881,53 | 0,7784 | 881,53 | 0,7741 | 881,54 | 0,7708 |
| 1700 | 866,70 | 0,8140 | 866,71 | 0,8037 | 866,71 | 0,7934 | 866,71 | 0,7874 | 866,71 | 0,7831 | 866,72 | 0,7797 |
| 1800 | 851,89 | 0,8225 | 851,89 | 0,8122 | 851,89 | 0,8019 | 851,90 | 0,7958 | 851,90 | 0,7915 | 851,19 | 0,7882 |
| 1900 | 837,08 | 0,8305 | 837,08 | 0,8202 | 837,08 | 0,8099 | 837,08 | 0,8038 | 837,09 | 0,7995 | 837,09 | 0,7962 |
| 2000 | 822,25 | 0,8381 | 822,25 | 0,8278 | 822,25 | 0,8175 | 825,25 | 0,8114 | 822,25 | 0,8071 | 822,26 | 0,8038 |

## Table 3 (cont'd)

| $T$, °K | $P$, atm. | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 20 | | 40 | | 60 | | 80 | | 100 | | 150 | |
| | $-I_{eff}$ | $S_{eff}$ | $-I_{eff}$ | $S_{eff}$ | $-I_{eff}$ | $S_{eff}$ | $-I_{eff}$ | $S_{eff}$ | $-I_{eff}$ | $S_{eff}$ | $-I_{eff}$ | $S_{eff}$ |
| 500 | — | — | 1108,50 | 0,4837 | 1109,12 | 0,4793 | 1109,49 | 0,4763 | 1109,75 | 0,4741 | 1110,14 | 0,4702 |
| 550 | — | — | 1096,31 | 0,5069 | 1097,73 | 0,5010 | 1098,58 | 0,4971 | 1099,16 | 0,4943 | 1100,07 | 0,4894 |
| 600 | 1075,24 | 0,5496 | 1081,03 | 0,5335 | 1083,72 | 0,5253 | 1085,36 | 0,5201 | 1086,49 | 0,5164 | 1088,25 | 0,5099 |
| 650 | 1054,44 | 0,5829 | 1062,71 | 0,5628 | 1066,89 | 0,5522 | 1069,53 | 0,5454 | 1071,38 | 0,5405 | 1074,35 | 0,5322 |
| 700 | 1034,34 | 0,6127 | 1043,09 | 0,5918 | 1048,22 | 0,5799 | 1051,68 | 0,5718 | 1054,23 | 0,5659 | 1058,46 | 0,5557 |
| 750 | 1018,00 | 0,6353 | 1025,05 | 0,6168 | 1029,92 | 0,6052 | 1033,55 | 0,5969 | 1036,38 | 0,5905 | 1041,42 | 0,5792 |
| 800 | 1005,47 | 0,6514 | 1010,25 | 0,6359 | 1014,03 | 0,6257 | 1017,12 | 0,6181 | 1019,70 | 0,6120 | 1024,66 | 0,6009 |
| 850 | 995,41 | 0,6637 | 998,41 | 0,6502 | 1001,01 | 0,6415 | 1003,30 | 0,6349 | 1005,32 | 0,6295 | 1009,50 | 0,6193 |
| 900 | 986,65 | 0,6737 | 988,52 | 0.6616 | 990,23 | 0,6538 | 991,80 | 0,6480 | 993,25 | 0,6433 | 996,44 | 0,6342 |
| 950 | 978,55 | 0,6825 | 979,73 | 0,6711 | 980,86 | 0,6640 | 981,92 | 0,6587 | 982,92 | 0,6545 | 985,23 | 0,6463 |
| 1000 | 970,78 | 0,6905 | 971,56 | 0,6795 | 972,31 | 0,6728 | 973,03 | 0,6678 | 973,73 | 0,6639 | 975,37 | 0,6565 |
| 1100 | 955,69 | 0,7049 | 956,06 | 0,6842 | 956,42 | 0,6879 | 956,78 | 0,6833 | 957,13 | 0,6797 | 957,98 | 0,6730 |
| 1200 | 940,82 | 0,7178 | 941,02 | 0,7073 | 941,22 | 0,7011 | 941,41 | 0,6967 | 941,60 | 0,6933 | 942,07 | 0,6869 |
| 1300 | 926,00 | 0,7297 | 926,12 | 0,7192 | 926,24 | 0,7131 | 926,36 | 0,7088 | 926,47 | 0,7054 | 926,76 | 0,6991 |
| 1400 | 911,20 | 0,7406 | 911,27 | 0,7303 | 911,35 | 0,7242 | 911,42 | 0,7198 | 911,50 | 0,7165 | 911,68 | 0,7103 |
| 1500 | 896,38 | 0,7508 | 896,43 | 0,7405 | 896,48 | 0,7344 | 896,53 | 0,7301 | 896,59 | 0,7268 | 896,71 | 0,7206 |
| 1600 | 881,56 | 0,7604 | 881,59 | 0,7501 | 881,63 | 0,7440 | 881,67 | 0,7397 | 881,70 | 0,7364 | 881,79 | 0,7303 |
| 1700 | 866,73 | 0,7694 | 866,76 | 0,7591 | 866,79 | 0,7530 | 866,81 | 0,7487 | 866,84 | 0,7454 | 866,91 | 0,7393 |
| 1800 | 851,91 | 0,7779 | 851,93 | 0,7675 | 851,92 | 0,7615 | 851,98 | 0,7572 | 852,00 | 0,7539 | 852,05 | 0,7478 |
| 1900 | 837,10 | 0,7859 | 837,11 | 0,7755 | 837,13 | 0,7695 | 837,15 | 0,7652 | 837,16 | 0,7619 | 837,21 | 0,7553 |
| 2000 | 822,26 | 0,7935 | 822,28 | 0,7832 | 822,29 | 0,7772 | 822,31 | 0,7728 | 822,32 | 0,7695 | 822,35 | 0,7634 |

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## NOTATION

$\Delta_z$ - isobaric-isothermal potential of the reaction $Al_2Cl_6 \rightleftarrows 2AlCl_3$ at temperature T; P - total pressure of the mixture; v- specific volume of the mixture; R - gas constant; $\alpha$ - degree of dissociation of $Al_2Cl_6 \rightleftarrows 2AlCl_3$ at P and T; $M_2$ - molecular weight of $Al_2Cl_6$; $I^o_{0j}$ and $S^0_{0j}$ - enthalpy and entropy of components at standard values $P_0$ and $T_0$; $i_1$; $S_1$; $i_2$; $S_2$ - relative enthalpy and entropy of the $AlCl_3$ and $Al_2Cl_6$ components.

