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EQUATIONS OF AVERAGE ISOBARIC HEAT CAPACITY OF AIR AND COMBUSTION GASES WITH INFLUENCE OF PRESSURE AND EFFECT OF THERMAL DISSOCIATION

All properties of thermomechanical systems working substance are two-parameter that is determined by two parameters, the most often they are temperature and pressure which are easily measured by experiment. Representing the isobaric heat capacity as a function of temperature cp = f(T) become a thing of the past. Analytical and tabular ways are used to represent dependencies as a function of temperature and pressure. The tabular method is convenient for single calculations, but the analytical one is more convenient for a series of calculations. The advantages of an analytical description in comparison with a tabular one are obvious, namely, compactness of information storage without reference to node points, the ability to integrate and differentiate, dependencies can be embedded directly in the program body and don't require special subroutines to access to the tables. Developers of the programs for calculating thermophysical properties, as a rule, use functional dependencies which may have a different appearance for temperature and pressure intervals of the same substance. This is explained by the fact that in the region close to the saturation curve, there is a steep change in all the thermophysical properties of substances including the isobaric heat capacity. In thermogasdynamic calculations of heat machines, the main physical parameter of the working fluid is its heat capacity, both true and average. The article presents the analytical dependencies of the average specific isobaric heat capacities of the main components of air and combustion products of hydrocarbon fuels which are united throughout the specified range of pressures and temperatures (nitrogen: p = 1 ... 200 bar, T = 150 ... 2870 K, oxygen: p = 1 ... 200 bar, T = 210 ... 2870 K, argon: p = 1 ... 200 bar, T = 190 ... 1300 K, the water vapor: p = 0,1 ... 200 bar, T = 700 ... 2600 K, carbon dioxide: p = 1 ... 200 bar, T = 390 ... 2600 K). The analytical dependencies were derived on the basis of previously obtained analytical expressions for the specific isobaric heat capacities of these gases. The average specific isobaric heat capacities of gases are also functions of temperature and pressure cp = f(T, P) and take into account the effect of thermal dissociation. Formulas for average specific isobaric heat capacities are obtained by integrating expressions for specific isobaric heat capacities. Verification of the obtained dependencies for different temperature ranges was done.

Keywords: average isobaric heat capacity; combustion products of heat machines; air; thermal dissociation; influence of pressure.

Introduction

The average heat capacity c_{p_m} traditionally is used for thermogasdynamic calculations of heat machines (HM) and gas turbine engines, in particular [1-3]. It is the average integral value of the isobaric heat capacity within a given temperature range [4, 5]

$$c_{p_m} = \frac{\int_{T_1}^{T_2} c_p(T,p)\, dT}{T_2 - T_1}. \qquad (1)$$

Ease of use c_{p_m} is obvious, as far as multiplied by the temperature increment during the process the average isobaric heat capacity allows to get immediately increase in the specific enthalpy of the working fluid Δi

$$\Delta i = c_{p_m} \Delta T$$

and specific heat of the isobaric process $q = \Delta i$, including thermal effect of isobaric chemical reactions [4].

Average adiabatic index k_m within a given temperature range can be expressed also through c_{p_m}

$$k_m = \left(1 - \frac{R}{c_{p_m}}\right)^{-1},$$

where R is the individual gas constant of the substance.

Starting from references [6–8], the average heat capacities were not determined experimentally, but by temperature integration of the existing values of the heat capacities c_p, according to the formula (1).

1. Analysis of Publications and Problem Statement

In the ideal gas model, the heat capacity is constant and depends only on the structure of the gas molecule.

The real working substance of the thermomechanical system is two-parameter, i.e. any parameter, including phenomenological coefficients (viscosity, thermal conductivity, heat capacity), is determined by two parameters of the system. The temperature and pressure are used the most commonly, because they are measured by experiment easily. Despite this, in the majority of references [8–10], the values of c_{p_m} are given only for the gas pressure $p \ll p_{cr}$ at a fixed lower temperature $T_1 = 0\,^\circ C$. In this case, c_{pm} depends only on the upper integration temperature T_2. The effect of thermal dissociation (ETD) for the obtained values of c_{p_m} is also not taken into account. The works [11–15] show that in a number of cases it is unacceptable to neglect the pressure and the ETD in the c_p determination. The calculation of ETD requires to use of other approaches, and the solution of the system of chemical kinetics equations, in particular, which includes the equilibrium constants of the reactions [8, 9, 13, 15].

There are software products [16, 17] that allow obtaining the isobaric heat capacities of gases as a function of temperature and pressure $c_p(T,p)$. In this case, $c_{p_m}(T,p)$ can be found by numerical integration of the generated spreadsheets. This is not always convenient because the user has to substitute manually the results into their own calculation or develop a special subroutine for accessing spreadsheets. It is much more convenient to use analytical dependencies in calculations.

The advantages of an analytical description in comparison with a tabular one are obvious, namely, compactness of information storage without reference to node points, the ability to integrate and differentiate, dependencies can be embedded directly in the program body and don't require special subroutines to access to the tables, obtaining the average heat capacity at T_1, other than 0 °C.

Authors of the article don't know analytical relationships that allow to count $c_{p_m}(T,p)$ taking into account the ETD.

In the reference [11], formulas for the specific isobaric heat capacities of the air and combustion products components (ACPC) of heat machines that taking into account temperature, pressure and ETD are presented. According to formula (1), it is possible to obtain $c_{p_m} = f(T,p)$ taking into account ETD.

The aim of the work is to obtain the average heat capacities of the ACPC of HM $c_{p_m} = f(T,p)$ within a given range of pressures and temperatures taking into account the effect of thermal dissociation.

2. Method of Obtaining of the Average Specific Isobaric Heat Capacities

The initial data for obtaining of c_{p_m} expressions of the ACPC were the equations of the specific isobaric heat capacities of these gases that were obtained by the authors in [11] which were derived from the tabular data of the references [18, 19].

Mathematically, the derivation of a formula $c_{p_m}(T,p)$ is reduced to finding of a definite integral within a given temperature range $T_1 \dots T_2$

$$\int_{T_1}^{T_2} c_p(T,p)\,dT$$

with fixed pressure p.

In all expressions below temperature T is measured in Kelvin degrees, pressure p – in bar, heat capacity c_{p_m} – in kJ/(kg·K).

3. Results

The working range of the obtained expressions for average heat capacities c_{p_m} coincides with the working range of the original heat capacities c_p. For low-boiling gases (N_2, O_2, Ar), the expressions for c_{p_m} are applicable in the temperature range from 150...210 to 2600...2870 K and pressure range from 0.1 to 200 bar. For high-boiling gases (CO_2, H_2O), the lower limit of the working range shifts towards higher temperatures, for CO_2 it is T_1 = 390 K and for H_2O it is T_1 = 700 K. Pressure range for water vapor is p = 0,1 ... 200 bar and for carbon dioxide is p = 1 ... 200 bar [11]. The reason of the high values for the lower temperature limit in the case of high-boiling components is determined by expectation to remain in the superheated steam region and to avoid the onset of condensation, which occurs in the case of subcritical temperatures at operating pressures above the saturation pressure.

Verification of the obtained expressions for the c_{p_m} of the ACPC was performed according to the data [9], where the initial temperature was taken T_1 = 273 K, the pressure was implied low enough ($p \ll p_{cr}$) and was not mentioned at all by reason of the hypothesis of

heat capacity independence from the pressure. In [9], the effect of thermal dissociation is also not taken into account.

For low-boiling gases (N_2, O_2, Ar) $c_{p_m}(T, p)$ were calculated at $p = 1\,bar$, $T_1 = 273\,K$ and were compared with the data [9].

For high-boiling gases (CO_2, H_2O) $c_{p_m}(T, p)$ were calculated at $p = 1\,бар$, $T_1 \neq 273\,K$. For verification tabular data c_{p_m} [9] were recalculated for the interval $T_1 \ldots T_2$ using the formula

$$c_{p_m}\Big|_{T_1}^{T_2} = \frac{(T_2 - 273) \cdot c_{p_m}\Big|_{273}^{T_2} - (T_1 - 273) \cdot c_{p_m}\Big|_{273}^{T_1}}{T_2 - T_1},$$

or

$$c_{p_m}\Big|_{T_1}^{T_2} = \frac{(T_2 - 273) \cdot c_{p_m}\Big|_{273}^{T_2} - \Delta i\Big|_{273}^{T_1}}{T_2 - T_1}.$$

Enthalpy difference at a fixed pressure $p = 1\,bar$ is a function of T_1 only $\Delta i\Big|_{273}^{T_1} = i(T_1) - i(T = 273\,K)$. Enthalpy difference for carbon dioxide CO_2 at $T_1 = 390\,K$ is $\Delta i\Big|_{273}^{390} = 103{,}13\,\frac{kJ}{kg}$ and for water vapor H_2O at $T_1 = 700\,K$ is $\Delta i\Big|_{273}^{700} = 833{,}7\,\frac{kJ}{kg}$.

3.1. Average Specific Isobaric Heat Capacity of Nitrogen

The specific isobaric heat capacity of nitrogen at the temperature range $T = 150 \ldots 2870\,K$ and pressures $p = 0{,}1 \ldots 200\,bar$ has the form of a fourth-degree polynomial by pressure [11]

$$c_p(T, p) = \sum_{i=0}^{4} X_i(T) \cdot p^i, \qquad (2)$$

with polynomial coefficients $X_i(T)$ depending only on the gas temperature.

The average heat capacity at the temperature range $T_1 \ldots T_2$ are determined according to expression (1) and for a polynomial of the 4th degree by pressure

$$c_{p_m} = \frac{1}{T_2 - T_1} \sum_{i=0}^{4} \left(\int_{T_1}^{T_2} X_i(T) dT \right) p^i. \qquad (3)$$

The coefficient X_0 is described by a polynomial of the 6th degree and has the form [11]

$$X_0 = \sum_{i=0}^{6} e_i T^i. \qquad (4)$$

The integral of the power polynomial (4) has the form

$$\int_{T_1}^{T_2} X_0(T) dT = \sum_{i=0}^{6} \frac{e_i}{i+1} \left(T_2^{i+1} - T_1^{i+1} \right), \qquad (5)$$

polynomial coefficients e_i are given in the Table 1 [11]

Table 1

Polynomial coefficients e_i for the expression (5)

e_i	Value
e_0	1,17485346 E+00
e_1	-1,00362980 E-03
e_2	2,41548607 E-06
e_3	-2,26418817 E-09
e_4	1,07944740 E-12
e_5	-2,58998975 E-16
e_6	2,47848087 E-20

The remaining coefficients of formula (3) for $i = 1 \ldots 4$ are described by a rational function ("Rational Model") [11]

$$X_i = \frac{a_i + b_i T}{1 + c_i T + d_i T^2}. \qquad (6)$$

The temperature integral of the expression (6) has the form

$$\int_{T_1}^{T_2} X_i(T) dT = \int_{T_1}^{T_2} \frac{a_i + b_i T}{1 + c_i T + d_i T^2} dT =$$

$$= a_i \int_{T_1}^{T_2} \frac{dT}{1 + c_i T + d_i T^2} + b_i \int_{T_1}^{T_2} \frac{T dT}{1 + c_i T + d_i T^2} \qquad (7)$$

The integrals of the expression (7) are tabular ones, and for the case $4d_i - c_i^2 > 0$ are equal

$$\int \frac{dT}{1 + c_i T + d_i T^2} =$$

$$= \frac{2}{\sqrt{4d_i - c_i^2}} \text{arctg} \left(\frac{2d_i T + c_i}{\sqrt{4d_i - c_i^2}} \right); \qquad (8)$$

$$\int \frac{T dT}{1 + c_i\,T + d_i\,T^2} = \frac{1}{2d_i} \ln\left|1 + c_i\,T + d_i\,T^2\right| -$$

$$-\frac{c_i}{2d_i} \int \frac{dT}{1 + c_i\,T + d_i\,T^2}. \qquad (9)$$

Expressions (8) and (9) are substituted in the (7)

$$\int \frac{a_i + b_i\,T}{1 + c_i\,T + d_i\,T^2}\,dT = \frac{b_i}{2d_i}\ln\left|1 + c_i\,T + d_i\,T^2\right| +$$

$$+\left(a_i - \frac{b_i c_i}{2d_i}\right)\int \frac{dT}{1 + c_i\,T + d_i\,T^2} =$$

$$= \frac{1}{d_i}\left(\frac{b_i}{2}\ln\left|1 + c_i\,T + d_i\,T^2\right| + \frac{2a_i d_i - b_i c_i}{\sqrt{4d_i - c_i^2}}\,\mathrm{arctg}\left(\frac{2d_i T + c_i}{\sqrt{4d_i - c_i^2}}\right)\right).$$

$$\qquad (10)$$

After that, the limits of integration T_1 and T_2 are substituted in expression (10)

$$\int_{T_1}^{T_2} X_i(T)\,dT = \frac{1}{d_i}\left(\frac{b_i}{2}\ln\left|\frac{1 + c_i\,T_2 + d_i\,T_2^2}{1 + c_i\,T_1 + d_i\,T_1^2}\right| +\right.$$

$$+\frac{2a_i d_i - b_i c_i}{\sqrt{4d_i - c_i^2}}\left(\mathrm{arctg}\left(\frac{2d_i T_2 + c_i}{\sqrt{4d_i - c_i^2}}\right) - \mathrm{arctg}\left(\frac{2d_i T_1 + c_i}{\sqrt{4d_i - c_i^2}}\right)\right)\Bigg)$$

$$\qquad (11)$$

Finally, the average specific heat capacity of nitrogen in the range of pressures p = 0.1 ... 200 bar and temperatures T = 150 ... 2870 K is described by the expression (12).

$$c_{p_m} = \frac{1}{T_2 - T_1}\left(\sum_{i=0}^{6}\frac{e_i}{i+1}\left(T_2^{i+1} - T_1^{i+1}\right) +\right.$$

$$+\sum_{i=1}^{4}\left(\frac{1}{d_i}\left(\frac{b_i}{2}\ln\left|\frac{1 + c_i\,T_2 + d_i\,T_2^2}{1 + c_i\,T_1 + d_i\,T_1^2}\right| +\right.\right.$$

$$+\frac{2a_i d_i - b_i c_i}{\sqrt{4d_i - c_i^2}}\left(\mathrm{arctg}\left(\frac{2d_i T_2 + c_i}{\sqrt{4d_i - c_i^2}}\right) -\right.$$

$$\left.\left.\left.-\mathrm{arctg}\left(\frac{2d_i T_1 + c_i}{\sqrt{4d_i - c_i^2}}\right)\right)\right)\right)p^i\Bigg). \qquad (12)$$

The coefficients a_i, b_i, c_i, d_i of the expression (12) are presented in the Table 2 [11].

The Fig. 1 presents the comparison results of the average specific isobaric heat capacity of nitrogen $\left(c_{p_m}\right)_{calc}$ that is calculated by the formula (12) with reference data $\left(c_{p_m}\right)_{ref}$ from the work [9]. The relative error of approximation was defined as

$$\Delta c_{p_m} = \frac{\left(c_{p_m}\right)_{calc} - \left(c_{p_m}\right)_{ref}}{\left(c_{p_m}\right)_{ref}}100\%.$$

As seen from the Fig. 1b, the error for the pressure p = 1 bar is $\Delta c_{p_m} < 1\%$, with the exception of the first point $T_2 = T_1 = 273$ K, where it is 1,15 %.

The simplified linear dependence of the isobaric heat capacity of nitrogen c_p on pressure p describes computational regions far from the critical point at which the temperature and pressure are $T_{cr} = 126,2$ K; $p_{cr} = 33,9$ bar.

The isobaric heat capacity of N_2 within a given range T = 210 ... 2870 K and p = 0,1 ... 200 bar is approximated by the simplified expression [11]

$$c_p(T;p) = \left(1 + \frac{\alpha}{T^\beta}(p-1)\right)\cdot c_p(T)_{p=1}, \qquad (13)$$

where $\alpha = 1434,2$; $\beta = 2,421$; $c_p(T)_{p=1}$ is the 6th degree polynomial that describes the specific isobaric heat capacity of nitrogen at the pressure p = 1 bar [11]

$$c_p(T)_{p=1} = \sum_{i=0}^{6} f_i T^i. \qquad (14)$$

According to the formula (1), the average heat capacity of N_2 for the specified range of temperatures and pressures can be written as

$$c_{pm} = \frac{1}{T_2 - T_1}\int_{T_1}^{T_2}\left(\left(1 + \frac{\alpha}{T^\beta}(p-1)\right)c_p(T)_{p=1}\right)dT. \qquad (15)$$

Table 2

Coefficients a_i, b_i, c_i, d_i for the equation (12)

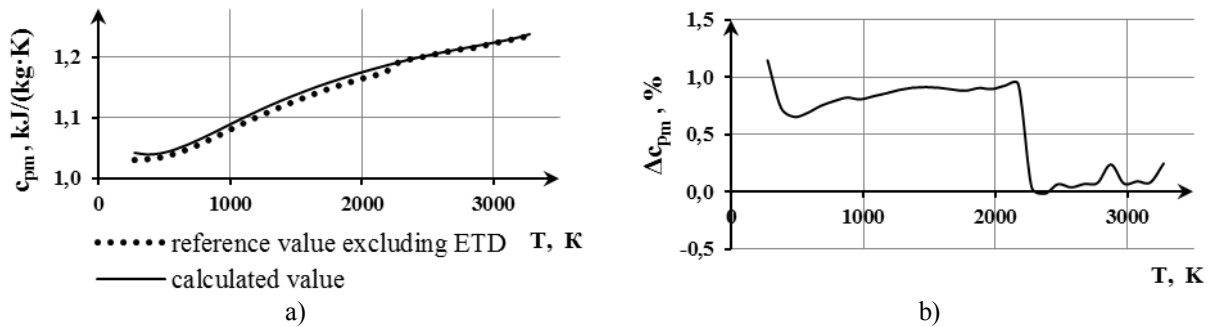| i	1	2	3	4
a_i	-1,135383459 E-03	3,455484448 E-05	-3,091140829 E-07	7,634837423 E-10
b_i	6,421029505 E-06	-1,225542135 E-07	1,116149284 E-09	-2,920723149 E-12
c_i	-1,144002151 E-02	-1,311713799 E-02	-1,323947412 E-02	-1,326425980 E-02
d_i	3,327677283 E-05	4,365761243 E-05	4,436704709 E-05	4,444797637 E-05

a)

b)

Fig. 1. The average specific isobaric heat capacity c_{p_m} (a) and approximation error Δc_{p_m} (b) for N_2 at $p = 1$ bar, $T_1 = 273$ K in the given range $T_2 = 273 \ldots 3273$ K; approximation c_{p_m} is carried out by the formula (12)

The subintegral function of the expression (15) is the sum of two power polynomials that are integrated separately for convenience

$$\int\left(\left(1+\frac{\alpha}{T^{\beta}}(p-1)\right)c_p(T)_{p=1}\right)dT = \int\left(\sum_{i=0}^{6}f_i T^i\right)dT +$$

$$+\alpha(p-1)\int\left(\sum_{i=0}^{6}f_i T^{i-\beta}\right)dT.$$

Finally, the average specific isobaric heat capacity of nitrogen in the given range of temperatures and pressures $T = 210 \ldots 2870$ K and $p = 0{,}1 \ldots 200$ bar has the form

$$c_{p_m} = \frac{1}{T_2-T_1}\left(\sum_{i=0}^{6}\frac{f_i}{i+1}\left(T_2^{i+1}-T_1^{i+1}\right)+\right.$$

$$\left.+\alpha(p-1)\sum_{i=0}^{6}\frac{f_i}{i-\beta+1}\left(T_2^{i-\beta+1}-T_1^{i-\beta+1}\right)\right), \quad (16)$$

polynomial coefficients are given in the Table 3 [11].

Table 3

Coefficients of f_i of the equation (16) for nitrogen

f_i	Value
f_0	1,14552 E+00
f_1	−7,80728 E-04
f_2	1,87175 E-06
f_3	−1,66208 E-09
f_4	7,46404 E-13
f_5	−1,69530 E-16
f_6	1,55002 E-20

The coincidence of the graphs in the Fig. 1 and 2 is explained by the fact that expressions (12) and (16) correlate well in the region of low pressures $p \ll p_{cr}$.

3.2. Average Specific Isobaric Heat Capacity of Oxygen

The physical properties of oxygen are close to nitrogen, which allowed using the same functional dependences $c_p = f(T, p)$ in [11], but only with different coefficients. The coefficients of $X_i(T)$ for $i = 2, 3, 4$ are described by the logistic regression model in the form [11]

$$X_i(T) = \frac{a_i}{1+\left(\dfrac{T}{b_i}\right)^{c_i}}. \quad (17)$$

Its integral

$$\int X(T)dT = a\int\frac{dT}{1+\left(\dfrac{T}{b}\right)^c},$$

unlike a rational model or a power function, has no analytical solution.

Therefore, to find the expression for the specific isobaric heat capacity of O_2 the linear dependence of pressure in the form (13) was used. In this case, the average specific heat is described by the expression (16), which coefficients $\alpha = 1418$, $\beta = 2{,}412$ and f_i are presented in the Table 4 [11].

Table 4

Coefficients f_i of the equation (16) for oxygen

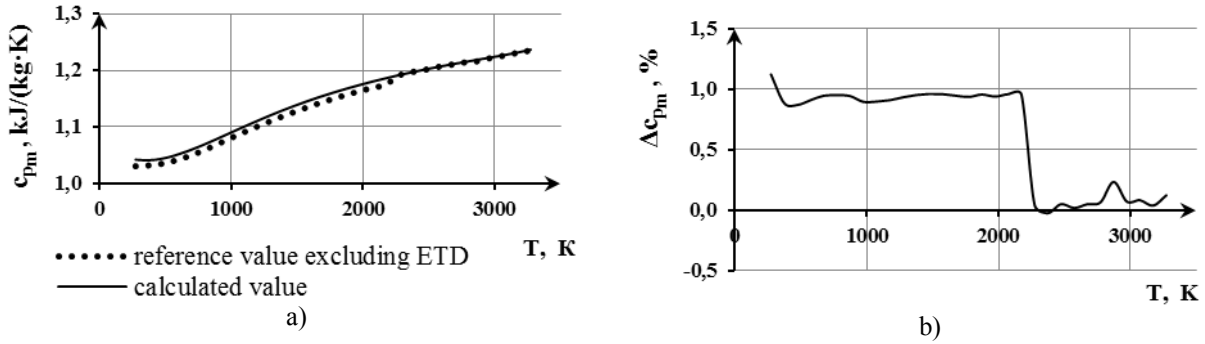| f_i	Value
f_0	9,41626 E-01
f_1	−4,90884 E-04
f_2	1,99973 E-06
f_3	−2,37238 E-09
f_4	1,34346 E-12
f_5	−3,70413 E-16
f_6	3,99917 E-20

Fig. 2. The average specific isobaric heat capacity c_{p_m} (a) and approximation error Δc_{p_m} (b) for N_2 at p = 1 bar, T_1 = 273 K in the given range T_2 = 273 ... 3273 K; approximation c_{p_m} is carried out by the formula (16)

In this case, the approximation error Δc_{p_m} for oxygen will be higher than for nitrogen, but within acceptable limits [11].

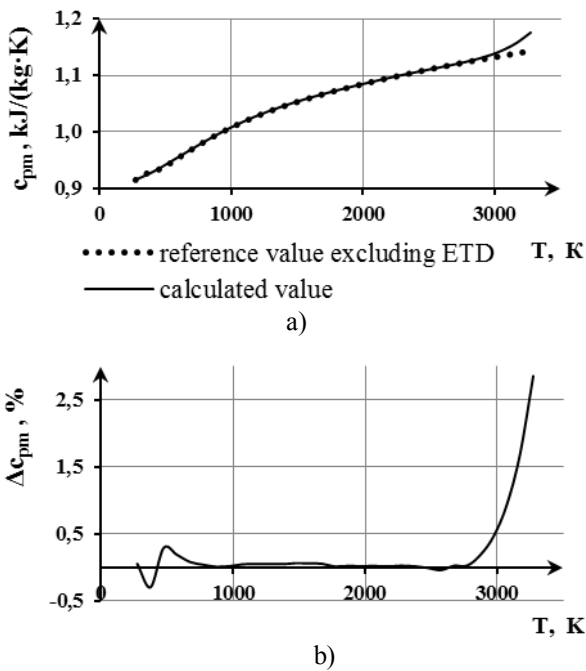The Fig. 3 shows the average specific isobaric heat capacity of oxygen c_{p_m} and the Δc_{p_m}.

Fig. 3. The average specific isobaric heat capacity c_{p_m} (a) and approximation error Δc_{p_m} (b) for O_2 at p = 1 bar, T_1 = 273 K in the given range T_2 = 273 ... 3273 K; approximation c_{p_m} is carried out by the formula (16)

As seen from the Fig. 3b, the approximation error at the pressure p = 1 bar up to the temperature T_2 = 3100K is $\Delta c_{p_m} < 1\%$. The Δc_{p_m} increases due to the manifestation of the ETD of oxygen, which was not considered in [9].

3.3. Average Specific Isobaric Heat Capacity of Argon

The effect of thermal dissociation for argon at the pressure p = 1 bar and higher must be considered when temperatures are above 5000 K [7]. Therefore, in the ranges of temperature T = 190 ... 1300 K and pressure p = 1 ... 200 bar, the linear dependence of the specific isobaric heat capacity on pressure is acceptable and along the isotherms can be written

$$c_p(T, p) = X_0(T) + X_1(T) \cdot p. \qquad (18)$$

The coefficients X_0 and X_1 of the equation (18) can be represented by polynomials of the 6th degree in the form (4) [11], with polynomial coefficients f_i and g_i, respectively.

Based on the equation (1) the average specific isobaric heat capacity of Ar in the ranges of temperature T = 190 ... 1300 K and pressure p = 1 ... 200 is equal to

$$c_{p_m} = \frac{1}{T_2 - T_1} \int_{T_1}^{T_2} \left(X_0(T) + X_1(T) \cdot p \right) dT =$$

$$= \frac{1}{T_2 - T_1} \left(\sum_{i=0}^{6} \frac{f_i}{i+1} \left(T_2^{i+1} - T_1^{i+1} \right) + \right.$$

$$\left. + p \sum_{i=0}^{6} \frac{g_i}{i+1} \left(T_2^{i+1} - T_1^{i+1} \right) \right)$$

or

$$c_{p_m} = \frac{1}{T_2 - T_1} \sum_{i=0}^{6} \frac{f_i + p \cdot g_i}{i+1} \left(T_2^{i+1} - T_1^{i+1} \right). \qquad (19)$$

For Ar, polynomial coefficients f_i and g_i of the expressions (19) are presented in the Table 5 [11].

Table 5

Coefficients f_i and g_i of the equation (16) for argon

f_i	Value	g_i	Value
f_0	3,8552028131 E-1	g_0	3,86799652 E-2
f_1	1,2621680194 E-3	g_1	-3,39272814 E-4
f_2	-4,6085746669 E-6	g_2	1,2108595 E-6
f_3	8,4972243889 E-9	g_3	-2,21920621 E-9
f_4	-8,4024021453 E-12	g_4	2,19770021 E-12
f_5	4,2499200354 E-15	g_5	-1,11699435 E-15
f_6	-8,634491379 E-19	g_6	2,28349314 E-19

There are not data for the c_{p_m} of argon in the reference books (including [9]). In this connection, it can be assumed that the verification of the isobaric heat capacity expressions which were carried out in [11], together with the observance of the formal integration rules ensure the correctness of the c_{p_m} for Ar.

To estimate the effect of pressure on the isobaric heat capacity of argon, the values of c_{p_m} for three different pressures p = 0,1; 20; 200 bar in the working temperature range T = 190 ... 1300 K were calculated and compared with its ideal gas value that equals to $c_p^{ig} = 0,52043 \frac{kJ}{кг \cdot K}$ [7]. The results of this calculation are shown on the Fig. 4.

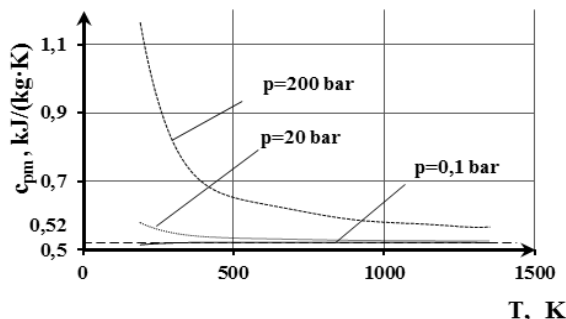Fig. 4. Comparison of the average specific isobaric heat capacity approximation of Ar, at p = 0,1; 20; 200 bar, T_1 = 273 K in the given range T_2 = 190 ... 1350 K which is carried out by the equation (16) with c_p^{ig} (dotted line).

As seen from the Fig. 4, for low pressures p < 20 bar in the wide range of temperatures starting from 200 K and up to the beginning of thermal dissociation (depending on pressure the temperature is T = 5000...8000 K), it can be recommended to use as the c_p and c_{p_m} for argon its ideal gas value [7]

$$c_{p_m} = c_p = c_p^{ig} = 0,52043 \frac{kJ}{кг \cdot K} .$$

The expression (19) is recommended when c_{p_m} is calculated for operating pressures p> 50 bar.

3.4. Average Specific Isobaric Heat Capacity of Water Vapor

For water vapor, the dependence of the specific isobaric heat capacity $c_p = f(T, p)$ is described by the universal model "polynomial in polynomial" [11]

$$c_p = \sum_{j=0}^{6} \left(\sum_{i=0}^{3} h_{ij}(p) \right) T^j . \tag{20}$$

According to the integration rules for a power function, the average specific isobaric heat capacity of H_2O that determined by the expression (1) has a polynomial in the form

$$c_{p_m} = \frac{1}{T_2 - T_1} \sum_{j=0}^{6} \frac{\sum_{i=0}^{3} h_{ij} p^i}{j+1} T^{j+1}. \tag{21}$$

The coefficients h_{ij} of the equation (21) are presented in the Table 6 [11].

The Fig. 5 shows the approximation error Δc_{p_m} for water vapor in the temperature range T_1 = 700 ... 2600 K at the pressure p = 1 bar.

As seen from the Fig. 5b, at the pressure p = 1 bar, significant discrepancies (Δc_{p_m} >20 %) between the calculated and reference values of c_{p_m} [9] are observed at the temperatures T_2>2250 K. This is caused by the manifestation of the ETD, which was not taken into account in [9].

3.5. Average Specific Isobaric Heat Capacity of Carbon Dioxide

For carbon dioxide, in the temperature T = 390 ... 2600 K and pressure p = 1 ... 200 bar ranges, the dependence of the specific isobaric heat capacity $c_p = f(T, p)$ as like as for water vapor, is described by the universal polynomial model [11]

$$c_p = \sum_{j=0}^{5} \left(\sum_{i=0}^{6} h_{ij}(p) \right) T^j . \tag{22}$$

Along isobars, the c_p of CO_2 is approximated by polynomials of the fifth degree of temperature, and then

Table 6

Coefficients h_{ij} of the equation (21) for water vapor

j \ i	0	1	2	3
0	3,72130648 E+00	6,09794432 E-02	2,78477950 E-04	2,62005726 E-06
1	-7,87119929 E-03	-1,71071169 E-04	-1,00020581 E-06	-8,81134559 E-09
2	1,29672771 E-05	2,01838542 E-07	1,37761696 E-09	1,18862334 E-11
3	-9,10704008 E-09	-1,37861935 E-10	-8,46198559 E-13	-8,50288119 E-15
4	2,89749137 E-12	6,25166859 E-14	1,83292082 E-16	3,53086519 E-18
5	-3,26763999 E-16	-1,67716888 E-17	1,20919120 E-20	-8,04176721 E-22
6	1,10942242 E-20	1,50509665 E-21	-2,90837997 E-24	6,71382535 E-26

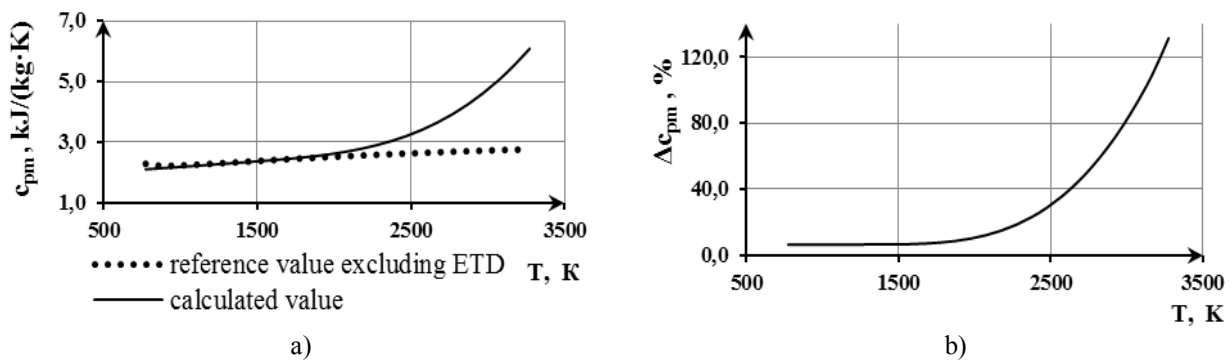a)   b)

Fig. 5. The average specific isobaric heat capacity c_{p_m} (a) and approximation error Δc_{p_m} (b) for H_2O at p = 1 bar,
T_1 = 700 K in the given range T_2 = 700 ... 2600 K; approximation c_{p_m} is carried out by the formula (21)

each polynomial coefficient is approximated by a polynomial of the sixth order of pressure.

The lower limit of the temperature range, as in the case of H_2O, is limited by the critical temperature (for CO_2 T_{cr} = 304,2 K) [11].

According to the rules for integrating of a power function, the polynomial of c_{p_m} of CO_2 which is determined by the expression (1) has the form

$$c_{p_m} = \frac{1}{T_2 - T_1} \sum_{j=0}^{5} \frac{\sum_{i=0}^{6} h_{ij}p^i}{j+1} T^{j+1}. \qquad (23)$$

For carbon dioxide, coefficients h_{ij} of the equation (23) are presented in the Table 7 [11].

For carbon dioxide, the Δc_{p_m}, at the pressure p = 1 bar in the temperature range T = 390 ... 2600 K is presented on the Fig. 6.

As seen from the Fig. 6b, at the pressure p = 1 bar, significant discrepancies (Δc_{p_m} >10%) between the calculated and reference values of c_{p_m} [9] are observed at temperatures T > 2100 K . This is caused by the manifestation of the ETD, which was not taken into account in [9].

Table 7

Coefficients h_{ij} of the equation (23) for carbon dioxide

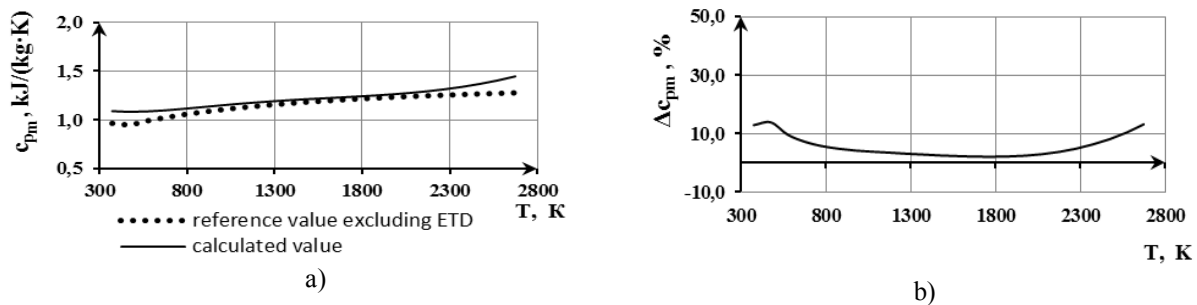| i\j	0	1	2	3	4	5
0	2,039177506 E-01	5,158916222 E-02	1,611004043 E-05	-1,029642891 E-03	-6,820993797 E-08	7,323524876 E-11
1	3,778692716 E-03	-3,045265412 E-04	-9,937532295 E-08	6,775455393 E-06	4,297034312 E-10	-5,106669842 E-13
2	-7,999577879 E-06	7,388788998 E-07	2,401932965 E-10	-1,735375108 E-08	-1,059662323 E-12	1,373170166 E-15
3	1,052717691 E-08	-9,224711889 E-10	-2,927782176 E-13	2,224236798 E-11	1,313768636 E-15	-1,823684483 E-18
4	-7,587121620 E-12	6,140246672 E-13	1,895088498 E-16	-1,499196077 E-14	-8,620109566 E-19	1,260737533 E-21
5	2,658838680 E-15	-2,026341930 E-16	-6,110020795 E-20	4,979046010 E-18	2,807777837 E-22	-4,262116081 E-25
6	-3,408673189 E-19	2,526330393 E-20	7,512383702 E-24	-6,235261470 E-22	-3,476054695 E-26	5,401552597 E-29

Fig. 6. The average specific isobaric heat capacity c_{p_m} (a) and approximation error Δc_{p_m} (b) for CO_2 at p = 1 bar, $T_1 = 700$ K in the given range $T_2 = 390 \dots 2600$ K; approximation c_{p_m} is carried out by the formula (23)

Conclusion

Analytical dependences of $c_{p_m} = f(T,p)$ that taking into account the ETD of the main GTE's ACPC were obtained by integrating of the functional dependencies presented in [11] in a given range of pressures and temperatures: nitrogen: p = 1 ... 200 bar, T = 150 ... 2870 K, oxygen: p = 1 ... 200 bar, T = 210 ... 2870 K, argon: p = 1 ... 200 bar, T = 190 ... 1300 K, water vapor: p = 0,1 ... 200 bar, T = 700 ... 2600 K, carbon dioxide: p = 1 ... 200 bar, T = 390 ... 2600 K.

The obtained dependences $c_{p_m} = f(T,p)$, which take into account ETD, can be used for calculation of the thermophysical properties of a working substance in the wide class of modeling problems of thermogasdynamic processes of heat machines.

Prospects for Further Research

1. The expressions of average isobaric heat capacity of ACPC in a given temperature range for isobaric processes, that are the combustion processes in GTE combustion chambers, piston internal combustion engines operating by the Diesel cycle and heat exchange processes in the heat exchangers were obtained. However, the processes occurring in the compressor, turbine, nozzle of the GTE, in the internal combustion engine working by the Otto cycle are not fundamentally isobaric, but require for their calculation the value of the c_{p_m}.

In the future, it is planned to obtain analytical expressions $c_{p_{mm}} = f(T,p)$ that are cumulative ones over a given range of temperatures and pressures

$$c_{p_{mm}} = \frac{1}{p_2 - p_1}\int_{p_1}^{p_2}\left(\frac{1}{T_2 - T_1}\int_{T_1}^{T_2} c_p(T,p)dT\right)dp .$$

2. The value of the average isobaric heat capacity of water vapor at various pressures and temperatures below the critical values, i.e. the range for which a phase transition is possible and which is not covered in this article, is practically interesting. It is planned to obtain the dependences of the c_p and c_{p_m} as functions of temperature and pressure in the ranges of temperature T = 273,16 ... 700 K and pressure p = 0,1 ... 200 bar.

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РІВНЯННЯ СЕРЕДНЬОЇ ПИТОМОЇ ІЗОБАРНОЇ ТЕПЛОЄМНОСТІ КОМПОНЕНТ ПОВІТРЯ ТА ПРОДУКТІВ ЗГОРАННЯ З УРАХУВАННЯМ ВПЛИВУ ТИСКУ І ЕФЕКТУ ТЕРМІЧНОЇ ДИСОЦІАЦІЇ

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Всі властивості робочих тіл термомеханічної системи є двопараметричними, тобто визначаються двома параметрами, найчастіше температурою і тиском, які найпростіше вимірюються експериментально. Практика представлення ізобарної теплоємності функцією тільки температури $c_p=f(T)$ відходить у минуле. Існує два способи представлення залежності: аналітичний і табличний. Для одиночних розрахунків зручний табличний спосіб, але для серії розрахунків зручніше аналітичний. Перевага аналітичного опису в порівнянні з табличним є зрозумілими: це компактність зберігання інформації без прив'язки до вузлових точок, можливість інтегрувати і диференціювати, залежності можуть бути вбудовані безпосередньо в тіло програми і не вимагати спеціальних підпрограм для звернення до таблиць. Розробники програм розрахунку теплофізичних властивостей, як правило, використовують функціональні залежності, які для різних діапазонів температур і тисків однієї речовини можуть мати різний вигляд. Пояснюється це тим, що в області близької до кривої насичення спостерігається різкі зміни всіх теплофізичних властивостей речовин, в тому числі і істинної теплоємності. У термогазодинамічних розрахунках теплових машин основним фізичним параметром робочого тіла є його теплоємність – як істина, так і середня. У статті представлені аналітичні залежності середніх питомих ізобарних теплоємностей основних компонентів повітря і продуктів згоряння вуглеводневих палив, єдині у всьому зазначеному діапазоні тисків і температур (азот: р = 0,1 ... 200 бар, Т = 150 ... 2870 К; кисень: р = 1 ... 200 бар, Т = 210 ... 2870 К; аргон: р = 1 ... 200 бар, Т = 190 ... 1300 К; пари води: р = 0,1 ... 200 бар, Т = 700 ... 2600 К; вуглекислий газ: р = 1 ... 200 бар, Т = 390 ... 2600 К), виведені на основі отриманих раніше аналітичних виразів для справжніх питомих ізобарних теплоємностей цих газів. Середні питомі ізобарні теплоємності газів також є функціями температури і тиску $c_p = f(T,P)$ і враховують ефект термічної дисоціації. Формули для середніх питомих ізобарних теплоємностей отримані шляхом інтегрування виразів для справжніх теплоємностей. Проведена верифікація отриманих залежностей для різних діапазонів температур.

Ключові слова: питома середня ізобарна теплоємність; продукти згоряння теплових машин; повітря; вплив термічної дисоціації; вплив тиску.

УРАВНЕНИЯ СРЕДНЕЙ УДЕЛЬНОЙ ИЗОБАРНОЙ ТЕПЛОЕМКОСТИ КОМПОНЕНТ ВОЗДУХА И ПРОДУКТОВ СГОРАНИЯ С УЧЕТОМ ВЛИЯНИЯ ДАВЛЕНИЯ И ЭФФЕКТА ТЕРМИЧЕСКОЙ ДИССОЦИАЦИИ

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Все свойства рабочих тел термомеханической системы являются двухпараметрическими, т.е. определяются двумя параметрами, чаще всего температурой и давлением, которые проще всего замеряются экспе-

риментально. Практика представления изобарной теплоемкости функцией только температуры $c_p=f(T)$ уходит в прошлое. Существует два способа представления зависимости: аналитический и табличный. Для одиночных расчетов удобен табличный способ, но для серии расчетов удобнее аналитический. Преимущество аналитического описания в сравнении с табличным очевидно: компактность хранения информации без привязки к узловым точкам, возможность интегрировать и дифференцировать, зависимости могут быть встроены непосредственно в тело программы и не требовать специальных подпрограмм для обращения к таблицам. Разработчики программ расчета теплофизических свойств, как правило, используют функциональные зависимости, которые для разных диапазонов температур и давлений одного вещества могут иметь различный вид. Объясняется это тем, что в области близкой к кривой насыщения наблюдается резкие изменение всех теплофизических свойств веществ, в том числе и истинной теплоемкости. В термогазодинамических расчетах тепловых машин основным физическим параметром рабочего тела является его теплоемкость - как истинная, так и средняя. В статье представлены аналитические зависимости средних удельных изобарных теплоемкостей основных компонентов воздуха и продуктов сгорания углеводородных топлив, единые во всем указанном диапазоне давлений и температур (азот: p = 0,1…200 бар, T = 150…2870 K; кислород: p = 1…200 бар, T = 210…2870 K; аргон: p = 1…200 бар, T = 190…1300 K; пары воды: p = 0,1…200 бар, T = 700…2600 K; углекислый газ: p = 1…200 бар, T = 390…2600 K), выведенные на основе полученных ранее аналитических выражений для истинных удельных изобарных теплоемкостей этих газов. Средние удельные изобарные теплоёмкости газов также являются функциями температуры и давления $c_p=f(T,P)$ и учитывают эффект термической диссоциации. Формулы для средних удельных изобарных теплоемкостей получены путем интегрирования выражений для истинных теплоемкостей. Произведена верификация полученных зависимостей для различных диапазонов температур.

Ключевые слова: удельная средняя изобарная теплоемкость; продукты сгорания тепловых машин; воздух; влияние термической диссоциации; влияние давления.

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