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MOLLIER-I,S-DIAGRAMS FOR COMBUSTION GASES IN DATA PROCESSING

Dr.-Ing. Friedemann Zacharias

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16. Abstract

In order to have all the thermal and caloric states of combustion gases accessible in a computer, closed mathematical approximation equations were established for the real factors, the enthalpy and the entropy of a real combustion gas. The equations approximate the various effects of molecular forces - real gas influence and dissociation - at temperatures of 200 - 6,000 K, pressures of 0.001 - 1,000 bar, and in the range from stoichiometric composition to air. Finally, a system of subprograms is listed in FORTRAN, by means of which thermodynamic calculations can be carried out in the same manner as with Mollier I,S diagrams.

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MOLLIER I,S DIAGRAMS FOR COMBUSTION GASES IN DATA PROCESSING

Dr.-Ing. Friedemann Zacharias

In order to have all the thermal and caloric states of combustion gases accessible in a computer, closed mathematical approximation equations were established for the real factors, the enthalpy and the entropy of a real combustion gas. The equations approximate the various effects of molecular forces - real gas influence and dissociation - at temperatures of 200 - 6,000 K, pressures of 0.001 - 1,000 bar, and in the range from stoichiometric composition to air. Finally, a system of subprograms is listed in FORTRAN, by means of which thermodynamic calculations can be carried out in the same manner as with Mollier I,S diagrams.

After the publication of the first I,S diagrams for gases in 1932 [1], Prof. Pflaum of the Technical University in Berlin made the thermodynamic fundamentals of combustion engines his objective. In 1960, the second edition of the Mollier I,S diagrams for combustion gases [2] was also published at his institute. This edition included the most modern physical data for the individual gases included in the combustion gases.

With the expanded use of programmed computer systems in engineering work, it had become desirable to supplement the graphic computing aid of the I,S diagrams for use with electronic data processing.

In the years 1963 to 1965, research work was carried out with the objective of representing, by means of equations, the thermodynamic functions, which also formed the basis of the I,S diagrams. The enthalpy, the entropy, and the

real factors of the thermal equation of state for combustion gases were developed as closed formulas valid over the entire range:

Temperature:	200 - 6,000 K
Pressure:	0.001 - 1,000 kp/cm^2 (absolute)
Air ratio:	stoichiometric gas - air.

In a further step, a programming system was established for computers to allow them to operate with these formulas in the same manner as manual operations with I,S diagrams.

This decisively simplified, or even made possible for the first time, computerized thermodynamic determinations on combustion engines, as well as stepwise simulations of real processes or optimization computations.

The Mollier I,S diagrams, though, remain essential for a survey of the establishment of thermodynamic computer procedures and for quick calculation of individual state points and simpler processes.

The work is arranged as follows:

1. General establishment of combustion gas system and assumptions.
2. In the temperature range from 200 to 1,500 K a modified form of the Bettie-Bridgman equation of state [3] is used to take into consideration the intermolecular forces at high pressures and lower temperatures. (The dew limits were not included in the expression.)
3. In the temperature range from 1,500 to 6,000 K, the real gas properties were calculated from the chemical reaction equilibrium for individual thermal states (every 100 K in temperature, and at orders of magnitude of pressure from 0.001 to 1,000 kp/cm^2). Twenty different partial reaction products were considered in the combustion gas.

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4. Using rational integral and transcendental polynomials, approximation equations were obtained for the enthalpy, entropy and the real factors, based on the derivations in (2) and the state points according to (3).
5. A practical system of subprograms in FORTRAN is listed for application of the equations determined. With this system it is possible to compute changes in thermodynamic states immediately.

Symbols Used

C_p specific heat capacity at constant pressure
F general thermodynamic property
H enthalpy (absolute)
M molecular weight
P absolute pressure
R, R_o gas constant
S entropy (absolute)
T absolute temperature
V volume
Z real factor for the state equation $Z = PV/RT$
n mole fraction of an individual gas in combustion mixture
r air content in the combustion gas mixture
i, j running indices
ϕ, ψ empirical functions
λ air ratio, DIN 1940

1. General Assumptions and Prerequisites

The necessary number of independent parameters sufficient for adequate description of a system of combustion gases can be determined from Gibbs' phase rule:

$$f = b - p + 2 \qquad (1)$$

b = number of independent components in the system
p = number of phases appearing
f = number of degrees of freedom or the number of parameters required to describe the system.