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# HEAT TRANSFER IN THE CHEMICALLY-REACTING EQUILIBRIUM SYSTEM $N_2O_4 \rightleftarrows 2NO_2$

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Heat transfer in a chemically-reacting flow has still not yet been investigated to a sufficient extent, although it is a very urgent problem in aircraft and rocket technology, and is a potential means for increasing the rate of heat processes in power- and chemical-engineering [6, 8-10]. The presently available analytic methods for computing heat exchange in a reacting flow system are extremely complex and laborious, while the great majority of studies in this field are concerned with the case of external flow around bodies. For engineering computations of heat-exchange apparatus, sufficient accuracy is achieved by the use of empirical relations. In this case, thermal and fluid flow computations for ducts (channels) are performed on one-dimensional models, where the (effective) coefficients of heat and mass transfer qualitatively allow for the specific nature of the one-dimensional description of real three-dimensional processes [7, 11].

The theory of diffusion and heat transfer shows that processes involving heat transfer via conduction and mass transfer by diffusion are similar. Theoretical and experimental results obtained in the study of molecular conduction can be applied directly to diffusion processes and vice-versa [1, 2].

The basic law of heat transfer via molecular (heat) conduction is Fourier's law

$$\mathbf{q} = -\lambda_f \operatorname{grad} T. \tag{1}$$

The corresponding law for diffusion is Fick's law

$$\mathbf{j}_k = -D_k \operatorname{grad} c_k. \tag{2}$$

Equations (1) and (2) hold rigorously only in the case of heat transfer in a medium with a constant and identical at all points concentration, and in isothermal diffusion. If both concentration and temperature gradients are present in the system, then one deals with phenomena, known as thermodiffusivity and diffusive heat conduction. In this case, one more term, proportional to the concentration gradient, is introduced into Eq. (1), and a term proportional to the temperature gradient is introduced into Eq. (2). However, the contribution made by cross-effects is usually small, and in most cases such effects can be neglected.

In the computation of processes involving transfer of heat and mass, one uses the heat transfer coefficient $\alpha$ and the mass transfer coefficient $\beta$:

$$\alpha_f = \frac{q}{\Delta T}, \tag{3}$$

$$\beta_k = \frac{j_k}{\Delta c_k}, \tag{4}$$

where $\Delta T$, $\Delta c_k$ are the temperature and concentration differences, respectively.

The heat and mass transfer coefficients are defined with the aid of criteria of similarity:

$$\mathrm{Nu}_f = \frac{\alpha_f L}{\lambda_f}, \tag{5}$$

$$\mathrm{Nu}_{fk} = \frac{\beta_k L}{D_k'}. \tag{6}$$

The similarity theory proves that in forced convection, the Nusselt number is a function of the Reynolds and Prandtl numbers at specific geometric and physical conditions:

$$\mathrm{Nu} = f(\mathrm{Re},\ \mathrm{Pr}).$$

The only difference between computation of a heat-transfer process and computation of diffusional process is that, in the first case, one uses the Prandtl thermal number, while in the latter case one uses the Prandtl diffusion number [2]:

$$\mathrm{Pr}_f = \frac{\nu}{a}, \tag{7}$$

$$\mathrm{Pr}_{fk} = \frac{\nu}{D_k}, \tag{8}$$

where $D_k$ is the kinematic diffusion coefficient ($m^2/sec$).

To compute heat transfer in a chemically reacting equilibrium flow we can write

$$q = q_f + q_r, \tag{9}$$

where

$$q_f = \alpha_f (T_{\text{ст}} - T_f); \tag{10}$$

$$q_r = \sum_{k=1}^{n} h_k \beta_k (x_{k\text{ст}} - x_k). \tag{11}$$

The molar concentrations $x_{kct}$, $x_k$ of each component in an equilibrium mixture are functions of the temperature and pressure and are determined, respectively, from the wall temperature and the mean calorimetric temperature of the flow.

Consequently, by analogy with the determination of thermophysical properties of a chemically-reacting mixture, the heat transfer coefficient can also be represented in the form of two additive components

$$\alpha_e = \alpha_f + \alpha_r, \tag{12}$$

where $\alpha_e$ is the "effective" heat transfer coefficient, defined by the equation

$$\alpha_e = \frac{q}{T_{\text{ст}} - T_r}; \tag{13}$$

$\alpha_f$ is the "frozen" component of the heat transfer coefficient, defined by the usual analytic or empirical relations for a "frozen" mixture; $\alpha_r$ is the "reactive" component of the heat transfer coefficient, defined by the equation

$$\alpha_r = \frac{\sum_{k=1}^{n} h_k \beta_k (x_{k\text{ст}} - x_k)}{T_{\text{ст}} - T_r}. \tag{14}$$

If $\mu$ chemical reactions take place in a multicomponent mixture, then in each j-th chemical reaction it is possible to select a component which does not participate in any other reaction. We shall index this component with the ordinal number of the j-th chemical reaction. Then we can write for the diffusional mass flow of each component

$$\frac{j_k}{m_k} = \sum_{j=1}^{n} \frac{a_{jk}}{a_{jj}} \frac{j_j}{m_j}. \tag{15}$$

Equation 15) is obtained from the diffusion equation at static conditions.

Using the fact that

$$Q_{pj} = \sum_{k=1}^{n} a_{jk} m_k h_k,$$

it is not difficult to find that the energy flow due to diffusion is

$$j_r = \sum_{k=1}^{n} h_k j_k = \sum_{j=1}^{\mu} \frac{Q_{pj} j_j}{a_{jj} m_j}. \tag{16}$$

To compute the heat transfer coefficient in a undimensional, chemically-reacting equilibrium flow with a stoichiometric ratio of molar diffusional flows in the radial direction, we can write

$$\alpha_r = \sum_{j=1}^{\mu} \frac{Q_{pj} \beta_j}{a_{jj} m_j} \frac{x_{j\text{ст}} - x_j}{T_{\text{ст}} - T_r}. \tag{17}$$

The thermophysical properties of the reversibly dissociating nitrogen tetroxide equilibrium system, necessary for the calculation of $\alpha_c$ (the thermal conductivity $\lambda_f$ of the "frozen" mixture, the coefficient of dynamic viscosity $\mu$), where determined from the equations obtained in [3, 4]. The kinematic diffusion coefficient $D_k$ was calculated from the well-known equation of mass transfer theory

$$D_k = \frac{1-x_k}{\sum\limits_{\substack{j=1\\ j\neq k}}^{n} x_j/D_{kj}\,\frac{m_k' m_j}{m^2}}, \tag{18}$$

where the generalized diffusion coefficients $D_{hj}$ were determined from the equations obtained in [5].

The method described above for computing the heat transfer coefficient for an equilibrium mixture was used to generalize the experimental data on heat transfer in the system $N_2O_4 \rightleftarrows 2NO_2$ during heating. In this study, we used the theoretical dependence of the Nusselt numbers on the Reynolds and Prandtl numbers in a forced turbulent pipe flow, postulated by M. A. Mikheyev and S. S. Kutateladze

$$Nu = 0{,}021\ Re^{0.8} Pr^{0.43} \left(\frac{T_{ст}}{T_r}\right)^{-0.55}. \tag{19}$$

Description of test units. Experimental studies of heat transfer to a chemically-reacting gas were carried out at the Institute of Nuclear Power Engineering of the Academy of Sciences of the Belorussian SSSR in the temperature range of 30-300°C, pressure range of 1-60 atm. abs, and Reynolds number range of $10^4$-$3\cdot 10^5$. In the unit used for studying heat transfer to a dissociating has at low pressure, the tests were carried out in the pressure range of 1-10 atm ($Re = 10^4 - 3\cdot 10^4$) [6]. A detailed description of this test unit is given in [6]. In the unit used for studying chemically reactive media in the high-pressure region the tests were carried out in the pressure range of 10-60 atm at Re of $3\cdot 10^4 - 3\cdot 10^5$. Steady-state conditions prevailed in both units during the study of the heat transfer.

The unit for the experimental study of media which are chemically-reactive at high pressures is a closed loop in which the liquid nitrogen tetroxide is circulated by a pump. The flow rate is regulated by varying the speed of the pump and by passing part of the flow through a by pass valve. The flow rate of the heat carrier in the loop is measured by the calorimetric method in a flow calorimeter [with self-recovery (compensation) of heat losses], placed in a Dewar flask. The temperature of the liquid at the inlet and outlet of the calorimeter is measured with thermocouples whose cold junctions are held at a constant temperature of 0°C. A carefully calibrated four-junction differential thermocouple, yielding twice the emf, is used for measuring the difference of temperatures at the inlet and outlet. Pressure in the system is created by filling it with the necessary amount of product; for this purpose, a special charging system is available. It consists of two preheated containers. The test unit is provided with a surge chamber for damping of pulsations created by the pump and with a mechanical filter for removing from the system any products of corrosion of the structural materials by $N_2O_4$. All parts of the unit in contact with $N_2O_4$ are made from 1Kh18N9T stainless steel.

The test section (Fig. 1) consists of a v-shaped tube made of 1Kh18N9T stainless; it has an O. D. of 4 mm, wall thickness of 1 mm and total length of 700 mm. The tube itself also functions as an electrical conductor and heater. The hot-line conductor is attached to the middle of the tube, while the ground conductor is attached to the flanged ends of the tube. Thus, it is not necessary to electrically insulate the test section of the tube from the rest of the system, thus avoiding a problem which is difficult in a system operating under these conditions. The section connecting the tube to the flange is finned to reduce heating of the flange. For protection against heat losses, screens are attached to the flange, while the jacket and flange surfaces are covered with heat-insulting material. A calorimeter is installed to measure the heat losses.

In the test section, we measured the inlet and outlet temperatures of the heat carrier, and also the wall temperatures along the tube (at equal intervals of 100 mm). Special thermometric wells were installed for measuring the inlet and outlet gas temperatures. The temperature sensors were inserted into internal tubes, over which the gas flowed. This arrangement prevents reaction between the thermocouples and the corrosive heat carrier and allows a simple replacement of the thermocouples. Chromel-alumel thermocouples with an electrode diameter of 0.3 mm were used as temperature sensors. The gas and wall temperatures in the test apparatus were measured with a P-307 potentiometer (accuracy of up to 1 microvolt). The pressure in the system was measured with reference manometers equipped with separators. These manometers were installed ahead and behind the test section and also on the calorimeter-flowmeter. The electric power liberated in the heating tube was measured from the readings of an ammeter and voltmeter. The current was measured with a type D-57 ammeter of 0.2% precision class through a type UTT-6 current transformer. The voltage was measured with voltmeters of type D-523 and E-59 0.5% precision class). Switching in the voltage-measurement circuit was effected by means of a type PMT-12 switch. All heat transfer experiments were repeated 2-3 times.

Workup of test data. By definition, the local "effective" heat transfer coefficient $\alpha_e$ in steady state is given by equation (13).

The electric power supplied to the test section was calculated from the measured current and voltage data. Then, making allowance for losses to the surrounding medium, the heat supplied to the heat carrier in each section was determined. Knowing the profile of the heat flux along the length of the channel and also the initial conditions from measurements of the temperature and gas pressure at the inlet of the test section, the gas temperature profile along the length of the channel was calculated with the aid of equations obtained in [7]; then the "effective" heat transfer coefficient ($\alpha_e$) in each section was calculated with the aid of (13). Experimental points located next to the start of the test section and behind the turn (see Fig. 1) and, consequently, lying in the region of hydrodynamic stabilization, were not taken into account in the calculations.

Results and discussion of experimental data. The table below gives calculated and experimental values of the "effective" heat transfer coefficient $\alpha_e$ for the chemically-reactive gaseous system $N_2O_4 \rightleftarrows 2NO_2$ in turbulent flow in the tube. Comparison of calculated data, obtained from the empirical relations proposed in this study, with experimental data for the equilibriated chemically-reactive system $N_2O_4 \rightleftarrows 2NO_2$ indicates a satisfactory correlation between these data, as well as the fact that the proposed empirical relations can be used to describe the mechanism of heat transfer in a chemically-reacting system.

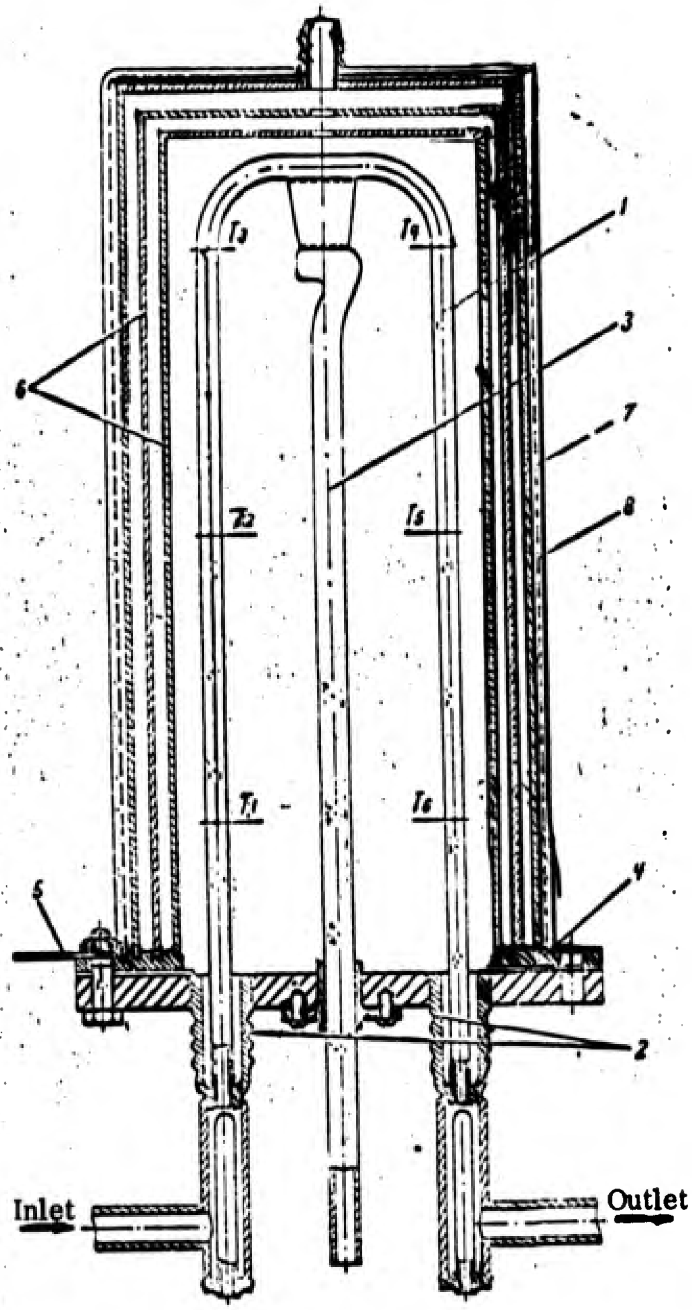

Fig. 1. Schematic of test apparatus:

1—test tube; 2—thermometric wells; 3—hot conductor; 4—flange; 5—ground conductor; 6—screens; 7—jacket; 8—calorimeter. $T_1$-$T_6$—thermocouples in temperature-measurement circuit.

Analysis of these experimental data on heat transfer shows that, in the case of turbulent flow in a circular tube, concentration gradient-induced diffusional heat transfer in the chemically reactive stream $N_2O_4 \rightleftarrows 2NO_2$, in the form of chemical enthalpy, is high and a 3-9-fold increase (factor of improvement) of heat transfer coefficients is achieved, as compared to data obtained with an inert gas ($CO_2$, $N_2$ and others).

Table 1. Comparison of Calculated "Effective" Heat Transfer Coefficients $\alpha_e$ with Experimental Results for the System $N_2O_4 \rightleftarrows 2NO_2$

| Наименование 1) | 2) Номер опыта | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 3) 48 ($P$=2,5 атм), участки | | | | | | 4) 49 ($P$=5 атм), участки | | | | | |
| | 1 | 2 | 3 | 4 | 9 | 10 | 1 | 2 | 3 | 4 | 6 | 10 |
| 8) Температура стенки, °K | 358 | 364 | 369 | 378 | 464 | 513 | 372 | 378 | 383 | 391 | 438 | 504 |
| 9) Температура газа, °K | 344 | 349 | 355 | 361 | 404 | 423 | 355 | 361 | 366 | 372 | 398 | 419 |
| 10) Число $Re \cdot 10^{-4}$ | 2,98 | 2,81 | 2,73 | 2,65 | 2,27 | 2,09 | 3,14 | 3,06 | 3,05 | 2,87 | 2,59 | 2,32 |
| 11) Расчетные значения $\alpha_f$ | 370 | 373 | 377 | 376 | 362 | 357 | 368 | 384 | 386 | 405 | 367 | 373 |
| 11) Расчетные значения $\alpha_{r_I}$ | 3150 | 2720 | 2340 | 2040 | 252 | 66 | 2290 | 2250 | 2030 | 2170 | 830 | 139 |
| 11) Расчетные значения $\alpha_e$ | 3520 | 3093 | 2717 | 2416 | 614 | 422 | 2658 | 2634 | 2416 | 2575 | 1197 | 512 |
| 12) Экспериментальные значеная $\alpha_e$ | 3310 | 3080 | 3300 | 2710 | 750 | 496 | 2630 | 2630 | 2630 | 2330 | 1060 | 511 |

| Наименование 1) | 2) Номер опыта | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 28 ($P$=53 атм), участки 5) | | | | | 6) 32 ($P$=42 атм), участки | | | | 7) 79 ($P$=22 атм), участки | | | |
| | 1 | 2 | 3 | 5 | 6 | 2 | 3 | 5 | 6 | 2 | 3 | 5 | 6 |
| 8) Температура стенки, °K | 468 | 508 | 506 | 590 | 632 | 476 | 586 | 542 | 561 | 477 | 493 | 529 | 543 |
| 9) Температура газа, °K | 431 | 441 | 452 | 484 | 503 | 444 | 452 | 476 | 488 | 443 | 450 | 472 | 484 |
| 10) Число $Re \cdot 10^{-5}$ | 2,05 | 1,97 | 1,91 | 1,76 | 1,69 | 1,88 | 1,83 | 1,72 | 1,68 | 1,96 | 1,92 | 1,82 | 1,78 |
| 11) Расчетные значения $\alpha_f$ | 3840 | 3740 | 3820 | 3740 | 3730 | 3720 | 3740 | 3700 | 3730 | 3810 | 3810 | 3850 | 3890 |
| 11) Расчетные значения $\alpha_{r_I}$ | 8320 | 4860 | 4370 | 1170 | 6130 | 5930 | 4720 | 1730 | 1160 | 4140 | 2950 | 1310 | 910 |
| 11) Расчетные значения $\alpha_e$ | 12200 | 8600 | 8190 | 4190 | 4350 | 9660 | 8470 | 5430 | 4890 | 7960 | 6760 | 5150 | 4800 |
| 12) Экспериментальные значения $\alpha_e$ | 12800 | 7190 | 8940 | 4530 | 3730 | 10300 | 9780 | 4950 | 4510 | 7510 | 5990 | 4500 | 4310 |

KEY: 1) Item; 2) No. of test; 3) 48 (p-2.5 atm) sections; 4) 49 (p-5 atm) sections; 5) 28 (p=53 atm); sections, 6) 32 (p=42 atm) sections; 7) 79 (p = 22 atm) sections; 8) Wall temperature, k°; 9) Gas temperature, k°; 10) Rena No. Re. $10^{-4}$; 11) Calculated values; 12) Experimental values $\alpha_e$.

At pressures of 40-50 atm. abs. and Re of $2 \cdot 10^5$, heat transfer coefficients of 10,000-13,000 kcal/m$^2$ - hr-deg were experimentally obtained in the chemically-reactive system.

Figure 2 compares calculated and experimental heat transfer data for in the reactive equilibriated system $N_2O_4 \rightleftarrows 2NO_2$ in the Re range $10^4$ - $2 \cdot 10^5$, P = 1-6 atm. abs. and T = 30-300 °C.

In the range investigated, the error in the experimental heat transfer coefficients is ±15%. The accuracy of experimental data can be substantially improved after more reliable experimental data on the heat capacity of liquid nitrogen tetroxide have been obtained, since inaccuracies in the calorimeteric determination of the $N_2O_4$ flow rate constitute the major fraction of the error.

In view of the satisfactory agreement between calculated and experimental data, it is possible to recommend the previously suggested unidimensional model for computing the axial temperature profile in a circular tube when studying heat transfer to a chemically-reactive gas [11], and also to recommend the empirical (numerical) relations for computing heat transfer in the chemically reactive system $N_2O_4 \rightleftarrows 2NO_2$ in the temperature range of 30-300°C, pressure range of 1-60 atm. abs., and Re range of $10^4$ - $3 \cdot 10^5$.

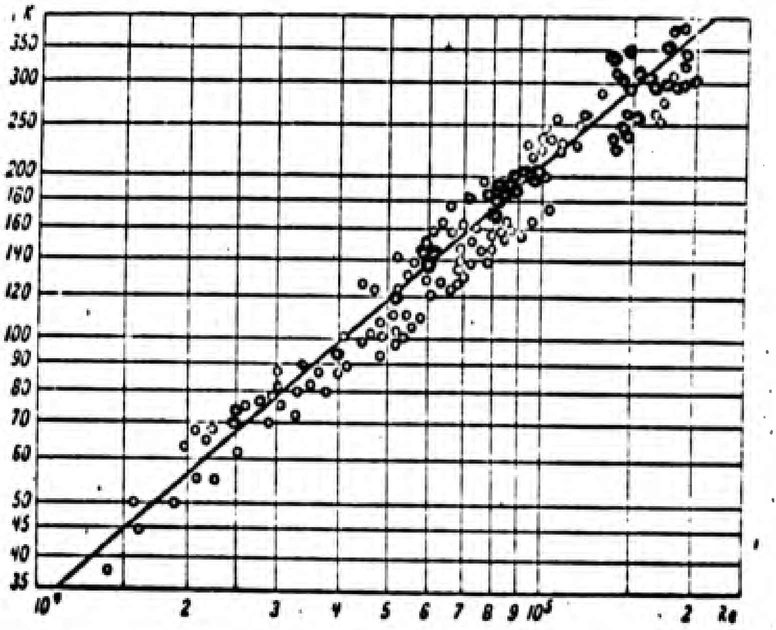

Fig. 2. Heat transfer for the forced turbulent flow of the chemically equilibriated system $N_2O_4 \rightleftarrows 2NO_2$ in tube.

$$K = Nu_f Pr_f^{-0.43} \left(\frac{T_{ct}}{T_r}\right)^{0.55} = Nu_{jk} Pr_{jk}^{-0.43} \left(\frac{T_{ct}}{T_r}\right)^{0.55}$$

In conclusion, the authors wish to thank A. K. Krasin, member of the Academy of Sciences of the Belorussian SSSR, for his constant concern with their work, and also their department associates A. N. Kremeshnyy, Yu. I. Bakalin and V. A. Nikolayev, who took part in this work or in its discussion.

## NOTATION

$\alpha_e$ - "effective" heat transfer coefficient; $\alpha_f$, $\alpha_r$ - "frozen" and "reactive" components of the heat transfer coefficient; $\beta_k$ - mass transfer coefficient; $Nu_f$, $Nu_{jk}$ - Nusselt numbers for heat transfer and diffusional processes; $Pr_f$, $Pr_{jk}$ - Prandtl numbers for heat transfer and diffusional processes; $\lambda_f$ - thermal conductivity of "frozen" mixture; $\nu$ - kinematic viscosity coefficient; a - thermal diffusivity coefficient; $D_k$ - kinematic diffusion coefficient; $D_k' = \rho D_k$ - dynamic diffusion coefficient; $\rho$ - mixture density; L - characteristic dimension; $h_k$ - specific enthalpy of each component; $x_{kct}$, $x_k$ - molar concentrations of each component near and away from the wall; $m_k$ - molecular weight of each component; $Q_{pf}$ - heat of the j-th reaction; $a_{kj}$ - stoichiometric factor; $D_{kf}$ - generalized diffusion coefficient; q - specific heat flow per unit surface from wall to heat carrier in a given cross-section; $T_{ct}$ - current (moving) temperature of channel wall; $T_r$ - mean calorimetric flow temperature in given section.

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# HEAT TRANSFER IN THE CHEMICALLY-REACTING SYSTEM $2NO_2 \rightleftarrows 2NO + O_2$ TAKING THE KINETICS OF THE CHEMICAL REACTION INTO ACCOUNT

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Previous studies of heat transfer in the presence of chemical reactions were concerned with systems in chemical equilibrium [1, 2, 5, 6]. When chemical reactions proceeding at a finite rate are present, the relations obtained for equilibrium flows are no longer satisfactory since they do not take the rate of the chemical process into account. The available analytic methods for computing heat transfer in a reacting flow are extremely complex and laborious even in the case of equilibrium systems. The calculation of heat transfer in chemically reactive media, taking the kinetics of chemical reactions into account, will require even more complex analytic methods, since the differential equations of heat transfer will include internal sources and mass flows of individual components, which exhibit a complex functional relationship.

For practical computations of heat-exchange units, designed for chemically-reactive heat carriers, a sufficient accuracy can be achieved by using empirical relations. For this reason, the aim of the theoretical and experimental study which we have undertaken is to obtain empirical relations for calculating the heat transfer coefficient in the case of a forced turbulent flow $2NO_2 \rightleftarrows 2NO+O_2$ in a tube, taking the kinetics of chemical reactions into account. In this case, a nonequilibrium chemical process is understood to represent a process in which the Maxwell-Boltzmann distribution of reacting particles is not disturbed to any significant extent, i.e. the system is in a static equilibrium. This is caused by the difference in the rates of the processes in the system, i.e. by the fact that equilibrium with respect to the motion of molecules (thermodynamic equilibrium) sets in much more rapidly than the equilibrium of chemical processes.

In this study, the method of integral analogs [4], widely used in the theory of similarity, has been utilized for the determination of a similarity criterion which takes the nonequilibrium nature of a chemical reaction into account. This method consists in reducing the equations of a physical process to a nondimensional form. If we analyze the analytic relations which describe heat and mass transfer in the presence of chemical reactions, we can easily obtain the following nondimensional complex:

$$N_h = \frac{I_k L}{\rho w}, \qquad (1)$$

which is a measure of the ratio between the velocity of the source or the mass flow rate of each component and the convective transfer rate. The criterion (number) $N_h$ is closely related in meaning to the criterion well-known in two-phase flow theory:

$$\frac{\mathrm{Nu}}{K\,\mathrm{Pe}} = \frac{q}{r \rho w}, \qquad (2)$$

which is a measure of the ratio between the phase conversion rate $q/r\rho$ and the flow rate of the given phase $\omega$.

In a flow in chemical equilibrium the gas composition is a single-valued function of the temperature (it is assumed that the pressure p is constant). In this case, the concentration gradients of individual components and, consequently, also the diffusion energy flows are uniquely dependent on the temperature gradient and can be determined without solving the diffusion equation. If the chemical reaction takes place at a finite rate, then not all molecules have a chance to react in view of the limited residence time in the channel. In this case, the concentration gradients of the components are determined by solving the diffusion equation and depend to a considerable extend on the profile of the axial component of the flow velocity $w_2$ along the radius. Variation of $w_z$ from zero near the channel wall to specific values at the boundary of the flow care results in a variation, within a very wide range, of the residence time of individual gas particles in a radial direction. For this reason, the nonequilibrium character of the chemical reaction will become more pronounced as one draws closer to the flow core, which the gas composition will vary from equilibrium values near the channel wall to values reflecting a considerable deviation of the gas composition from equilibrium values near the flow core.

The Nusselt number $Nu_{jk}$ for the diffusion process in a chemically-reactive flow, when one nonequilibrium reaction is present, is a function of the following numbers (criteria):

$$Nu_{jk\ \text{non eq.}} = f(Re,\ Pr_{jk},\ N_k). \tag{3}$$

The mass transfer coefficient $\beta_k$ in this case is equal to

$$\beta_k = \frac{Nu_{jk\,\text{non eq.}} D_k}{d_{\text{э}}} \tag{4}$$

The heat transfer coefficient $\alpha_e$ in a nonequilibrium flow was calculated from the relations given in [2]:

$$\begin{gathered}\alpha_e = \alpha_f + \alpha_r,\\ \alpha_f = \frac{Nu_f \lambda_f}{d_{\text{э}}}\\ \alpha_r = \frac{\sum\limits_{k=1}^{n} h_k \beta_k (x_{k\,\text{ст}} - x_k)}{T_{\text{ст}} - T_r}.\end{gathered} \tag{5}$$

of, if the calculation is carried out in terms of the thermal effects of the reaction, from the formula

$$\alpha_r = \sum_{j=1}^{k} \frac{Q_{pj} \beta_j}{a_{ij} m_j} \frac{x_{j\text{ст}} - x_j}{T_{\text{ст}} - T_r}.$$

The specific heat flow, q, per unit surface in the given section from the wall to the heat carrier is determined by the equations

$$q = \alpha_e (T_{\text{ст}} - T_{\text{г}}) \tag{6}$$

or

$$q = q_l + q_r,$$

where

$$q_l = \alpha_l (T_{\text{ст}} - T_{\text{г}}); \quad q_r = \sum_{k=1}^{n} h_k \beta_k (x_{k\,\text{ст}} - x_k) \tag{7}$$

or

$$q_r = \sum_{j=1}^{n} \frac{Q_{pj} \beta_j}{a_{ij} m_j} (x_{j\text{ст}} - x_j).$$

The thermophysical properties of the chemically-reactive system $2NO_2 \rightleftarrows 2NO + O_2$, necessary for calculating $\alpha_e$ and q, were determined in the same manner as in [2], except that the composition of the mixture was determined with the aid of equations taking the kinetics of the chemical reaction into account.

The method, described above, for calculating the heat transfer coefficient in a chemical reaction was used to generalize experimental data on heat transfer during heating for the system $2NO_2 \rightleftarrows 2NO + O_2$. Tests aimed at studying heat transfer in the case of a forced turbulent flow in a tube for the system $2NO_2 \rightleftarrows 2NO + O_2$ were carried out at the Institute of Nuclear Power Engineering of the Academy of Sciences of the Belorussian SSR in the range of gas temperatures of 140-550°C, pressures of 10-60 atm. abs. and Reynolds number Re = $3 \cdot 10^4 - 3 \cdot 10^5$. The test section and experimental method used in this case were the same as those used in the experimental study of heat transfer in the equilibrium system $N_2O_4 \rightleftarrows 2NO_2$ [2].

In order to calculate the temperature profiles of the reacting flow along the length of the channel from the equations given in [3], it is necessary to know the initial conditions with respect to the flow temperature T(z = 0) and concentration of the component $O_2 \rho_{40} (z = 0)$. Since the concentration of the $O_2$ component was not determined in this case, tests aimed at studying heat transfer in the system $2NO_2 \rightleftarrows 2NO + O_2$ were carried out under the condition that a binary mixture $N_2O_4 \rightleftarrows 2NO_2$, was fed at the inlet of the test section, while the reaction $2NO_2 \rightleftarrows 2NO + O_2$ took place already far away from the initial section.

From the analysis of experimental heat transfer data in the case of forced turbulent flow in a tube we obtained the following criterial dependence for the determining component:

$$Nu_{j4\,\text{non eq.}} = Nu_{j4} N_{k4}, \tag{8}$$

wher $Nu_{j4}$ is the Nusselt number defined in terms of the critial dependence proposed by

M. A. Mikheyev

$$\mathrm{Nu}_{jk} = 0{,}021\,\mathrm{Re}^{0{,}8}\,\mathrm{Pr}_{jk}^{0{,}43}\,e_T; \qquad (9)$$

$e_T$ is a coefficient characterizing the variability of the physical parameters.

As recommended by S. S. Kutateladze

$$e_T = \left(\frac{T_{cr}}{T_r}\right)^{-0{,}55}. \qquad 10)$$

The criterion of chemical nonequilibrium was defined as

$$N_{k4} = \frac{l_4 z}{\rho w}, \qquad (11)$$

where z is the moving coordinate;

$$l_4 = \frac{m_4}{m_2^2}\,K_{\text{СПА}}(\rho\rho_{20})^2; \quad 0 \leqslant N_4 \leqslant 1.$$

In case $N_4 > 1$, chemical equilibrium takes place and the "reaction" component $\alpha_r$ is calculated by the method described in [2] for equilibrium systems.

The composition of the mixture in the flow was determined with the aid of equations obtained in [3], taking the kinetics of the chemical reaction into account. The molar concentrations of components at the wall, $x_{hct}$, were determined from the wall temperature in the assumption that chemical equilibrium is established here ($w_{\text{ст}} = 0$). This assumption, which is valid for equilibrium systems, may not be fulfilled when the rate of the chemical reaction is finite. The decisive factor is the ratio of the chemical relaxation and diffusion times. However, even in this case, the assumption of a chemical equilibrium at the wall will not result in a large error, since under conditions close to a "frozen" flow the contribution made by the "reaction" component is infinitely small: $\alpha_r \approx 0$ since $N_k \approx 0$. The contribution made by $\alpha_r$ becomes significant when the number $N_k$ increases. In this case, the rate of the chemical reaction is comparable with the rate of convective transfer. The chemical reaction rate will play a decisive role in regard to diffusion transfer in the layer located near the wall and also in the region where temperatures near the channel wall are higher than in the flow during heating, and the composition of the mixture will be close to the equilibrium composition.

Calculated and experimental values of the "effective" heat transfer coefficient $\alpha_e$ are given in the table.

The experimental study of heat transfer in the second stage of the reaction was carried out with residence times of the gas in the heated channel of 0.01–0.03 sec.

Comparison of calculated and experimental data shows a satisfactory agreement between these data and also that the proposed empirical relations can be used in describing

Table 1. Comparison of Calculated "Effective" Heat Transfer Coefficient $\alpha_e$ With Experimental Results for the $2NO_2 \rightleftarrows 2NO + O_2$ System Taking the Kinetics of the Chemical Reactions Into Account

| Наименование 1) | 2) Номер опыта | | | | | | |
|---|---|---|---|---|---|---|---|
| | 3) 71 ($P = 23$ ата), участки | | | | 4) 46 ($P = 33,5$ ата), участки | | |
| | 2 | 3 | 5 | 6 | 3 | 5 | 6 |
| 8) Температура стенки, °K | 632 | 710 | 802 | 802 | 891 | 921 | 942 |
| 9) Температура газа, °K | 475 | 520 | 659 | 704 | 671 | 760 | 781 |
| 10) Число $Re\cdot10^{-4}$ | 9,47 | 8,72 | 7,21 | 6,84 | 6,46 | 5,80 | 5,66 |
| 11) Число $N_{O_2}$ | 0 | 0 | 0,012 | 0,045 | 0,023 | 0,193 | 0,262 |
| 12) Расчетные значения $\alpha_f$ | 2087 | 2146 | 2539 | 2705 | 2270 | 2490 | 2516 |
| 13) Расчетные значения $\alpha_{rI}$ | 309 | 75 | 0 | 0 | 0 | 0 | 0 |
| 14) Расчетные значения $\alpha_{rII}$ | 0 | 0 | 65 | 620 | 156 | 1453 | 1737 |
| 15) Расчетные значения $\alpha_e$ | 2396 | 2222 | 2604 | 3325 | 2426 | 3943 | 4253 |
| 16) Экспериментальные значения $\alpha_e$ | 2306 | 1906 | 2523 | 3684 | 2688 | 3948 | 3939 |

| Наименование 1) | 2) Номер опыта | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | 5) 30 ($P=55,5$ ата), участки | | | 6) 31 ($P=57,5$ ата), участки | | | 7) 35 ($P=42$ ата), участки | | |
| | 3 | 5 | 6 | 3 | 5 | 6 | 3 | 5 | 6 |
| 8) Температура стенки, °K | 804 | 874 | 878 | 928 | 950 | 945 | 684 | 802 | 812 |
| 9) Температура газа, °K | 557 | 709 | 726 | 646 | 743 | 766 | 512 | 642 | 656 |
| 10) Число $Re\cdot10^{-5}$ | 1,45 | 1,20 | 1,17 | 1,27 | 1,13 | 1,10 | 1,56 | 1,30 | 1,23 |
| 11) Число $N_{O_2}$ | 0,0007 | 0,126 | 0,180 | 0,015 | 0,182 | 0,278 | 0 | 0,014 | 0,0535 |
| 12) Расчетные значения $\alpha_f$ | 3446 | 4142 | 4213 | 3590 | 3970 | 4090 | 3438 | 3937 | 4167 |
| 13) Расчетные значения $\alpha_{rI}$ | 86 | 0 | 0 | 12 | 0 | 0 | 290 | 13 | 0 |
| 14) Расчетные значения $\alpha_{rII}$ | 5 | 1563 | 2118 | 120 | 1705 | 2560 | 0 | 155 | 815 |
| 15) Расчетные значения $\alpha_e$ | 3537 | 5705 | 6331 | 3722 | 5675 | 6650 | 3728 | 4105 | 4982 |
| 16) Экспериментальные значения $\alpha_e$ | 3984 | 6001 | 6521 | 3910 | 5310 | 6140 | 3842 | 4144 | 5276 |

KEY: 1) Item; 2) No. of test; 3) 71 (P = 23 atm. abs.), sectors; 4) 46 P = 33.5 atm. abs.), sectors; 5) 50 (P = 55.5 atm. abs.), sectors; 6) 31 (P = 57.5 atm. abs.), sectors; 7) 35 (P = 42 atm. abs.), sectors; 8) Wall temperature, °K; 9) Gas temperature, °K; 10) Rena No. $Re \cdot 10^4$; 11) No. $N_{O2}$; 12) Calculated values $\alpha_f$; 13) Calculated values $\alpha_{rI}$; 14) Calculated values $\alpha_{rII}$; 15) Calculated Values $\alpha_e$; 16) Experimental values $\alpha_e$.

the mechanism of heat transfer in a chemically reacting system with allowance for the actual finite rates of chemical reactions.

In the above figure, a comparison is given in criterial form of calculated and experimental heat transfer data in the system $2NO_2 \rightleftarrows 2NO+O_2$ for the Re number range of $3\cdot 10^4$ - $2\cdot 10^5$. Analysis of the results obtained in a study of heat transfer in the case of forced turbulent flow in a circular tube shows that, even at short residence times of the gas in the heated channel, heat transfer in the form of chemical enthalpy due to concentration diffusion is high and that a 1.5-2-fold increase of the heat transfer coefficient is achieved as compared to heat transfer data for an inert gas ($N_2$, $CO_2$ and others).

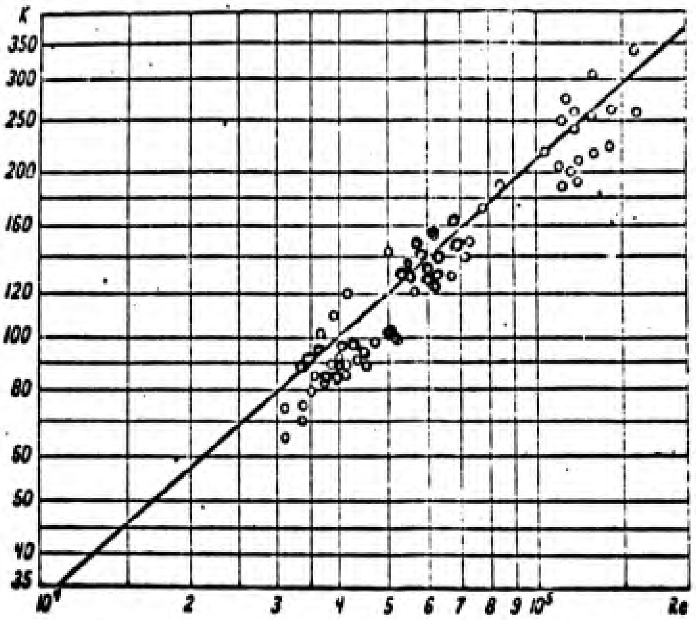

Fig. 1. Heat transfer during forced flow of the chemically nonequilibrium flow ($2NO_2 \rightleftarrows 2NO + O_2$) in a tube.

$$K = Nu_f Pr_f^{-0.43} \left(\frac{T_{ст}}{T_г}\right)^{0.55} = Nu_{jk} Pr_{jk}^{-0.43} N_k^{-1} \left(\frac{T_{ст}}{T_г}\right)^{0.55}$$

The error in the experimental data on heat transfer coefficients in the studied temperature and pressure range amounts to ± 15%. The experimental accuracy can be substantially improved after more reliable experimental data on the heat capacity of liquid nitrogen tetroxide have been obtained, since errors in the calorimetric determination of the flow rate of $N_2O_4$ constitute the major portion of the experimental error.

On the basis of the experimental and theoretical studies which have been carried out, it is possible to recommend the criterial relations proposed here for the computation of heat transfer in the chemically-reacting system $2NO_2 \rightleftarrows 2NO + O_2$, with allowance for the kinetics of chemical reactions, in the temperature range of 140-700°C, pressure range of 1-60 atm. abs., and Reynolds number range of $10^4 - 3 \cdot 10^5$.

In conclusion, the authors wish to thank Academician A. K. Krasin (Acad. Sci. Belorussian SSR) for his constant concern and interest in this work, and also their divisional colleagues for active participation in the tests, calculations on an electronic digital computer, and discussion of the results of this work.

## NOTATION

$\alpha_e$ - "effective" heat transfer coefficient, kcal/m$^2$-hr-$^\circ$K; $\alpha_f$, $\alpha_r$ - "frozen" and "reaction" component of heat transfer coefficient; $Nu_f$, $Nu_{jk}$ - Nu numbers for the heat transfer and diffusion process, respectively; $Pr_{jk}$ - Pr no. for the diffusion process;

$\lambda_f$ - thermal conductivity for the "frozen" mixture; $D_k$ - dynamic diffusion coefficient; L - characteristic length; $h_k$ - specific enthalpy for each component; $x_{kct}$, $x_k$ - molar concentration of each component at the wall and from the wall; $m_k$ – molecular weight of each component; $Q_{pj}$ - thermal effect of the j-th reaction; $a_{jk}$ - stochiometric coefficient; p - mixture density.

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