Equations and Computer Program for Calculating the Properties of Gases and Combustion Products

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Abstract—Equations are presented for calculating the isobaric heat capacity, enthalpy and entropy of gases resulting from the combustion of fuels (taking dissociation into account). A computer program is described that was developed for determining the thermodynamic properties of these gases and their mixtures as a function of temperature, enthalpy, or entropy.

The properties of gases in the ideal gas state are calculated for substances most frequently encountered in calculations of thermal power processes. Among these are nitrogen N_2, oxygen O_2, carbon oxide CO, carbon dioxide CO_2, water steam H_2O, sulfur dioxide SO_2, air, atmospheric nitrogen, nitrogen oxide NO, nitrogen dioxide NO_2, argon Ar, neon Ne, and hydrogen H_2.

Air consists (by volume) of 78.03% nitrogen, 20.99% oxygen, 0.94% argon, 0.01% hydrogen, and 0.03% carbon dioxide [1].

Atmospheric nitrogen consists (by volume) of 98.76% nitrogen, 1.19% argon, 0.01% hydrogen, and 0.04% carbon dioxide [1].

The following constants are used in these calculations: the absolute gas constant $R = 8.31451$ J/(mol K), the molar masses of individual gases (Table 1), and the standard pressure $p_0 = 0.1$ MPa.

THE PROCEDURE FOR CALCULATING THE THERMODYNAMIC PROPERTIES OF INDIVIDUAL GASES

The thermodynamic properties of substances and their mixtures in the ideal gas state are described by the system of equations from [2], which employs a unified form of the equation for isobaric heat capacity

$$\frac{c_p}{R} = \sum_{i=0}^{6} a_i \tau^i + \sum_{i=7}^{12} a_i \left(\frac{1}{\tau}\right)^{i-6}, \qquad (1)$$

where $\tau = T/T^*$ is the relative temperature (T is the gas temperature, K, and $T^* = 1000$ K); a_i is the array of coefficients that are specific for each gas; R is the absolute gas constant, J/(mol K); and c_p is the isobaric heat capacity, J/(mol K).

The coefficients a_i for all substances except water steam and single-atom gases have been determined using the least square method; they are based on the data from [3] for the temperature range from 200 to 2500 K and are given in Table 2. These coefficients

allow the values from [3] to be calculated with the following standard error: 0.67×10^{-5} for oxygen, 0.23×10^{-4} for nitrogen, 0.60×10^{-4} for carbon dioxide, 0.19×10^{-4} for carbon oxide, 0.80×10^{-5} for nitrogen oxide, 0.54×10^{-5} for nitrogen dioxide, 0.44×10^{-5} for sulfur dioxide, and 1.5×10^{-5} for hydrogen.

When water steam is in the ideal gas state, its isobaric heat capacity has previously been described in the International equation (IF-95) [4] in terms of an equation that was taken from [5], where it was derived using

Table 1. List of unique gas identifiers

Gas	Molar mass, kg/mol	Unique identifier
Nitrogen N_2	0.0280134	0
Oxygen O_2	0.0319988	1
Carbon oxide CO	0.0280104	2
Carbon dioxide CO_2	0.0440098	3
Water steam H_2O	0.0180152	4
Sulfur dioxide SO_2	0.064059	5
Air as a single gas Air	0.02896431986	6
Atmospheric nitrogen as a single gas N_2^{air}	0.02815922054	7
Nitrogen oxide NO	0.0300061	8
Nitrogen dioxide NO_2	0.0460055 [3]	9
Argon Ar	0.039948 [3]	10
Neon Ne	0.020179 [3]	11
Hydrogen H_2	0.0020158 [3]	12
Air as a mixture of gases Air_{mix}	0.02896431986	13
Atmospheric nitrogen as a mixture of gases $N_{2_{mix}}^{air}$	0.02815922054	14

Table 2. Values of the coefficients a_i in Eq. (1)

i	N$_2$	O$_2$	CO	CO$_2$	H$_2$O	SO$_2$
0	-0.92984251×10	0.171190127×10^2	0.58627934×10	-0.18188731×10^1	$3.10409601236035 \times 10^1$	0.129839174×10^2
1	0.20007476×10^2	-0.11550976×10^2	0.34431824×10	0.12903022×10^2	$-3.91422080460869 \times 10^1$	-0.70975523×10
2	-0.16763488×10^2	0.70056996×10	-0.48382992×10	-0.96634864×10	$3.79695277233575 \times 10$	0.54433743×10
3	0.86903787×10	-0.28621429×10	0.30512615×10	0.42251879×10	$-2.18374910952284 \times 10$	-0.26855652×10
4	-0.27510686×10	0.79318027	-0.1065302×10	-0.1042164×10	7.42251494566339	0.83220003
5	0.48793873	-0.13392554	0.1992689	0.12683515	-1.38178929609470	-0.14690738
6	$-0.37167758 \times 10^{-1}$	$0.10209172 \times 10^{-1}$	$-0.15612248 \times 10^{-1}$	$-0.49939675 \times 10^{-2}$	$1.08807067571454 \times 10^{-1}$	$0.11260596 \times 10^{-1}$
7	0.40387289×10^1	-0.8967597×10^1	-0.48401746×10^1	0.24950242×10	$-1.20771176848589 \times 10^1$	-0.28695081×10
8	-0.30781129	0.33796419×10^1	0.30051634×10^1	-0.8272375	3.39105078851732	-0.21889887
9	-0.19090602	-0.76513147	-0.97260373	0.15372481	$-5.84520979955060 \times 10^{-1}$	0.35974571
10	0.6465393×10^{-1}	0.10340806	0.17723571	$-0.15861243 \times 10^{-1}$	$5.89930846488082 \times 10^{-2}$	$-0.92149906 \times 10^{-1}$
11	$-0.82736889 \times 10^{-2}$	$-0.770090528 \times 10^{-2}$	$-0.17272462 \times 10^{-1}$	0.8601715×10^{-3}	$-3.12970001415882 \times 10^{-3}$	$0.99973132 \times 10^{-2}$
12	$0.39772373 \times 10^{-3}$	$0.24408174 \times 10^{-3}$	$0.70218924 \times 10^{-3}$	$-0.19222165 \times 10^{-4}$	$6.57460740981757 \times 10^{-5}$	$-0.39568472 \times 10^{-3}$

i	Air	N$_2^{\text{air}}$	NO	NO$_2$	H$_2$	Ar, Ne
0	-3.62171168554944	-9.15141475338944	0.175012975×10^2	0.22897799×10^2	$2.68742461056112 \times 10$	2.5
1	13.1878685737717	$1.97612585131717 \times 10$	-0.10232606×10^2	-0.15733398×10^2	$-3.28599322826549 \times 10$	0
2	-11.61002657829	$-1.655656033537 \times 10^1$	0.5309077×10	0.10595966×10^2	$2.92580798999686 \times 10$	0
3	6.1800155085671	8.5827173265771	-0.1756358×10	-0.4722968×10	$-1.59075270290400 \times 10$	0
4	-1.97996023924462	-2.71684951509762	0.34469268	0.13348353×10	5.22699862384258	0
5	0.352570060264284	$4.81843413354284 \times 10^{-1}$	$-0.33561691 \times 10^{-1}$	-0.21315607	$-9.56104537163882 \times 10^{-1}$	0
6	-0.026853107411115	$-3.67013882440646 \times 10^{-2}$	$0.90748482 \times 10^{-3}$	$0.14608561 \times 10^{-1}$	$7.48714373539927 \times 10^{-2}$	0
7	1.26880226994069	3.98857888363069	-0.10716017×10^2	-0.10408705×10^2	$-1.06778768930899 \times 10$	0
8	$4.69260613574416 \times 10^{-1}$	$-3.04018225402584 \times 10^{-1}$	0.471147653×10	0.30661019×10	3.07099601416186	0
9	$-3.09569582156729 \times 10^{-1}$	$-1.88527932068729 \times 10^{-1}$	-0.12288023×10	-0.49285332	$-5.06366407292404 \times 10^{-1}$	0
10	$7.21534908248886 \times 10^{-2}$	$6.38493125955586 \times 10^{-2}$	0.18875565	$0.37617693 \times 10^{-1}$	$3.43582478595844 \times 10^{-2}$	0
11	$-8.07371553566351 \times 10^{-3}$	$-8.17063504476351 \times 10^{-3}$	$-0.15404104 \times 10^{-1}$	$-0.5705258 \times 10^{-3}$	$1.16044276488724 \times 10^{-3}$	0
12	$3.61550066177588 \times 10^{-4}$	$3.92763515964088 \times 10^{-4}$	$0.51348154 \times 10^{-3}$	$-0.46213031 \times 10^{-4}$	$-2.07509179117432 \times 10^{-4}$	0

data from [6]. In subsequent years, however, new calculations of the properties of water steam in this state were carried out [7–9], whose results at high temperatures differ from data in [6]. A new equation for water steam is therefore presented in this paper, which is based on the data from [7] and describes these properties with a root-mean-square error not exceeding 0.32×10^{-2}. The coefficients of Eq. (1) for air and atmospheric nitrogen were determined by summing the coefficients for components (using the procedure for calculating mixtures, which is described below) taking into account their concentrations given above.

The discrepancies between the isobaric heat capacity values calculated from Eq. (1) and similar values obtained from some other studies are presented in Fig. 1.

The greatest discrepancies are observed for water steam. When temperatures are below 1200 K, all data except those from [3] are in strong agreement with one another (the error does not exceed ±0.1%). As the temperature increases, however, discrepancies grow. It is interesting to note that at $T = 2500$ K, the values calculated from [5] are 0.8% greater and those calculated from [7] are 0.8% lower than those obtained using the proposed method. Deviations in the values calculated using the equation from [1] within its applicability limits from 223 to 1773 K do not exceed 0.2%.

The results calculated by Eq. (1) for carbon dioxide coincide with the values from [3, 10, 11] over the entire temperature range with an error not exceeding 0.04%. Discrepancies with the data from [12] remain within 0.1% only at temperatures not exceeding 1300 K; the discrepancies with data from [1] reach 0.4% at 1800 K.

The results obtained for nitrogen and oxygen were found to be in very strong agreement with the data from [10]: the discrepancy for nitrogen was within 0.016% and for oxygen 0.003%. At temperatures below 1500 K a similarly strong agreement is observed with the values calculated from the data in [13] (within 0.01%), and from [14] (within 0.03%). The discrepancy from the data in [1] is somewhat greater: for nitrogen it is 0.08%, and for oxygen it is more than 0.1% (at the boundaries of the temperature range). Accordingly, for air at temperatures to 2000 K the difference from the data in [15] is not more than 0.02%, and from the data in [1] it is not more than 0.06%.

Strong agreement is observed between the figures calculated by (1) and the data from [10] for sulfur dioxide (within 0.01%), and for carbon oxide (within 0.04%). The discrepancy between the results for carbon dioxide and the data in [1] does not exceed 0.09%.

Expressions for calculating other properties of gases can be obtained from Eq. (1) using well-known thermodynamic relationships. For example, the following expression was obtained for calculating enthalpy h

$$\frac{h}{R} = T^* \left[\sum_{i=0}^{6} \frac{a_i}{i+1} \tau^{i+1} + a_7 \ln\tau \right. \tag{2}$$
$$\left. + \sum_{i=8}^{12} \frac{a_i}{7-i} \left(\frac{1}{\tau}\right)^{i-7} \right] + \frac{h_{\text{int}}}{R},$$

where h_{int} is an integration constant, which is determined from [3].

The following relation holds for calculating gas entropy s at pressure p:

$$s = s_0 - R\ln\left(\frac{p}{p_0}\right), \tag{3}$$

where s_0 is the entropy at standard pressure $p_0 = 100$ kPa, which is calculated by the formula

$$\frac{s_0}{R} = a_0 \ln\tau + \sum_{i=1}^{6} \left(\frac{a_i}{i}\tau^i\right) \tag{4}$$
$$+ \sum_{i=7}^{12} \frac{a_i}{6-i}\left(\frac{1}{\tau}\right)^{i-6} + \frac{s_{\text{int}}}{R},$$

where s_{int} is an integration constant (which was determined from the data in [3] taking into account the changeover from the old standard pressure $p_0 = 101.325$ kPa to its modern value $p_0 = 100$ kPa), and p is the gas pressure kPa.

The integration constants in (2) and (4) are determined from the condition of equality of the specific enthalpy and specific entropy calculated from these equations to their values at the check points taken from [3] (Table 3).

THE COMPUTER PROGRAM FOR CALCULATING THE THERMODYNAMIC PROPERTIES OF INDIVIDUAL GASES

Relations (1)–(4) were used to develop computer programs for calculating the properties of gases in accordance with a procedure similar to that used for developing the WaterSteamPro, a computer program for calculating the properties of water and water steam [16]. These two programs have now been incorporated into a single unit. This enables users to employ the functions for calculating properties of gases in all computer programs where the WaterSteamPro can be used.

The following basic functions have been determined in the package for calculating the properties of gases, which correspond to relationships (1)–(4):

$$\text{wspgCPIDT}(id, T); \tag{5}$$
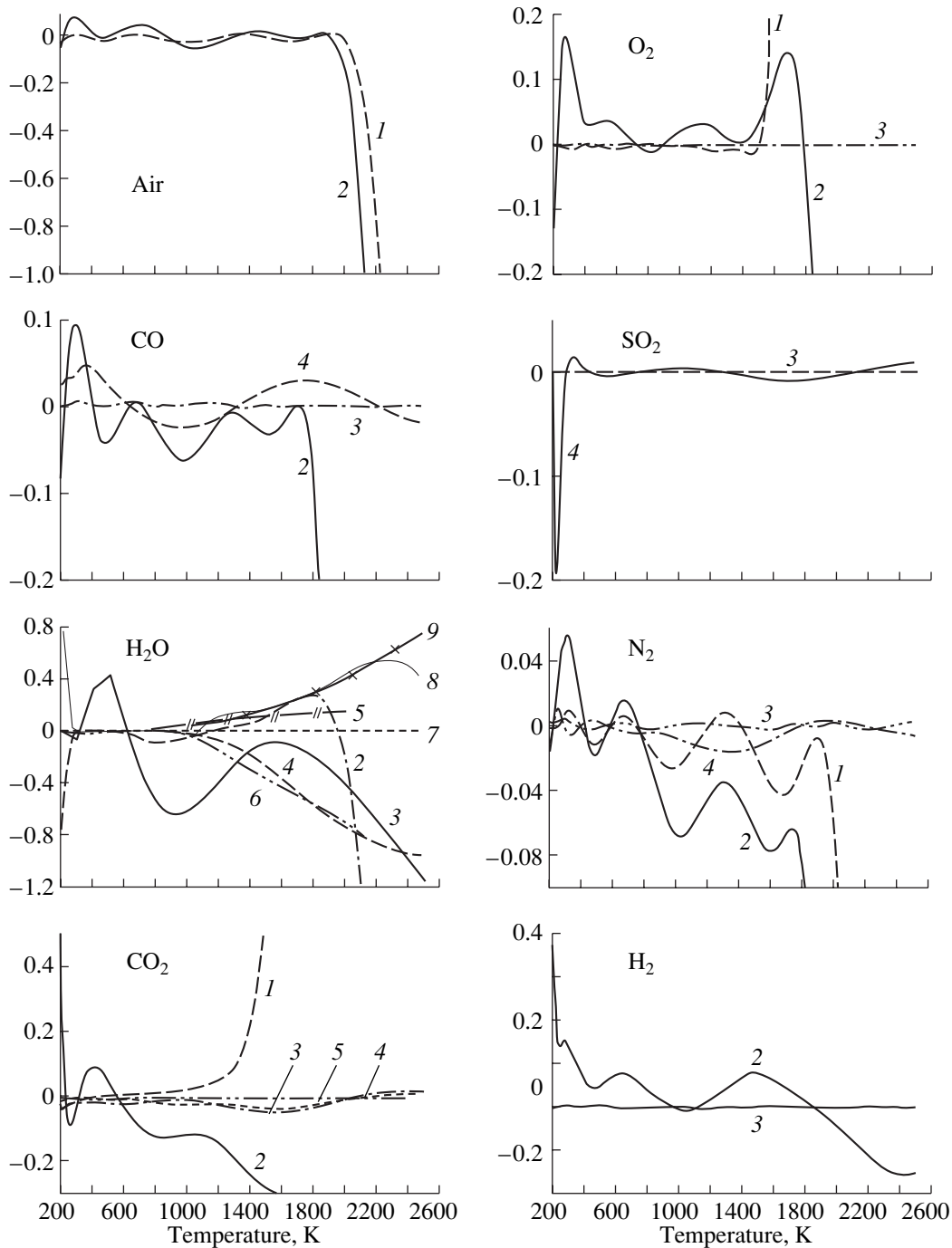$$\text{wspgHIDT}(id, T); \tag{6}$$
$$\text{wspgS0IDT}(id, T); \tag{7}$$

Fig. 1. Discrepancies between the isobaric heat capacity values calculated by (1) and data of other researchers. Source of data: (*1*) [12–15]; (*2*) [1]; (*3*) [3]; (*4*) [10]; (*5*) [8, 11]; (*6*) [9]; (*7*) [7]; (*8*) [16], and (*9*) [4, 5].

$$\text{wspgSIDPT}(id, p, T), \qquad (8)$$

where *id* is a unique gas identifier, T is the temperature, K, and p is the pressure, Pa.

When the user wishes to calculate the properties of a specific gas, he or she must specify its unique identifier (Table 1). This identifier specified, the program itself then finds the coefficients for relations (1)–(4). It

is important to note that the same identifier will be assigned to each gas in subsequent versions of the program.

Notice that air and atmospheric nitrogen appear twice in Table 1. In the first case they appear as individual gases (the program regards them not as a mixture of gases but as a unique gas, whose properties are equivalent to those of the mixture of the gases constituting it).

Dissociation cannot be taken into account for them because the program does not store information on their components. In the second case these are mixtures of gases, and for them it is possible to calculate dissociation and to determine their components. This was done to facilitate a comparison and generate calculations using the proposed procedure. The user himself can select the best suitable option.

Apart from initial functions (5)–(8), there are additional functions, which allow the following parameters to be calculated:

molar mass, kg/mol

$$\text{wspgMMID}(id); \qquad (9)$$

specific gas constant, J/(kg K)

$$\text{wspgGCID}(id); \qquad (10)$$

specific volume determined from the Clapeyron-Mendeleyev equation

$$\text{wspgVIDPT}(id, p, T), \qquad (11)$$

$$\text{wspgVIDT}(id, T). \qquad (12)$$

The last function is calculated at standard pressure.

The program can also be used to determine inverse relations, namely, to calculate temperatures from specific enthalpy or entropy. To this end, we developed the following functions (using the Newton method), which allow the roots of functions (6)–(8) to be determined more exactly:

$$\text{wspgTIDH}(id, h); \qquad (13)$$

$$\text{wspgTIDS0}(id, s_0); \qquad (14)$$

$$\text{wspgTIDPS}(id, p, s). \qquad (15)$$

These functions make possible the quick and easy calculation of adiabatic expansion and compression processes.

THE PROCEDURE FOR CALCULATING THE THERMODYNAMIC PROPERTIES OF GAS MIXTURES

The properties of gas mixtures can be determined using the same functional relations (1)–(4) that were used for individual gases

$$\frac{c_{p,\text{mix}}}{R} = \sum_{i=0}^{6} a_{i,\text{mix}}\tau^i + \sum_{i=7}^{12} a_{i,\text{mix}}\left(\frac{1}{\tau}\right)^{i-6}; \qquad (16)$$

$$\frac{h_{\text{mix}}}{R} = T^*\left[\sum_{i=0}^{6}\frac{a_{i,\text{mix}}}{i+1}\tau^{i+1} + a_{7,\text{mix}}\ln\tau\right.$$
$$\left. + \sum_{i=8}^{12}\frac{a_{i,\text{mix}}}{7-i}\left(\frac{1}{\tau}\right)^{i-7}\right] + \frac{h_{\text{int,mix}}}{R}. \qquad (17)$$

Table 3. Values of enthalpy and entropy at check points ($T_{\text{ch}} = 298.15$ K and $p_{\text{ch}} = 101.325$ kPa)

Gas	k_{ch}, kJ/mol	s_{ch}, J/(mol K)
N_2	8.670	191.498
O_2	8.680	205.035
CO	8.671	197.548
CO_2	9.365	213.674
H_2O	9.908	188.724
SO_2	10.548	248.110
Air_{mix}	8.6490411	198.721001
$N_{2_{\text{mix}}}^{\text{air}}$	8.6408291	191.637836
NO	9.179	210.636
NO_2	10.208	240.057
Zr	6.197	154.732
Ne	6.197	146.214
H_2	8.468	130.570

However, the relation for standard entropy, which is given by

$$\frac{s_{0,\text{mix}}}{R} = a_{0,\text{mix}}\ln\tau + \sum_{i=1}^{6}\left(\frac{a_{i,\text{mix}}}{i}\tau^i\right)$$
$$+ \sum_{i=7}^{12}\frac{a_{i,\text{mix}}}{6-i}\left(\frac{1}{\tau}\right)^{i-6} + \frac{s_{0,\text{int,mix}}}{R} + \frac{\Delta s_{0,\text{mix}}}{R} \qquad (18)$$

now contains a term that expresses the change in the entropy when the gases are mixed

$$\frac{\Delta s_{0,\text{mix}}}{R} = -\sum_{j=1}^{N} x_j\ln(x_j). \qquad (19)$$

The coefficients for the mixture are calculated by the following formulas:

$$a_{i,\text{mix}} = \sum_{j=1}^{N} x_j a_{i,j}; \qquad (20)$$

$$h_{\text{int,mix}} = \sum_{j=1}^{N} x_j h_{\text{int},j}; \qquad (21)$$

$$s_{\text{int,mix}} = \sum_{j=1}^{N} x_j s_{\text{int},j}, \qquad (22)$$

where x_j is the molar (or volume) share of the jth gas appearing in a mixture consisting of N gases, and $a_{i,j}$ is the ith coefficient of the jth gas.

The following volumetric fractions of the air components are assumed

· nitrogen: $x_{N_2} = 78.03\%$ wspgMMID(wspgN$_2$) = 28.0134 g/mol

· oxygen: $x_{O2} = 20.99\%$ wspgMMID(wspgO$_2$) = 31.9988 g/mol

· argon: $x_{O_2} = 0.94\%$ wspgMMID(wspgAr) = 39.948 g/mol

· hydrogen: $x_{H_2} = 0.01\%$ wspgMMID(wspgH$_2$) = 2.0158 g/mol

· carbon dioxide: $x_{CO_2} = 0.03\%$ wspgMMID(wspgCO$_2$) = 44.0098 g/mol

The identifier of a new mixture is obtained: air_mix = wspgNEWMIX(0) air_mix = 8

Gases are "added" to the mixture:

wspgADDGASMO2MIX(air_mix, wspgN$_2$, x_{N_2}) = 0

wspgADDGASMO2MIX(air_mix, wspgO$_2$, x_{O_2}) = 1

wspgADDGASMO2MIX(air_mix, wspgAr, x$_{Ar}$) = 2

wspgADDGASMO2MIX(air_mix, wspgH$_2$, x_{H_2}) = 3

wspgADDGASMO2MIX(air_mix, wspgCO$_2$, x_{CO_2}) = 4

The volumetric or mass fractions of the initial gases in the mixture are determined:

· by volume: wspgGASMFINMIX(air_mix, wspgO$_2$) = 20.99%

· by mass: wspgGASMFINMIX(air_mix, wspgO$_2$) = 23.1890%

The parameters of the mixture are calculated and the unique identifier for the mixturebased gas is formed:

air_id = wspgNEWGASFROMMIX(air_mix) air_id = 20

It is now possible to calculate, for example, the molar mass of the mixture or specific enthalpy:

wspgMMID(air_id) = 28.96431996 g/mol wspgHIDT(air_id, 500 K) = 503 kJ/kg

Fig. 2. Example of calculating a mixture (air consisting of nitrogen, oxygen, argon, hydrogen, and carbon dioxide).

THE PROGRAM FOR CALCULATING THE THERMODYNAMIC PROPERTIES OF GAS MIXTURES

A concept of creating mixtures was proposed for calculating mixtures of initial gases. This concept consists in the following. The user notifies the program that a new mixture has to be calculated. This is done by calling the function

$$wspgNEWMIX(). \qquad (23)$$

Function (23) assigns a unique identifier to the new mixture, which will then be used for determining the parameters of this mixture. Every time this function is called it gives a new identifier to the mixture. Their total number is limited by the resources of the system; its maximal value cannot be greater than 2 147 483 647.

The identifier thus obtained is then used to call a function that takes into account the "addition" of gases to the mixture:

$$wspgADDGASM2MIX(\textit{mix\_id, gas\_id, mass}), \qquad (24)$$

where *mix_id* is the mixture identifier obtained earlier when function (23) was called; *gas_id* is the identifier of the gas that is added (see Table 1); and *mass* is the mass of the gas that is added. It should be noted that the user can specify not only absolute, but also relative values of the mass of a gas in the mixture (for example, mass content *d*).

Another function for taking into account the addition of a gas into a mixture appears as follows:

$$wspgADDGASMO2MIX(\textit{mix\_id, gas\_id, moles}), (25)$$

where *moles* is the quantity of moles of the gas that is added.

The approach implemented in these functions is somewhat different from the commonly adopted one, in which the fractions (mass and volume) of the substances composing the mixture are usually specified. Everything is much easier in the new approach.

Suppose, for example, that the user wants to calculate the properties of a mixture consisting of 1 kg of air and 10 g of water steam. There is no need to find the relative fractions of these substances in the mixture; the only thing that has to be done is to call function (24) with the following parameters: *gas_id* = 7, *mass* = 1, *gas_id* = 4, and *mass* = 0.01. The program itself will determine the necessary fractions of substances in the mixture.

Function (25) is used in a similar way. The parameter *moles* can be specified as a quantity of moles or as a volume fraction of the substance in the mixture.

Figure 2 shows a fragment of the calculation of the properties of air as a mixture of gases.

After all of the components are added to the mixture, the coefficients for Eqs. (16)–(19) must be determined. This is done by calling the following function:

$$\text{wspgNEWGASFROMMIX}(mix\_id). \tag{26}$$

Once all required parameters are calculated, function (26) will return the gas identifier *gas_id* for the mixture specified by the parameter *mix_id*. The gas identifier *gas_id* thus obtained can be used when calling functions (5)–(15) for calculating the properties of gases.

The program can identify for the user the fraction of each component in a mixture at any time in the course of calculating its properties. This is done by introducing the following functions:

for the mass fraction of the gas with the identifier *gas_id* in the mixture with the identifier *mix_id*

$$\text{wspgGASWFINMIX}(mix\_id, gas\_id),$$

for the molar (volume) fraction of the gas with the identifier *gas_id* in the mixture with the identifier *mix_id*

$$\text{wspgGASMFINMIX}(mix\_id, gas\_id).$$

The program that has been developed can be used to calculate mixtures of gases that are themselves mixtures of other gases; that is, a mixture composed of mixtures of primary gases can be calculated.

To this end, Eq. (19) is written in the form

$$\frac{\Delta s_{0,\,\text{mix}}}{R} = -\sum_{j=1}^{N}\left[x_j\left(\ln x_j - \frac{\Delta s_{0,\,\text{mix}}^j}{R}\right)\right],$$

where $\Delta s_{0,\,\text{mix}}^j$ is the mixing entropy of the mixture of which gas j is composed.

The function for calculating the fraction of a gas that is a component of a mixture is augmented with a special mechanism, which allows the total fraction of the gas to be determined even though it is part of mixtures of which the mixture being studied is composed. This possibility can be used to calculate, for example, the fraction of oxygen in flue gases from a gas-turbine unit; it may also be used when a consecutive calculation of mixtures has to be carried out: first for dry air, then for humid air (a mixture of dry air and water steam), then for a mixture of humid air and the products that result from burning fuel in the combustion chamber, and then for the mixing of the mixture thus obtained with the cooling air, and so on. The program will itself scan all components of the mixture and determine the fraction of the gas in it.

When calling functions (23) and (26), the program allocates a memory space for saving data on the mixtures and gases composed of them. If the user wishes to allocate this memory, this can be done using the following special functions:

to allocate the memory occupied by data on a gas composed using a mixture
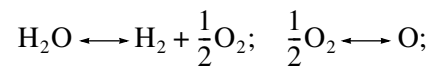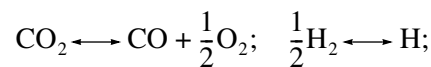
$$\text{wspgDELETEGAS}(gas\_id);$$

to allocate the memory occupied by data on a mixture

$$\text{wspgDELETEMIX}(mix\_id).$$

THE PROCEDURE FOR TAKING INTO ACCOUNT DISSOCIATION IN GAS MIXTURES AT HIGH TEMPERATURES

The equations described above were set up without considering the dissociation of gases at high temperatures. If we wish this effect to be taken into account, the chemical equilibrium of the components in the given mixture must be calculated. Quite a number of methods and computer programs are now available for calculating this equilibrium [17–19]. Most of these methods and programs require a considerable amount of iterative calculation for the precise determination of the chemical equilibrium of a mixture, because this involves the necessity of solving systems of nonlinear equations.

However, the calorific effect of dissociation within the required temperature range can be approximated accurately enough without knowing the precise equilibrium composition of the mixture. An approximate method was therefore used to calculate this effect, which was proposed in [10]. This method is based on the assumption that under conditions typically encountered in power engineering applications and at temperatures below 2000 K, the change in the properties of interest depends mostly on the formation of products of the following reactions:

$$CO_2 \longleftrightarrow CO + \tfrac{1}{2}O_2; \quad \tfrac{1}{2}H_2 \longleftrightarrow H;$$

$$H_2O \longleftrightarrow H_2 + \tfrac{1}{2}O_2; \quad \tfrac{1}{2}O_2 \longleftrightarrow O;$$

$$\tfrac{1}{2}H_2O + \tfrac{1}{4}O_2 \longleftrightarrow OH; \quad \tfrac{1}{2}N_2 + \tfrac{1}{2}O_2 \longleftrightarrow NO.$$

The equilibrium constants for these reactions were represented in [10] (using the data from [18, 19]) by the empirical formula

$$K_j = A_j \exp(B_j/T). \tag{27}$$

The values of A_j and B_j are given in Table 4. The variables U_j are then introduced, which characterize the concentration of the reaction products

$$U_1 = A_1 \frac{x_{CO_2}}{\sqrt{x_{O_2}}}\left(\frac{p}{p_0}\right)^{-0.5}\exp\left(\frac{B_1}{T}\right); \tag{28}$$

Table 4. Coefficients of Eqs. (27)–(34)

Gas	A_j	B_j, K	C_j, J/(mol K)	D_j, J/mol	E_j, GJ × × K/mol
CO	20413.2	−33086.5	−19.5	-1.15×10^5	9.483
H_2	1075.5	−30283.3	−65.2	3.03×10^5	7.277
OH	165.95	−19526.8	−18.7	5.72×10^4	3.136
H	1491.75	−27488.0	−3.60	3.93×10^5	5.826
O	3235.34	−30807.8	−21.8	1.50×10^5	7.659
NO	4.55420	−10973.6	−5.60	1.62×10^4	9.940

$$U_2 = A_2 \frac{x_{H_2O}}{\sqrt{x_{O_2}}} \left(\frac{p}{p_0}\right)^{-0.5} \exp\left(\frac{B_2}{T}\right); \qquad (29)$$

$$U_3 = A_3 \sqrt{x_{H_2O}} \sqrt[4]{x_{O_2}} \left(\frac{p}{p_0}\right)^{-0.25} \exp\left(\frac{B_3}{T}\right); \qquad (30)$$

$$U_4 = A_4 \sqrt{U_2} \left(\frac{p}{p_0}\right)^{-0.5} \exp\left(\frac{B_4}{T}\right); \qquad (31)$$

$$U_5 = A_5 \sqrt{x_{O_2}} \left(\frac{p}{p_0}\right)^{-0.5} \exp\left(\frac{B_5}{T}\right); \qquad (32)$$

$$U_6 = A_6 \sqrt{x_{N_2}} \sqrt{x_{O_2}} \exp\left(\frac{B_6}{T}\right) \qquad (33)$$

and the total value

$$U_{tot} = 1 + \sum_{j=1}^{6} U_j.$$

The contribution that the thermal effect of each reaction introduces into the isobaric heat capacity at temperatures from 1000 to 2000 K is given by the formula

$$V_j = C_j + \frac{D_j}{T} + \frac{E_j}{T^2}. \qquad (34)$$

The coefficients of (34) are also given in Table 4; changes in the thermodynamic properties of the mixture due to dissociation are calculated as follows:

$$\Delta^{dis} c_p^0 = \frac{1}{U_{tot}} \sum_{j=1}^{6} U_j V_j;$$

$$\Delta^{dis} h^0 = -\frac{T^2}{U_{tot}} \sum_{j=1}^{6} \frac{U_j V_j}{B_j};$$

$$\Delta^{dis} s^0 = \frac{\Delta^{dis} h^0}{T} = -\frac{T}{U_{tot}} \sum_{j=1}^{6} \frac{U_j V_j}{B_j}.$$

After that, the properties of the mixture of dissociating gases are determined by summing the values thus obtained with the values calculated by (16)–(19)

$$c_{p,\,dis}^0 = c_{p,\,mix}^0 + \Delta^{dis} c_p^0;$$

$$h_{dis}^0 = h_{mix}^0 + \Delta^{dis} h^0;$$

$$s_{dis}^0 = s_{mix}^0 + \Delta^{dis} s^0.$$

When implemented in practice, this method will allow the user to determine, without iterative calculations, the thermodynamic properties of a mixture of dissociating gases with high accuracy at temperatures to 2000 K.

The user can specify settings for the mode when the dissociation effect is taken into account, using the following function:

wspgSETCALCDISSMODE(*mode*),

where *mode* is the number of the mode connected with taking the dissociation effect into account (when *mode* = 0, the thermal effect of dissociation is not calculated; when *mode* = 1, the effect of dissociation is calculated at all temperatures; and when *mode* = 2, the effect of dissociation is calculated only for temperatures above 1200 K).

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