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In all combustion engines, the combustion gas appears only in the gas phase; that is, $p = 1$. The combustion gases under consideration here arise from oxidation of hydrocarbons in air. The air has a fixed composition except for humidity. Air humidity will not be considered here, though. Hydrocarbons of different compositions are used in combustion engines. In order to limit the range of computed points, it is necessary to select a fixed carbon/hydrogen ratio for the fuel. This ratio is taken here as $C/H = 85.63/14.37$. This is exactly true for mono-olefins and naphthenes. From a comparison of various fuels for combustion engines, this average value seems suitable for a general representation.

Such an assumed fuel, along with the air of fixed composition, makes up the two components of the total system; that is, $b = 2$. Then for the number of independent parameters, one finds that $f = 3$; that is, three independent parameters are required.

For combustion gases, the following parameters are generally required as characteristic quantities and properties:

a) Characterization of the type of gas
Statement of the air/fuel mixture ratio;
e. g.:

λ . . . air ratio . . . $\dfrac{\text{air volume before combustion}}{\text{stoichiometric air volume}}$

or

F . . . Air/Fuel mass ratio

or

r . . . air content . . . $\dfrac{\text{volume of air in the combustion gas after combustion}}{\text{total combustion gas volume}}$

b) Thermal parameters:
Absolute temperature T; absolute pressure P and volume V.

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c) Caloric parameters:
Enthalpy H; entropy S; and specific heat capacity at constant pressure, C_p.

Among the parameters in a), the air content, r, is especially suitable for an analytical representation, as Schüle suggested in the Z. VDI 60, p. 630, (1916) for fire gases. This is because the thermodynamic properties of combustion gases in the ideal gas state are linearly dependent on this parameter, due to the mixing rule.

Aside from the generally common air content, r, the temperature and pressure must also be selected as independent variables. Then every combustion state with the assumed fuel is unambiguously characterized by the following parameters:

T absolute temperature
P absolute pressure
r air content

Accordingly, the other parameters listed in a), b) and c) are dependent quantities.

The relations between the dependent and the independent parameters are further represented by the thermal equation of state

$$V = \Phi(T, P, r) \tag{2}$$

and the caloric equation of state

$$H = \psi(T, P, r) \tag{3}$$

The thermal equation of state represents the extra-molecular processes, and the caloric equation the intra-molecular processes. Both relations are empirical for real gases.

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Because of the wide range of the temperature and pressure for this representation, the chemical reactions at high temperature (dissociation) and the pressure-dependence of the caloric properties must be taken into consideration by the thermal euqation of state at low temperatures and high pressures.

If the empirical relations are known according to Equations (2) and (3), then the other thermodynamic properties can be derived mathematically; for instance:

$$S = \int dH/T \qquad \text{or} \qquad C_p = (dH/dT)_p$$

2. The Thermal Equation of State for Combustion Gases at High Pressures and Low Temperatures

In order to consider the effects of real gases, euqations of state with several virial coefficients were used. The best-known generally applicable real equations of state are those of Beattie-Bridgman [3] and Benedict-Webb-Rubin. The Beattie-Bridgman equation of state is sufficient for the simpler technological gases. In its virial form it is as follows:

$$\frac{PV}{RT} = 1 + \left[B_o - \frac{A_o}{RT} - \frac{c}{T^3}\right]\frac{1}{V} + \left[\frac{A_o a}{RT} - B_o b - \frac{B_o c}{T^3}\right]\frac{1}{V^2} + \left[\frac{B_o bc}{T^3}\right]\frac{1}{V^3} \tag{4}$$

$$\frac{PV}{RT} = 1 + \frac{B(T)}{V} + \frac{C(T)}{V^2} + \frac{D(T)}{V^3} = Z$$

B(T), C(T) and D(T) are the second, third, and fourth virial coefficients. Z indicates the real factor, which has a value of Z = 1 for an ideal gas. Keyes, Smith and Gerry [4] changed the second virial coefficients of the

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Beattie-Bridgman state equation in order to consider equally the behavior of polar and nonpolar gases. The original Beattie-Bridgman equation is not suitable for representation of polar gases. The altered second virial coefficient of Keyes, Smith and Gerry is:

$$B(T) = B_o - \frac{A_o e^{D/T^2}}{RT} \tag{5}$$

Stockmayer [5] tested this form of the virial coefficient on binary gas mixtures: H_2O-CO_2, N_2-NH_3, and N_2-H_2O. The gases CO_2 and N_2 are not polar. H_2O and NH_3 are polar. Because of the polar water vapor content in the combustion gas, the altered second virial coefficient, Equation (5), should be used in the state equation, Equation (4). The constants for the pure gas components appearing here are known from measurements.

The constants for the mixture are determined here according to the following equation

$$K_m = \sum_i \sum_j n_i \cdot n_j \cdot K_{ij} \tag{6}$$

in which the summations are to be carried out over all components of the mixture.

n_i, n_j	Volume proportions of pure gas components
$K_{ij}(i=j)$	Constants for the pure gas components
$K_{ij}(i \neq j)$	Mixture constants due to interactions between two different types of gas molecules [6].

As yet there is no valid theory from which the constants K_{ij} for $i \neq j$ can be calculated from the constants for the pure components. But from various measurements and computations for binary mixtures [5, 7]

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the following relations can be used as approximations for the constants in the second virial coefficients of equation (5):

$$
\begin{aligned}
A_{ii} &= (A_{ii} \cdot A_{ii})^{1/2} \\
B_{ii} &= (1/8)(B_{ii}^{1/3} \cdot B_{ii}^{1/3})^{3} \\
D_{ii} &= (D_{ii} \cdot D_{ii})^{1/2}
\end{aligned}
\qquad (7)
$$

After application of these relations to combustion gas components in the range from pure air up to stoichiometric combustion gases, it could be established that the constants A, B and D in Equation (5) show an approximately linear dependence on the air content, r, in the form: $K_m = K_0 + K_1 r$.

Because of insufficient reliability in the formation of the interaction constants K_{ij} with $i \neq j$ in the third and fourth virial coefficients, and because of the relatively minor contributions of the latter virial coefficients in the technological computations, only the first and second virial coefficients are considered for the combustion gas mixture. With the further approximation that $1/V$ may be expressed as P/RT, one obtains the following initial solution for the thermal equation of state:

$$V = \frac{RT}{P} + (B_0 + B_1 r) - \frac{(A_0 + A_1 r)}{RT} \exp\left[(D_0 + D_1 r)\, T^2\right] \qquad (8)$$

Here the volume, V, is shown to be explicitly dependent on the independent parameters T, P, and r.

With this equation of state, then it is also possible to obtain the pressure-dependence of the enthalpy, H, and

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the entropy, S, by means of the following differential equations (9):

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

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

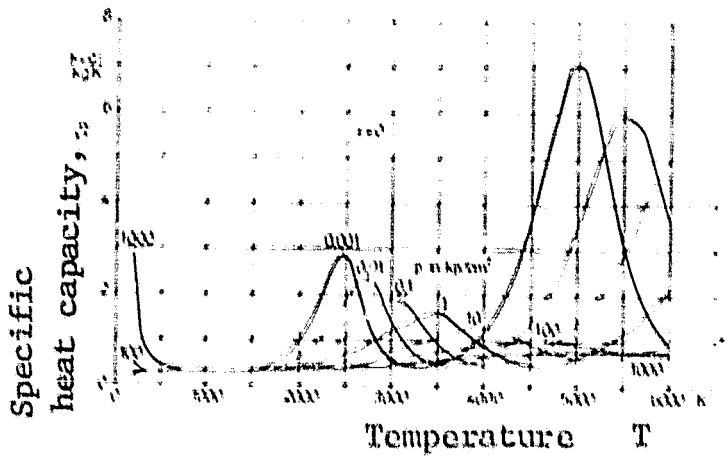

Figure 1. Specific heat capacity C_p of the real stoichiometric combustion gas at pressures of 0.001 to 1000 kp/cm^2.

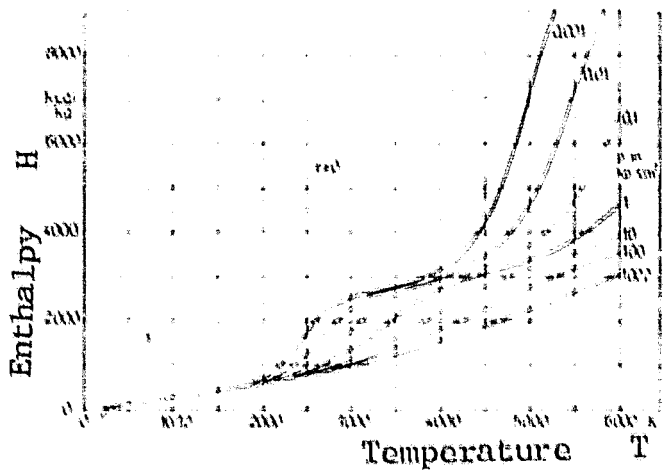

Figure 2. Enthalpy, H, of the real, stoichiometric combustion gas at pressures from 0.001 to 1000 kp/cm^2.

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3. Chemical Equilibrium Reactions in the Combustion Gas

Chemical reactions in the combustion gas must be taken into consideration in the temperature range above 1500 K. As the effect of the intermolecular forces decreases with rising temperature in this temperature range, and the real equation of state approaches the ideal one, the ideal thermal state equation can be used as the basis in this region. It is also apparent that the modified Beattie-Bridgman state equation selected also transforms into the ideal state equation at higher temperatures, even at relatively high pressures. At high temperatures the thermodynamic properties of a gas mixture are expressed by intra-molecular processes. The gas stores energy in the form of various states of motion, which lead to dissociation of the molecule into atoms or groups of atoms (radicals). An apparent equilibrium composition, dependent on T, P and r, is established between the reciprocal dissociating and bonding reactions.

The calculation of the gas composition and, from that, the thermodynamic properties of the dissociating combustion gas are presented in [8] and [9] with respect to application of electronic data processing. The calculations performed here are closely based on [9] and are extensively described in [10]. The equilibrium composition must be determined for every thermal state point by means of a long iterative computation from the mass action law, the atomic balances (unchangeable number of the various types of atoms in different combintations) and Dalton's Law (sum of the partial pressures = 1).

In order to get a sufficient number of supporting values for the following approximations, the gas composition and all the thermodynamic properties of interest were computed every 100 K from 1500 to 6000 K at all orders of

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magnitude of pressure between 0.001 and 1,000 kp/cm^2, and for the air contents (air ratios) r (λ) 0 (1); 0,2 (1,267); 0,4 (1,713); 0,6 (2,603); 0,8 (5,278); 1,0 (∞)

This set of steps gave computations for about 2,000 state points.

In the dissociating combustion gas, 20 different reaction products were considered as potential gas components:

H_2O, CO_2, HCN, N_2O, NO_2, H_2, C_2, O_2, N_2, NO, CO, CN, OH, CH, NH, H, C, O, N, and the noble gases of the air.

The required absolute thermodynamic functions C_p/R, $(H - H_0)/RT$ and S/R for the 20 individual gases in the ideal gas state, and the reaction enthalpies, were taken from [8] and [9], because they presented a critical selection of the latest data up to 1959. The data for the triatomic gases were from McBride and Gordon [11]. All the data used are tabulated in [10].

Of the results of computations from the reaction equilibria, only the heat capacity, C_p in kcal/kg K and the enthalpy, H, in kcal/kg, are shown here in Figure 1 and 2 for stoichiometric combustion gas ($r = 0$ or $\lambda = 1$). The absolute temperature in K is the abscissa for each figure. The seven curves presented in each figure correspond to the absolute pressures 0.001; 0.01; 0.1; 1; 100; and 1000 kp/cm^2.

In these diagrams, two distinct reaction steps are recognizable from the wave-shaped course with rising temperatures. These are due to the prevailing decompositions appearing in the various temperature ranges. The first step is for decomposition of the triatomic molecules into diatomic ones. The second step is for decomposition of diatomic molecules into monatomic ones.

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4. Establishment of Approximation Equations

In order to be able to work with the thermodynamic gas properties on programmed computer systems, these properties must be presented as mathematical equations. The following three functions are approximated:

1. Real factor $Z = \frac{PV}{RT} = Z(T, P, r)$

2. Enthalpy $H = H(T, P, r)$

3. Entropy $S = S(T, P, r)$

The entropy is to be provided for the minimal system from the thermal state equation (2) and the caloric state equation (3) in order to avoid derivative errors in computing the entropy from differential calculus.

Corresponding to the various effects of molecular processes on the thermodynamic properties, one can decompose the three functions shown above into three parts each: ideal behavior, correction according to the real state equation (second virial coefficient) and dissociation correction. Accordingly, the three functions shown can be represented in the general form

$$F = F_{ideal} + \Delta F_{Realgas} + \Delta F_{Dissoziation} \qquad (10)$$

Here the ideal gas properties, F_{ideal}, contain only the temperature dependence of the specific heat capacity in the undissociated ideal gas mixture. They are approximated by rational integral polynomials. The Tschebyscheff approximation procedure was used as the most practical method of approximation.

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The correction term due to the selected second virial coefficients in the state equation, $\Delta F_{real\ gas}$, is known analytically directly from the previous section, as are effects on the enthalpy and entropy from the differential equations (9).

The effect of dissociation, $\Delta F_{dissociation}$, must be considered in the high-temperature range. The wave-form appearance of the dissociation contradicts an approximation by simple rational integral polynomials. For this reason it is advantageous to use transcendental types of functions for the approximation. For this case, a mathematical model was established by means of which the constants can be determined from a formula made up arbitrarily of transcendental and rational functions. On applying the principal of minimizing the squared errors, one gets with mixed transcendental-rational formulas non-linear determination equations for the constants. These can be solved by a Newtonian iteration. For this purpose, coarsely estimated numerical values are input into the computation for the constants which are initially unknown [10]. This approximation procedure makes it possible to match the most practical mathematical formulas to the curve form to be represented with enough free constants.

After detailed studies and back-calculations with various types of functions for the curves of the real factors, enthalpy and entropy, the correction term $\Delta F_{dissociation}$ was represented by the following formula:

$$\Delta F_{Dissoziation} = a_1/(1+e^{y_1}) + a_2/(1+e^{y_2}) \qquad (11)$$

In Equation (11) the exponential functions y_1 and y_2 and the amplitude functions a_1 and a_2 can be solved with the aid of the curve to be approximated, specified point-wise; and they can further be approximated by the best-matching function types according to the method cited.

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While y_1 and y_2 are usable equally for the state equation, enthalpy and entropy, a_1 and a_2 must be matched separately to the particular thermodynamic properties.

Applying the summation of Equation (10) to each of the thermodynamic functions to be represented here, one finally obtains as a result the approximation equations according to Table 1, which always contain the sequence $F = \Delta F_{real\ gas} + F_{ideal} + \Delta F_{dissociation}$. The real effect is superimposed in the ideal functions from the low-temperature side, and the dissociation effects from the high-temperature side. The approximation functions of Table 1 are shown in Figures 3, 4, and 5 for stoichiometric combustion gases.

The three thermodynamic functions are referred to the kmol of undissociated combustion gases, and made dimensionless with the ideal gas constant R_o and the absolute temperature. By multiplication with the corresponding ideal gas constants, the thermodynamic data may be obtained immediately in the dimensions desired. The ideal molecular weight, M_o, of Table 1 must be used in relation to the weight (kg).

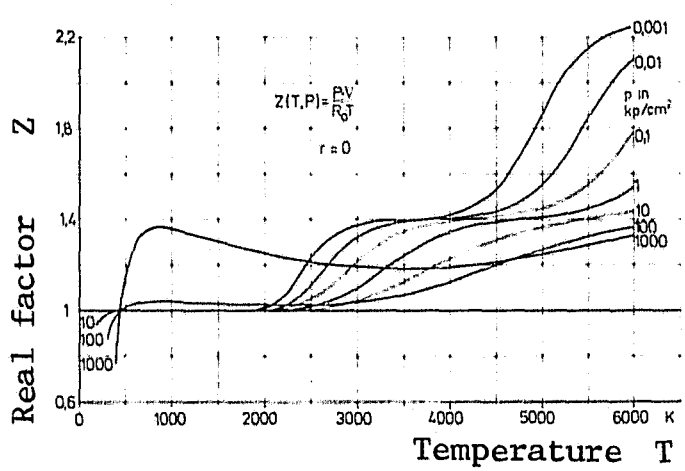

Figure 3. