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OPTIMIZING THE PARAMETERS OF POWER PLANTS USING DISSOCIATING WORKING MEDIA

by

M. A. Bazhin, V. P. Bubnov, et al.

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В в	*В в*	V, v	Т т	*Т т*	T, t
Г г	*Г г*	G, g	У у	*У у*	U, u
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О о	*О о*	O, o	Ю ю	*Ю ю*	Yu, yu
П п	*П п*	P, p	Я я	*Я я*	Ya, ya

* ye initially, after vowels, and after ъ, ь; e elsewhere. When written as ё in Russian, transliterate as yё or ё. The use of diacritical marks is preferred, but such marks may be omitted when expediency dictates.

FOLLOWING ARE THE CORRESPONDING RUSSIAN AND ENGLISH DESIGNATIONS OF THE TRIGONOMETRIC FUNCTIONS

Russian	English
sin	sin
cos	cos
tg	tan
ctg	cot
sec	sec
cosec	csc
sh	sinh
ch	cosh
th	tanh
cth	coth
sch	sech
csch	csch
arc sin	$\sin^{-1}$
arc cos	$\cos^{-1}$
arc tg	$\tan^{-1}$
arc ctg	$\cot^{-1}$
arc sec	$\sec^{-1}$
arc cosec	$\csc^{-1}$
arc sh	$\sinh^{-1}$
arc ch	$\cosh^{-1}$
arc th	$\tanh^{-1}$
arc cth	$\coth^{-1}$
arc sch	sech^{-1}
arc csch	csch^{-1}

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rot	curl
lg	log

In this book we present features of calculating the thermodynamic functions of chemically reacting systems used in cycle calculation. We calculate the thermodynamic diagrams of chemically reacting systems. We examine possible schemes for thermodynamic cycles in chemically reacting systems. We give a method of calculating the regenerator effectiveness. We examine the influence of the basic parameters on the efficiency of power-plant cycles. We present the thermodynamic optimization of gas and gas-liquid cycles.

The book contains 6 tables, 35 figures, and 38 references.

The book is designed for scientific workers and engineers studying questions of the thermodynamic analysis and selection of working media for power plants.

INTRODUCTION

The problem of a working medium/coolant at the present time is one of the pressing problems of both thermal and atomic power engineering. New working media and coolants are being sought both for temperatures and pressures which have already been realized in power engineering as well as for future plants. This work is devoted to studies of the thermodynamic cycles using chemically reacting working media.

The development of fixed and transportable power engineering, including nuclear, is based mainly on the use of steam as the working medium. Recent technical and economic studies have shown that in thermodynamic cycles using steam, the economically optimum parameters and limiting efficiencies have been achieved [1-4]. In addition, the physicochemical properties of steam are such that there are considerable limitations on the unit power of single-shaft turbine units [4].

In this regard, at the present time there is an urgent need for finding new coolants and working media. This problem is particularly pressing for atomic power engineering with nuclear reactors using fast neutrons [5-7].

One of the ways for solving the given problem might be the use, as working media and coolants, of chemically reacting mixtures in which there are reversible chemical reactions accompanied by the heat effects of chemical reactions and a change in the number of moles [8-12]. An increase in the number of moles during heating and a decrease during cooling result in increased efficiency of the thermodynamic cycle, while the presence of the heat of chemical reactions assures high thermophysical properties of the mixture due to transfer of a significant quantity of heat by concentration diffusion [8].

The class of chemically reacting mixtures is large; certain of the mixtures examined by us are given in Table 1.

Of the large class of chemically reacting mixtures in which reactions occur with an increase in the number of moles and the absorption of heat during dissociation, the chemically reacting mixture $N_2O_4 \rightleftharpoons 2NO_2 \rightleftharpoons 2NO + O_2$ has been studied most completely.

To study the efficiency of thermodynamic cycles we must know the change in thermodynamic properties over a broad range of temperatures and pressures. There have been practically no methods developed for calculating the thermodynamic properties of chemically reacting mixtures [8]. The occurrence of chemical reactions, however, imposes its own specific nature on the calculation of thermodynamic properties; therefore, the obtained thermodynamic dependences, from the assumption of constant composition, cannot always be used when calculating the properties of chemically reacting mixtures. The specific nature of the behavior of the thermodynamic properties imposes its features in the calculation of the parameters of thermodynamic cycles using chemically reacting mixtures as the working medium.

In this book we present the methodology for calculating the thermodynamic properties of chemically reacting mixtures and thermodynamic cycles using chemically reacting mixtures as the working media.

The book was written using data from research at the Institute of Nuclear Power Engineering of the Academy of Sciences of the Belorussian SSR during the period from 1964 thru 1969.

Table 1. Chemically reacting mixtures.

(1) Диссоциирующие системы (ж) = liquid	(2) Коэффициент увеличения газовой постоянной	(3) Температура диапазона реакции, °K	(4) Тепловой эффект химической реакции, ккал/моль
$N_2O_4 \rightleftarrows 2NO_2$	2,0	300—450	13,7
$2NO_2 \rightleftarrows 2NO+O_2$	1,5	400—1300	27.0
$N_2O_4 \rightleftarrows 2NO_2 \rightleftarrows 2NO+O_2$	3,0	300—1300	13,7/27
$Al_2Cl_6 \rightleftarrows 2AlCl_3$	2,0	475—1300	29,8
$Al_2Br_6 \rightleftarrows 2AlBr_3$	2,0	600—1600	30,0
$Al_2I_6 \rightleftarrows 2AlI_3$	2,0	500—1600	26,4
$2NOBr \rightleftarrows 2NO+Br_2$	1,5	300—800	—
$2NOCl \rightleftarrows 2NO+Cl_2$	1,5	300—1200	—
$HgCl_2 \rightleftarrows Hg+Cl_2 \rightleftarrows Hg+2Cl$	3,0	1300—3000	—
$HgI_2 \rightleftarrows Hg+I_2 \rightleftarrows Hg+2I$	3,0	900—1500	—
$I_2 \rightleftarrows 2I$	2,0	700—1700	—
$CH_4+2H_2O \rightleftarrows CO_2+4H_2$	2,0	700—1500	—
$CH_4+CO_2 \rightleftarrows 2CO+2H_2$	2,0	600—1600	—
$C_2H_6 \rightleftarrows C_2H_4+H_2$	2,0	700—1500	—
$Al_2Cl_6+4Al(ж) \rightleftarrows 6AlCl$	6,0	930—1300	263,8
$Al_2Br_6+4Al(ж) \rightleftarrows 6AlBr$	6,0	930—1600	282,4
$Al_2I_6+4Al(ж) \rightleftarrows 6AlI$	6,0	930—1600	196,4
$HgCl_2+Hg(ж) \rightleftarrows 2HgCl$	2,0	550—950	70,4
$HgBr_2+Hg(ж) \rightleftarrows 2HgBr$	2,0	520—950	63,7
$SnCl_2+Sn(ж) \rightleftarrows 2SnCl$	2,0	780—1500	208,0
$SnBr_2+Sn(ж) \rightleftarrows 2SnBr$	2,0	550—1500	178,2
$SnI_2+Sn(ж) \rightleftarrows 2SnI$	2,0	650—1000	—
$Fe(CO)_5 \rightleftarrows Fe+5CO$	5,0	350—1200	55,7
$Ni(CO)_4 \rightleftarrows Ni+4CO$	4,0	320—1000	70,0
$SnCl_4+3Sn(ж) \rightleftarrows 4SnCl$	4,0	500—1200	425,0
$SnBr_4+3Sn(ж) \rightleftarrows 4SnBr$	4,0	500—1200	372,0
$SnI_4+3Sn(ж) \rightleftarrows 4SnI$	4,0	500—1200	—
$Hg_2Cl_4 \rightleftarrows 2HgCl_2$	2,0	—	1,9
$Hg_2Br_4 \rightleftarrows 2HgBr_2$	2,0	—	1,9
$Hg_2I_4 \rightleftarrows 2HgI_2$	2,0	—	1,9
$(HF)_6 \rightleftarrows 6HF$	6,0	—	—
$S_8 \rightleftarrows 4S_2$	4,0	700—1200	—

KEY: (1) Dissociating systems, (2) Gas-constant increase factor, (3) Temperature of the reaction range, °K, (4) Thermal effect of chemical reaction, kcal/mole.

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CHAPTER I

THE THERMODYNAMIC PROPERTIES OF CHEMICALLY REACTING SYSTEMS

1. CALCULATING THE THERMODYNAMIC PROPERTIES OF MIXTURES OF REAL GASES

Let us examine the following basic approaches to calculation of the thermodynamic properties of gas mixtures [13]. Here we use the term "partial pressure" of the gas in the mixture to designate the product of its molar fraction in the mixture times the total pressure of the mixture; we use the term "equilibrium pressure" as the pressure of this gas in isothermal equilibrium with a mixture through a diaphragm which can be penetrated only by this gas.

The ideal-gas approach. In accordance with these definitions, in the ideal-gas approach we assume that 1) the equilibrium pressure of the gas in the mixture is equal to its partial pressure, and 2) the equation of state of the mixture is as follow $pV = \Sigma n_i RT$. In place of the second assumption we can simply require that the internal energy of the mixture component be a function only of temperature. The relationships for the thermodynamic properties, obtained using this approach, are well-known.

Now let us derive formulas for calculating the thermodynamic properties of pure gases using a generalized method of passage to the limit, since these formulas are used in the other approaches.

When deriving the formulas, let us direct our attention only to enthalpy and entropy.

The generalized method of passage to the limit for pure gases. Let us examine two regions of pressure:

a) low pressure, in which terms of the order of p^2 are negligibly small compared with terms of the order of p or one;

b) very low pressures, in which terms of the order of p are negligibly slight compared with one.

Let us assume that at all temperatures the product of volume times pressure for a fixed mass of a real gas can be represented by the following expression with constant temperature in the region of low pressures:

$$pV = F(T,\ m) + A(T,\ m)p + O(p^2), \tag{1.1}$$

where F(T, m) and A(T, m) depend for the given gas only on temperature and mass, while A(T, m) and its derivatives with respect to temperature are limited; $O(p^2)$ are terms of the order of p^2. Further let us assume that at all temperatures the enthalpy of a fixed mass of real gas can be represented by the following expression with constant temperature in the low-pressure region:

$$H = f(T,\ m) + B(T,\ m)p + O(p^2). \tag{1.2}$$

where f(T, m) and B(T, m) depend for the given gas only on the temperature and mass, while B and its temperature derivatives are limited.

Substituting equations (1.1) and (1.2) into the relationship

$$\left(\frac{\partial H}{\partial p}\right)_T = V - T\left(\frac{\partial V}{\partial T}\right)_p, \tag{1.3}$$

we get

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

This equation is valid provided

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

Integration of this relationship with constant mass gives

$$F=r(m)T, \tag{1.4}$$

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

Considering this, we obtain the following from equation (1.1):

$$pV=r(m)T+A(T,\ m)p+O(p^2), \tag{1.5}$$

while for the region of very low pressures

$$p^*V^*/rT=1. \tag{1.6}$$

Since volume is an extensive magnitude, if we replace V in equation (1.6) by V/m, r becomes a magnitude characteristic for each gas. If, however, the mass of the given gas is expressed in moles, r will not depend on the nature of the gas and we will designate it by R. Then

$$pV=nRT+n\beta p/RT+O(p^2), \tag{1.7}$$

where n is the number of moles in volume V, β is a pure temperature function.

When integrating the differential relationships for enthalpy and entropy let us select the following path from the point of the normal state (p_0, T_0) to an arbitrary point (p, T), changing:

1) the pressure from p_0 to p^* with the temperature constant and equal to T_0;

2) the temperature from T_0 to T with constant pressure p^*;

3) the pressure from p* to p with constant temperature T.

From the ordinary differential relationships we get

$$H(p,T)-H(p_0,T_0)=\int_{T_0p_0}^{p^*}\left[V-T\left(\frac{\partial V}{\partial T}\right)_p\right]dp+\int_{p^*T_0}^{T}nc_p^*dT+$$

$$+\int_{Tp^*}^{p}\left[V-T\left(\frac{\partial V}{\partial T}\right)_p\right]dp; \qquad (1.8)$$

$$S(p,T)-S(p_0,T_0)=-\int_{T_0p_0}^{p^*}\left(\frac{\partial V}{\partial T}\right)_p dp+\int_{p^*T_0}^{T}\frac{nc_p^*}{T}dT-$$

$$-\int_{Tp^*}^{p}\left(\frac{\partial V}{\partial T}\right)_p dp. \qquad (1.9)$$

In order that the definite pressure integrals in formula (1.9) not diverge as the limit of p* tends toward zero, let us add the term nR/p to the integrand and subtract nR ln p/p_0 from all terms. We get

$$S(p,T)-S(p_0,T_0)=\int_{T_0p_0}^{p^*}\left[\frac{nR}{p}-\left(\frac{\partial V}{\partial T}\right)_p\right]dp+$$

$$+\int_{p^*T_0}^{T}\frac{nc_p^*}{T}dT+\int_{Tp^*}^{p}\left[\frac{nR}{p}-\left(\frac{\partial V}{\partial T}\right)_p\right]dp-nR\ln p/p_0. \qquad (1.10)$$

Let

$$h^*=h_0^0+\int_{T_0}^{T}c_p^*dT;\ nh_0^0=H(p_0,T_0)+$$

$$+\int_{T_0p_0}^{p^*}\left[V-T\left(\frac{\partial V}{\partial T}\right)_p\right]dp; \qquad (1.11)$$

$$S^*=S_0^0+\int_{T_0}^{T}\frac{c_p^*}{T}dT;\quad nS_0^0=S(p_0,T_0)+$$

$$+\int_{T_0p_0}^{p^*}\left[\frac{nR}{p}-\left(\frac{\partial V}{\partial T}\right)_p\right]dp+nR\ln p/p_0. \qquad (1.12)$$

From equation (1.2) and the relationship $c_p = \left(\frac{\partial H}{\partial T}\right)_p$ we find that

$$c_p^* = \left(\frac{\partial f}{\partial T}\right)_m + O(p) \tag{1.13}$$

and, consequently, c_p^* is a function only of temperature.

From equation (1.7) we find that

$$\lim_{p^*\to 0}\int_{p^*}^{0}\left[V - T\left(\frac{\partial V}{\partial T}\right)_p\right]dp = \lim_{p^*\to 0}\int_{p^*}^{0}\left[\frac{nR}{p} - \left(\frac{\partial V}{\partial T}\right)_p\right]dp = 0. \tag{1.14}$$

The definite pressure integrals in expressions (1.11) and (1.12) for normal pressure are small compared with $H(p_0, T_0)$ and $S(p_0, T_0)$, and we disregard them.

Considering equalities (1.11)-(1.14), we obtain the following expression from equations (1.8) and (1.10):

$$H(p, T) = nh^0 + \int_0^p\left[V - T\left(\frac{\partial V}{\partial T}\right)_p\right]dp; \tag{1.15}$$

$$S(p, T) = nS^0 + \int_0^p\left[\frac{nR}{p} - \left(\frac{\partial V}{\partial T}\right)_p\right]dp - nR\ln p, \tag{1.16}$$

where

$$nh^0 = H(p_0, T_0) + n\int_{T_0}^{T} c_p^* dT,$$

$$nS^0 = S(p_0, T_0) + n\int_{T_0}^{T}\frac{c_p^*}{T}\,dT + nR\ln p_0.$$

The equations for calculating enthalpy and entropy in coordinates T, V are as follows:

$$H = \int_V^{\infty}\left[p - T\left(\frac{\partial p}{\partial T}\right)_V\right]dV + pV + ne^0; \tag{1.17}$$

$$S=\int_{V}^{\infty}\left[\frac{nR}{V}-\left(\frac{\partial p}{\partial T}\right)_{V}\right]dV+nR\ln\frac{V}{nRT}+nS^{0}, \tag{1.18}$$

where

$$e^{0}=e_{0}^{0}+\int_{T_0}^{T}c_V^{0}\,dT,\quad e_0^{0}=h_0^{0}-RT_0,$$

$$S^{0}=S_0^{0}+\int_{T_0}^{T}\frac{c_V^{0}}{T}\,dT+R\ln p/p_0$$

The Gibbs-Dalton law. The Gibbs-Dalton law states that the total pressure of a mixture of various gases is equal to the sum of the pressures which these gases would have if they each existed individually, at the mixture temperature and with those chemical potentials which they have in the mixture. This statement contains an idea of equilibrium, essential and necessary for general thermodynamic studies of gas mixtures. Obviously, the various gases having those chemical potentials which they had in the mixture and being at the mixture temperature will be in equilibrium with the mixture through the diaphragm which is permeable only for the given gas, while the pressure of each such gas is the equilibrium pressure.

From the Gibbs-Dalton law it follows that the concentration and number of moles of a pure gas in equilibrium with a mixture through a diaphragm permeable only to it are the same as in the mixture, hence

$$p=\sum p_{\text{см}} \tag{1.19}$$

$$H=\sum H_{\text{см}} \tag{1.20}$$

$$S=\sum S_{\text{см}} \tag{1.21}$$

Equation (1.19) is the ordinary statement of the Dalton law. The Dalton law follows from the Gibbs-Dalton law, but the inverse is not true, since the idea of equilibrium is lacking in the formulation of the Dalton law.

The Gibbs-Dalton law leads to total solution of the problem of determining the thermodynamic properties of mixtures of gases from information on the behavior of the pure gases of which the mixture consists.

Having substituted into equations (1.20) and (1.21) the expressions for the enthalpy and entropy of pure gases (1.17) and (1.18), we obtain the following for the enthalpy and entropy of a gas mixture subject to the Gibbs-Dalton law:

$$H=\sum\left\{\int_V^{\infty}\left[p_{\text{к}}-T\left(\frac{\partial p_{\text{к}}}{\partial T}\right)_{V_{\text{к}}}\right]dV_{\text{к}}+p_{\text{к}}V+ne_{\text{к}}^{0}\right\}; \qquad (1.22)$$

$$S=\sum\left\{\int_V^{\infty}\left[\frac{n_{\text{к}}R}{V_{\text{к}}}-\left(\frac{\partial p_{\text{к}}}{\partial T}\right)_{V_{\text{к}}}\right]dV_{\text{к}}+\right.$$

$$\left.+n_{\text{к}}R\ln\frac{V}{n_{\text{к}}RT}+n_{\text{к}}S_{\text{к}}^{0}.\right. \qquad (1.23)$$

The Gibbs-Dalton law leads to the following expression for the law of mass action:

$$\ln\frac{K_p}{K_p^{\circ}}=-\frac{1}{RT}\sum\left\{v_{\text{к}}\left[\int_V^{\infty}\left[\left(\frac{\partial p_{\text{к}}}{\partial T}\right)_{V_{\text{к}}}-\right.\right.\right.$$

$$\left.\left.\left.-\frac{RT}{V_{\text{к}}}\right]dV_{\text{к}}\right]\right\}+\sum v_i\ln\frac{pV}{\Sigma n_i RT}; \qquad (1.24)$$

$$\ln K_p^{\circ}=-\frac{1}{RT}\sum\left[v_{\text{к}}\left(e_{\text{к}}^{0}+RT-TS_{\text{к}}^{0}\right)\right]. \qquad (1.25)$$

Calculation of K_p for given p and T of the mixture is performed by the method of successive approximations. First we give $K_p = K_p^*$ and determine the composition of the mixture. The mixture composition allows us to estimate the right-hand side of the equation (1.24) and obtain a second approximation of K_p. The process is repeated until the composition of the mixture becomes constant.

The Lewis-Randall rule. The Lewis-Randall rule states that the fugacity f_1 of a gas in a mixture is equal to the product of its molar fraction in the mixture times the fugacity $f_{p\text{к}}$ of this pure gas with total pressure and temperature of the mixture:

$$f_i = x_i f_{p\kappa} \tag{1.26}$$

The fugacity of a pure gas is defined by the relationship

$$\mu = RT \ln f + \psi(T), \ \lim_{p \to 0} \frac{f}{p} = 1. \tag{1.27}$$

Let us examine a pure gas in isothermal equilibrium with a mixture through a diaphragm which is permeable only to this gas. The chemical potential of a gas in a mixture is μ_i, while that of a pure gas is μ_κ, and $\mu_i = \mu_\kappa$. According to the Lewis-Randall rule μ_κ and, consequently, μ_i can be calculated by substituting equation (1.26) into (1.27):

$$\mu_i = RT \ln f_{p\kappa} x_i + \psi_\kappa(T). \tag{1.28}$$

Equation (1.28) can be rewritten as follows:

$$\mu_i = \mu_{p\kappa} + RT \ln x_i, \tag{1.29}$$

considering that $RT \ln f_{p\kappa} + \psi_\kappa(T) = \mu_{p\kappa}$. Let us differentiate equation (1.29) with respect to p and T under the following conditions which result from the Lewis-Randall rule: the temperature of each pure gas is equal to the temperature of the mixture; the pressure of each pure gas is equal to the pressure of the mixture; $n_i = n_\kappa$.
We get

$$\left(\frac{\partial \mu_i}{\partial p}\right)_{T,n} = \left(\frac{\partial \mu_{p\kappa}}{\partial p}\right)_T; \tag{1.30}$$

$$\left(\frac{\partial \mu_i}{\partial T}\right)_{p,n} = \left(\frac{\partial \mu_{p\kappa}}{\partial T}\right)_p + R \ln x_i. \tag{1.31}$$

From the general theory of thermodynamics we know that the left sides of equations (1.30) and (1.31) are equal, respectively, to the partial molar volume and the partial molar entropy taken with a minus sign for the i-th gas in the mixture, while the right sides are equal to the corresponding molar values for a pure gas.

Thus,

$$\left(\frac{\partial V}{\partial n_i}\right)_{p,T,n} = \frac{V_{p\text{к}}}{n_{\text{к}}}; \tag{1.32}$$

$$\left(\frac{\partial S}{\partial n_i}\right)_{p,T,n} = \frac{S_{p\text{к}}}{n_{\text{к}}} - R\ln x_i. \tag{1.33}$$

From the Euler theorem on homogeneous functions

$$V = \sum n_i \left(\frac{\partial V}{\partial n_i}\right)_{p,T,n} = \sum V_{p\text{к}}; \tag{1.34}$$

$$S = \sum n_i \left(\frac{\partial S}{\partial n_i}\right)_{p,T,n} = \sum S_{p\text{к}} - \sum n_i R\ln x_i. \tag{1.35}$$

Using relationships from general thermodynamics, we get

$$H = \sum H_{p\text{к}}. \tag{1.36}$$

Using equations (1.15) and (1.16), we finally obtain the following expressions for the enthalpy and entropy of a gas mixture subject to the Lewis-Randall rule:

$$H = \sum\left\{\int_0^p \left[V_{\text{к}} - T\left(\frac{\partial V_{\text{к}}}{\partial T}\right)_{p_{\text{к}}}\right] dp_{\text{к}} + nh_{\text{к}}^0\right\}; \tag{1.36a}$$

$$S = \sum\left\{\int_0^p \left[\frac{n_{\text{к}}R}{p_{\text{к}}} - \left(\frac{\partial V_{\text{к}}}{\partial T}\right)_{p_{\text{к}}}\right] dp_{\text{к}} + n_{\text{к}}S_{\text{к}}^0\right\} - \sum H_i R\ln px_i. \tag{1.37}$$

However, the expression for the law of mass action is as follows:

$$\ln\frac{K_p}{K_p^0} = -\frac{1}{RT}\sum\left\{\nu_{\text{к}}\left[\int_0^p \left[\frac{V_{\text{к}}}{n_{\text{к}}} - \frac{RT}{p_{\text{к}}}\right] dp_{\text{к}}\right]\right\}. \tag{1.38}$$

The generalized method of passage to the limit for gas mixtures. The generalized method of passage to the limit is based on the following assumption on the behavior of gas mixtures: at all temperatures the ratio of the equilibrium pressure of each gas in the mixture to its partial pressure can be represented in the low-pressure region by the expression

$$\frac{p_{e\text{к}}}{px_i} = 1 + D_i(T,\, x_1,\, x_2,\, \ldots)p + O(p^2), \tag{1.39}$$

where D_i depends only on the temperature and composition of the mixture, and its derivatives with respect to T, n_1, n_2, ... are limited. Let us examine a gas mixture consisting of Σn_i moles and "κ" systems. Let us assume in all measurements that the temperature of each pure gas is equal to the temperature of the mixture and the volume of each pure gas is equal to the volume of the mixture, $\mu_i = \mu_\kappa$.

Let us also assume that T, μ_1, μ_2, ... are independent variables for the gas mixture, T and μ_κ are independent variables for each pure gas. Then we rewrite equation (1.39) as follows:

$$p_{e\kappa} = p x_i (1 + D_i p). \tag{1.40}$$

From this

$$\sum p_{e\kappa} = p (1 + D_m p), \tag{1.41}$$

where $D_m = \Sigma x_i D_i$.

Differentiating equation (1.41) first with respect to one of the μ's with T and the remaining μ's constant, and then with respect to T with all μ's constant, we obtain the following for the low-pressure region:

$$\left(\frac{\partial p_{e\kappa}}{\partial \mu_\kappa}\right)_T = \left(\frac{\partial p}{\partial \mu_i}\right)_{T,\mu} (1 + 2D_m p); \tag{1.42}$$

$$\sum \left(\frac{\partial p_{e\kappa}}{\partial T}\right)_{\mu_\kappa} = \left(\frac{\partial p}{\partial T}\right)_{\mu} (1 + 2D_m p). \tag{1.43}$$

From equation (1.42) we have

$$\frac{n_{e\kappa}}{V} = \frac{n_i}{V} (1 + 2D_m p), \tag{1.44}$$

while from equation (1.43) we derive

$$\sum S_{e\kappa} = S (1 + 2D_m p). \tag{1.45}$$

Dividing expression (1.40) by equation (1.44) we get

$$\frac{p_{e\kappa} V}{n_{e\kappa}} = \frac{pV}{\Sigma n_i} [1 + (D_i - 2D_m) p]. \tag{1.46}$$

From known thermodynamic relationships

$$\sum H_{\text{ек}} = H(1 + 2D_m p). \tag{1.47}$$

For the region of very low pressures we have

$$p^*_{\text{ек}} = (px_i)^*;\ \left(\sum p_{\text{ек}}\right)^* = p^*;\ n^*_{\text{ек}} = n^*_i; \tag{1.48}$$

$$c^*_p = \sum c^*_{p\text{к}}, \tag{1.49}$$

$$S^* = \sum S^*_{\text{ек}}, \tag{1.50}$$

$$H^* = \sum H^*_{\text{к}}, \tag{1.51}$$

$$(pV)^* = \sum n_i RT. \tag{1.52}$$

In accordance with equations (1.8) and (1.9) for the enthalpy and entropy of a pure gas for Σn_i moles of the gas mixture of constant composition

$$H(p,\ T) - H(p_0,\ T_0) = \int\limits_{T_0 p_0}^{p^*} \left[V - T\left(\frac{\partial V}{\partial T}\right)_{p,n}\right] dp + \\ + \int\limits_{p^* T_0}^{T} c^*_p\, dT + \int\limits_{T p^*}^{p} \left[V - T\left(\frac{\partial V}{\partial T}\right)_{p,n}\right] dp, \tag{1.53}$$

$$S(p,\ T) - S(p_0,\ T_0) = -\int\limits_{T_0 p_0}^{p^*} \left[\frac{\Sigma n_i R}{p} - \left(\frac{\partial V}{\partial T}\right)_{p,n}\right] dp + \\ + \int\limits_{p^* T_0}^{T} \frac{c^*_p}{T}\, dT + \int\limits_{T p^*}^{p} \left[\frac{\Sigma n_i R}{p} - \left(\frac{\partial V}{\partial T}\right)_{p,n}\right] dp - \\ - \sum n_i R \ln p/p_0. \tag{1.54}$$

Considering expressions (1.51), (1.15) and (1.48) we get

$$H(p^*,\ T_0) = \sum H_{\text{к}}(p^*,\ T_0) = \sum n_{\text{ск}} h^0_{0\text{к}} = \sum n_i h^0_{0i}. \tag{1.55}$$

From equations (1.50), (1.16) and (1.48) we have

$$S(p^*,\ T) = \sum S_{\text{ск}}(p^*_{\text{ек}},\ T_0) = \sum n_{\text{ск}} S^0_{0\text{к}} - \\ - \sum n_{\text{ек}} R \ln p^*_{\text{ек}} = \sum n_i S^0_{0i} - \sum n_i R \ln p^* x_i. \tag{1.56}$$

Considering equations (1.48) and (1.49) we get

$$c_p^\circ = \sum c_{px}^\circ = \sum n_{0x} c_{px}^\circ = \sum n_i c_{pi}^{\circ *}. \qquad (1.57)$$

Thus, from equalitites (1.53) and (1.55) we finally obtain

$$H(p_0, T_0) + \int\limits_{T_0 p_0}^{p^*} \left[V - T \left(\frac{\partial V}{\partial T} \right)_{p,n} \right] dp =$$
$$= H(p^*, T_0) + \sum n_i h_{0i}^\circ, \qquad (1.58)$$

while from equations (1.54) and (1.56)

$$S(p_0, T_0) + \int\limits_{T_0 p_0}^{p^*} \left[\frac{\Sigma n_i R}{p} - \left(\frac{\partial V}{\partial T} \right)_{p,n} \right] dp + \sum n_i R \ln p_0 =$$
$$= S(p^*, T_0) + \sum n_i R \ln p^* = \sum n_i S_{0i}^0 - \sum n_i R \ln x_i. \qquad (1.59)$$

Let us substitute expressions (1.57), (1.58), and (1.59) into formulas (1.53)-(1.54), replacing in this case the limit p* by 0, considering equation (1.46), and we finally obtain the following equalities for the enthalpy and entropy of the gas mixture:

$$H(p, T) = \int\limits_0^p \left[V - T \left(\frac{\partial V}{\partial T} \right)_{p,n} \right] dp + \sum n_i h_i^\circ. \qquad (1.60)$$

$$S(p, T) = \int\limits_0^p \left[\frac{\Sigma n_i R}{p} - \left(\frac{\partial V}{\partial T} \right)_{p,n} \right] dp -$$
$$- \sum n_i R \ln p x_i + \sum n_i S_i^\circ. \qquad (1.61)$$

The expression for the law of mass action, obtained by the generalized method of passage to the limit, is as follows:

$$\ln \frac{K_p}{K_p^\circ} = - \frac{1}{RT} \sum \left\{ \nu_i \left[\int\limits_0^p \left[\left(\frac{\partial V}{\partial n_i} \right)_{p,T,n} - \frac{RT}{p} \right] dp \right] \right\}. \qquad (1.62)$$

In view of the fact that the right side of this equation depends on the composition, it must be calculated by the method of successive approximations.

In order to calculate the thermodynamic properties of gas mixtures having constant composition using relationships derived by the generalized method of passage to the limit, we must know the equation of state of the mixture in such a form that it explicitly includes the number of moles of the components. The equation of state of a gas mixture of constant composition is usually given the same form as the equations of state of pure gases, and each parameter of the mixture, let us say B_m, is associated with the corresponding parameters of the components by the relationship $B_m = \Sigma x_i s_j B_{ij}$. The parameters of interaction of unlike molecules B_{ij} are associated with parameters of the components by specific combination rules which have been the object of numerous theoretical studies.

2. CALCULATING THE THERMODYNAMIC PROPERTIES OF REAL CHEMICALLY REACTING SYSTEMS

The thermodynamic properties of real mixtures of constant composition can also be calculated from relationships derived by the generalized method of passage to the limit for pure gases, if we know the composition of the mixture, its volumetric behavior, and data on the heat capacity of the mixture components at low pressure. For chemically reacting real equilibrium gas systems the question of calculating the thermodynamic properties from the known volumetric behavior of the systems (or from the known equation of state) has not been developed with the same degree of strictness as for pure gases and gas mixtures of constant composition. In view of the fact that for chemically reacting systems the assumptions of the generalized method of passage to the limit for pure gases have not been carried out, the relationships derived for pure gases cannot be used when calculating the thermodynamic properties of chemically reacting systems. We can show this in another way. Let us differentiate, for example, expression (1.16) to calculate the entropy with respect to pressure, bearing in mind that $n = \Sigma n_i$ is a function of the pressure in terms of the chemical reaction equilibrium constant.

We get

$$\left(\frac{\partial S}{\partial p}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_p - \left(\frac{\partial n}{\partial p}\right)_T R \ln p. \qquad (1.63)$$

Since

$$\left(\frac{\partial n}{\partial p}\right)_T R \ln p \neq 0, \qquad (1.64)$$

one of the general differential relationships of thermodynamics

$$\left(\frac{\partial S}{\partial p}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_p \qquad (1.65)$$

is not satisfied, which proves the inapplicability of formula (1.16) for calculating the entropy of chemically reacting systems. All other methods for calculating the thermodynamic properties of mixtures of real gases having constant composition can also be used when calculating the thermodynamic properties of chemically reacting systems with consideration of nonideality. But it is most convenient to use in this case a method based on the Lewis-Randall rule, for the following reasons.

To calculate the thermodynamic properties of chemically reacting systems with consideration of nonideality in all approaches we must know the heat capacity of the mixture components at low pressure and their volume behavior, given either in the form of tables or in the form of the equation of state. Ordinarily the equations of state of mixture components are given either for a very narrow range or not at all. In this case, to describe the volume behavior of the components we use the law of corresponding state. When calculating the thermodynamic properties of substances which have been studied only little or not at all, we often use generalized tables of the dependence of the fugacity coefficient on the reduced parameters. When calculating the thermodynamic properties of chemically reacting systems by the Lewis-Randall rule, corrections for the nonideality of the mixture components are very simply expressed in terms of the fugacity coefficients. It is also easy to take into account the influence of the nonideality of the components of the mixture on its composition. In this case the composition is determined directly, not by the method of successive approximations as in the case of calculations using the Gibbs-Dalton law or by the generalized method of passage to the limit.

The hypothesis of corresponding states, advanced by van der Waals, has been carefully discussed by Hougen and Watson [14]. They showed that the maximum error in predicting the volume behavior of a substance is 15%, while the error in predicting the other properties is in the range 5-35%. This shows the degree to which real substances are subject to the hypothesis of corresponding states. Pitzer [15] has proposed another scheme for predicting properties which is somewhat more complex, since it includes, in addition to the critical parameter, one more parameter, but it gives results which are one order of magnitude more accurate.

Statistical theory has shown [16] that a group of substances will be subject to the principle of corresponding states only when their intermolecular potentials are identical in form, although the depth of the minimum of potential and the minimum intermolecular distance associated with the critical temperature and the critical volume, respectively, are characteristic for each substance. The intramolecular motions should be classical, i.e., quantum effects should be disregarded. The only group of substances corresponding to these requirements – heavy inert gases Ar, Kr, Xe – correspond precisely to the law of corresponding states. These are called simple gases. We can expect that various types of the forms of molecules and molecular dipole moments will lead to various deviations from the macroscopic properties of simple gases. It was found, however, that the relative second theoretical virial coefficients of a broad class of the molecular type of substances fall within a single family of curves which can be characterized by one parameter. Molecules with a high dipole moment are an exception. The substances making up this class are usually called normal gases. According to the principle of corresponding states, all substances should have identical saturation length in relative coordinates. Actually, this is not so. These lines comprise one family of straight lines which differ from one another in their slopes. It was this slope which was taken as the characteristic parameter in describing the family of curves of virial coefficients and as the supplementary parameter for a more precise system of correlation of the nonideality of behavior of substances. To this we must add that the saturation lines were measured very accurately.

The third correlation parameter ω is defined by the following relationship:

$$\omega = -\lg \frac{p_s}{p_{кр}} - 1,$$

where $p_s/p_{кр}$ is taken with $T_s/T_{кр} = 0.7$ at a point rather far from the critical point. This formula was selected such that ω is equal to zero for the simple gases Ar, Kr, Xe with simple spherical molecules. Normal gases have small positive values of ω. The parameter ω is called the acentric factor, in view of the fact that it shows the measure of the deviation of the intramolecular potential function from the potential function of simple spherical molecules. The p-V-t-data of a number of substances were interpolated by series with equal p_r - T and constructed as a function of ω. Such graphs show that the coefficients of compressibility of substances are described quite well by a linear dependence of ω: $Z = Z^{(0)}(p_r, T_r) + \omega \times Z^{(')}(p_r, T_r)$. The smoothed values of $Z^{(0)}$ and $Z^{(')}$, taken from these graphs, are given in tables $Z^{(0)}(p_r, T_r)$ and $Z^{(')}(p_r, T_r)$ in works [15, 17, 18]. From these values of the coefficient of compressibility we calculated the fugacity coefficients and log $\gamma^{(0)}$, log $\gamma^{(')}$, and also corrections for nonideality of the enthalpy of substances $\left(\frac{H^0 - H}{RT_{кр}}\right)^{(0)}$, $\left(\frac{H^0 - H}{RT_{кр}}\right)^{(')}$, corresponding to the dependences

$$\log \gamma = \log \gamma^{(0)} + \omega \log \gamma^{(')}, \quad (1.66)$$

$$\left(\frac{H^0 - H}{RT_{кр}}\right) = \left(\frac{H^0 - H}{RT_{кр}}\right)^{(0)} + \omega \left(\frac{H^0 - H}{RT_{кр}}\right)^{(')}. \quad (1.67)$$

When calculating the thermodynamic properties of gas mixtures we can use the very useful Kay postulate [19] which states that a gas mixture conforms to the behavior of a hypothetical pure substance with pseudocritical constants, calculated on the basis of known critical constants of the components of the mixture and the composition of the mixture from specific combination rules. Pitzer and Hultgren [20] have proposed a generalization of this postulate with consideration of the theory of the acentric factor of pure substances.

3. CALCULATING THE THERMODYNAMIC PROPERTIES OF A REAL CHEMICALLY REACTING SYSTEM

$(N_2O_4 \rightleftarrows 2NO_2 \rightleftarrows 2NO + O_2;\ Al_2Cl_6 \rightleftarrows 2AlCl_3;\ Al_2Br_6 \rightleftarrows 2AlBr_3)$

Let us examine the method of calculating the thermodynamic properties of real chemically reacting systems using as our example the mixture $N_2O_4 \rightleftarrows 2NO_2 \rightleftarrows 2NO + O_2$. A feature of the behavior of the chemically reacting system $N_2O_4 \rightleftarrows 2NO_2 \rightleftarrows 2NO + O_2$, as others, is the fact that its components N_2O_4 and NO_2 do not exist in pure form. They always comprise an equilibrium mixture, 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 nonideality in their behavior. Because of this fact, it is impossible to obtain individual data on the volume behavior of these components and, consequently, it is impossible to compile an equation of state for the components. Although the volume behavior of this system has been studied rather well, particularly near the exageration line, the absence of a strict method for calculating the thermodynamic properties of chemically reacting systems from a known equation of state does not allow us to use this information for calculating the thermodynamic properties. The only way for considering nonideality when calculating the thermodynamic properties of such systems is to use some modification of the law of corresponding states. Here, the need for knowing the real composition forces us to ascribe to the components N_2O_4 and NO_2 specific critical parameters and, consequently, various saturation lines. At the same time, we know that the chemically reacting 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.

If we assume, for example, that in the phase diagram, in addition to the curve of phase equilibrium of the system $N_2O_4 \rightleftarrows 2NO_2$ there also exist curves of the phase equilibrium of pure components, it is easy to conclude as to the possibility of achieving total dissociation of the system by isothermal compression (Fig. 1). Along line 1-2 we should have $(\partial x/\partial p)_T > 0$, while with total association of the

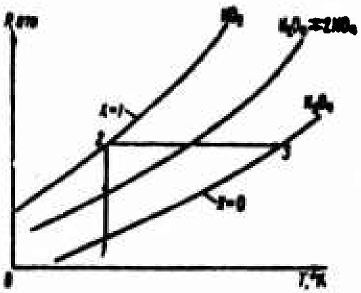

Fig. 1. Phase diagram of the system $N_2O_4 \rightleftarrows 2NC_2$ from the point of view of the mixture. Designation: ата = atm (abs).

molecules of the system with isobaric heating along line 2-3, $(\partial x/\partial p)_T < 0$.[1] Here x is the percentage of dissociated molecules of N_2O_4.

This conclusion is at complete odds with the known behavior of the degree of dissociation of the system $N_2O_4 \rightleftarrows 2NO_2$ as a function of temperature and pressure. Let us note that the question discussed in detail in [21] of the possible deflections of the phase equilibrium curve says nothing in favor of the existence of one, two, or three curves, but is connected merely with the relationship of the rates of dissociation and vapor formation.

The critical parameters of the components N_2O_4 and NO_2 are determined as follows. There are two approaches toward defining the critical parameters of substances which have been little studied. The first uses the rule of additivity, the second uses experimental dependences. The percentages of atoms, molecules, and bonds used in the first approach are obtained from experimental data on hydrocarbons, and therefore this approach is justified for organic compounds. It was noted, however, that the percentages of N_2 and O_2 in organic compounds do not correspond to the percentage of these molecules in inorganic compounds. From this it follows that the first approach cannot be used for molecules of NO_2 and N_2O_4.

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[1] The mutual position of the curves of the phase equilibrium of the system and the pure components, shown in Fig. 1, follows from the experiments by J. W. Smith [22] on the shift of equilibrium with drying toward the more volatile components.

We examined the following methods based on the second approach.

1. Definition of the critical temperature:

a) the Smith, Greenbaum, and Rutledge method [23]. The equation for defining $T_{\text{кр}}$:

$$T_{\text{кр}} = \frac{T_2 - T_1}{(\rho_1/\rho_2)^{10/3} - 1} + T_2 + 6, \tag{1.68}$$

where ρ_1 is the density of the liquid with $T = T_1$, ρ_2 is the density of the liquid with $T = T_2$. From the Eötvös and Segden relationship we find that $\gamma' - \gamma'' = \gamma_0'(1-\theta)^{3/10}$, where $\theta = T/T_{\text{кр}}$, γ_0' is the specific weight of the liquid with $T = 0$. In order to obtain suitable values of $T_{\text{кр}}$, the following conditions must be satisfied:

$$T_2 - T_1 > 20, \ \frac{T_2 + T_1}{2} \approx 3/4 T_{\text{кр}}. \tag{1.69}$$

The mean calculation error $\Delta T_{\text{кр}} \approx 3\%$;

b) the graphic Altenburg method [23]. It is necessary to know the density of the liquid at two temperatures. The mean definition error $\Delta T_{\text{кр}} = 1.5\%$ (the maximum does not exceed 5%);

c) the Rydell method [17]. It is necessary to know the boiling point at a pressure of 760 mm, the temperature at which the saturated vapor pressure is 100 mm, and the density of the liquid at a specific temperature. The method guarantees definition of $T_{\text{кр}}$ with a mean error of 0.8%;

d) the Watson method [24]. According to Watson, for nonpolar substances capable of association and dissociation, we have the simple empirical relationship

$$T_e/T_{\text{кр}} = 0{,}283(M/\gamma_s)^{0.18}, \tag{1.70}$$

where γ_s is the weight of the liquid at the normal boiling point; M is the molecular weight; T_e is the temperature at which the saturated vapor of 1 g-mole of liquid is contained in 22.4 *l*.

The following equation has been compiled to define T_e:

$$\ln T_e = 9{,}8\,\frac{T_s}{T_e} - 4{,}2.$$

Using it, we can construct a curve in coordinates T_s and $\Delta = T_e - T_s$, with which, using the known boiling point, we can uniquely define T_e. Relationship (1.70) was verified for 36 nonpolar substances. Its mean error was 2%.

Determining the critical density or critical volume. The most accurate relationship for determining the critical density is the following Goldhammer equation [24]:

$$\gamma_{\text{кр}}^{3} - \frac{\gamma' - \gamma''}{2}\,\gamma_{\text{кр}}^{2} + \frac{(\gamma' - \gamma'')^{3}}{64} = 0. \qquad (1.71)$$

This relationship was checked for 64 normal and abnormal substances, and good agreement with experimental values was obtained.

Determining the critical pressure. The critical pressure can be calculated using the relationship

$$\frac{RT_{\text{кр}}}{p_{\text{кр}}V_{\text{кр}}} = 0{,}291 - 0{,}08\omega, \qquad (1.72)$$

where ω is the acentric Pitzer factor.

The value of ω can be obtained by the Rydell graphic method [17]. If this is impossible, $p_{\text{кр}}$ can be defined from the empirical dependence [24]

$$\frac{RT_{\text{кр}}}{p_{\text{кр}}V_{\text{кр}}} = 3{,}75. \qquad (1.73)$$

The value 3.75 is not the same for all substances. It depends greatly, as has been established, on the position of the binodal in the lg p-1/T diagram, and it is the greater, the steeper the binodal.

However, for substances for which there are no experimental data, these methods cannot be used.

To determine the critical parameters of such substances we can use a relative method, i.e., use a reference substance for which the critical parameters are known. The molecular-kinetic theory indicates a connection between critical parameters and force constants σ (the collision diameter) and ε (the depth of the potential hole).

Thodos and Flunn obtained the following empirical connections between $p_{кр}$, $T_{кр}$, $V_{кр}$ and ε/k, σ [25]:

$$\sigma = 0{,}618 V_{кр}^{1/3} T_{кр}^{-1/18}; \qquad (1.74)$$

$$\sigma = 0{,}561 V_{кр}^{1/3}; \qquad (1.75)$$

$$\sigma = 0{,}1866 V_{кр}^{1/3} Z_{кр}^{-6/5}, \qquad (1.76)$$

from which

$$V_{кр2}^{4/13} = \frac{\sigma_2 V_{кр1}^{4/13}}{\sigma_1}; \qquad (1.77)$$

$$T_{кр2}^{-1/18} = \frac{\sigma_2 V_{кр1}^{1/3} T_{кр1}^{-1/18}}{\sigma_1 V_{кр2}^{1/3}};$$

$$Z_{кр2}^{-6/5} = \frac{\sigma_2 V_{кр1}^{1/3} Z_{кр1}^{-6/5}}{\sigma_1 V_{кр2}^{1/3}}. \qquad (1.78)$$

from $Z_{кр}$ we define $p_{кр}$ by the relationship

$$p_{кр} = \frac{Z_{кр} R T_{кр}}{V_{кр}}. \qquad (1.79)$$

The collision diameter σ can be determined relatively accurately from data on the crystal lattice.

The critical temperature of N_2O_4 can be determined using the Smith (a), Altenburg (b), and Watson (d) methods. We obtained the following values: a) $T_{кр}$ = 489.3 °K, b) $T_{кр}$ = 489.7 °K, d) $T_{кр}$ = = 495.0 °K. These values agree within limits of error guaranteed by each method. The region in which the errors of all methods overlap gives a value of the critical temperature $T_{кр}$ = 491 °K. The critical volume of N_2O_4 is defined from formula (1.77); the critical pressure is defined from relationship (1.79). The critical parameters of NO_2 are defined by the relative method. As the reference substance we used N_2O_4.

Thus, we obtained the following critical parameters of N_2O_4 and NO_2:

	$T_{кр}$, °K	$p_{кр}$, atm	$V_{кр}$, cm^3/mole
N_2O_4	491	51,6	205,6
NO_2	293,6	66,6	94,45

As we know, the critical parameters of the mixture $N_2O_4 \rightleftarrows 2NO_2$ are as follows [2]: $T_{кр} = 431.35$ °K; $p_{кр} = 99.99$ atm (tech); $V_{кр} = 163$ cm^3/mole. With calculation of the composition of the mixture $N_2O_4 \rightleftarrows 2NO_2 \rightleftarrows 2NO + O_2$ with consideration of nonideality, the attributing of various critical parameters of the components N_2O_4 and NO_2 has the result that, in the temperature region 431 °K < T < 491 °K, near the saturation line of the mixture $N_2O_4 \rightleftarrows 2NO_2$ in its gas phase, we obtain corrections for nonideality for the component N_2O_4 by the law of corresponding states in the liquid phase, while for the component NO_2 in the gas phase this is far from the generalized saturation line. For this reason, great error is introduced when calculating the composition of the mixture in this region. A similar error in this region is introduced, both in the enthalpy and the entropy of the mixture when calculating the corrections for nonideality, into the entropy and enthalpy of the components N_2O_4 and NO_2 with respect to their pseudocritical parameters. All this greatly distorts the H-S diagram in this region. Less distortion of the H-S diagram near the saturation line can be obtained if we calculate the correction for nonideality introduced into the entropy and enthalpy of the mixture as follows.

For each value of temperature and pressure let us represent the mixture $N_2O_4 \rightleftarrows 2NO_2 \rightleftarrows 2NO+O_2$ by a homogeneous substance with pseudocritical parameters calculated by the Kay rule, and molecular weight equal to $M = M_0/\sum n_i$, where M_0 is the molecular weight of one mole of the initial nondissociated composition of the mixture, while $\sum n_i$ is the number of moles of the mixture. For such a homogeneous substance with variable molecular weight and current pseudocritical parameters, in view of the change in composition, the correction in the entropy and enthalpy of the mixture for nonideality, sought from the pseudocritical parameters, lies only in the gas phase for temperatures

$431 < T < 491$ °K, although the above-indicated errors are preserved in the composition, as before.

Such a calculation scheme is identical to calculation under the assumption of identical corrections for nonideality in the entropy and enthalpy of all components of the mixture, provided that these corrections are sought from its pseudocritical parameters.

Below we give an algorithm for calculating the thermodynamic properties of a chemically reacting real mixture $N_2O_4 \rightleftarrows 2NO_2 \rightleftarrows 2NO + O_2$ from the scheme of a homogeneous substance with variable molecular weight and current pseudocritical parameters. The law of corresponding states is used in the Pitzer modification. Using an analogous method we calculated the thermodynamic properties of the chemically reacting systems $Al_2Cl_6 \rightleftarrows 2AlCl_3$, $Al_2Br_6 \rightleftarrows 2AlBr_3$.

The equation for the equilibrium constant from the first stage of the reaction is taken from [26]; for the second reaction stage it is taken from [28]. Smoothed Pitzer tables of $\log \gamma^{(0)}$, $\log \gamma^{(')}$, $\left(\frac{H^0 - H}{RT_{кр}}\right)^{(0)}$, and $\left(\frac{H^0 - H}{RT_{кр}}\right)^{(')}$ are given in [17, 18]. The critical parameters of N_2O_4 and NO_2 were previously determined; the acentric factors of N_2O_4 and NO_2 were defined from the condition of agreement with the Pitzer relationship:

$$Z_{кр} = Z_{кр}^{(0)} + \omega Z_{кр}^{(1)},$$

i.e.,

$$\omega_i = \frac{0{,}291 - Z_{кр\,i}}{0{,}08}.$$

The critical parameters of NO and O_2 were taken from [28]; the acentric factors were determined from data on p_s-T_s given in [28].

In accordance with the assumed dependence of the equilibrium constant of the first stage of the reaction on the temperature for ΔH_{R1}^0 (reaction heat) and for ΔS_{R1}^0 (change in entropy during the reaction) with $T = 298.15$ °K we obtain the following values: $\Delta H_{R1}^0 = 13{,}680$ cal/mole, $\Delta S_{R1}^0 = 42.06$ cal/mole·deg. For the second stage we obtain the following values: ΔH^0_{R2} = 27,200 cal/mole, ΔS^0_{R2} = = 34.87 cal/mole·deg. For N_2O_4 we assume $\Delta H^0_{298.15}$ = 2140 cal/mole and $S^0_{298.15}$ = 72.72 [29]. From this, for NO_2 $\Delta H^0_{298.15}$ = 7910 [29], $S^0_{298.15}$ = 57.39; for NO $\Delta H^0_{298.15}$ = 21,510 cal/mole, $S^0_{298.15}$ = 50.315. For O_2 $S^0_{298.15}$ = 49.0065 [31]. From the polynomial for the dependence of heat capacity of N_2O_4 on temperature T [8] we obtained the below-given polynomials for the enthalpy and entropy of the N_2O_4 component The polynomials for the dependence of enthalpy and entropy of NO_2, NO and O_2 components on temperature are as follows [31]:

1) $$\ln K_{p10} = 14{,}19712 + 1{,}121226 \ln T - 1{,}813894 \cdot 10^{-3} T + 0{,}131186 \cdot 10^{-6} T^2 - \frac{4{,}47727 \cdot 10^4}{T^2} - \frac{6403{,}298}{T};$$

2) $$\ln K_{p20} = -0{,}5845 \ln (10^{-4} T) + \frac{12{,}5862 \cdot 10^4}{T^2} - \frac{147{,}088 \cdot 10^2}{T} + 17{,}5121 - 0{,}3079 \cdot 10^{-4} T - 1{,}6017 \cdot 10^{-8} T^2 - 0{,}1183 \cdot 10^{-12} T^3;$$

3) we are given the tables

$$A - \log \gamma^{(0)};\ B - \log \gamma^{(')};\ C - \left(\frac{H^0 - H}{RT_{кр}}\right)^{(0)};\quad D - \left(\frac{H^0 - H}{RT_{кр}}\right)^{(')};\ \text{from } T_r = T/T_{ci};\ P_r = P/P_{ci},$$

where $i = 1, 2, 3, 4;$ $1 - N_2O_4,\ 2 - NO_2,\ 3 - NO,\ 4 - O_2;$

4) $$\gamma_i = e^{2.3026\,(A + \omega_i B)};$$

5) $$K_{p1} = \frac{K_{p10}\gamma_1}{\gamma_2^2};$$

6) $$K_{p2} = \frac{K_{p20}\gamma_2^2}{\gamma_3^2\gamma_4};$$

7) $$(4K_{p2}^2 + K_{p1}K_{p2} - pK_{p1})\alpha_2^6 - 24K_{p2}^2\alpha_2^5 + (60K_{p2}^2 - 3K_{p1}K_{p2})\alpha_2^4 + (2K_{p1}K_{p2} - 80K_{p2}^2)\alpha_2^3 + 60K_{p2}^2\alpha_2^2 - 24K_{p2}^2\alpha_2 + 4K_{p2}^2 = 0;$$

8) $\alpha_1 = \dfrac{\alpha_2 + \sqrt{\alpha_2^2 + 4\left[4p(1-\alpha_2)^2/K_{p1} + (\alpha_2+1)\right]}}{2\left[4p(1-\alpha_2)^2/K_{p1} + (\alpha_2+1)\right]};$

9) $i_1 = 37{,}077(T-298) + 36{,}938\cdot 10^{-6}(T^2 - 298^2) - 6878{,}84$
$\ln/T298 - 641{,}424\cdot 10^{3}(1/T - 1/298);$

10) $S_1 = 34{,}077\ln T/298 + 73{,}876\cdot 10^{-6}(T\,298) + 6878{,}84(1/T - 1/298) - 320{,}712\cdot 10^{3}(1/T^2 - 1/298^2);$

11) $i_i = 10^7(h^0 + h_{-1}x^{-1} + h_1x + h_2x^2 + h_3x^3 + h_4x^4 + h_5x^5 + h_6x^6 + h_7x^7 + h_8x^8), \quad x = 10^{-4}T;$

12) $S_i = h_1\ln x + \frac{h_{-1}}{2}x^{-2} + 2h_2x + \frac{3}{2}h_3x^2 + \frac{4}{3}h_4x^3 +$
$+ \frac{5}{4}h_5x^4 + \frac{6}{5}h_6x^5 + \frac{7}{6}h_7x^6 + \frac{8}{7}h_8x^7,\ i = 2,\ 3,\ 4$ (Table 2);

13) $x_1 = \dfrac{1-\alpha_1}{1+\alpha_1+\alpha_1\alpha_2}; \quad x_2 = \dfrac{2\alpha_1(1-\alpha_2)}{1+\alpha_1+\alpha_1\alpha_2}; \quad x_3 = \dfrac{2\alpha_1\alpha_2}{1+\alpha_1+\alpha_1\alpha_2}; \quad x_4 + \dfrac{x_3}{2};$

14) $T_{cr} = \sum_{i=1}^{4} x_iT_{ci}; \quad p_{cr} = \sum_{i=1}^{4} x_ip_{ci}; \quad \omega_r = \sum_{i=1}^{4} x_i\omega_i;$

15) $H_i = \Delta H_i^0 + i_i;$

16) $S_i = S_i + S_i^0;$

17) $\Delta H = 1{,}98726\ T_{cr}(C + \omega_r D)(1 + \alpha_1 + \alpha_1\alpha_2);$

18) $\Delta S = \dfrac{\Delta H}{T} + 4{,}57586(A + \omega_r B)(1 + \alpha_1 + \alpha_1\alpha_2)$ from $T_r = \dfrac{T}{T_{cr}}; \ p_r = \dfrac{p}{p_{cr}};$

19) $H_e = \dfrac{1}{92}\left[(1-\alpha_1)H_1 + 2\alpha_1(1-\alpha_2)H_2 + 2\alpha_1\alpha_2H_3 + \alpha_1\alpha_2H_4 - \Delta H\right] + 100;$

20) $S_e = \dfrac{1}{92}\left[(1-\alpha_1)S_1 + 2\alpha_1(1-\alpha_2)S_2 + 2\alpha_1\alpha_2S_3 + \alpha_1\alpha_2S_4 - \Delta S\right] - \dfrac{1{,}98726}{92}\left[(1-\alpha_1)\ln(1-\alpha_1) +\right.$
$\left. + 2\alpha_1(1-\alpha_2)\ln 2\alpha_1(1-\alpha_2) + 2\alpha_1\alpha_2 + \ln\alpha_1\alpha_2 + \alpha_1\alpha_2\ln\alpha_1\alpha_2 - (1+\alpha_1+\alpha_1\alpha_2)\ln(1+\alpha_1+\alpha_1\alpha_2)/p\right];$

21) $C_{pe} = \left(\dfrac{\partial H_e}{\partial T}\right)_p.$

Table 2. Coefficients for calculating the properties of the mixture mixture $N_2O_4 \rightleftarrows 2NO_2 \rightleftarrows 2NO + O_2$

(1) Условное обозначение	(2) Величины			
	N_2O_4	NO_2	NO	O_2
T_{ci}	491,0	293,6	180,2	154,8
P_{ci}	51,60	66,61	64,60	50,10
ω_i	0,3463	0,3740	0,5757	0,024
ΔH_i^0	2140	7910	21510	0
S_i^0	72,2	75,0036	66,15562	65,8072
h^0	—	—0,24562	—0,240348	—0,160748
h_{-1}	—	4,114·10⁻⁴	—7,935·10⁻⁴	—2,689·10⁻⁴
h_1	—	6,0784	4,83286	5,20537
h_2	—	64,9703	29,0791	30,47837
h_3	—	—296,017	—120,2217	—146,8618
h_4	—	766,17	276,738	421,1702
h_5	—	—919,213	—334,5202	—584,5064
h_6	—	44,094	32,0833	132,5398
h_7	—	954,35	308,769	525,966
h_8	—	—649,71	—212,369	—400,939

KEY: (1) Arbitrary designation, (2) Values.

The results of the calculation are given in Table 2 of the Appendix.

4. CALCULATING THE DENSITY OF CHEMICALLY REACTING SYSTEMS

The density of chemically reacting gas systems is calculated from the scheme of a homogeneous substance with variable molecular weight by the law of corresponding states in the Pitzer modification. The pseudocritical parameters of a homogeneous substance and its acentric factor are calculated from the following dependences:

$$T_{\text{ст}} = \sum_{i=1}^{4} x_i T_{ci}; \quad P_{\text{ст}} = \sum_{i=1}^{4} x_i P_{ci}; \quad \omega_{\text{ст}} = \sum_{i=1}^{4} x_i \omega_i.$$

From the reduced parameters $T_r = T/T_{\text{ст}}$, $P_r = P/P_{\text{ст}}$ and ω_{CT} we find Z_{CT}: $Z_{\text{ст}} = Z^{(0)} + \omega_{\text{ст}} Z^{(')}$. From this,

$$\rho = \frac{M_0 P}{nRTZ_{\text{ст}}}, \tag{1.81}$$

where $n = \Sigma n_i$ is the sum of the moles of the mixture components, M_0 is the molecular weight of the initial nondissociated single mole of the mixture; $Z^{(0)}$ and $Z^{(')}$ are tabulated [17-19].

The results of calculation of the density of the chemically reacting mixture $N_2O_4 \rightleftarrows 2NO_2 \rightleftarrows 2NO+O_2$ are given in Table 2 of the Appendix.

CHAPTER II

METHODS OF CALCULATING THERMODYNAMIC CYCLES FOR CHEMICALLY REACTING SYSTEMS

1. THERMODYNAMIC CYCLES FOR CHEMICALLY REACTING WORKING MEDIA

In most of the stationary power plants, thermal as well as atomic, which have been created or are being developed, as the working medium for the turbines we use steam with a condensation cycle. In modern steam-turbine plants (STP) [ПТУ] steam parameters have been achieved relative to temperatures of 565-580°C and pressure 240 atm (abs) with a thermodynamic efficiency of the condensation cycle with one industrial superheating of 45-47%, which corresponds to a 41-42% net efficiency of the plant [4]. However, successes in creating reactor units with powers of 600-800 MW allow us to obtain an output temperature of the gas from type AGR reactors of 650°C, from HTGR reactors – 750-850°C. The use of steam for these temperatures, as shown by research carried out at the Central Scientific Research, Planning, and Design Boiler and Turbine Institute im. I. I. Polzunov, the Moscow Power-Engineering Institute, the Siberian Power-Engineering Institute of the Siberian Branch of the Academy of Sciences of the USSR, and others, is economically unfeasible [1-3]. Steam has a second major disadvantage when creating high-power turbine units: the physicochemical properties of steam are such that for the existing structural materials, per unit discharge of the turbine we can obtain powers to 125-135 MW [4]. This creates considerable difficulties in designing large single-shaft turbine units [4].

In connection with these features of steam, in recent years intense studies have been carried out for both new schemes for thermodynamic cycles as well as for more effective working media which will make it possible to obtain technical-economic plant indicators which are better than in the steam-turbine cycle.

One of the ways for solving this problem can be the use of chemically reacting substances as the working medium. Certain of these have physicochemical properties which are such that they can be used as working media for both gas-turbine as well as gas-liquid (condensation) cycles. For example, we have the chemically reacting mixtures $N_2O_4 \rightleftarrows 2NO_2 \rightleftarrows 2NO+O_2$, $Al_2Cl_6 \rightleftarrows 2AlCl_3$, $Al_2Br_6 \rightleftarrows 2AlBr_3$, and others.

The possible use of chemically reacting (dissociating) systems as working media for thermodynamic cycles and coolants was first indicated in the works by Lighthill (USA) [9] and Kovtun, Naumov, et al. (USSR) [10].

Let us examine the disadvantages of a gas-turbine cycle using inert gases. The low effective efficiency of gas-turbine plants (GTP) [ГТУ] is explained by the high losses to internal irreversibility in the cycle. The degree of influence of internal losses of the effective efficiency of the cycle is characterized by the work ratio

$$\varphi = \frac{L_m - L_к}{L_m}, \qquad (2.1)$$

where L_m is the expansion work, $L_к$ is the compression work.

In inert-gas GTP's, the work ratio is low: ~0.3-0.5. This is due to the great influence of losses in turbines and lines on the effective efficiency of the cycle

$$\eta_e = \frac{L_{тад}\eta_T - L_{кад}/\eta_к}{Q_{под}}, \qquad (2.2)$$

η_T is the internal efficiency of the expansion process, $\eta_к$ is the internal efficiency of the compression process, $Q_{под}$ is the heat fed in the cycle. To increase the work ratio, as follows from formula (2.1), we must increase the expansion work or decrease the compression work. From the formula for the expansion work

$$AL_m = \frac{ART}{\kappa-1}\left(1-\frac{1}{\pi_T^{\frac{\kappa-1}{\kappa}}}\right)\eta_T \qquad (2.3)$$

we see which parameters influence its value. Actually, the expansion work is proportional to the gas constant, and increases with a decrease in the specific heat ratio.

The compression work is also proportional to the gas constant of the working medium, but decreases with decreasing specific heat ratio

$$AL_\kappa = \frac{ART}{\kappa-1}\left(\pi_\kappa^{\frac{\kappa-1}{\kappa}}-1\right)\frac{1}{\eta_\kappa}. \qquad (2.4)$$

Consequently, if the cycle is arranged so that the process of expansion occurs in the region of a high gas constant, while the process of compression occurs in the region of the low gas constant, this effect should lead to an increase in the work ratio and, consequently, the efficiency of the plant.

The effect of a variable gas "constant" was first used in a cycle with supercritical compression [29], where the effect of "adhesion" of molecules was used, which lead to an increase in the molecular weight of the substance, while the gas constant was inversely proportional to the molecular weight of the substance R = = 848 M. The supercritical GTP cycle was arranged such that the process of compression was carried out in the supercritical region, close to critical (Fig. 2). Then in the compressor a gas having the properties of an imperfect gas is compressed, and the equation of state of such a gas has the form

$$PV = RTZ, \qquad (2.5)$$

where Z is the coefficient of compressibility which takes into account the difference between a real gas and a perfect gas as a result of

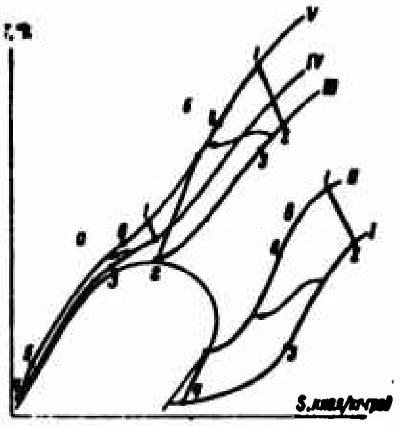

Fig. 2. T-S diagram of gas cycles using nitrogen tetroxide: a – with supercritical compression, b – with compression from the critical point, c – with subcritical compression, d – critical point, ($P_{кр}$ = = 99 atm (abs), $T_{кр}$ = 431°K); I – P-1 atm (abs), II – 4, III – 99, IV – 110, V – 200 atm (abs).

Designation: ккал/кг•град = = kcal/kg•deg.

the finite dimensions of the molecule, the presence of intermolecular forces, and association of molecules in the supercritical region.

For a gas-turbine cycle, as shown above, it is important that the complex ZR, which can be called the arbitrary gas constant, be significantly less during the compression process than the gas constant during the expansion process. However, a great disadvantage of gas cycles with supercritical compression is the fact that the lower pressure of the cycle should be above the critical pressure of the selected gas; for most substances, however, it is rather high and, as a result, we cannot have a high upper pressure of the cycle with an optimum compression ratio. In addition, the compressor operates in a region where the gas constant changes very greatly as a function of temperature, and therefore even a slight change in gas temperature at the compressor inlet (2-5°) leads to an abrupt change in gas flow through the compressor. Plants with such a cycle, operating under variable conditions, are especially sensitive to a change in temperature.

This effect of a change of gas constant in a cycle with supercritical compression is most clearly manifested in cycles using, as the GTP working medium, chemically reacting systems in which a change in the gas constant is observed with thermal and radiation dissociation of the substances.

During the heating or cooling of such systems there is a change in the number of moles and, consequently, the molecular weight of the mixture with absorption or release of the heat of chemical reactions.

Using such systems as the working medium in closed-cycle OTP's, the gas in the initial state with maximum molecular weight, i.e., minimum gas constant, is compressed in the compressor and heated in the regenerator and heater to the maximum temperature of the cycle. Here there is dissociation of the gas with absorption of heat to chemical reactions, and an increase in the number of moles and, consequently, a decrease in the molecular weight and an increase in the gas "constant." After expanding in the turbine the gas, cooled in the regenerator and the cooler, recombines with the release of the heat of chemical reactions and a decrease of the number of moles to the initial state, and the cycle is repeated. The high gas "constant" of the working medium in the turbine compared with the gas "constant" of the working medium in the compressor makes it possible to decrease the percentage of power expended on compressing the gas in the compressor to 30-40% instead of 70-80% for inert gases, which leads to an increase in the effective efficiency of the cycle using chemically reacting mixtures compared with cycles using inert gases.

The nonmonotonic nature of the change in thermophysical properties of chemically reacting systems considerably complicates calculation of the characteristics of the thermodynamic cycle: the specific heat ratio, the heat of regeneration, and the regenerator effectiveness. Below we examine methods for calculating the specific heat ratio of a chemically reacting system and the regenerator effectiveness of thermodynamic cycles using chemically reacting systems as the working medium.

2. THE SPECIFIC HEAT RATIO OF A MIXTURE OF CHEMICALLY REACTING GASES

On this question we have the vast work by Irene Sänger-Bredt [35]. Unfortunately, although she gives a correct general approach to the problem, there are a number of errors which cause incorrect derivation of formulas for the true isentropic indices for various pairs of thermodynamic independent variables.

In the section dealing with chemically variable isentropic flow, with differentiation of the entropy of the mixture components with respect to independent variables the fact is disregarded that the entropy of the mixture components is selected not with the total pressure of the mixture but with partial pressures of the components. And since the partial pressure of the component is equal to the product of the total pressure of the mixture times the molar percentage of the component in the mixture, the derivatives of the entropy of the component contain terms, derivatives of the molar percentage relative to independent variables, which were not taken into account by the author of [35]. This was what led to incorrect derivation of all general formulas for the isentropic indices of chemically reacting gases, and also to the incorrect assertion that for a chemically variable equilibrium system we do not have the equalities

$$\left(\frac{\partial H}{\partial T}\right)_p = T\left(\frac{\partial S}{\partial T}\right)_p; \quad \left(\frac{\partial U}{\partial T}\right)_v = T\left(\frac{\partial S}{\partial T}\right)_v. \qquad (2.6)$$

In this work formulas were again derived for the true isentropic indices of chemically reacting systems, and results were given for calculation of the isentropic index in coordinates T, P for the chemically reacting system $N_2O_4 \rightleftarrows 2NO_2 \rightleftarrows 2NO + O_2$. For comparison, the results are given of the calculation of the equilibrium specific heat ratio c_{pe}/c_{ve}.

Let us examine an ideal gas in which we have the equilibrium reaction $\nu_1 R_1 + \cdots + \nu_i R_i \rightleftarrows \nu_{i+1} R_{i+1} + \cdots + \nu_k R_k$.

The equation for the reaction equilibrium constant $K_p(T) = \prod p_i^{\nu_i} = p^{\nu} \prod x_i^{\nu_i}$, where $\nu = \sum_{i=1}^{i=k} \nu_i$. Taking the logarithm of this equation, we obtain the following expression:

$$\ln K_p(T) = \sum_{i=1}^{l} \nu_i \ln x_i + \nu \ln p. \qquad (2.7)$$

For convenience in further mathematical transformations, let us replace x_1 by ξ - the degree of completeness of the reaction [36]:

$$x_i = \frac{n_i^0 + \nu_i \xi}{n^0 + \nu \xi}, \qquad (2.8)$$

where $n_0 = \sum_{i=1}^{l} n_i^0$.

Then equation (2.7) is written as follows:

$$\ln K_p(T) = \sum_{i=1}^{l} \nu_i \ln(n_i^0 + \nu_i \xi) - \nu \ln(n^0 + \nu \xi) + \nu \ln p. \qquad (2.9)$$

Let us derive the differential equations of isentropy for the examined reaction in T, p; ρ, T; ρ, p-coordinates.

I. Coordinate T, p. The entropy of the mixture

$$S = \frac{\sum_{i=1}^{l} n_i S_i}{M}, \qquad (2.10)$$

where M is the mass of one mole of the initial composition of the mixture, corresponding to $\xi = 0$; S_1 is the entropy of the 1-th component:

$$S_i = S_i^0 + \int_{T_0}^{T} \frac{c_{pi}}{T} dT - R \int_{p_0}^{p_i} \frac{dp}{p}.$$

Since $p_1 = x_1 p$, while p_0 is the standard pressure per 1 atm,

$$S_i = S_i^0 + \int_{T_0}^{T} \frac{c_{pi}}{T} dT - R \ln x_i p. \qquad (2.11)$$

The equation of isentropy with consideration of expression (2.10) is as follows:

$$dS = \left(\frac{\partial S}{\partial T}\right)_p dT + \left(\frac{\partial S}{\partial p}\right)_T dp + \frac{1}{M}\left\{\sum_{i=1}^{l}\left[S_i\left(\frac{\partial n_i}{\partial T}\right)_p + \right.\right.$$

$$\left.\left. + n_i\left(\frac{\partial S_i}{\partial T}\right)_p\right]dT + \sum_{i=1}^{l}\left[S_i\left(\frac{\partial n_i}{\partial p}\right)_T + n_i\left(\frac{\partial S_i}{\partial p}\right)_T\right]dp\right\} = 0. \qquad (2.12)$$

Since $n_i = n_i^0 + \nu_i \xi$,

$$\left(\frac{\partial n_i}{\partial T}\right)_p = \nu_i\left(\frac{\partial \xi}{\partial T}\right)_p, \quad \left(\frac{\partial n_i}{\partial p}\right) = \nu_i\left(\frac{\partial \xi}{\partial p}\right)_p. \qquad (2.13)$$

From equation (2.11) we have

$$\left(\frac{\partial S_i}{\partial T}\right)_p = \frac{c_{pi}}{T} - \frac{R}{x_i}\left(\frac{\partial x_i}{\partial T}\right)_p;$$

$$\left(\frac{\partial S_i}{\partial p}\right)_T = -\frac{R}{p} - \frac{R}{x_i}\left(\frac{\partial x_i}{\partial p}\right)_T. \qquad (2.14)$$

From equality (2.8) we get

$$\left(\frac{\partial x_i}{\partial T}\right)_p = \frac{\nu_i n^0 - \nu n_i^0}{n^2}\left(\frac{\partial \xi}{\partial T}\right)_p; \quad \left(\frac{\partial x_i}{\partial p}\right)_T = \frac{\nu_i n^0 - \nu n_i^0}{n^2}\left(\frac{\partial \xi}{\partial p}\right)_T. \qquad (2.15)$$

Let us substitute expressions (2.13)-(2.15) into equation (2.12) and, after certain transformations, considering that $x_1 = n_1/n$, we get

$$\frac{1}{M}\sum_{i=1}^{l}\left[\nu_i S_i\left(\frac{\partial \xi}{\partial T}\right)_p + \frac{n_i c_{pi}}{T} - \frac{R(\nu_i n^0 - \nu n_i^0)}{n}\left(\frac{\partial \xi}{\partial T}\right)_p\right]dT +$$

$$+ \frac{1}{M}\sum_{i=1}^{l}\left[\nu_i S_i\left(\frac{\partial \xi}{\partial p}\right)_T - \frac{n_i R}{p} - \right.$$

$$\left. - \frac{R(\nu_i n^0 - \nu n_i^0)}{n}\left(\frac{\partial \xi}{\partial p}\right)_T\right]dp = 0. \qquad (2.16)$$

But

$$\sum_{i=1}^{l}\frac{R(\nu_i n^0 - \nu n_i^0)}{n} = \frac{R(\nu n^0 - n^0 \nu)}{n} = 0. \qquad (2.17)$$

The expression ahead of $(\partial\xi/\partial T)_p$ and $(\partial\xi/\partial p)_T$ is transformed such that, considering the solution (2.7):

$$\sum_{i=1}^{l}\nu_i S_i = \sum_{i=1}^{l}\nu_i\left(S_i^0 + \int_{T_0}^{T}\frac{c_{pi}}{T}\,dT\right) - R\sum_{i=1}^{l}\nu_i \ln p x_i =$$

$$= \Delta S - R\ln K_p(T). \qquad (2.18)$$

where ΔS is the change of entropy of the reaction.

Using the familiar relationship

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

where ΔH is the normal effect of the reaction, equal to $\Delta H = \sum_{i=1}^{l} \nu_i H_i$, $H_i = H_i^0 + \int_{T_0}^{T} c_{pi}\,dT$ (H_i is the enthalpy of the i-th component of the mixture), from equation (2.18) we get the following:

$$\sum_{i=1}^{l} \nu_i S_i = \frac{\Delta H}{T}. \tag{2.19}$$

Substituting expression (2.19) into equation (2.16) and considering the solution of (2.17), we get

$$\frac{1}{M}\left[\sum_{i=1}^{l} \frac{c_{pi} n_i}{T} + \frac{\Delta H}{T}\left(\frac{\partial \xi}{\partial T}\right)_p\right] dT + \frac{1}{M}\left[\frac{\Delta H}{T}\left(\frac{\partial \xi}{\partial p}\right)_T - nR/p\right] dp = 0. \tag{2.20}$$

Differentiating equation (2.19) with respect to T and making certain transformations, we obtain the following expression for $\left(\frac{\partial \xi}{\partial T}\right)_p$:

$$\left(\frac{\partial \xi}{\partial T}\right)_p = \left(\frac{\partial \ln K_p}{\partial T}\right)_p \Big/ \left(\sum_{i=1}^{l} \frac{\nu_i^2}{n_i} - \frac{\nu^2}{n}\right).$$

But, from the Van't Hoff isobar equation

$$\left(\frac{\partial \ln K_p}{\partial T}\right)_p = \frac{\Delta H}{RT^2}.$$

Therefore,

$$\left(\frac{\partial \xi}{\partial T}\right) = \Delta H / RT^2 \left(\sum_{i=1}^{l} \frac{\nu_i^2}{n_i} - \frac{\nu^2}{n}\right). \tag{2.21}$$

From equality (2.15) we find

$$\left(\frac{\partial\xi}{\partial p}\right)_T = -\nu/p\left(\sum_{i=1}^{s}\frac{\nu_i^2}{n_i} - \frac{\nu^2}{n}\right). \qquad (2.22)$$

Substituting expressions (2.21) and (2.22) into equations (2.20), we get

$$\frac{1}{M}\left[\frac{\Delta H^2}{RT^2\left(\sum_{i=1}^{s}\frac{\nu_i^2}{n_i} - \frac{\nu^2}{n}\right)} + \sum_{i=1}^{s} n_i c_{pi}\right]\frac{dT}{T} +$$

$$+\frac{1}{M}\left[-\frac{\nu\Delta H}{T\left(\sum_{i=1}^{s}\frac{\nu_i^2}{n_i} - \frac{\nu^2}{n}\right)} - nR\right]\frac{dp}{p} = 0. \qquad (2.23)$$

Let us show that the expression in the first set of brackets is the equilibrium heat capacity c_{pe}. For this let us use the equality

$$c_{pe} = \left(\frac{\partial H}{\partial T}\right)_p.$$

Since

$$H = \frac{\sum_{i=1}^{s} n_i H_i}{M},$$

then

$$\left(\frac{\partial H}{\partial T}\right)_p = \frac{1}{M}\left\{\sum_{i=1}^{s}\left[\left(\frac{\partial n_i}{\partial T}\right)_p H_i + n_i\left(\frac{\partial H_i}{\partial T}\right)_p\right]\right\}. \qquad (2.24)$$

Considering the solutions of (2.13) and (2.21), we get

$$\left(\frac{\partial H}{\partial T}\right)_p = \frac{1}{M}\left\{\sum_{i=1}^{s}\left[\nu_i H_i \frac{\Delta H}{RT^2\left(\sum_{i=1}^{s}\frac{\nu_i^2}{n_i} - \frac{\nu^2}{n}\right)} + \right.\right.$$

$$\left.\left. + n_i\left(\frac{\partial H_i}{\partial T}\right)_p\right]\right\}.$$

while since

$$\left(\frac{\partial H_i}{\partial T}\right) = c_{pi},$$

while

$$\sum_{i=1}^{e} \nu_i H_i = \Delta H,$$

then

$$c_{pe} = \left(\frac{\partial H}{\partial T}\right)_p = \frac{1}{M}\left[\frac{\Delta H^2}{RT^2\left(\sum_{i=1}^{e}\frac{\nu_i^2}{n_i} - \frac{\nu^2}{n}\right)} + \sum_{i=1}^{e} n_i c_{pi}\right].$$

Thus, the final form of the isentropy equation equation is as follows:

$$\frac{c_{pe}}{T}\,dT - \frac{1}{M}\left[\frac{\nu\Delta H}{T\left(\sum_{i=1}^{e}\frac{\nu_i^2}{n_i} - \frac{\nu^2}{n}\right)} + nR\right]\frac{dp}{p} = 0. \qquad (2.25)$$

II. Coordinates ρ, T. The equation of isentropy, considering that $\rho = 1/V$, looks as follows:

$$dS = \left(\frac{\partial S}{\partial T}\right)_\rho dT + \left(\frac{\partial S}{\partial \rho}\right)_T d\rho = \left(\frac{\partial S}{\partial T}\right)_V dT - V^2\left(\frac{\partial S}{\partial V}\right)_T d\rho = 0. \qquad (2.26)$$

Since

$$\left(\frac{\partial S}{\partial T}\right)_V = \frac{c_{pe}}{T}, \quad \left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V,$$

$$\left(\frac{\partial T}{\partial p}\right)_V \left(\frac{\partial p}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_p = -1, \qquad (2.27)$$

from which

$$\left(\frac{\partial S}{\partial V}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_p \Big/ \left(\frac{\partial V}{\partial p}\right)_T,$$

then

$$\frac{c_{pe}}{T}\,dT + \frac{V^2\left(\frac{\partial V}{\partial T}\right)_p}{\left(\frac{\partial V}{\partial p}\right)_T}\,d\rho = 0.$$

Since

$$V = \frac{\sum_{i=1}^{e} n_i RT}{MP},$$

then

$$\left(\frac{\partial V}{\partial p}\right)_T = -\frac{nRT}{Mp^2} + \frac{RT}{Mp}\sum_{i=1}^{c}\left(\frac{\partial n_i}{\partial p}\right)_T .$$

Considering expression (2.13) and (2.21) we get

$$\left(\frac{\partial V}{\partial p}\right)_T = -\frac{nRT}{Mp^2} - \frac{\nu^2 RT}{Mp^2\left(\sum\limits_{i=1}^{c}\frac{\nu_i^2}{n_i} - \frac{\nu^2}{n}\right)} . \tag{2.28}$$

For $(\partial V/\partial T)_p$ we obtain the following:

$$\left(\frac{\partial V}{\partial T}\right)_p = \frac{1}{Mp}\left[nR + \frac{\nu\Delta H}{T\left(\sum\limits_{i=1}^{c}\frac{\nu_i^2}{n_i} - \frac{\nu^2}{n}\right)}\right] . \tag{2.29}$$

Considering relationships (2.28) and (2.29), after certain transformations we finally obtain the isentropy equation:

$$c_{ve}\frac{dT}{T} - \frac{\left[nRT\left(\sum\limits_{i=1}^{c}\frac{\nu_i^2}{n_i} - \frac{\nu^2}{n}\right) + \nu\Delta H\right]}{T\sum\limits_{i=1}^{c}\frac{\nu_i^2}{n_i}}\frac{d\rho}{\rho} = 0. \tag{2.30}$$

For the examined thermodynamic system

$$c_{ve} = c_{pe} - \frac{\left[nRT\left(\sum\limits_{i=1}^{c}\frac{\nu_i^2}{n_i} - \frac{\nu^2}{n}\right) + \nu\Delta H\right]^2}{MRT^2\left(\sum\limits_{i=1}^{c}\frac{\nu_i^2}{n_i} - \frac{\nu^2}{n}\right) n \sum\limits_{i=1}^{c}\frac{\nu_i^2}{n_i}} . \tag{2.31}$$

III. Coordinates ρ, p. The equation of isentropy is as follows:

$$dS = \left(\frac{\partial S}{\partial p}\right)_\rho \partial p + \left(\frac{\partial S}{\partial \rho}\right)_p d\rho = \left(\frac{\partial S}{\partial p}\right)_V dp - V^2\left(\frac{\partial S}{\partial V}\right)_p d\rho = 0, \tag{2.32}$$

but

$$\left(\frac{\partial S}{\partial p}\right)_V = \frac{c_{ve}}{T}\left(\frac{\partial T}{\partial p}\right)_V , \quad \left(\frac{\partial S}{\partial V}\right)_p = \frac{c_{pe}}{T}\left(\frac{\partial T}{\partial V}\right)_p . \tag{2.33}$$

From relationship (2.27) we get

$$\left(\frac{\partial T}{\partial p}\right)_V = -\left(\frac{\partial V}{\partial p}\right)_T \left(\frac{\partial T}{\partial V}\right)_p. \qquad (2.34)$$

Having substituted expressions (2.33) and (2.34) into equations (2.32), and reducing by a multiplier not equal to zero, taking into account equality (2.28), we get

$$c_{ve}\left(\frac{\nu^2}{\sum\limits_{i=1}^{c}\frac{\nu_i^2}{n_i} - \frac{\nu^2}{n}} + n\right)\frac{dp}{p} - nc_{pe}\frac{d\rho}{\rho} = 0. \qquad (2.35)$$

Defining the isentropic index in coordinates p, T as a function which satisfies the equation analogous to the Poisson specific heat equation

$$\frac{\varkappa_{p,T} - 1}{\varkappa_{p,T}} = \frac{p}{T}\left(\frac{dT}{\partial p}\right)_s, \qquad (2.36)$$

for $\kappa_{p,T}$ we get the following expression which takes into account equation (2.25):

$$\varkappa_{p,T} = \frac{c_{pe}}{c_{pe} + \frac{1}{M}\left[\frac{\Delta H}{T\left(\sum\limits_{i=1}^{c}\frac{\nu_i^2}{n_i} - \frac{\nu^2}{n}\right)} + nR\right]}. \qquad (2.37)$$

By analogy, in ρ, T coordinates, from

$$\varkappa_{\rho,T} - 1 = \frac{\rho}{T}\left(\frac{dT}{d\rho}\right)_s$$

we obtain for $\kappa_{\rho,T}$ with consideration of equation (2.30)

$$\varkappa_{\rho,T} = 1 + \frac{nRT\left(\sum\limits_{i=1}^{c}\frac{\nu_i^2}{n_i} - \frac{\nu^2}{n}\right) + \nu\Delta H}{c_{ve}T\sum\limits_{i=1}^{c}\frac{\nu_i^2}{n_i}}. \qquad (2.38)$$

In ρ, p coordinates we obtain for

$$\varkappa_{p,\rho} = \frac{\rho}{p}\left(\frac{dp}{d\rho}\right)_s$$

with consideration of equation (2.35), the following:

$$\varkappa_{p,\rho} = \frac{c_{pe}\left(\sum_{i=1}^{c}\frac{\nu_i^2}{n_i} - \frac{\nu^2}{n}\right)}{c_{ve}\sum_{i=1}^{c}\frac{\nu_i^2}{n_i}}.$$

Figure 3 shows the dependence of $\kappa_{p,T}$ and c_{pe}/c_{ve} on temperature and pressure for the mixture $N_2O_4 \rightleftarrows 2NO_2 \rightleftarrows 2NO + O_2$.

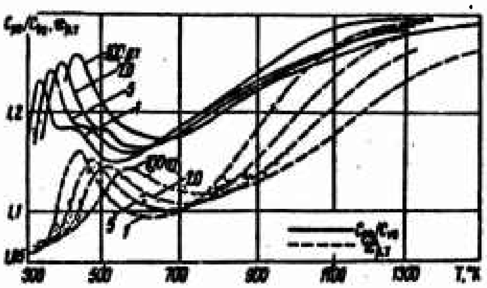

Fig. 3. Dependence of $\kappa_{p,T}$ and c_{pe}/c_{ve} on temperature and pressure.

As can be seen from this graph, $\kappa_{p,T}$ differs greatly from the specific heat ratio c_{pe}/c_{ve}. Therefore, in gas-dynamic calculations and in calculations of thermodynamic cycles with chemically reacting working media when using methods based on use of the specific heat ratio we must make use of the averaged values of $\kappa_{p,T}$. The nonmonotonic nature of the change in $\kappa_{p,T}$ with respect to temperature and the strong stratification with respect to pressure lead to great errors when averaging $\kappa_{p,T}$ with respect to temperature and pressure. This does not allow us to use, during the calculation of thermodynamic cycles for chemically reacting systems, methods of calculating gas-turbine cycles using inert gases [37]. The most suitable method for calculating thermodynamic cycles with such working media is the use of the H-S (enthalpy-entropy) diagrams which, although it is laborious particularly (as will be shown below) when calculating regeneration cycles, involves no errors of a numerical nature.

3. CALCULATING THE HEAT OF REGENERATION IN CYCLES USING CHEMICALLY REACTING MIXTURES WITH VARIABLE HEAT CAPACITY

Calculation of the regenerated heat in cycles using chemically reacting systems is complicated because of the dependence of the heat capacity of such systems on the temperature and pressure (Fig. 4), which does not allow us to use ordinary formulas to determine the regenerator effectiveness and the regenerated heat.

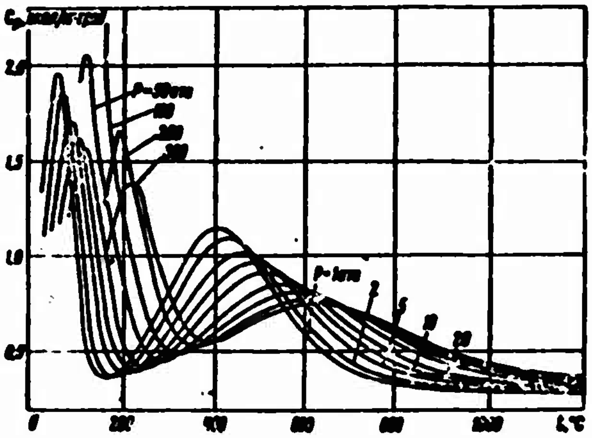

Fig. 4. Dependence of the effective isobaric heat capacity c_{pe} on temperature and pressure.
Designations: ккал/кг·град = kcal/kg·deg; ата = atm (abs).

Below we present calculation of the regeneration heat in cycles using working media with variable heat capacity for the case of unidirectional flow and backflow. Here we assume that the mass flows of working medium along the heated and warmed sides of the regenerator are equal, and pressure losses can be disregarded.

Unidirectional flow. Let us examine the behavior of the current temperature head

$$\delta = T^{*} - T \qquad (2.39)$$

as a function of the change in temperature of the warm wall of the regenerator, which we took as an independent variable. For this we use the connection between the current values of the temperature of the warmed and heated walls of the regenerator in terms of the heat-balance equation for the current value of the temperature of the heated wall of the regenerator

$$H(p_4,\ T_4)-H(p_4,\ T^*)=H(p_2,\ T)-H(p_2,\ T_2). \qquad (2.40)$$

For the derivative of the temperature head with respect to T*

$$\delta'_{T^*}=1-[T]'_{T^*},$$

considering equation (2.40) and the known relationship $c_{pe} = \left(\frac{\partial H}{\partial T}\right)_p$, we obtain the following expression:

$$\delta'_{T^*}=1+\frac{c_p(p_4,\ T^*)}{c_p(p_2,\ T)}. \qquad (2.41)$$

From this we see that in the interval of change of $T^*[T_{4p},\ T_4]$, due to the fact that the heat capacity is a positive magnitude, $\delta'_{T^*} \neq 0$. Consequently, there is no extremum of δ within the interval $[T_{4p},\ T_4]$ and it is reached at the ends of the interval. Obviously, the minimum δ is reached with $T^* = T_{4p}$. Let us show that Q_{per} will have a maximum with $\delta_{min} = 0$. Let us examine the change in Q_{per} with a change in δ:

$$Q_{per}=H(p_4,\ T_4)-H(p_4,\ T^*). \qquad (2.42)$$

Considering dependences (2.41) and (2.42), for the derivative of Q_{per} with respect to δ we obtain the following expression:

$$\frac{dQ_{per}}{d\delta}=\frac{dQ_{per}}{dT^*}\,\frac{dT^*}{d\delta}=-\frac{c_p(p_2,\ T)\,c_p(p_4,\ T^*)}{c_p(p_2,\ T)+c_p(p_4,\ T^*)}. \qquad (2.43)$$

Since $[Q_{per}]'_{\delta} \neq 0$, within the interval of change of δ from its maximum value to the minimum, we have the possible value δ = 0, with no extremum of Q_{per}. Consequently, both the maximum and minimum of Q_{per} are achieved at the ends of interval δ. Obviously, the maximum Q_{per} is obtained with δ = 0. Thus, with unidirectional flow of a working substance with variable heat capacity, as well as a working substance with constant heat capacity, the minimum temperature head is achieved at the output from the regenerator, while Q_{per} is maximum at δ_{min}. Calculation of the maximum heat of regeneration Q^0_{per} reduces to solution of the equation

$$H(p_4, T_4) - H(p_4, T^*) = H(p_2, T^* - \delta_{min}) - H(p_2, T_2) \qquad (2.44)$$

with $\delta_{min} = 0$, from which we find T* and substitute it into equation (2.42).

With given regenerator effectiveness μ of the heat of regeneration

$$Q_{per} = \mu Q^0_{per}. \qquad (2.45)$$

We must note that it is not very convenient to give the regenerator effectiveness when calculating the heat of regeneration in cycles using working media with variable heat capacity, since it is necessary each time to calculate the minimum temperature head in order to arrive at the technically realizable head. It is much more convenient to give immediately the minimum temperature head δ_{min}, find T* from equation (2.44), and, substituting T* into equation (2.42), determine Q_{per}. This is even more true of calculations of the heat of regeneration in the case of backflow, which we will now discuss.

Backflow. The heat balance equation for the given case is written as follows:

$$H(p_4, T_4) - H(p_4, T^*) = H(p_2, T_{2p}) - H(p_2, T). \qquad (2.46)$$

Let us examine the behavior of the current temperature head with a change of T* from T_{4p} to T_4, considering T_{2p} as fixed. For δ'_{T^*} we obtain, with consideration of equation (2.46), the following expression:

$$\delta'_{T^*} = 1 - \frac{c_p(p_4, T^*)}{c_p(p_2, T)}. \qquad (2.47)$$

From this we see that δ can have an extremum not only at the ends of the interval $[T_{4p}, T_4]$, as in the case of unidirectional flow, but also within it. The points which we suspect to be on the extremum δ are determined from the equation

$$c_p(p_4, T^*) = c_p(p_2, T). \qquad (2.48)$$

where T is defined from expression (2.46).

Let us assume that in the interval of change of T^* equation (2.48) has one root T_0^* and it corresponds to the minimum δ. This minimum δ was obtained for a fixed value of T_{2p}. If we are given not T_{2p} but δ_{min}, from the equation

$$c_p(p_r, T^*) = c_p(p_r, T^* - \delta_{min}) \tag{2.49}$$

we can find the root T_0^* which corresponds to δ_{min}, and from T_0^* we can find T_{2p} from the equation

$$H(p_r, T_0) - H(p_r, T_0^*) = H(p_r, T_{2p}) - H(p_r, T_0^* - \delta_{min}) \tag{2.50}$$

Knowing T_{2p}, we can calculate Q_{per} which corresponds to the given δ_{min}, as follows:

$$Q_{per} = H(p_r, T_{2p}) - H(p_r, T_0). \tag{2.51}$$

Let us show that maximum Q_{per} is obtained if we set $\delta_{min} = 0$. For this let us examine the change of T_{2p} with a change in δ_{min}. Since

$$(\delta_{min})'_{T_{2p}} = (T_0^*)'_{T_{2p}} - (T_0)'_{T_0^*}(T_0^*)'_{T_{2p}}, \tag{2.52}$$

with consideration of equations (2.47), (2.49), and (2.50) we get

$$(\delta_{min})'_{T_{2p}} = -\frac{c_p(p_r, T_{2p})}{c_p(p_r, T_0)}, \tag{2.53}$$

from which

$$(T_{2p})'_{\delta_{min}} = -\frac{c_p(p_r, T_0)}{c_p(p_r, T_{2p})}. \tag{2.54}$$

From equation (2.54) it follows that T_{2p} reaches an extremum at the ends of the interval of change of δ_{min}; in this case T_{2p} is maximum with $\delta_{min} = 0$. From this, Q_{per} is maximum with $\delta_{min} = 0$, as seen from equation (2.51), since enthalpy is an increasing function of temperature.

If with given δ_{min} the root of equation (2.49) T_0^* corresponds not to the minimum δ, but to the maximum, i.e., at the ends of the interval $[T_{4p}, T_4]$ we have δ which is less than the given δ_{min}, δ_{min} must be given either at the right or the left end of the interval of change T^*, depending on where δ is least. It is easy to see that the given δ_{min} must be selected at that end of the interval $[T_{4p}, T_4]$ for which the heat of regeneration is the minimum of the two values calculated from the ends of the interval. Let us assume that δ_{min} is given with $T^* = T_{4p}$. Then

$$Q_{per} = H(p_1, T_{4p}) - H(p_1, T_2), \tag{2.55}$$

where $T_{4p} = T_4 - \delta_{min}$. As we see from equation (2.55), Q_{per} is maximum with $\delta_{min} = 0$. The same is true if δ_{min} is given with $T^* = T_{4p}$. In this case,

$$Q_{per} = H(p_1, T_4) - H(p_1, T_{4p}), \tag{2.56}$$

where $T_{4p} = T_2 + \delta_{min}$.

Equation (2.49) with given δ_{min} might have no route within the interval $[T_{4p}, T_4]$. In this case the given δ_{min} must be selected only from the ends of the interval $[T_{4p}, T_4]$. If in the entire interval $c_p(p_1, T^* - \delta_{min}) > c_p(p_2, T^*)$, δ_{min} must be given with $T^* = T_{4p}$ and Q_{per} is calculated from formula (2.56), while if in the entire interval $[T_{4p}, T_4]$ $c_p(p_1, T^* - \delta_{min}) < c_p(p_2, T^*)$, δ_{min} must be given with $T^* = T_4$ and Q_{per} is calculated from fromula (2.55). Here the maximum Q_{per} is obtained in the same manner as when $\delta_{min} = 0$.

If equation (2.49) in the interval of change of T^* has several roots, and we are given one of these roots δ_{min}, from the value of this root and the given δ_{min} we determine T_{2p}, while from T_{2p} we determine δ for all other roots. Comparing the obtained values of δ and δ_{min} to one another, we find the smallest of the δ and the root of equation (2.49) corresponding to this δ. With this value of the root we select the given δ_{min}, and from expressions (2.50) and (2.51) we find Q_{per}.

Thus, in the case of backflow of working media with variable heat capacity, the minimum temperature head can also be within the interval of change of the independent variable, unlike backflow using working media with constant heat capacity, but the heat of regeneration is also maximum with $\delta_{min} = 0$. The expression for the regenerator effectiveness in the general case is written as follows: $\mu = Q_{per}/Q^0_{per}$, where Q_{per} is the heat of regeneration with given δ_{min}, Q^0_{per} is the heat of regeneration with $\delta_{min} = 0$.

There is a graphic method for determining the heat of regeneration in cycles with working media with variable heat capacity using the H-T diagram of the working medium. Figure 5 shows an example of the low- and high-pressure isobars corresponding to the hot and cold walls of the regenerator. Heat can be regenerated on isobar sections 4'-2 and 2'-4 which are cut off by isotherms T_2 = const and T_4 = const. Moving within this temperature interval the low-pressure isobar such that at one point it touches the high-pressure isobar (which indicates equality of the temperature head to zero at this point of the regenerator), while at all other points the condition $\delta > 0$ would be observed, we obtain the maximum quantity of heat which can be thermodynamically fed to the regenerator, $Q_{4p-2p} = H_{4p} - H_{2p}$. In this case the regenerator effectiveness is equal to one. The regenerated heat, corresponding to the given regenerator efficiency, $Q_{per} = \mu Q_{4p-2p}$. Now the low-pressure isobar should be moved downward (within limits of temperatures T_2 and T_4) such that the regenerated heat is equal to Q_{per}, after which we can determine here the temperatures of the gas at the inlet and outlet of the regenerator along the high- and low-pressure sides, and the minimum temperature head. If we are given immediately the minimum temperature head, we can shift the low-pressure isobar downward such that we obtain the given minimum temperature head, and using the previously described procedure find Q_{per} and the outlet temperatures from the regenerator.

There is a second method for graphically determining the heat of regeneration using H-T or H-S diagrams and the graph of the dependence of the heat capacity of the working medium on the temperature and pressure. Moving along the low-pressure isobar on the graphs $c_p = f(p, T)$ (see Fig. 4), we reach a position such that

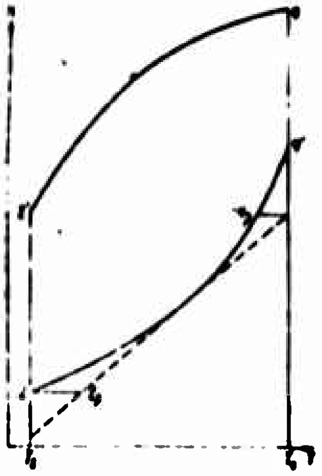

Fig. 5. H-T diagram in a regenerator in cycles using working media with variable heat capacity.

between the low- and high-pressure isobars the distance along the temperature axis is exactly equal to the given δ_{min}. The temperature on the low-pressure isobar, corresponding to this position, will be (as we can easily see) the root of equation (2.49). Calculation of Q_{per} and the temperatures at the regenerator outlet with the known root T_0^* can be done using H-T or H-S diagrams, using equations (2.50) and (2.51).

As an example, let us examine the calculation of the heat of regeneration in a cycle using a chemically reacting gas system $N_2O_4 \rightleftarrows 2NO_2 \rightleftarrows 2NO + O_2$.

Equation (2.49), depending on the magnitude and position of the range $[T_2, T_4]$ can have in it one-three roots or it may not have them. Depending on this, calculation of the heat of regeneration is divided into four cases.

I. In the range $[T_2, T_4]$ with given δ_{min} equation (2.49) has three roots: T_{10}^*, T_{20}^*, T_{30}^*.

Let us assume that δ_{min} corresponds to temperature T_{10}^*, and find the temperature heads which correspond to the two other points which we suspect of being the extremum - T_{20}^* and T_{30}^*. This can be done as follows. Based on δ_{min} and T_{10}^*, from the equation

$$H(p_2, T'_{2p}) - H(p_2, T^*_{10} - \delta_{\min}) = H(p_4, T_4) - H(p_4, T^*_{10}) \qquad (2.57)$$

we can find T'_{2p}, and based on T'_{2p}, from the equations

$$H(p_2, T'_{2p}) - H(p_2, T^*_{20} - \delta_{\min}) = H(p_4, T_4) - H(p_4, T^*_{20}), \qquad (2.58)$$
$$H(p_2, T'_{2p}) - H(p_2, T^*_{30} - \delta_{\min}) = H(p_4, T_4) - H(p_4, T^*_{30}) \qquad (2.59)$$

we can find δ_2 and δ_3 which are, respectively, the temperature heads at points T^*_{20} and T^*_{30}. Comparing δ_2, δ_3, and δ_{min} among themselves, we find the smallest of them and, at a temperature corresponding to the smallest temperature head, give δ_{min}.

This comparison of temperature heads at points T^*_{10}, T_{20}, and T^*_{30} can be done without seeking T'_{2p}, δ_2, and δ_3. Let us subtract equation (2.57) from expressions (2.58) and (2.59). We obtain the following relationships:

$$H(p_2, T^*_{20} - \delta_2) - H(p_2, T^*_{10} - \delta_{\min}) = H(p_4, T^*_{10}) - H(p_4, T^*_{20}),$$
$$H(p_2, T^*_{30} - \delta_3) - H(p_2, T^*_{10} - \delta_{\min}) = H(p_4, T^*_{10}) - H(p_4, T^*_{30}).$$

In these equalities in place of δ_2 and δ_3 we substitute δ_{min}, and find the sign of the following expression:

$$H(p_2, T^*_{20} - \delta_{\min}) - H(p_2, T^*_{10} - \delta_{\min}) -$$
$$- H(p_4, T^*_{10}) + H(p_4, T^*_{20}); \qquad (2.60)$$
$$H(p_2, T^*_{30} - \delta_{\min}) - H(p_2, T^*_{10} - \delta_{\min}) -$$
$$- H(p_4, T^*_{10}) + H(p_4, T^*_{30}). \qquad (2.61)$$

If both expressions are greater than zero, obviously the temperature head at points T^*_{20} and T^*_{30} is greater than δ_{min} and, consequently, δ_{min} corresponds to T^*_{10}. If at least one of expressions (2.60) or (2.61)is less than zero, the temperature head corresponding to it is less than δ_{min} and, consequently, δ_{min} must be given with the value of the root of equation (2.49).corresponding to this expression.

If both expressions (2.60) and (2.61) are less than zero, both δ_2 and δ_3 are less than δ_{min}. In this case, assuming that δ_{min} corresponds to T^*_{20}, from the sign of the expression

$$H(p_2, T^*_{20} - \delta_{\min}) - H(p_2, T^*_{30} - \delta_{\min}) - \\ - H(p_4, T^*_{20}) + H(p_4, T^*_{30}) \qquad (2.62)$$

we find the temperature head at point T^*_{30}. If expression (2.62) is greater than zero, the temperature head at point T^*_{30} is greater than at point T^*_{20} and, consequently, $\delta_{\min}$ must be given at point T^*_{20}. If expression (2.62) is less than zero, the temperature head at point T^*_{30} is less than at point T^*_{20}, and $\delta_{\min}$ must be given at T^*_{30}. Equality of expressions (2.60)-(2.62) to zero obviously indicates equality of the compared temperature heads. Then $\delta_{\min}$ can be given at any of the compared points.

Having defined the root of T^*_{10}, at which we must give $\delta_{\min}$, from the equation $H(p_2, T_{2p}) - H(p_2, T^*_{10} - \delta_{\min}) = H(p_4, T_4) - H(p_4, T^*_{10})$ we find T_{2p} and then calculate the heat of regeneration $Q_{\text{рег}} = H(p_2, T_{2p}) - H(p_2, T_2)$. If we seek the roots of equation (2.49) in ascending order, i.e., $T^*_{10} < T^*_{20} < T^*_{30}$, as we see from the graph of the dependence of the heat capacity of the chemically reacting system $N_2O_4 \rightleftharpoons 2NO_2 \rightleftharpoons 2NO + O_2$ on the temperature and pressure (see Fig. 4), by replacing the sign of expression $c_p(p_4, T^*) - c_p(p_2, T^* - \delta_{\min})$ on passage through these roots we can conclude that T^*_{10} and T^*_{30} will always correspond to minimum δ, while T^*_{20} corresponds to maximum δ. From this it follows that minimum δ is never reached at the ends of the interval $T^*[T_2, T_4]$, and we can compare the temperature heads only at the two points corresponding to T^*_{10} and T^*_{30}.

II. In the range $[T_2, T_4]$ equation (2.49) has two roots - T^*_{10} and T^*_{20}.

Using the same method as in the case of three roots, let us compare the temperature heads at the points corresponding to the roots. Let us compare the smallest of these with the temperature heads at the ends of the interval $[T_2, T_4]$.

In order to compare, for example, the temperature head at the end of T_4 with the temperature head at T^*_{10}, it is necessary to determine the sign of the expression $H(p_2, T_4 - \delta_{\min}) - H(p_2, T^*_{10} - \delta_{\min}) - H(p_4,$

$T_4) + H(p_4, T^*_{10})$, which is obtained from the same concepts as expressions (2.60)-(2.62).

III. In the interval $[T_2, T_4]$ equation (2.49) has one root T^*_{10}.

This root can correspond either to the minimum or the maximum of the temperature head. This can be determined by alternating the sign of δ'_{T^*} upon passage of T^* through T^*_{10}, i.e., by changing the sign of the expression

$$c_p(p_2, T^* - \delta_{\min}) - c_p(p_4, T^*). \tag{2.63}$$

If T^*_{10} corresponds to the minimum temperature head, by setting it equal to $\delta_{\min}$ we can define Q_{per}. If T^*_{10} corresponds to the maximum temperature head, the minimum, consequently, is found at either end of the interval $[T_2, T_4]$. This is easy to establish by determining the sign of the following expression:

$$\begin{gathered} H(p_4, T_4) - H(p_4, T_2 + \delta_{\min}) - \\ - H(p_2, T_4 - \delta_{\min}) + H(p_2, T_2). \end{gathered} \tag{2.64}$$

If this expression is less than zero, the temperature head is obviously minimum at temperature T_2. In this case the heat of regeneration is calculated as follows: $Q_{per} = H(p_4, T_4) - H(p_4, T_2 + \delta_{\min})$.

If expression (2.64) is greater than zero, the temperature head is minimum at temperature T_4 and the heat of regeneration $Q_{per} = H(p_2, T_4 - \delta_{min}) - H(p_2, T_2)$.

IV. Equation (2.49) has no roots in the interval $[T_2, T_4]$.

From this it follows that the minimum and maximum temperature heads are located at the ends of the interval $[T_2, T_4]$. If $\delta'_{T^*} > 0$ in the entire interval $[T_2, T_4]$, i.e.,

$$c_p(p_2, T^* - \delta_{\min}) - c_p(p_4, T^*) > 0, \tag{2.65}$$

the minimum temperature head obviously corresponds to T_2, and the heat of regeneration $Q_{per} = H(p_4, T_4) - H(p_4, T_2 + \delta_{min})$.

If $\delta'_{T^{\#}} < 0$ in the entire interval $[T_2, T_4]$, i.e.,

$$c_p(p_2, T^{*} - \delta_{min}) - c_p(p_4, T^{*}) < 0, \tag{2.66}$$

the temperature head is minimum at T_4 and the heat of regeneration $Q_{per} = H(p_2, T_4 - \delta_{min}) - H(p_2, T_2)$.

Based on the above, we can write as follows the algorithm for calculating the heat of regeneration in the cycle with $N_2O_4 \rightleftarrows 2NO_2 \rightleftarrows 2NO + O_2$.

I. Equation $c_p(p_4, T^{*}) = c_p(p_2, T^{*} - \delta_{min})$ has the roots $T^{\#}_{10}$, $T^{\#}_{20}$, $T^{\#}_{30}$ and $T^{\#}_{10} < T^{\#}_{20} < T^{\#}_{30}$.

1) If $H(p_2, T^{*}_{20} - \delta_{min}) - H(p_2, T^{*}_{10} - \delta_{min}) - H(p_4, T^{*}_{20}) + H(p_4, T^{*}_{10}) : > 0$, proceed to No. 2; < 0, proceed to No. 3;

2) if $H(p_2, T^{*}_{30} - \delta_{min}) - H(p_2, T^{*}_{10} - \delta_{min}) - H(p_4, T^{*}_{30}) + H(p_4, T^{*}_{10}) : > 0$, proceed to No. 4; < 0, proceed to No. 6;

3) if $H(p_2, T^{*}_{30} - \delta_{min}) - H(p_2, T^{*}_{20} - \delta_{min}) - H(p_4, T^{*}_{30}) + H(p_4, T^{*}_{20}) : > 0$, proceed to No. 5; < 0, proceed to No. 6;

4) the equation for finding T_{2p}, $H(p_2, T_{2p}) - H(p_2, T^{*}_{10} - \delta_{min}) = H(p_4, T_4) - H(p_4, T^{\#}_{10})$;

5) the equation for finding T_{2p}: $H(p_2, T_{2p}) - H(p_2, T^{\#}_{20} - \delta_{min}) = H(p_4, T_4) - H(p_4, T^{\#}_{20})$;

6) the equation for finding T_{2p}: $H(p_2, T_{2p}) - H(p_2, T^{\#}_{30} - \delta_{min}) = H(p_4, T_4) - H(p_4, T^{\#}_{30})$;

7) $Q_{per} = H(p_2, T_{2p}) - H(p_2, T_2)$.

II. The equation $c_p(p_4, T^*) = c_p(p_2, T^* - \delta_{min})$ has the roots T^*_{10}, T^*_{20}.

1) If $H(p_2, T^*_{20} - \delta_{min}) - H(p_2, T^*_{10} - \delta_{min}) - H(p_4, T^*_{20}) + H(p_4, T^*_{10})$: >0, go to No. 2; <0, go to No. 7;

2) if $H(p_2, T_4 - \delta_{min}) - H(p_2, T^*_{10} - \delta_{min}) - H(p_4, T_4) + H(p_4, T^*_{10})$: >0, go to No. 3; <0, go to No. 5;

3) the equation for finding T_{2p}: $H(p_2, T_{2p}) - H(p_2, T^*_{10} - \delta_{min}) = H(p_4, T_4) - H(p_4, T^*_{10})$;

4) $Q_{per} = H(p_2, T_{2p}) - H(p_2, T_2)$;

5) $T_{2p} = T_4 - \delta_{min}$;

6) $Q_{per} = H(p_2, T_{2p}) - H(p_2, T_2)$;

7) if $H(p_2, T^*_{20} - \delta_{min}) - H(p_2, T_2) - H(p_4, T^*_{20}) + H(p_4, T_2 + \delta_{min})$: >0,

8) $T_{4p} = T_2 + \delta_{min}$;

9) $Q_{per} = H(p_4, T_4) - H(p_4, T_{4p})$;

10) the equation for finding T_{2p}: $H(p_2, T_{2p}) - H(p_2, T^*_{20} - \delta_{min}) = H(p_4, T_4) - H(p_4, T^*_{20})$;

11) $Q_{per} = H(p_2, T_{2p}) - H(p_2, T_2)$.

III. The equation $c_p(p_4, T^*) = c_p(p_2, T^* - \delta_{min})$ has one root T^*_{10}.

1) If $c_p(p_2, T^* - \delta_{min}) - c_p(p_4, T^*)$ on passage through T^*_{10} changes sign from + to -, go to No. 2; from - to +, go to No. 5;

2) if $H(p_4, T_4) - H(p_4, T_2 + \delta_{min}) - H(p_2, T_4 - \delta_{min}) + H(p_2, T_2)$: >0, go to No. 3; <0, go to No. 4;

3) $Q_{per} = H(p_2, T_4 - \delta_{min}) - H(p_2, T_2)$;

4) $Q_{per} = H(p_4, T_4) - H(p_4, T_2 + \delta_{min})$;

5) the equation for finding T_{2p}: $H(p_2, T_{2p}) - H(p_2, T^*_{10} - \delta_{min}) = H(p_4, T_4) - H(p_4, T^*_{10})$;

6) $Q_{per} = H(p_2, T_{2p}) - H(p_2, T_2)$.

IV. The equation $c_p(p_2, T^* - \delta_{min}) = c_p(p_4, T^*)$. No roots.

1) If $c_p(p_2, T^* - \delta_{min}) - c_p(p_4, T^*)$: >0, go to No. 2; <0, go to 3;

2) $Q_{per} = H(p_4, T_4) - H(p_4, T_2 + \delta_{min})$;

3) $Q_{per} = H(p_2, T_4 - \delta_{min}) - H(p_2, T_2)$.

For systems of the type $Al_2Cl_6 \rightleftarrows 2AlCl_3$, $Al_2Br_6 \rightleftarrows AlBr_3$ the heat of regeneration can be calculated much more simply in view of the fact that equation (2.49) has only one root or none. In this case, if there is one root, it must correspond to the minimum temperature head, and there is no need to verify the minimum of the end of the interval $[T_2, T_4]$.

Algorithm for calculating the heat of regeneration.

I. Equation $c_p(p_2, T^* - \delta_{min}) = c_p(p_4, T^*)$ has the root T^*_0:

1) the equation for finding T_{2p}: $H(p_2, T_{2p}) - H(p_2, T^*_0 - \delta_{min}) = H(p_4, T_4) - H(p_4, T^*_0)$;

2) $Q_{per} = H(p_2, T_{2p}) - H(p_2, T_2)$.

II. The equation $c_p(p_2, T^* - \delta_{min}) = c_p(p_4, T^*)$ has no roots:

1) if $c_p(p_2, T^* - \delta_{min}) - c_p(p_4, T^*)$; a) >0, go to No. 2; b) <0, go to No. 3;

2) $Q_{per} = H(p_4, T_4) - H(p_4, T_2 + \delta_{min})$;

3) $Q_{per} = H(p_2, T_4 - \delta_{min}) - H(p_2, T_2)$.

4. FEATURES OF THE THERMAL CALCULATION OF HEAT EXCHANGERS USING CHEMICALLY REACTING MIXTURES

The calculation of heat circuits for power plants using dissociating gases has certain features and difficulties. It is quite complex to calculate the heat of regeneration in cycles, the thermal calculations of intermediate heat exchangers in binary plants, coolants, etc. These difficulties are caused by the nonlinear nature of the change in thermodynamic properties of the dissociating gases as a function of temperature and pressure [8]; this in turn leads to a nonmontonic change in temperature head along the heat exchanger, as a result of which the minimum temperature head can be found not only at the ends but also in the inner regions of the heat exchanger. Therefore, thermal calculation of heat exchangers must be done with this condition taken into account. Below we give a solution of the problem of finding the point of minimum temperature head and a method of thermal calculation of a heat exchanger with a given minimum temperature head.

The problem was solved for a backflow circuit of motion of coolant without considering losses of pressure and with different flows along the heating and warmed sides of the heat exchanger.

Figure 5a shows a diagram of the distribution of temperatures as a function of heat flow.

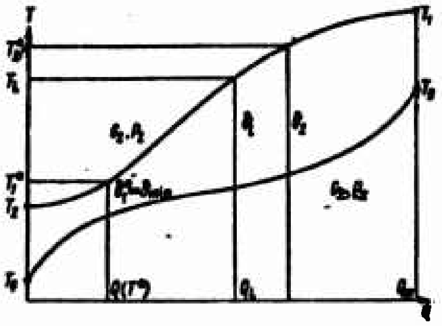

Fig. 5a. Diagram of the distribution of temperatures in a heat exchanger as a function of heat flow.

The form of solution of the problem will depend on the manner in which the initial data are given. We will examine two methods here.

I. Let us consider that the following values are given (see Fig. 5a): T_4, T_1, p_2, p_x, G_2, G_x, δ_{min}. We must determine the output temperatures of the coolant, i.e., T_2 and T_3. We are given the value T_2. Then the heat-balance equation for the i-th section is written as follows:

$$Q_i = G_2[H(p_2, T_i) - H(p_2, T_2)] = \\ = G_x[H(p_x, T_i - \delta_i) - H(p_x, T_3)]. \qquad (2.67)$$

where H(p, T), the enthalpy of the gas, is a function of temperature and pressure; Q_i is the heat flow for the i-th section of heat exchangers; T_i is the current temperature in the i-th section along the hot side of the heat exchanger; $T_i - \delta_i$ is the current temperature in the i-th section along the cold wall of the heat exchanger; δ_i is the current temperature head for the i-th section; G_2 is the flow of coolant along the hot side of the heat exchanger; G_x is the flow of coolant along the cold side of the heat exchanger.

Let us differentiate expression (2.67) with respect to current temperature:

$$\left(\frac{\partial Q_i}{\partial T}\right)_p = G_2\left[\frac{\partial H(p_2, T_i)}{\partial T}\right]_p = G_x\left[\frac{\partial H(p_x, T_i - \delta_i)}{\partial T}\right]_p. \qquad (2.68)$$

Since

$$\left[\frac{\partial H(p_2, T_i)}{\partial T}\right]_p = c_p(p_2, T_i),$$

while

$$\left[\frac{\partial H(p_x, T_i - \delta_i)}{\partial T}\right]_p = c_p(p_x, T_i - \delta_i) \times \\ \times \frac{\partial(T_i - \delta_i)}{\partial T} = c_p(p_x, T_i - \delta_i)\left(1 - \frac{\partial \delta_i}{\partial T}\right).$$

where $c_p(p, T)$, the isobaric heat content of the gas, is a function of temperature and pressure, by substituting these transformations into equation (2.68) we get

$$G_2 c_p(p_2, T) = G_x c_p(p_x, T - \delta)\left(1 - \frac{\partial \delta}{\partial T}\right). \qquad (2.69)$$

After certain transformations of expression (2.69) we obtain the following:

$$\frac{\partial\delta}{\partial T}=\frac{G_2}{G_x}\,\frac{c_p(p_2,\ T)}{c_p(p_x,\ T-\delta)}-1. \tag{2.70}$$

Let us verify function δ(T) for the extremum, equating its derivative to zero:

$$\frac{G_2}{G_x}\,\frac{c_p(p_2,\ T^*)}{c_p(p_x,\ T^*-\delta^*)}=1, \tag{2.71}$$

i.e., $G_2c_p(p_2,\ T^*)=G_xc_p(p_x,\ T^*-\delta^*)$, where T^* is the extremal point; δ^* is the temperature head at the extremal point, equal in magnitude to δ_{min} (given).

As can be seen from expression (2.71), the extremal point in a heat exchanger can be reached when the "water" equivalent $Gc_p(p, T)$ are equal.

Thus, given the value $\delta^* = \delta_{min}$, we can always find the extremal point T^* (if it exists in the investigated range of temperature). The unknown values of the output temperatures of the flow (T_2 and T_3) can be found from the system of equations

$$\begin{gathered}G_x\left[H(p_x,\ T^*-\delta^*)-H(p_x,\ T_4)\right]=\\=G_2\left[H(p_2,\ T^*)-H(p_2,\ T_2)\right],\\G_x\left[H(p_x,\ T_3)-H(p_x,\ T^*-\delta^*)\right]=\\=G_2\left[H(p_2,\ T_1)-H(p_2,\ T^*)\right].\end{gathered} \tag{2.72}$$

II. We are given the following values: T_1, T_2, T_4, G_2, δ_{min}. We must determine T_3 and G_x.

In this case, solving the system of equations written for section T^*,

$$\begin{gathered}\frac{G_2}{G_x}=\frac{H(p_x,\ T^*-\delta^*)-H(p_x,\ T_4)}{H(p_2,\ T^*)-H(p_2,\ T_2)},\\\frac{G_2}{G_x}=\frac{c_p(p_x,\ T^*-\delta^*)}{c_p(p_2,\ T^*)},\end{gathered} \tag{2.73}$$

we obtain the following expression for determining the position of the extremal point T^*:

$$\frac{H(\rho_2, T^*)-H(\rho_2, T_2)}{c_p(\rho_2, T^*)}=\frac{H(\rho_x, T^*-\delta^*)-H(\rho_x, T_4)}{c_p(\rho_x, T^*-\delta^*)}. \tag{2.74}$$

Equation (2.74) allows us to find the extremal point T^* with given temperature head in it, and then determine the unknown flow and the unknown output temperature, solving the following system of equations:

$$\begin{aligned} G_x &= G_2\,\frac{H(\rho_2, T^*)-H(\rho_2, T_2)}{H(\rho_x, T^*-\delta^*)-H(\rho_x, T_4)},\\ H(\rho_x, T_3) &= H(\rho_x, T_4)+G_2\,\frac{H(\rho_2, T_1)-H(\rho_2, T_2)}{G_x}. \end{aligned} \tag{2.75}$$

We examined two basic methods for solving this problem. The point of minimum temperature head can be found either from equation (2.71) or from (2.74). Let us study the solution of these equations.

1) Equations (2.71) and (2.74) can contain several roots, i.e., several extremal points T^*. In this case we select that solution which satisfies the condition $\delta \geq \delta_{min}$ in the investigated temperature range.

2) The presence of an extremal point in the investigated temperature range assumes a minimum in it as well as a maximum temperature head, i.e., in the latter case $\delta \leq \delta_{min}$, which leads to incorrect calculation of the heat exchanger. To avoid possible errors in the calculation, we must verify the boundary points at the minimum.

3) If the flows of coolant are identical along the heating and heated walls of the heated exchanger, equation (2.71) assumes the form obtained previously:

$$c_p(\rho_2, T^*)=c_p(\rho_x, T^*-\delta^*). \tag{2.76}$$

CHAPTER III

GAS AND GAS-DYNAMIC CYCLES USING CHEMICALLY REACTING WORKING MEDIA

1. THE GAS CYCLE

Unlike gas-turbine plants using inert gases (He, N_2, and others), in cycles using dissociating gases we should expect an influence of the shape of the boundary curve on the thermodynamic indices of the gas-turbine cycle, since most of the dissociating systems pertain to substances with relatively high boiling point. In addition, at atmospheric pressure in gas cycles with dissociating gases we should expect a significant influence of the absolute pressure of the gas on the thermodynamic indices due to the dependence of the thermophysical properties not only on temperature but also on pressure.

During thermodynamic studies of gas cycles we examined a number of closed-cycle GTP's using dissociating N_2O_4 gas. We studied a simple circuit (Fig. 6c), a circuit with regeneration of heat (Fig. 6a), and a circuit with regeneration and intermediate heating of the gas (Fig. 6b).

Thermodynamic calculations of simple gas cycles for GTP's using dissociating N_2O_4 gas with a change of minimum temperature of the cycle in the range 40-158°C and maximum pressure of 6-200 atm (abs) and temperature of 600-1200°C showed that the optimum compression ratio $\pi_к$ is 60-80, which considerably exceeds the optimum values of the compression ratio using inert gases [37].

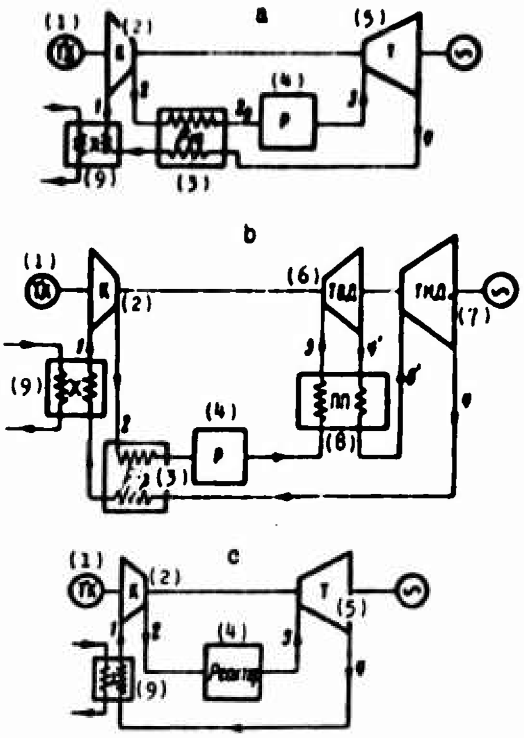

Fig. 6. Circuits for gas cycles: a — with regeneration, b — with regeneration and intermediate superheating, c — simple.

KEY: (1) gas generator, (2) compressor, (3) regeneration, (4) reactor, (5) turbine, (6) high-pressure turbine, (7) low-pressure turbine, (8) intermediate superheater, (9) coolant.

The occurrence of chemical reactions with absorption and release of heat during heating and cooling has a favorable influence on the effectiveness of regeneration in the cycles, which results in increased cycle efficiency. Therefore, chemically reacting working media are used to best advantage in cycles regeneration.

When analyzing gas cycles with regeneration we examined the influence of the minimum parameters (temperature T_1 and pressure p_1), the maximum parameters (temperature T_3 and pressure p_3), the coefficient of low-space and high-pressure losses, and the heat of regeneration on the effectiveness of the cycle.

2. THE INFLUENCE OF THE PARAMETERS OF THE GAS CYCLE ON ITS EFFICIENCY

The influence of heat regeneration on the effectiveness of the cycle. To raise the thermal economy of OTP's we use regeneration of heat in the cycle; in this case the heat of the gas spent in the turbine is used to heat a compressed gas which makes it possible to decrease the irreversibility of the cycle. An analysis of gas cycles using N_2O_4 as the working medium showed that the use of regeneration increases the cycle efficiency by a factor of 1.5-2 and, in addition, shifts the optimum efficiency toward lower values of the compression ratio ($\pi_к$) (Fig. 7), which decreases the dimensions of the compressor and the turbine. The shift of maximum efficiency toward lower values of $\pi_к$ is explained by the fact that at low values of $\pi_к$ the temperature at the end of isentropic compression rises insignificantly; thus, the region of the isobar in which regeneration is possible increases, approaching T_3 and T_1, respectively.

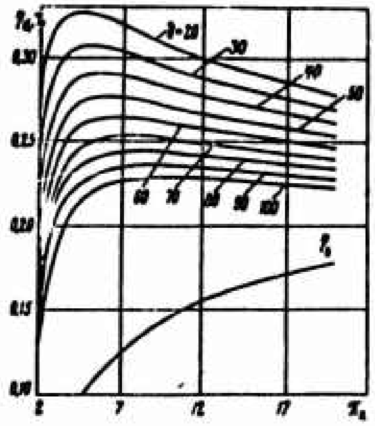

Fig. 7. Dependence of thermal efficiency on the compression ratio $\pi_к$: $T_3 = 1073°K$; $T_1 = 390°K$; $p_2 = 50$ atm (abs); $\sigma_{в.д} = 0.91$; $\sigma_{н.д} = 0.90$; $\eta_T = 0.90$; $\eta_к = 0.88$.

When examining regeneration in a cycle with nondissociating (inert) gases it is theoretically possible to permit total regeneration of the heat in a given temperature range, i.e., regeneration can be considered a reversible process in the presence of an infinite heat-exchange surface.

However, regeneration in a gas cycle with dissociating gases even theoretically is an irreversible process. Here the completeness of regeneration is estimated in ratio to the maximum possible quantity of heat which can be used in the regeneration, i.e., when the minimum temperature head is equal to zero. The magnitude of regenerator effectiveness depends on the value of the minimum temperature head in the regenerator and the temperature range, and in practice varies from zero to one.

In the case at hand we examined the influence of the value of minimum temperature head on the effectiveness of the cycle. Figures 8 and 9 show the dependences $\eta_{ц}(\delta_{min})$ and the dependence $Q_{per}(\delta_{min})$. As can be seen from the graphs, regeneration raises the internal efficiency very abruptly, with the optimum $\eta_{ц}(\pi_{к})$ shifted toward high values of $\pi_{к}$ with an increase in minimum temperature head in the regenerator. A comparison of cycles using He and N_2O_4 showed a weaker dependence of $\eta_{ц}(\delta_{min})$ and $Q_{per}(\delta_{min})$ for N_2O_4 than for He (see Fig. 8).

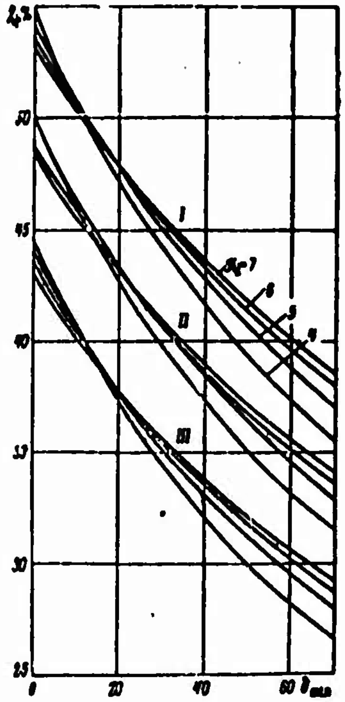

Fig. 8. Dependence of the efficiency of a GTP cycle on the value of minimum temperature head δ_{min}: (p_2 = 10 atm; η_T = 0.88; $\eta_{к}$ = 0.86) I – T_3 = 1473, II – T_3 = 1273, III – 1073°K.

The influence of minimum temperature and pressure on cycle effectiveness. In the analysis we examined the influence of gas temperature, having both subcritical and supercritical, ahead of the compressor.

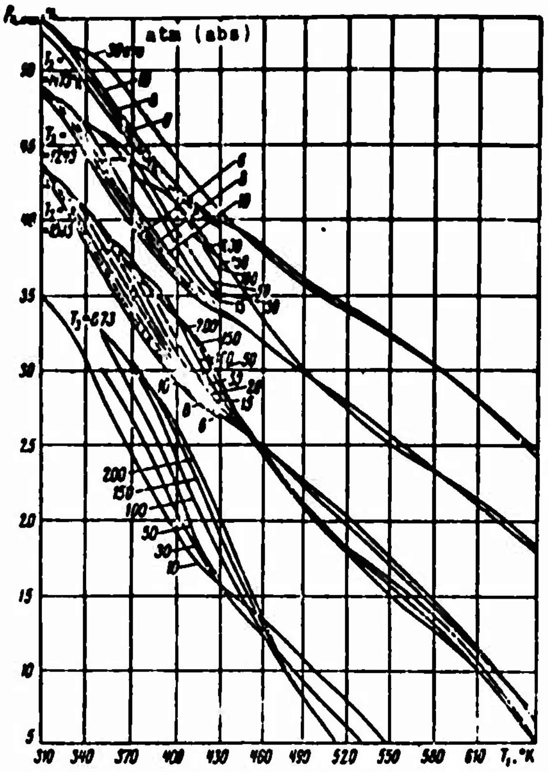

Fig. 9. Dependence of maximum thermal efficiency on the minimum T_1 and maximum T_3 temperatures and the pressure after the compressor p_2: $\eta_T = 0.88$; $\eta_к = 0.86$; $\sigma_{в.д} = 0.91$; $\sigma_{н.д} = 0.9$; $\delta_{min} = 10°$; $T_1 = 310\text{-}650°K$.

With $T_1 \leq T_{кр}$ the efficiency shifts toward high values of $\pi_к$ for the compression ratio in the compressor. With the permissibly low values of T_1 the optimum value of pressure behind the compressor p_2 is in the low-pressure region. With an increase in T_1 to the range 370-430°K the optimum p_2 shifts to the high-pressure region (see Fig. 9).

With T_1 = 450-650°K > $T_{кр}$ the optimum again shifts to the region of low values of p_2 (see Fig. 9). Such a phenomenon is easily explained after examination of the behavior of the effective specific power of the cycle $N_{уд} = f(T_1)$ (Fig. 10) and the work of gas compression in the compressor $AL_к = f(T_1)$ (Fig. 11). The first stage of dissociation ($N_2O_4 \rightleftarrows 2NO_2$) occurs in the region of temperatures up to 450°K.

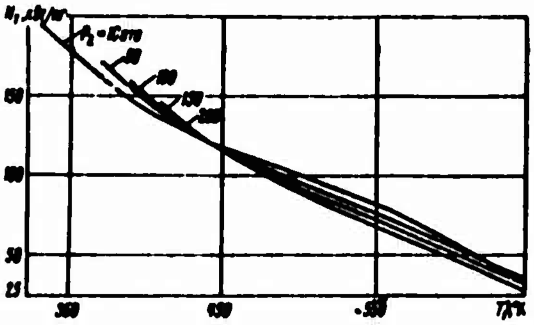

Fig. 10. The dependence of specific GTP power $N_{уд}$ on the minimum temperature of the cycle T_1 and pressure p_2.

Designations: квт/кг = kW/kg; ата = atm (abs).

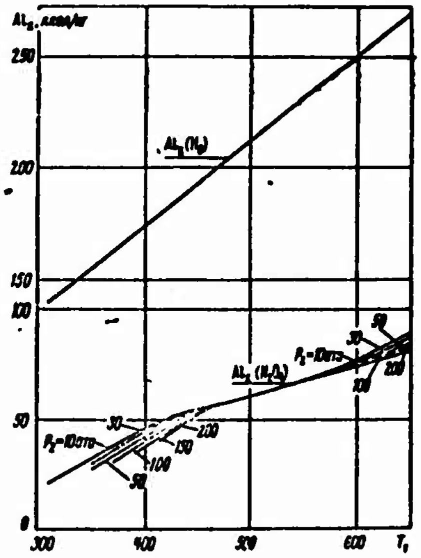

Fig. 11. Dependence of the work of gas compression in the compressor $AL_к$ on the minimum temperature of the cycle T_1 and pressure p_2 for a GTP using helium and nitrogen tetroxide.

Designations: ккал/кг = = kcal/kg; ата = atm (abs).

A rise in pressure shifts the reaction toward the region of higher temperature, i.e., at high pressures the compressor operates using a gas with a lower gas constant, which also leads to a lower value of the compression work of the compressor.

At temperatures T_1 = 450-650°K the first stage of the reaction is complete, while the second is just beginning; therefore the compression work of the gas is practically independent of pressure.

The influence of the temperature of the gas ahead of the turbine T_3 on the effectiveness of the cycle. We know that a rise in temperature ahead of the turbine influences the thermal economy of a GTP, increasing the average temperature of heat input. In the study, the range of change of the upper temperature of the cycle included temperatures of 600-800°C which are already used in power engineering as well as temperatures of 1000-1200°C which are perspective temperatures.

Analysis showed that a rise in gas temperature from 600 to 800°C gives the maximum cycle efficiency increment, approximately 10% (see Fig. 9); with a further increase this increment is significantly reduced:

$$\Delta\eta = \eta(T_3 = 1273\ ^\circ\mathrm{K}) - \eta(T_3 = 1073\ ^\circ\mathrm{K}) \approx 6{,}5\%.$$
$$\Delta\eta = \eta(T_3 = 1473\ ^\circ\mathrm{K}) - \eta(T_3 = 1273\ ^\circ\mathrm{K}) \approx 5\%.$$

This phenomenon can probably be explained as follows: with $T_3 < 1073$°K the second stage of dissociation $2NO_2 \rightleftarrows 2NO + O_2$ has its most developed nature, i.e., there is the most intense increase in the gas "constant" which is proportional to the gas expansion work in the turbine. At temperatures $T_3 > 1073$°K, however, the reaction of dissociation actually terminates, and the gas "constant" is stabilized which leads to a lower efficiency increment. But at the same time, the work of regeneration depends on the pressure, since it is in the region of the second stage of the reaction $2NO_2 \rightleftarrows 2NO + O_2$ (Fig. 12). Therefore, in this region low pressure values are optimum.

As T_1 increases, the optimum $\eta_{\text{ц}}(\pi_{\text{к}})$ goes toward lower values of $\pi_{\text{к}}$. In the supercritical region of temperatures T_1 the

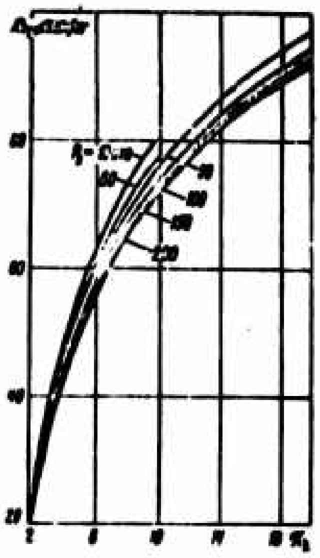

Fig. 12. Dependence of gas expansion work in the turbine AL_T on the compression ratio $\pi_к$ and pressure p_2 (T_3 = = 873°K).

Designations: ккал/кг = kcal/kg; ата = atm (abs).

optimum value $\pi_к$ = 4 is characteristic for the entire studied pressure range p_2 = 6-200 atm (abs) (Fig. 13).

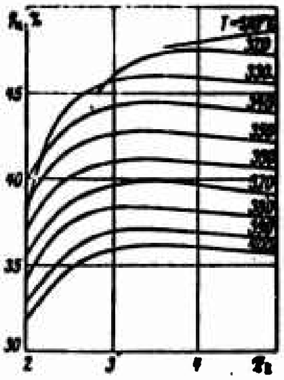

Fig. 13. Dependence of psychoefficiency on the compression ratio in the compressor $\pi_к$ and the minimum temperature of the cycle T_1 for pressure p_2 = 6 atm (abs): p_2 = = 6 atm (abs); T_3 = 1273°K; η_T = = 0.88; η_K = 0.86; $\sigma_{в.д}$ = 0.91; $\sigma_{н.д}$ = 0.90; $\Delta t^{min}_{рег}$ = 10°.

The influence of the coefficients of pressure losses on the cycle effectiveness. Hydraulic resistances account for losses in pressure in the inlet and outlet devices of the compressor and turbine in the gas line and the regenerator, in the cooler, and in the heater. Obviously the compression ratio in the compressor will always be somewhat greater than the expansion ratio in the turbine; here part of the effective work of the cycle is spent on overcoming hydraulic resistances.

The study was carried out for the following pressure loss coefficient: $\sigma_{\text{н.д}}$ = 0.85-1 along the low-pressure line; $\sigma_{\text{в.д}}$ = = 0.85-1 along the high-pressure line.

As can be seen from Figures 14 and 15, the GTP efficiency is sensitive to pressure lost to overcoming resistances. Consideration of resistances changes the optimum compression ratio toward high values of $\pi_{\text{к}}$.

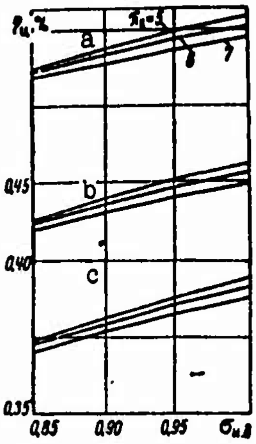

Fig. 14.

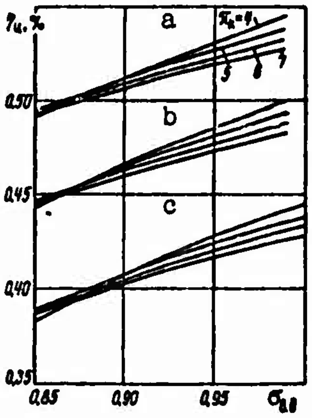

Fig. 15.

Fig. 14. Dependence of cycle efficiency on the coefficient of pressure losses on the low-pressure side $\sigma_{\text{н.д}}$: a — T_3 = 1473°K; b — T_3 = 1273°K; c — T_3 = 1073°K (p_2 = 30 atm (abs); $\sigma_{\text{в.д}}$ = 0.85).

Fig. 15. Dependence of cycle efficiency on the coefficient of pressure losses toward high pressure $\sigma_{\text{в.д}}$: a — T_3 = 1273°K, T_1 = = 330°K; b — T_3 = 1173°K; c — T_3 = 1073°K (T_1 = 330°K, p_2 = 10 atm (abs)).

Analysis of the results showed that a change in the coefficient of losses along the high-pressure line in the indicated range has a more significant influence on the effectiveness of the cycle (3-4%) than does a change in the coefficients of pressure losses along the low-pressure line in this same range of change of $\sigma(\Delta\eta = 1\text{-}1.5\%)$.

To compare the influence of $\sigma_{н.д}$ and $\sigma_{в.д}$ on the efficiency of a GTP using dissociating and inert (He) working media we calculated cycles using He for the same range of change of σ; these showed that the dependence of cycle efficiency on the values of pressure losses with inert gases is more abrupt (Δη ≈ 20%) (Fig. 16).

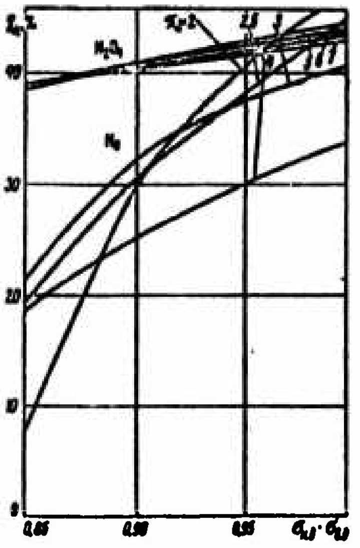

Fig. 16. The dependence of cycle efficiency on the coefficient of pressure losses $\sigma_{н.д}$ and $\sigma_{в.д}$ in a GTP using inert and chemically reacting working media: $T_3 = 1073°K$, $p_2 = 10$ atm (abs), $T_1(N_2O_4) = 330°K$, $T_1(He) = 303°K$, $\sigma_{н.д} = \sigma_{в.д}$, $\eta_T = 0.88$, $\eta_K = 0.86$, $\delta_{min} = 10°$.

The lower influence of pressure losses along the line on the efficiency of gas cycles using dissociating working media allows us to permit high pressure losses, which has a positive influence on the dimensional characteristics of the device and, consequently, leads to better technical-economic characteristics of a GTP using dissociating working media than one using inert gases.

In GTP's using dissociating N_2O_4 gas a decrease in efficiency of the turbines has a much greater influence on the effective efficiency of the cycle than in GTP's using inert gases (Figs. 17, 18). This is explained by the high work ratio of the gas cycle of a GTP using dissociating gas. Higher values of the work ratios in the gas cycles of dissociating-gas GTP's (Fig. 19) allows us to conclude that the introduction of intermediate cooling during compression of the gas in the compressor is less effective than in cycles of GTP's using inert gases. Therefore, GTP schemes using intermediate cooling were not examined. The introduction, however, of intermediate superheating in a GTP with a dissociating working medium makes it possible to increase the cycle efficiency by 3-5 abs. %.

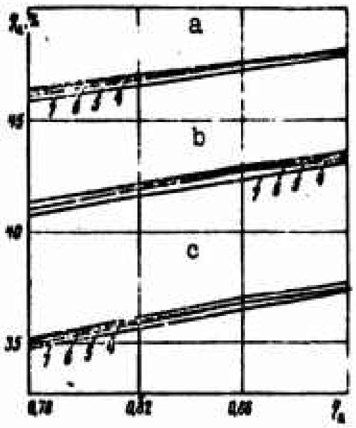

Fig. 17.

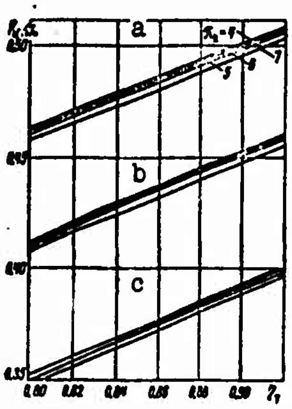

Fig. 18.

Fig. 17. Dependence of cycle efficiency on compressor efficiency η_{κ}: a – p_2 = 10 atm (abs); b – T_3 = 1273°K; c – T_3 = 1073°K (π_{κ} = 4-7; η = = 0.9; T_1 = 330°K).

Fig. 18. Dependence of cycle efficiency on turbine efficiency η_T: a – T_3 = 1473, b – T_3 = 1273, c – T_3 = 1073°K; (p_2 = 10 atm (abs); T_1 = 330°K; η_K = 0.78; δ_{min} = 10°).

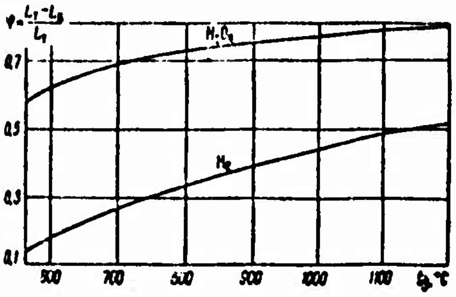

Fig. 19. Dependence of the work ratio on the maximum temperature for the cycle of a GTP using dissociating and inert gases.

Our thermodynamic analysis of gas cycles using a dissociating working medium $N_2O_4 \rightleftarrows 2NO_2 \rightleftarrows 2NO + O_2$ allowed us to explain their considerable advantages for the maximum gas temperatures used at present in stationary gas-turbine construction (600-800°C). The use of dissociating gases, in a GTP, in this temperature range allows us to obtain an effective GTP efficiency of 40-45%.

3. A GAS-LIQUID CYCLE USING CHEMICALLY REACTING SYSTEMS

The chemically reacting systems $N_2O_4 \rightleftarrows 2NO_2 \rightleftarrows 2NO+O_2$, $Al_2Cl_6 \rightleftarrows 2AlCl_3$, $Al_2Br_6 \rightleftarrows 2AlBr_3$ have a saturation line (p_s-T_s) which is such that with these working media, simple and complex gas-liquid cycles can be constructed. For example, for the system $N_2O_4 \rightleftarrows 2NO_2$ gas-liquid cycle can be realized with the following minimum parameters in the cycle: pressure 1.1-1.4 atm (abs), temperature 20-25°C [12] with a cycle effectiveness which is 3-5 abs. % higher than using steam.

An outstanding feature of the gas-liquid cycle using a dissociating working medium compared with a condensation medium is the fact that it combines the following positive qualities of the thermodynamic cycles:

1) gas-turbine – high mean-integral temperature of heat input;

2) steam-turbine – low power expended on pumping the working medium, low mean-integral temperature of heat removal;

3) a cycle using low-boiling working media – low heat of vaporization, low critical pressure;

4) a cycle using dissociating working media – high effectiveness of regeneration in the cycle.

These features allow us to have a gas-cooled reactor or a gas-cooled boiler in a device with a condensation (gas-liquid) cycle.

The operating principle of a device with a closed gas-liquid cycle is as follows (Fig. 20). The working medium in the liquid phase enters pump 1, where the pressure is raised to the maximum;

it then enters regenerator-evaporator 2, in which there is heating of the liquid, vaporization, and partial superheating of the gas due to the heat of the gases spent in the turbine. Then the gas enters mean heater 3, where it is superheated to the maximum temperature; it then goes to turbine 4. During the heating process there is dissociation (decomposition) of the initial substance with the release of the heat of chemical reactions, which facilitates the isothermal nature of the process of heat feed. The gas, expanding in the turbine, accomplishes effective work.

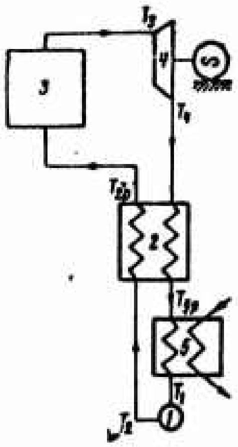

Fig. 20. Diagram of a device with a closed gas-liquid cycle.

From the turbine the spent gas enters the regenerator-evaporator and uses its remaining heat to heat the "cold" working medium. The gas which is cooled in the regenerator-evaporator enters the cooler-condenser, where its condensation and partial supercooling occurs, and the cycle is repeated. During cooling there is recombination of the components into the initial state with the release of heat of chemical reaction, which favorably influences the process of regeneration in the cycle.

When examining possible schemes for atomic power plants with a fast reactor using a chemically reacting working medium-coolant we analyzed the following schemes: with regeneration using N_2O_4, with regeneration and intermediate superheating using N_2O_4, with intermediate regeneration using N_2O_4, and with intermediate regeneration and intermediate superheating using N_2O_4.

The results of the analysis are given below.

When analyzing the thermodynamic cycles we varied the following parameters: the pressure p_3 and the temperature T_3 at the turbine inlet; the pressure p_4 at the turbine outlets; the turbine efficiency η_T; the minimum temperature head in the regenerator-evaporator $\Delta T^{min}_{рег}$; the pressure losses along the low-pressure line $\sigma_{н.д}$; and the pressure of intermediate superheating.

The various calculations were performed on the Minsk-22 computer using the compiled algorithm.

4. ANALYSIS OF A GAS-LIQUID CYCLE WITH REGENERATION

The influence of the pressure and temperature ahead of the turbine on the cycle efficiency. The results of calculating the dependence of cycle efficiency on the parameters at the turbine inlet for the regeneration scheme are given in Fig. 21. As can be seen from Fig. 21, the cycle efficiency increases most intensely to pressures of 100-140 atm (abs).

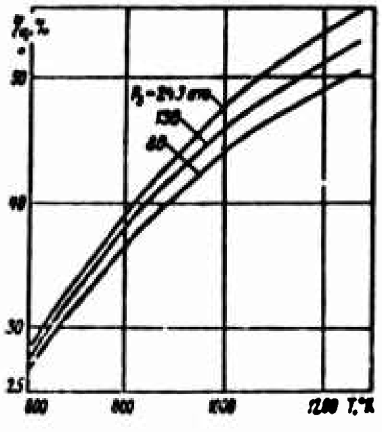

Fig. 21. The influence of parameters at the turbine inlet on the cycle efficiency (without intermediate superheating): $T_1 = 290°K$; $p_1 = 1.12$ atm (abs); $\Delta T^{min}_{ег} = 10°$; $\sigma_{н.д} = 0.8$; $\sigma_{в.д} = 0.93$; $\eta_T = 0.88$; $\eta_н = 0.7$.

Designation: ата = atm (abs).

Thus, in the pressure range 10-80 atm (abs) with $p_2 = 10$ atm (abs) the cycle efficiency increases by 1.5-2%; in the interval 80-140 atm (abs) it increases by 0.5-1%; from a pressure of 140 atm (abs) to the optimum pressure the increase is ~0.2%.

The intensity of the increase in cycle efficiency as a function of temperature at the turbine inlet and in the range T_3 = 600-1000°K remains constant and is ∿2% at $\Delta T = 50°$ (see Fig. 21).

In the temperature range 1000-1300°K the increment is ∿1% at $\Delta T = 50°$.

Such a change in cycle efficiency in a regeneration scheme can be explained by the fact that for temperatures above 1000°K the chemical reaction ceases; consequently, a change in regeneration efficiency will occur only due to a change in heat capacity due to temperature.

From an analysis of the obtained dependences (see Fig. 21) we can state that in schemes having a cycle with regeneration using the chemically reacting mixture $N_2O_4 \rightleftarrows 2NO_2 \rightleftarrows 2NO + O_2$ the use of pressure greater than 150 atm (abs) at the turbine inlet is unfeasible.

The dependence of cycle efficiency on counterpressure p_4. Figure 22 shows the dependence of efficiency, in a scheme with regeneration, on pressure on the turbine outlet. The intense drop in cycle efficiency to a pressure of 5 atm (abs) occurs due to the abrupt decrease in operation of the turbine; with an increase in counterpressure from 1 to 5 atm (abs) the work of the turbine decreases to 40 kcal/kg, while with an increase in counterpressure from 5 to 10 atm (abs) the work decreases to 20 kcal/kg, i.e., approximately 20 kcal/kg less than with an increase in counterpressure from 1 to 5 atm (abs). With an increase in counterpressure by more than 10 atm (abs) the intensity of the drop in head in the turbine is reduced.

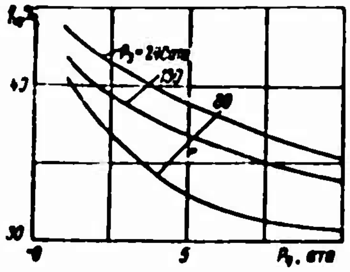

Fig. 22. Dependence of the cycle efficiency on counterpressure: T_3 = 873°K; η_T = 0.88; η_K = 0.7; $\Delta T^{min}_{рег}$ = 10°; $\sigma_{н.д}$ = 0.8; $\sigma_{в.д}$ = 0.93; T_1 = 290°K.

Designation: ата = atm (abs).

This is explained by the fact that the process of the cycle in T-S diagram shifts to the left, i.e., to the region of a more effective change in the degree of dissociation α_1, α_2. With a pressure of 1 atm (abs) the degree of dissociation at the turbine inlet is $\sim$1, at the outlet – $\sim$1; at the inlet $\alpha_2 = 0.8$, at the outlet $\alpha_2 = 0.2$. With a counterpressure of 10 atm (abs), however, the interval of change is smaller, namely: at the inlet $\alpha_2 = 0.8$, at the outlet $\alpha_2 = 0.6$ due to the high temperature at the turbine outlet. Consequently, the average value of the gas "constant" in the turbine in the latter case will be greater, which favorably influences the change of head in the turbine.

The influence of turbine efficiency on cycle effectiveness. In the examined range of change of turbine efficiency and parameters at the turbine inlet we obtained a linear dependence of turbine and cycle efficiencies. With a decrease in turbine efficiency by 0.5 the cycle efficiency drops by $\sim$1.2%. The intensity of the change is independent of pressure.

The influence of minimum temperature head in the regenerator on the cycle efficiency. An analysis of the influence of minimum temperature head in the regenerator (ΔT_{per}^{min}) on the cycle efficiency is given in Fig. 23. We obtained a practically linear dependence of cycle efficiency on ΔT_{per}^{min}. The increase in minimum temperature head in the regenerator by 10° decreases the cycle efficiency by 0.5%. Selection of the minimum temperature head in the regenerator should be stipulated by the weight and dimensional characteristics of the regenerator-evaporator, i.e., final selection of ΔT_{per}^{min} is determined in the stage of technical-economic estimates.

On the basis of this thermodynamic analysis of gas-liquid cycles with regeneration we can state that the use of the chemically reacting mixture $N_2O_4 \rightleftarrows 2NO_2 \rightleftarrows 2NO + O_2$ as the working medium makes it possible to obtain an efficiency for the gas-liquid cycle with regeneration at the pressures and temperatures presently used in power engineering ($p \leq 240$ atm (abs), $T \leq 838$°K), up to $\sim$43%.

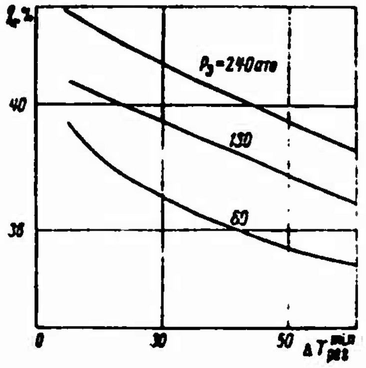

Fig. 23. Influence of the minimum temperature head in the regenerator on the cycle efficiency: T_1 = 290°K; p_1 = = 1.12 atm (abs); T_3 = 873°K; η_T = 0.88; η_K = 0.7.

Designation: ата = atm (abs).

5. ANALYSIS OF A GAS-LIQUID CYCLE WITH REGENERATION AND INTERMEDIATE SUPERHEATING

To raise the efficiency of the thermodynamic cycle and the unit as a whole we use secondary superheating of the steam (gas). The use of intermediate superheating in a cycle which uses the chemically reacting mixture $N_2O_4 \rightleftarrows 2NO_2 \rightleftarrows 2NO + O_2$ as the working medium is also expedient, since an increase of temperature during expansion increases the average gas "constant" in the turbine due to the smaller interval of change of the degree of dissociation and, secondly, increases the effectiveness of regeneration. The operating principle of a cycle with regeneration and intermediate superheating (Fig. 24) is as follows: the working medium in the liquid phase enters pump 1, is "compressed" to the maximum pressure of the cycle p_2 and enters regenerator-evaporator 2 where it is heated, vaporized, and partially superheated due to the heat of the gas spent in the turbine. The superheated working medium (gas) enters reactor 3 (intermediate heat exchanger, boiler), where it is superheated to the maximum cycle temperature T_3.

The gas with maximum temperature T_3 enters high-pressure turbine 4, is expanded (accomplishing work), and enters heat exchanger (reactor) 3 for secondary superheating of the gas; this gas then enters low-pressure turbine 4'. The spent gas in low-pressure turbine 4' enters regenerator-evaporator 2, where it gives its remaining heat for heating, evaporation, and partial superheating of the "cold"

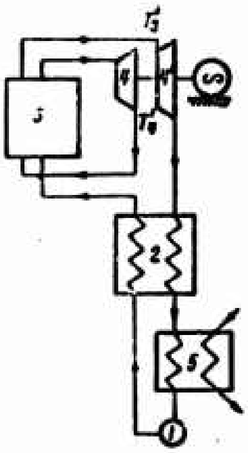

Fig. 24. Diagram of a gas-liquid cycle with regeneration and intermediate superheating.

working medium. The gas which gives off heat in regenerator-evaporator 2 enters cooler-condenser 5, where it is partially recooled to the saturation point, condensed, and supercooled. The supercooled working medium enters pump 1, and the cycle is repeated.

The influence of the pressure of intermediate superheating on cycle efficiency. To perform thermodynamic analysis of a scheme with intermediate superheating we must examine the influence of the pressure of intermediate superheating on the cycle efficiency and determine its optimum values, since the technical-economic calculations performed using other working media (H_2O, CO_2) showed that the optimum pressures of intermediate superheating from thermodynamic and technical-economic calculations coincide.

We determined the optimum pressures of intermediate superheating for initial pressures of 80, 130, and 240 atm (abs) in the temperature range 773-1273°K. The optimum pressure of intermediate superheating, for all practical purposes, for all initial pressures is in the range 15-30 atm (abs). With a rise in temperature the optimum pressure shifts toward high pressures (Fig. 25). At a temperature of 1173°K and a pressure of 240 atm (abs) the optimum cycle efficiency with a pressure intermediate superheating greater than 15 atm (abs) remains practically constant. Such a flat dependence has a favorable influence on the weight and dimensional characteristics of the installation.

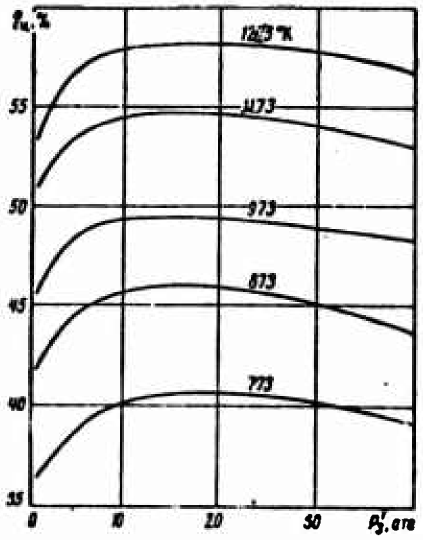

Fig. 25. The dependence of optimum pressure of intermediate superheating p_3' on the temperature of the gas at the turbine inlet with pressure $p_3 = 130$ atm (abs): $p_1 = 1.12$ atm (abs); $T_1 = 290°K$; $\eta_T = 0.88$; $\eta_H = 0.9$; $\sigma_{н.д} = 0.8$; $\sigma_{в.д} = 0.93$; $\sigma_{п/п} = 0.95$; $\Delta T^{min}_{рег} = 10°$.

Designation: ата = atm (abs).

To estimate the efficiency of introducing second intermediate superheating we carried out various calculations whose results are given in Fig. 26. Calculation was performed for pressure $p_3 = 240$ atm (abs) and $T_3 = 838°K$; we varied the pressures of the first and second intermediate superheating.

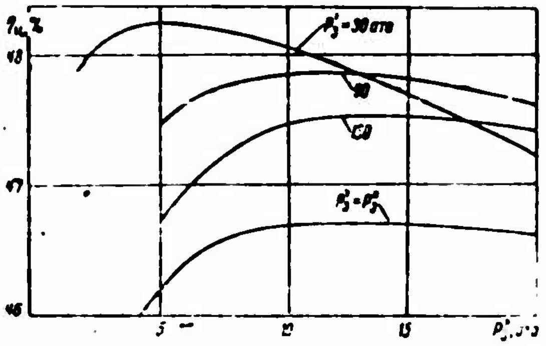

Fig. 26. The influence of intermediate superheating pressures on efficiency with two intermediate superheatings: $p_3 = 240$ atm (abs), $T_3 = 838°K$.

Designation: ата = atm (abs).

From an examination of the efficiency dependence we see that the optimum value of the pressure of second intermediate superheating p_3''

is in the range 10-14 atm (abs). The dependence of optimum efficiency on intermediate superheating pressure p_3'' is steeper than for a cycle with single intermediate superheating; the steepness increases with a decrease in the pressure of the first intermediate superheating.

From Fig. 26 it also follows that the values of the optimum pressures of the first intermediate superheating in a scheme with dual intermediate superheating are in the range 50-70 atm (abs). Such a relationship of p_3, p_3', and p_3'' allows us to produce turbines whose expansion ratios are close to one another, for example, with $p_3 = 240$ atm (abs), $p_3' = 60$ atm (abs), $p_3'' = 12$ atm (abs); $\pi_{ТВД} = 4$, and $\pi_{ТСД} = 5$, $\pi_{ТНД} = 8.5$, respectively.

From comparison of the optimum values of efficiency for single and dual intermediate superheatings we see that in the latter case the cycle efficiency increase by approximately 1.4 abs. %.

From an analysis of schemes with one and two intermediate superheatings it follows that the introduction of second intermediate superheating can hardly be justified by introducing a third hot heat exchanger, which leads to complication of the scheme and might not be economically justified by a 1.4% increase in thermoefficiency.

Selection of second intermediate superheating can be justified only by technical-economic calculations.

The dependence of cycle efficiency on the parameters at the turbine inlet. Figure 27 gives dependences of efficiency on temperature and pressure at the turbine inlet, from which it follows that the intensity of a change of cycle efficiency in the temperature range 600-1000°K is 2 abs. % at $\Delta T = 50°$. With a rise in temperature the intensity of the change of cycle efficiency drops, and at temperatures of 1000-1300°K is 1 abs. % at $\Delta T = 50°$. The peculiarity of such a change is indicated in an examination of a regeneration system without intermediate superheating. The dependence of cycle efficiency on pressure at the turbine inlet (Fig. 27) shows that an increase in pressure ahead of the turbine above 250-260 atm (abs) is hardly advisable, since the increment of cycle efficiency at p = = 250-300 atm (abs) is only 0.4 abs. %.

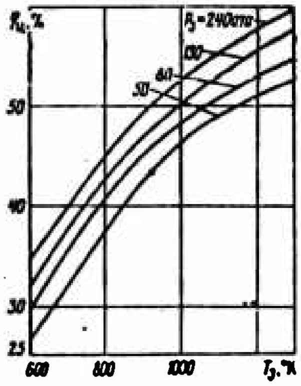

Fig. 27. Influence of pressure and temperature at the turbine inlet on the cycle efficiency in a scheme with intermediate superheating and regeneration: $p_3' = 240$ atm (abs); $T_1 = 290°K$; $p_1 = 1.12$ atm (abs); $\Delta T_{per}^{min} = 10°$; $\sigma_{н.д} = 0.8$; $\sigma_{в.д} = 0.93$; $\eta_T = 0.88$; $\eta_н = 0.7$; $\sigma_{n/n} = 0.95$.

Designation: ата = atm (abs).

The influence of minimum temperature head in the regenerator on cycle efficiency. Figure 28 gives the dependence of cycle efficiency on the minimum temperature head in the regenerator-evaporator ΔT_{per}^{min}. As seen from Fig. 28, we obtain a practically linear dependence of cycle efficiency on ΔT_{per}^{min}. With a change in ΔT_{per}^{min} by 10° the cycle efficiency changes by 1 abs. %, i.e., in a scheme with intermediate superheating the change of cycle efficiency versus ΔT_{per}^{min} is steeper than in a scheme with regeneration without intermediate superheating (see Fig. 24). Such a difference can be explained by the greater efficiency of regeneration in a cycle with intermediate superheating, since the introduction of intermediate superheating raises the temperature at the regenerator inlet on the low-pressure side, which leads to an increase in regeneration due to the difference $Q\Delta\alpha$ for high and low pressures. With a change in minimum head, however, the effect of a change in the difference of the heats of chemical reactions will vary. In a scheme without intermediate superheating it will be less, since the temperature at the regenerator inlet is lower, while the temperature on the low-pressure side at the regenerator outlet is identical for both schemes.

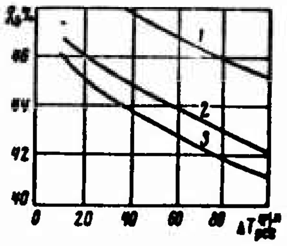

Fig. 28. The influence of minimum temperature head in the regenerator on the cycle efficiency: 1 – T_3 = 973°K, p_3 = 130 atm (abs); 2 – T_3 = 838°K, p_3 = = 240 atm (abs); 3 – T_3 = 873°K, p_3 = = 430 atm (abs) (with p_3 = 20 atm (abs), $\eta_T = 0.88$; $\eta_K = 0.7$; $\sigma_{н.д} = 0.8$; p_1 = = 1.12 atm (abs); T_1 = 290°K; $\sigma_{в.д}$ = = 0.93).

The influence of counterpressure p_4 on cycle efficiency. The efficiency of a cycle depends on the compression ratio in the cycle as well as the absolute values of the counterpressure. Figure 29 shows the dependence of cycle efficiency on counterpressure p_4. As can be seen from Fig. 29 the cycle efficiency depends on the change in counterpressure. Therefore, selection of counterpressure should be determined by the purpose of the installation, since, first, the increase in pressure behind the turbine leads to a reduction in size of the regenerator-evaporator, and also to a decrease in the exhaust area and the diameter of the exhaust lines, and second, an increase in counterpressure makes it possible to use an economic quantitative method for controlling the installation in partial-power regimes.

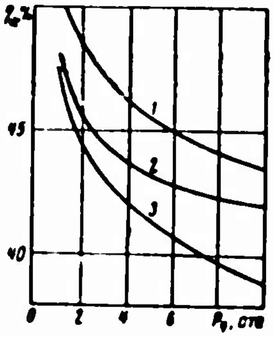

Fig. 29. Dependence of cycle efficiency on counterpressure: 1 – T_3 = = 973°K, p_3 = 130 atm (abs); 2 – T_3 = = 838°K, p_3 = 240 atm (abs); 3 – T_3 = = 873°K, p_3 = 130 atm (abs) (with η_T = = 0.88; $\eta_н = 0.7$; $\sigma_{н.д} = 0.8$; $\sigma_{в.д}$ = = 0.93; $\delta_{n/n} = 95$; p'_3 = 20 atm (abs); ΔT^{min}_{per} = 10°).

Designation: ата = atm (abs).

The minimum value of counterpressure is determined by the temperature of the cooling medium.

Figure 30 gives the dependence of cycle efficiency on turbine efficiency. In giving the dependence of cycle efficiency on η_T assumed that $\eta_{ТВД} = \eta_{ТНД}$. We obtained a practically linear dependence. The nature of change is practically independent of temperature and pressure at the turbine inlet.

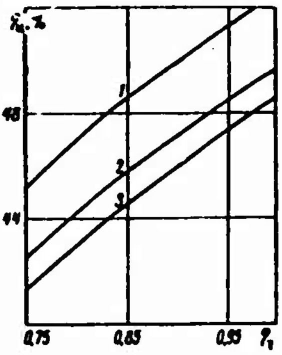

Fig. 30. The influence of turbine efficiency on cycle efficiency: 1 — T_3 = 973°K, p_3 = 130 atm (abs); 2 — T_3 = 838°K, p_3 = 240 atm (abs); 3 — T_3 = 873°K, p_3 = 130 atm (abs) (p_1 = 1.12 atm (abs); T_1 = 290°K; $\sigma_{н.д}$ = 0.8; $\sigma_{в.д}$ = 0.93; $\Delta T^{min}_{рег}$ = 10°; $\eta_T = \eta_T'$; η_e = = 0.1; p_3' = 20 atm (abs); $\sigma_{n/n}$ = 0.95).

Figure 31 gives the results of calculating the influence of pressure losses in the low-pressure line on cycle efficiency. From Fig. 31 it follows that with use of the chemically reacting mixture $N_2O_4 \rightleftarrows 2NO_2 \rightleftarrows 2NO + O_2$ as the working medium of the cycle, pressure losses up to 20% reduce the cycle efficiency by 0.5 abs. %.

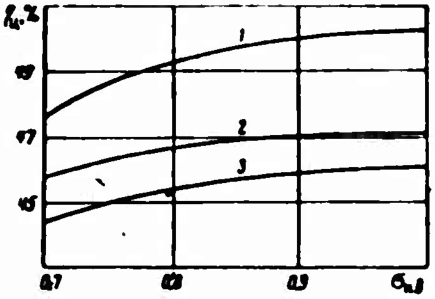

Fig. 31. Dependence of cycle efficiency on pressure losses: 1 — T_3 = 973°K, p_3 = 130 atm (abs); 2 — T_3 = 838°K, p_3 = 240 atm (abs); 3 — T_3 = 873°K, p_3 = 130 atm (abs) (p_3' = 20 atm (abs); p_1 = 1.12; T_1 = 290°K, η_T = 0.88; η_K = 0.7; $\Delta T^{min}_{рег}$ = 10°; $\sigma_{в.д}$ 0.93; $\sigma_{n/n}$ = = 0.95).

On the basis of thermodynamic analysis of cycle with single and dual intermediate heating we can draw the following conclusions:

1) with an increase in pressure the relative increase in efficiency and specific work increases, which limits the feasibility of using high pressures;

2) with a rise in temperature ahead of the turbine, the cycle efficiency sharply increases. An increase in temperature by 100° (in the range T_3 = 600-1200°K) raises the cycle efficiency by 4 abs. %, regardless of the pressure. At temperatures above 1200°K the intensity of an increase in efficiency decreases, and is 1.5-2%. Consequently, it is expedient to use the chemically reacting mixture $N_2O_4 \rightleftarrows 2NO_2 \rightleftarrows 2NO + O_2$ as a working medium for temperatures of 600-1200°K.

The disadvantages of these cycles using N_2O_4 include the relatively high temperature of the gas at the inlet to the cooler-condenser (about 80°C). In the recooler we get a heat of approximately 90% of the condensation heat. To reduce this temperature, and also to reduce the dimensions of the regenerator-evaporator we analyzed cycles with intermediate regeneration.

6. A GAS-LIQUID CYCLE WITH INTERMEDIATE REGENERATION

Figure 32 shows a diagram of a cycle with intermediate regeneration. A feature of this cycle is that in the high-pressure turbine (ТВД) [H-PT] the gas is expanded to a certain intermediate pressure, after which it enters the regenerator. In the regenerator the gas gives off part of its heat for heating, evaporation, and superheating of the coolant coming from the pump; after this it goes to the low-pressure turbine (ТНД) [L-PT] where it is expanded to the minimum pressure of the cycle and enters the condenser. A rise in pressure and temperature of the gas on the hot side of the regenerator is reflected in an improvement of the weight and dimensional characteristics of the regenerator and the regeneration process.

The pressure of the intermediate regeneration was selected based on the following conditions.

First, with an increase in pressure at the H-PT outlet there is an increase in enthalpy of the gas at outlet H_4 from the H-PT, which

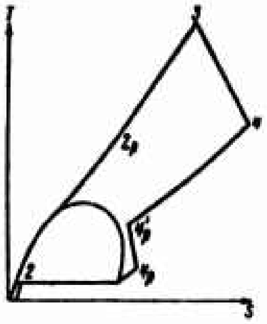

Fig. 32. T-S diagram of a cycle with intermediate regeneration.

increases the head in the regenerator; this increase in head is more intense than the increase in enthalpy of the gas at the outlet from the H-PT. Thus, the enthalpy of N_2O_4 at the outlet from the regenerator on the hot side H_{4p} decreases. From the t-H diagram it follows that a decrease in enthalpy of the gas at the regenerator outlet on the hot side together with a rise in pressure results in approach to the saturation line, i.e., at the inlet to the L-PT turbine saturated vapor may appear.

Second, increasing the pressure in the regenerator on the hot side, we thus lower the enthalpy of the gas at the point of minimum temperature head in the regenerator on the hot side $H^{\Gamma}_{\kappa p}$, which leads to an increase in regeneration heat.

Third, with an increase on the hot side of the regenerator the steepness of the isobar in the t-H diagram decreases, i.e., the point of minimum temperature head in the regenerator shifts to the region of high temperatures; consequently, the enthalpy of N_2O_4 at point ΔT^{min}_{per} on the cold side $H^{x}_{\kappa p}$ increases, which increases the heat of regeneration.

Expansion in the L-PT occurs in the region of isobars close to one another; therefore the total work of the turbine decreases compared with that during ordinary regeneration. We examined schemes with regeneration and intermediate superheating and with regeneration without intermediate superheating.

The maximum increase in cycle efficiency without intermediate superheating and with intermediate regeneration was 3.5 abs. % and only 1.2 abs. % lower than in a cycle with intermediate superheating without intermediate regeneration. The optimum pressure of intermediate regeneration in the given scheme with initial pressure 240 atm (abs) $p_{пр}$ = 15-20 atm (abs); with an initial pressure of 130 atm (abs) it was 10-15 atm (abs).

The introduction of intermediate regeneration into the scheme of a cycle with intermediate superheating also causes a rise in cycle efficiency, approximately 1 abs. %, but in this case the optimum pressure of intermediate regeneration reduces to 8-12 atm (abs).

To analyze the efficiency of a cycle with intermediate regeneration we also examined the influence of pressure losses in the regenerator on cycle efficiency. Figure 33 gives the results of these calculations and compares them with the efficiency of an ordinary cycle.

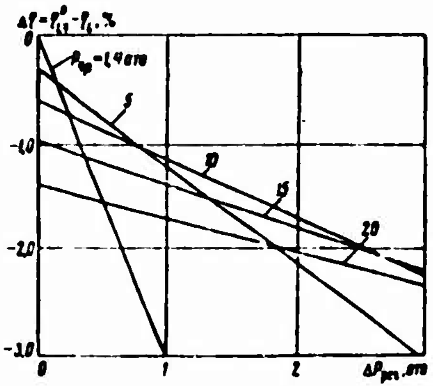

Fig. 33. The influence of pressure losses in the regenerator on the hot side on cycle efficiency.

Designation: ата = atm (abs).

As can be seen from this dependence (Fig. 34), the efficiency of cycles with intermediate regeneration is higher than those using steam, in the entire investigated temperature range.

These investigations of thermodynamic cycles using chemically reacting working media show that their use opens new possibilities for improving the technical-economic indices of power plants.

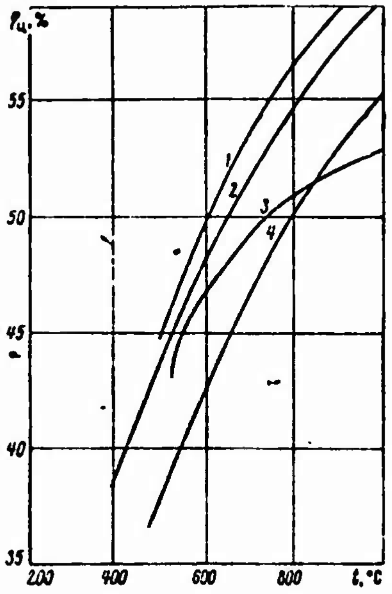

Fig. 34. Comparison of the efficiency of cycles using the chemically reacting mixture $N_2O_4 \rightleftarrows 2NO_2 \rightleftarrows 2NO + O_2$ and steam: 1 — cycle with intermediate superheating and intermediate regeneration using N_2O_4, 2 — cycle with intermediate superheating using N_2O_4, 3 — cycle with intermediate superheating using H_2O, 4 — simple cycle with regeneration using N_2O_4 (p_3 = 240 atm (abs)).

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APPENDIX

Table 1. Density, enthalpy, and entropy in the saturation line $N_2O_4 \rightleftarrows 2NO_2$

t, °C	p, ат	ρж, г/см³	ρг, г/см³	Hж, ккал/кг	Sж, ккал/кг·град	Hг, ккал/кг	Sг, ккал/кг·град
30	1,54	1,4220	0,00473	48,0	0,541	150,0	0,8780
35	1,92	1,4090	0,00571	49,5	0,547	153,1	0,8832
40	2,37	1,3961	0,00692	51,3	0,552	156,1	0,8876
45	2,91	1,3831	0,00832	53,1	0,559	159,1	0,8925
50	3,55	1,3701	0,01000	55,0	0,565	161,8	0,8963
55	4,31	1,3571	0,01198	57,1	0,572	164,6	0,8997
60	5,22	1,3440	0,01422	59,5	0,578	167,2	0,9026
65	6,30	1,3307	0,01688	61,7	0,582	169,7	0,9053
70	7,54	1,3170	0,01996	64,0	0,592	172,0	0,9075
75	9,00	1,3037	0,02329	66,6	0,601	173,9	0,9094
80	10,65	1,2896	0,02760	69,0	0,607	176,5	0,9116
85	12,55	1,2741	0,03231	71,6	0,614	178,6	0,9134
90	14,85	1,2575	0,03780	74,4	0,621	180,9	0,9151
95	17,45	1,2397	0,04430	77,2	0,629	182,9	0,9165
100	20,35	1,2200	0,05140	80,1	0,637	184,6	0,9175
105	23,80	1,1993	0,05955	83,2	0,645	186,4	0,9186
110	27,55	1,1770	0,06890	86,7	0,654	187,9	0,9191
115	32,10	1,1525	0,08025	90,6	0,665	189,1	0,9195
120	37,15	1,1255	0,09325	95,0	0,676	190,2	0,9189
125	42,75	1,0963	0,10930	99,5	0,688	191,0	0,9181
130	49,20	1,0645	0,12700	104,3	0,699	191,6	0,9160
135	56,40	1,0280	0,14820	109,7	0,712	191,7	0,9135
140	64,50	0,9860	0,17520	115,9	0,728	191,2	0,9100
145	73,65	0,9335	0,21140	123,7	0,746	190,0	0,9052
150	84,00	0,8670	0,26200	132,5	0,766	187,0	0,8958
155	95,30	0,7560	0,35500	143,6	0,789	181,5	0,8780
158	103,30	0,5500	0,55000	160,8	0,836	160,8	0,8360

Designations: ам = atm (tech); г/см³ = = g/cm³; ккал/кг = kcal/kg; ккал/кг·град = = kcal/kg·deg.

Table 2. Enthalpy, entropy, heat capacity, and density in the gas phase. Designations: ккал/кг = kcal/kg; ккал/кг·град = kcal/kg × × deg; кг/см = kg/cm.

t, °C	H, ккал/кг	S, ккал/кг·град	cp, ккал/кг·град	ρ, кг/см³
		p = 1 кг/см²		
30	157,37	0,9142	1,40520	2,983
40	172,91	0,9647	1,69690	2,673
50	191,06	1,0217	1,91350	2,381
60	210,62	1,0813	1,96920	2,126
70	229,72	1,1378	1,82200	1,917
80	246,53	1,1862	1,52630	1,756
90	260,08	1,2240	1,18600	1,634
100	270,39	1,2521	0,88648	1,543
110	278,06	1,2724	0,66082	1,473
120	285,08	1,2907	0,54250	1,413
130	290,00	1,3031	0,45079	1,368
140	294,23	1,3134	0,39800	1,324

Table 2 (continued).

t, °C	H, ккал/кг	S, ккал/(кг·град)	c_p, ккал/(кг·град)	ρ, кг/см³
150	298,06	1,3226	0,37131	1,287
160	301,71	1,3311	0,36210	1,252
170	305,34	1,3394	0,36490	1,220
180	309,04	1,3477	0,37652	1,189
190	312,90	1,3561	0,39481	1,160
200	316,96	1,3648	0,41842	1,132
250	341,96	1,4150	0,59537	1,000
300	377,49	1,4797	0,83044	0,880
350	424,73	1,5586	1,04800	0,767
400	480,34	1,6444	1,15190	0,668
450	537,14	1,7258	1,09690	0,586
500	588,12	1,7939	0,93296	0,522
550	630,03	1,8465	0,74727	0,473
600	663,36	1,8859	0,59414	0,436
650	690,15	1,9157	0,48553	0,406
700	712,50	1,9393	0,41379	0,381
750	731,94	1,9588	0,36773	0,360
800	749,54	1,9756	0,33836	0,341
850	765,95	1,9905	0,31958	0,325
900	781,60	2,0042	0,30748	0,311
950	796,77	2,0168	0,29964	0,297
1000	811,61	2,0287	0,29455	0,285
1050	826,25	2,0400	0,29126	0,276
1100	840,76	2,0508	0,28915	0,264
1150	855,18	2,0611	0,28785	0,255
1200	869,56	2,0710	0,28709	0,246
		$p = 2$ кг/см²		
40	159,06	0,9019	1,34650	5,876
50	173,83	0,9482	1,60100	5,265
60	190,89	1,0002	1,79580	4,702
70	209,30	1,0547	1,86030	4,212
80	227,56	1,1072	1,76410	3,805
90	244,12	1,1535	1,53110	3,484
100	258,00	1,1912	1,23840	3,237
110	268,96	1,2202	0,95840	3,049
120	278,36	1,2447	0,76048	2,898
130	285,14	1,2617	0,60270	2,780
140	290,62	1,2752	0,49820	2,683
150	295,25	1,2863	0,43314	2,598
160	299,38	1,2959	0,39657	2,524
170	303,25	1,3047	0,37908	2,455
180	307,02	1,3131	0,37542	2,392
190	310,80	1,3214	0,38145	2,332
200	314,67	1,3297	0,39459	2,275
250	337,38	1,3752	0,52865	2,016
300	368,64	1,4323	0,72768	1,783
350	410,29	1,5018	0,93399	1,567
400	460,86	1,5798	1,07170	1,372
450	515,29	1,6578	1,08420	1,205
500	567,23	1,7272	0,97989	1,071
550	612,30	1,7837	0,82070	0,967
600	649,35	1,8275	0,66680	0,885
650	679,49	1,8611	0,54555	0,821
700	704,47	1,8874	0,45945	0,768
750	725,88	1,9089	0,40129	0,724
800	744,91	1,9271	0,36279	0,886
850	762,37	1,9430	0,33741	0,652
900	778,79	1,9573	0,32062	0,623
950	794,52	1,9704	0,30945	0,596
1000	809,80	1,9826	0,30197	0,571
1050	824,76	1,9942	0,29695	0,549
1100	839,52	2,0051	0,29358	0,529
1150	854,14	2,0156	0,29134	0,510
1200	868,67	2,0256	0,28987	0,492

Table 2 (continued).

t, °C	H, $\frac{ккал}{кг}$	S, $\frac{ккал}{кг \cdot град}$	c_p, $\frac{ккал}{кг \cdot град}$	ρ, $\frac{кг}{см^3}$
		$p = 3$ кг/см²		
50	165,04	0,9102	1,40620	8,427
60	180,25	0,9565	1,62640	7,528
70	197,35	1,0071	1,77160	6,731
80	215,23	1,0586	1,78510	6,051
90	232,66	1,1072	1,66180	5,495
100	248,22	1,1495	0,43030	5,055
110	261,21	1,1839	0,15910	4,716
120	272,42	1,2130	0,93228	4,447
130	280,73	1,2339	0,73464	4,241
140	287,36	1,2502	0,59304	4,073
150	292,79	1,2632	0,49748	3,933
160	297,45	1,2741	0,45803	3,811
170	301,65	1,2837	0,40556	3,702
180	305,59	1,2925	0,38735	3,604
190	309,44	1,3009	0,38378	3,511
200	313,30	1,3091	0,38926	3,424
250	335,04	1,3527	0,49673	3,037
300	364,16	1,4059	0,67479	2,693
350	402,84	1,4705	0,87003	2,376
400	450,35	1,5438	1,01750	2,088
450	502,81	1,6189	1,06120	1,838
500	554,52	1,6880	0,99266	1,632
550	600,87	1,7461	0,85594	1,469
600	639,90	1,7922	0,70821	1,342
650	672,03	1,8280	0,58314	1,241
700	698,71	1,8562	0,48980	1,159
750	721,46	1,8790	0,42449	1,090
800	741,50	1,8981	0,38013	1,032
850	759,70	1,9147	0,35030	0,981
900	776,68	1,9295	0,33025	0,935
950	792,83	1,9430	0,31670	0,895
1000	808,43	1,9555	0,30750	0,858
1050	823,63	1,9672	0,30121	0,824
1100	838,58	1,9783	0,29691	0,793
1150	853,35	1,9889	0,29397	0,764
1200	868,00	1,9990	0,29198	0,738
		$p = 4$ кг/см²		
60	173,20	0,9275	1,49750	10,560
70	189,14	0,9746	1,67190	9,430
80	206,41	1,0242	1,75190	8,454
90	223,86	1,0730	1,70300	7,656
100	240,22	1,1175	1,53860	6,981
110	254,50	1,1553	1,29750	6,467
120	267,05	1,1879	1,06660	6,058
130	276,65	1,2120	0,84832	5,746
140	284,30	1,2308	0,67974	5,496
150	290,48	1,2456	0,55953	5,290
160	295,67	1,2577	0,48062	5,115
170	300,22	1,2681	0,43109	4,961
180	304,38	1,2774	0,40362	4,824
190	308,35	1,2861	0,39155	4,698
200	312,26	1,2945	0,39042	4,579
250	333,49	1,3370	0,47730	4,061
300	361,26	1,3877	0,64053	3,607
350	397,97	1,4491	0,82664	3,190
400	443,33	1,5190	0,97747	2,811
450	494,19	1,5918	1,03910	2,478
500	545,42	1,6603	0,99483	2,201
550	592,37	1,7192	0,87622	1,979
600	632,64	1,7667	0,73589	1,804
650	666,17	1,8041	0,61020	1,665
700	691,10	1,8336	0,51268	1,552
750	717,87	1,8574	0,44252	1,459
800	738,70	1,8773	0,39389	1,379
850	757,51	1,8914	0,36068	1,310

Table 2 (continued).

t, °C	H, ккал/кг	S, ккал/кг·град	c_p, ккал/кг·град	ρ, кг/м³
900	774,94	1,9096	0,33808	1,248
950	791,43	1,9234	0,32264	1,194
1000	807,28	1,9361	0,31205	1,144
1050	822,69	1,9480	0,30474	1,099
1100	837,80	1,9592	0,29967	1,057
1150	852,69	1,9698	0,29616	1,019
1200	867,43	1,9800	0,29373	0,983

$p = 5$ кг/см²

t, °C	H, ккал/кг	S, ккал/кг·град	c_p, ккал/кг·град	ρ, кг/м³
70	182,97	0,9502	1,58890	12,290
80	199,55	0,9979	1,70180	10,990
90	216,79	1,0461	1,70970	9,897
100	233,49	1,0916	1,59630	9,005
110	248,59	1,1316	1,39460	8,294
120	262,14	1,1666	1,17370	7,726
130	272,82	1,1935	0,94494	7,294
140	281,37	1,2145	0,75826	6,950
150	288,27	1,2311	0,61876	6,670
160	293,97	1,2444	0,52287	6,436
170	298,87	1,2556	0,46021	6,232
180	303,27	1,2654	0,42184	6,054
190	307,39	1,2744	0,40196	5,890
200	311,37	1,2829	0,39479	5,739
250	332,34	1,3250	0,46414	5,087
300	359,16	1,3739	0,61583	4,523
350	394,41	1,4329	0,79433	4,008
400	438,14	1,5003	0,94588	3,538
450	487,68	1,5712	1,01920	3,124
500	539,35	1,6390	0,99266	2,775
550	585,60	1,6982	0,88888	2,493
600	626,73	1,7467	0,75592	2,269
650	661,30	1,7852	0,63107	2,092
700	690,22	1,8158	0,53101	1,948
750	714,82	1,8404	0,45733	1,829
800	736,30	1,8610	0,40539	1,727
850	755,61	1,8786	0,36946	1,639
900	773,43	1,8941	0,34476	1,562
950	790,21	1,9081	0,32775	1,493
1000	806,29	1,9210	0,31598	1,430
1050	821,87	1,9330	0,30780	1,374
1100	837,11	1,9443	0,30208	1,322
1150	852,11	1,9550	0,29807	1,274
1200	866,94	1,9653	0,29527	1,229

$p = 6$ кг/см²

t, °C	H, ккал/кг	S, ккал/кг·град	c_p, ккал/кг·град	ρ, кг/м³
70	178,06	0,9309	1,51240	15,320
80	194,00	0,9768	1,65420	13,660
90	220,91	1,0240	1,69210	12,260
100	227,71	1,0698	1,62790	11,110
110	243,33	1,1112	1,46080	10,190
120	257,65	1,1482	1,25810	9,452
130	269,20	1,1773	1,02910	8,885
140	278,58	1,2003	0,82954	8,435
150	286,13	1,2184	0,67432	8,072
160	292,32	1,2329	0,56382	7,772
170	297,58	1,2450	0,48905	7,515
180	302,23	1,2553	0,44106	7,292
190	306,50	1,2647	0,41384	7,090
200	310,57	1,2734	0,40104	6,905
250	331,41	1,3152	0,45468	6,115
300	357,51	1,3628	0,59685	5,441
350	391,64	1,4199	0,76887	4,829
400	434,07	1,4853	0,92000	4,269
450	482,49	1,5546	1,0014	3,774
500	532,61	1,6216	0,98847	3,353
550	579,98	1,6810	0,89766	3,010
600	621,72	1,7303	0,77111	2,738
650	657,10	1,7697	0,64786	2,521

Table 2 (continued).

t, °C	H, ккал/кг	S, ккал/кг·град	c_p, ккал/кг·град	ρ, кг/см
700	686,84	1,8011	0,54626	2,345
750	712,13	1,8264	0,46993	2,199
800	734,18	1,8475	0,41532	2,076
850	753,93	1,8655	0,37713	1,970
900	772,08	1,8813	0,35064	1,876
950	789,12	1,8955	0,33227	1,792
1000	805,40	1,9086	0,31947	1,717
1050	821,14	1,9207	0,31052	1,649
1100	836,50	1,9321	0,30422	1,586
1150	851,59	1,9429	0,29978	1,528
1200	866.50	1,9532	0,29664	1,475
		$p = 7$ кг/см²		
70	173,99	0,9150	1,44640	18,510
80	189,35	0,9591	1,60090	16,470
90	205,91	1,0055	1,67600	14,740
100	222,66	1,0510	1,63810	13,310
110	238,61	1,0933	1,50730	12,160
100	253,49	1,1318	1,32410	11,230
130	265,80	1,1628	1,10010	10,510
140	275,90	1,1876	0,89407	9,951
150	284,06	1,2072	0,72844	9,497
160	290,72	1,2228	0,60369	9,126
170	296,33	1,2356	0,51780	8,811
180	301,22	1,2466	0,46074	8,539
190	305,65	1,2563	0,42667	8,297
200	309,83	1,2652	0,40847	8,075
250	330,64	1,3069	0,44767	7,145
300	356,18	1,3535	0,58166	6,361
350	389,40	1,4091	0,74805	5,651
400	430,74	1,4728	0,89819	5,002
450	478,20	1,5408	0,98545	4,427
500	527,78	1,6070	0,98333	3,935
550	575,17	1,6665	0,90315	3,531
600	617,37	1,7162	0,78301	3,209
650	653,42	1,7564	0,66175	2,952
700	683,83	1,7885	0,55927	2.743
750	709,73	1,8145	0,48090	2,571
800	732,26	1,8360	0,42409	2,426
850	752,40	1,8544	0,38396	2,300
900	770,85	1,8704	0,35592	2,190
950	788,13	1,8849	0,33634	2,092
1000	804,59	1,8981	0,32264	2,004
1050	820,47	1,9103	0,31299	1,923
1100	835,94	1,9218	0,30618	1,850
1150	851,12	1,9327	0,30134	1,782
1200	866,10	1,9430	0,29789	1,720
		$p = 8$ кг/см²		
80	185,35	0,9441	1,55100	19,400
90	201,54	0,9894	1,61840	17,320
100	218,18	1,0346	1,63660	16,590
110	234,31	1,0774	1,54000	14,190
120	249,66	1,1171	1,37710	13,030
130	262,57	1,1496	1,16110	12,180
140	273,31	1,1760	0,95251	11,490
150	282,04	1,1970	0,77754	10,940
160	289,15	1,2136	0,64206	10,490
170	295,10	1,2272	0,54622	10,110
180	300,24	1,2387	0,48065	9,795
190	304,84	1,2488	0,44005	9,510
200	309,13	1,2580	0,41674	9,251
250	329,96	1,2998	0,44238	8,177
300	355,06	1,3455	0,56914	7,281
350	387,52	1,3998	0,73056	6,475
400	427,93	1,4621	0,87940	5,738
450	474,55	1,5289	0,97102	5,082
500	523,62	1,5945	0,97773	4,519
550	570,97	1,6539	0,80675	4,055

Table 2 (continued).

t, °C	H, ккал/кг	S, ккал/кг·град	c_p, ккал/кг·град	ρ, кг/см
600	613,52	1,7041	0,79255	3,682
650	650,12	1,7448	0,67348	3,384
700	681,11	1,7776	0,57058	3,143
750	707,54	1,8041	0,49060	2,944
800	730,51	1,8260	0,43194	2,776
850	751,00	1,8447	0,39014	2,631
900	769,73	1,8610	0,36072	2,504
950	787,22	1,8756	0,34007	2,391
1000	803,84	1,8869	0,32554	2,290
1050	819,85	1,9013	0,31527	2,198
1100	835,42	1,9128	0,30798	2,114
1150	850,68	1,9237	0,30277	2,037
1200	865,72	1,9341	0,29905	1,965
		$p = 9$ кг/см²		
80	181,86	0,9310	1,50480	22,460
90	197,67	0,9753	1,61670	20,010
100	214,17	1,0201	1,63830	17,940
110	230,39	1,0631	1,55920	16,300
120	246,05	1,1036	1,42200	14,950
130	259,50	1,1375	1,21320	13,900
140	277,82	1,1653	1,00470	13,070
150	280,07	1,1875	0,82369	12,410
160	287,61	1,2052	0,67891	11,880
170	293,90	1,2196	0,57409	11,430
180	299,28	1,2316	0,50071	11,060
190	304,05	1,2421	0,45381	10,730
200	308,46	1,2515	0,42560	10,430
250	329,37	1,2935	0,43831	9,210
300	354,09	1,3385	0,55859	8,203
350	385,91	1,3918	0,71555	7,300
400	425,53	1,4529	0,86295	6,475
450	471,39	1,5185	0,95789	5,740
500	519,98	1,5835	0,97197	5,106
550	567,26	1,6427	0,90902	4,580
600	610,07	1,6933	0,80032	4,157
650	647,13	1,7346	0,68355	3,818
700	678,63	1,7678	0,58055	3,544
750	705,53	1,7948	0,49930	3,317
800	728,90	1,8171	0,43906	3,126
850	749,70	1,8361	0,39578	2,962
900	768,68	1,8526	0,36513	2,819
950	736,37	1,8674	0,34350	2,691
1000	803,14	1,8808	0,32822	2,576
1050	819,27	1,8933	0,31738	2,473
1100	834,93	1,9049	0,30965	2,378
1150	850,27	1,9159	0,30411	2,290
1200	865,38	1,9263	0,30014	2,210
		$p = 10$ кг/см²		
80	178,73	0,9194	1,47470	25,670
90	194,22	0,9627	1,58480	22,790
100	210,52	1,0071	1,62540	20,400
110	226,78	1,0502	1,57000	18,470
120	242,66	1,0912	1,45380	16,890
130	256,60	1,1263	1,25860	15,650
140	268,41	1,1554	1,05210	14,680
150	278,14	1,1788	0,86719	13,910
160	286,10	1,1974	0,71446	13,280
170	292,71	1,2125	0,60162	12,770
180	298,33	1,2251	0,52070	12,330
190	303,29	1,2359	0,46787	11,950
200	307,80	1,2456	0,43487	11,610
250	326,83	1,2878	0,43520	10,240
300	353,25	1,3323	0,54955	9,126

Table 2 (continued).

t, °C	H, ккал/кг	S, ккал/кг·град	c_p, ккал/кг·град	ρ, кг/см³
350	384,51	1,3846	0,70247	8,126
400	423,42	1,4446	0,81836	7,213
450	468,61	1,5093	0,94693	6,400
500	516,76	1,5737	0,96618	5,695
550	563,92	1,6328	0,91035	5,108
600	606,95	1,6836	0,80674	4,634
650	644,39	1,7253	0,69230	4,253
700	676,35	1,7590	0,58943	3,945
750	703,66	1,7864	0,50718	3,691
800	727,40	1,8091	0,44558	3,477
850	748,49	1,8283	0,40099	3,293
900	767,70	1,8451	0,36923	3,133
950	785,57	1,8600	0,34671	2,990
1000	802,48	1,8736	0,33073	2,863
1050	818,72	1,8861	0,31936	2,747
1100	834,48	1,8978	0,31122	2,641
1150	849,89	1,9088	0,30537	2,544
1200	865,05	1,9193	0,30115	2,455
$p = 20$ кг/см²				
110	200,71	0,9607	1,56360	44,130
120	216,96	1,0027	1,56150	39,350
130	232,67	1,0423	1,47990	35,590
140	247,28	1,0783	1,34700	32,650
150	260,32	1,1096	1,18140	30,280
160	271,60	1,1362	1,00630	28,410
170	281,14	1,1581	0,84585	26,890
180	289,16	1,1761	0,71281	25,650
190	295,94	1,1910	0,61080	24,630
200	301,78	1,2035	0,53737	23,780
250	324,88	1,2500	0,43053	20,680
300	347,89	1,2919	0,50127	18,390
350	376,02	1,3389	0,62567	16,410
400	410,72	1,3925	0,75815	14,630
450	451,51	1,4509	0,86428	13,040
500	496,33	1,5103	0,91562	11,640
550	542,13	1,5682	0,90302	10,440
600	585,87	1,6199	0,83684	9,453
650	625,50	1,6641	0,74304	8,645
700	660,27	1,7008	0,64595	7,987
750	690,43	1,7311	0,56021	7,447
800	716,69	1,7562	0,49117	6,996
850	739,91	1,7775	0,43835	6,612
900	760,82	1,7957	0,39910	6,280
950	780,04	1,8118	0,37032	5,988
1000	798,01	1,8263	0,34930	5,727
1050	815,08	1,8395	0,33394	5,492
1100	831,48	1,8516	0,32265	5,278
1150	847,39	1,8630	0,31430	5,082
1200	862,93	1,8737	0,30807	4,901
$p = 30$ кг/см²				
120	200,61	0,9494	1,56140	67,880
130	216,49	0,9893	1,54160	60,010
140	231,80	1,0270	1,45100	53,970
150	246,16	1,0616	1,32950	49,270
160	259,12	1,0921	1,18230	45,510
170	270,52	1,1183	1,02430	42,560
180	280,35	1,1404	1,87545	40,110
190	288,72	1,1588	0,74628	38,150
200	295,87	1,1742	0,64418	36,560
250	321,89	1,2268	0,44525	31,280
300	344,72	1,2685	0,48205	27,710
350	371,42	1,3130	0,58830	24,730
400	403,99	1,3633	0,71044	22,080
450	442,39	1,4183	0,81647	19,730
500	485,08	1,4754	0,87869	17,640
550	529,53	1,5311	0,88681	15,840

Table 2 (continued).

t, °C	H, ккал/кг	S, ккал/кг·град	c_p, ккал/кг·град	ρ, кг/см
600	573,03	1,5824	0,84230	14,320
650	613,38	1,6274	0,76436	13,080
700	649,46	1,6656	0,67512	12,060
750	681,15	1,6974	0,59083	11,220
800	708,91	1,7240	0,51941	10,520
850	733,46	1,7464	0,46268	9,937
900	755,50	1,7657	0,41928	9,428
950	775,64	1,7826	0,38673	8,982
1000	794,36	1,7976	0,36253	8,586
1050	812,02	1,8113	0,34458	8,229
1100	828,90	1,8238	0,33124	7,905
1150	815,20	1,8355	0,32128	7,608
1200	861,06	1,8464	0,31379	7,334
		$p=40$ кг/см^2		
130	203,40	0,9489	1,54840	90,380
140	219,11	0,9875	1,48330	79,390
150	234,07	1,0235	1,42480	71,090
160	248,07	1,0564	1,29040	64,800
170	260,71	1,0855	1,14790	59,850
180	271,87	1,1107	1,00430	55,830
190	281,57	1,1321	0,86601	52,570
200	289,93	1,1502	0,74678	50,030
250	319,19	1,2095	0,46812	42,040
300	342,36	1,2518	0,47382	37,070
350	368,25	1,2950	0,56438	33,060
400	399,41	1,3431	0,67924	29,520
450	436,21	1,3958	0,78376	26,810
500	477,40	1,4509	0,85042	23,660
550	520,76	1,5052	0,87070	21,240
600	563,87	1,5560	0,84074	19,200
650	604,50	1,6013	0,77480	17,500
700	641,34	1,6402	0,69720	16,110
750	674,02	1,6730	0,61098	14,970
800	702,81	1,7005	0,53902	14,010
850	728,31	1,7238	0,48019	13,210
900	751,18	1,7438	0,43418	12,520
950	772,01	1,7612	0,39908	11,910
1000	791,30	1,7767	0,37267	11,380
1050	809,43	1,7907	0,35289	10,900
1100	826,69	1,8036	0,33808	10,470
1150	843,29	1,8155	0,32698	10,070
1200	659,41	1,8266	0,31862	9,714
		$p=50$ кг/см^2		
140	205,21	0,9478	1,54580	112,700
150	220,74	0,9850	1,44590	98,280
160	235,79	1,0205	1,39440	87,780
170	249,82	1,0529	1,25970	79,710
180	262,42	1,0815	1,12130	73,550
190	273,57	1,1062	0,98031	68,600
200	283,30	1,1272	0,85219	64,590
250	316,53	1,1949	0,49595	52,940
300	340,32	1,2384	0,47087	46,430
350	365,75	1,2808	0,54902	41,360
400	395,94	1,3273	0,65558	36,930
450	431,46	1,3882	0,75768	33,070
500	471,33	1,4315	0,82641	29,650
550	513,60	1,4845	0,85488	26,640
600	556,13	1,5346	0,83632	24,090
650	596,75	2,5798	0,78093	21,960
700	634,04	1,6191	0,70608	20,210
750	667,44	1,6526	0,62779	18,770
800	697,07	1,6809	0,55633	17,580
850	723,39	1,7049	0,49627	16,570
900	747,01	1,7255	0,44824	15,710
950	768,49	1,7435	0,41097	14,960
1000	788,33	1,7594	0,38251	14,290

Table 2 (continued).

t, °C	H, ккал/кг	S, ккал/(кг·град)	c_p, ккал/(кг·град)	ρ, кг/м³
1050	806,92	1,7738	0,36095	13,690
1100	824,56	1,7870	0,34467	13,150
1150	841,49	1,7991	0,33237	12,650
1200	857,87	1,8105	0,32305	12,180
$p = 60$ кг/см²				
150	205,47	0,9438	1,50290	136,000
160	221,18	0,9809	1,43320	117,300
170	236,52	1,0165	1,37360	104,100
180	250,94	1,0494	1,24850	94,370
190	263,96	1,0784	1,10630	86,800
200	275,46	1,1034	0,96718	80,770
250	313,91	1,1821	0,52762	64,130
300	338,59	1,2272	0,47282	55,870
350	363,83	1,2693	0,53693	49,680
400	393,35	1,3148	0,63665	44,360
450	427,94	1,3644	0,73785	39,740
500	466,88	1,4165	0,80857	35,660
550	508,43	1,4686	0,84114	32,040
600	550,57	1,5182	0,83146	28,970
650	591,21	1,5635	0,78238	26,430
700	628,83	1,6033	0,71350	24,340
750	662,75	1,6373	0,63772	22,640
800	692,95	1,6663	0,56679	21,230
850	719,84	1,6909	0,50605	20,040
900	743,95	1,7120	0,45684	19,030
950	765,86	1,7304	0,41827	18,140
1000	786,05	1,7467	0,38865	17,360
1050	804,93	1,7613	0,36615	16,640
1100	822,81	1,7747	0,34915	15,990
1150	839,94	1,7870	0,33634	15,370
1200	856,50	1,7985	0,32671	14,800
$p = 70$ кг/см²				
150	191,31	0,9036	1,68460	190,000
160	208,06	0,9460	1,46780	155,100
170	224,07	0,9833	1,41530	133,500
180	239,62	1,0187	1,33900	118,300
190	254,17	1,0514	1,21180	107,100
200	267,24	1,0799	1,07120	98,420
250	311,14	1,1702	0,56513	75,650
300	337,01	1,2176	0,47930	65,380
350	362,24	1,2597	0,53205	57,980
400	391,27	1,3045	0,62518	51,750
450	425,16	1,3531	0,72226	46,370
500	463,40	1,4042	0,79493	41,620
550	504,41	1,4556	0,83132	37,380
600	546,25	1,5050	0,82629	33,800
650	586,86	1,5503	0,78297	30,820
700	624,66	1,5903	0,71668	28,380
750	658,88	1,6247	0,64270	26,390
800	689,43	1,6541	0,57224	24,730
850	716,64	1,6791	0,51118	23,330
900	741,04	1,7006	0,46134	22,160
950	763,18	1,7192	0,42215	21,130
1000	783,57	1,7358	0,39206	20,210
1050	802,61	1,7506	0,36930	19,370
1100	820,64	1,7641	0,35226	18,610
1150	837,92	1,7765	0,33964	17,890
1200	854,64	1,7880	0,33038	17,210
$p = 80$ кг/см²				
150	176,85	0,8699	2,43760	288,400
160	196,93	0,9170	1,60180	203,600
170	213,79	0,9560	1,46400	167,800
180	229,96	0,9929	1,38310	145,200

Table 2 (continued).

t, °C	H, ккал/кг	S, ккал/кг·град	c_p, ккал/кг·град	ρ, кг/м³
190	245,34	1,0274	1,28030	129,100
200	259,43	1,0583	1,14390	117,200
250	308,09	1,1587	0,60787	87,290
300	335,36	1,2089	0,48785	74,770
350	360,72	1,2512	0,52787	66,120
400	389,40	1,2954	0,61483	59,000
450	422,77	1,3432	0,70980	52,850
500	460,45	1,3937	0,78358	47,440
550	501,01	1,4445	0,82251	42,650
600	542,54	1,4936	0,82116	38,580
650	583,07	1,5388	0,78228	35,180
700	621,00	1,5790	0,71980	32,390
750	655,49	1,6139	0,64784	30,100
800	686,37	1,6437	0,57827	28,210
850	713,92	1,6691	0,51721	26,630
900	738,63	1,6910	0,46688	25,280
950	761,05	1,7100	0,42703	24,100
1000	781,67	1,7268	0,39629	23,060
1050	800,91	1,7418	0,37299	22,110
1100	819,10	1,7555	0,35555	21,230
1150	836,52	1,7680	0,34266	20,410
1200	853,37	1,7796	0,33328	19,640
		$p=90$ кг/см²		
150	162,48	0,8345	2,75140	469,400
160	187,44	0,8926	1,82490	267,400
170	205,47	0,9341	1,55100	206,800
180	222,20	0,9722	1,42440	174,300
190	238,04	1,0076	1,32930	152,400
200	252,75	1,0400	1,20150	136,800
250	305,06	1,1482	0,64726	99,420
300	333,79	1,2011	0,49499	84,310
350	359,28	1,2437	0,52432	74,400
400	387,70	1,2875	0,60672	66,360
450	420,65	1,3347	0,69924	59,460
500	457,68	1,3845	0,77292	53,400
550	498,08	1,4349	0,81427	48,000
600	539,47	1,4837	0,81745	43,400
650	580,10	1,5291	0,78283	39,580
700	618,32	1,5696	0,72308	36,440
750	653,20	1,6048	0,65275	33,870
800	684,49	1,6350	0,58343	31,760
850	712,40	1,6607	0,52194	30,000
900	737,43	1,6828	0,47090	28,500
950	760,08	1,7019	0,43032	27,190
1000	780,88	1,7188	0,39894	26,030
1050	800,25	1,7339	0,37513	24,970
1100	818,53	1,7475	0,35730	23,990
1150	836,01	1,7600	0,34413	23,060
1200	852,88	1,7716	0,33455	22,180
		$p=100$ кг/см²		
160	177,53	0,8679	2,19180	362,600
170	197,82	0,9142	1,60670	254,800
180	215,08	0,9533	1,48950	207,300
190	231,33	0,9896	1,37000	177,800
200	246,50	1,0230	1,26580	157,700
250	302,03	1,1381	0,68824	111,700
300	332,36	1,1940	0,50206	93,870
350	358,03	1,2369	0,52196	82,620
400	386,23	1,2804	0,59948	73,650
450	418,72	1,3269	0,68899	65,960
500	455,38	1,3760	0,76231	59,220
550	495,03	1,4257	0,80549	53,220
600	535,94	1,4740	0,81185	48,110
650	576,26	1,5189	0,78124	43,870
700	614,35	1,5591	0,72533	40,400
750	649,27	1,5941	0,65783	37,570

Table 2 (continued).

t, °C	H, ккал/кг	S, ккал/(кг·град)	c_p, ккал/(кг·град)	ρ, кг/м³
800	680,73	1,6242	0,59009	35,250
850	708,89	1,6499	0,52913	33,310
900	734,19	1,6720	0,47792	31,660
950	757,13	1,6912	0,43680	30,220
1000	778,19	1,7081	0,40474	28,940
1050	797,81	1,7233	0,38027	27,770
1100	816,33	1,7371	0,36197	26,660
1150	834,03	1,7499	0,34838	25,650
1200	851,12	1,7617	0,33852	24,660
$p=150$ кг/см²				
160	143,78	0,78675	1,58050	786,600
170	161,99	0,82750	1,79810	631,000
180	182,40	0,87246	1,91460	459,600
190	201,[illegible]3	0,91412	1,61060	356,500
200	218,63	0,95125	1,45380	296,600
250	286,62	1,0920	0,89444	178,000
300	325,18	1,1637	0,57658	142,300
350	352,97	1,2102	0,52419	123,100
400	380,58	1,2527	0,57096	109,100
450	411,62	1,2971	0,65395	97,630
500	446,55	1,3440	0,72474	87,760
550	484,55	1,3916	0,77370	79,020
600	524,31	1,4384	0,79276	71,510
650	561,28	1,4829	0,77633	65,190
700	602,75	1,5236	0,73223	59,950
750	638,54	1,5596	0,67221	55,640
800	671,10	1,5909	0,60776	52,090
850	700,40	1,6179	0,54707	49,130
900	726,74	1,6412	0,49449	46.610
950	750,58	1,6615	0,45137	44,430
1000	772,40	1,6793	0,41735	42,500
1050	792,62	1,6951	0,39125	40,750
1100	811,64	1,7095	0,37214	39,120
1150	829,76	1,7226	0,35778	37,600
1200	847,21	1,7347	0,34758	36,140
$p=200$ кг/см²				
160	132,74	0,7591	1,25950	892,900
170	146,65	0,7898	[illegible]	802,900
180	162,50	0,8244	[illegible]	692,200
190	179,93	0,8620	[illegible]	572,100
200	197,81	0,9001	1,55610	469,100
250	272,47	1,0536	1,05040	251,900
300	318,18	1,1391	0,63919	192,200
350	348,11	1,1895	0,53902	163,100
400	376,15	1,2327	0,56809	144,100
450	406,62	1,2762	0,63232	128,700
500	440,52	1,3215	0,69904	115,400
550	477,67	1,3680	0,75336	104,000
600	516,88	1,4141	0,77734	94,230
650	556,66	1,4584	0,76917	85,840
700	595,37	1,4993	0,73337	78,850
750	631,76	1,5359	0,67972	73,070
800	665,14	1,5681	0,61896	68,300
850	695,32	1,5960	0,55963	64,330
900	722,49	1,6202	0,50687	60,980
950	747,04	1,6411	0,46281	58,080
1000	769,43	1,6595	0,42758	55,530
1050	790,11	1,6759	0,40033	53,220
1100	809,46	1,6905	0,37980	51,090
1150	827,79	1,7038	0,36475	49,100
1200	845,39	1,7160	0,35411	47,200
$p=250$ кг/см²				
160	127,32	0,7443	1,06600	944,300
170	139,33	0,7708	1,19770	884,700
180	152,66	0,7998	1,31500	802,700
190	167,62	0,8317	1,46780	716,300
200	183,50	0,8653	1,48750	624,600
250	259,87	1,0211	1,14400	331,200

Table 2 (continued).

t, °C	H, $\frac{ккал}{кг}$	S, $\frac{ккал}{кг \cdot град}$	c_p, $\frac{ккал}{кг \cdot град}$	ρ, $\frac{кг}{см}$
300	310,65	1,1164	0,73124	241,500
350	341,11	1,1727	0,56408	202,000
400	372,06	1,2167	0,59016	177,800
450	402,58	1,2595	0,61864	158,000
500	435,65	1,3037	0,68106	142,400
550	471,84	1,3490	0,73573	128,400
600	510,19	1,3940	0,76312	116,300
650	549,44	1,4376	0,76150	106,000
700	588,00	1,4784	0,73232	97,360
750	624,56	1,5153	0,68399	90,280
800	658,33	1,5460	0,62060	84,450
850	689,01	1,5766	0,56877	79,630
900	716,72	1,6015	0,51619	75,560
950	741,79	1,6232	0,47158	72,070
1000	764,64	1,6422	0,43556	68,980
1050	785,72	1,6590	0,40758	66,170
1100	805,43	1,6741	0,38555	63,570
1150	824,09	1,6878	0,37130	61,090
1200	841,99	1,7002	0,36068	58,700
		$p = 300$ кг/см²		
160	123,92	0,7340	1,96242	981,300
170	134,66	0,7578	1,08090	929,300
180	146,64	0,7840	1,17810	869,600
190	159,91	0,8120	1,32680	795,600
200	174,48	0,8426	1,35070	722,800
250	249,13	0,9941	1,19510	410,300
300	303,96	1,0965	0,80864	289,500
350	340,26	1,1579	0,59145	240,600
400	369,41	1,2029	0,55628	210,400
450	399,02	1,2453	0,61033	187,500
500	431,48	1,2887	0,66757	168,500
550	466,87	1,3329	0,72214	152,100
600	504,35	1,3770	0,74944	138,000
650	542,71	1,4195	0,74973	125,900
700	580,49	1,4593	0,72425	115,700
750	616,48	1,4954	0,68004	107,300
800	649,90	1,5274	0,62622	100,300
850	680,44	1,5555	0,57098	94,580
900	708,16	1,5800	0,52004	89,690
950	733,34	1,6015	0,47641	85,480
1000	756,39	1,6204	0,44108	81,750
1050	777,74	1,6374	0,41377	78,380
1100	797,78	1,6527	0,39362	75,260
1150	816,85	1,6667	0,37956	72,290
1200	835,26	1,6797	0,37059	69,430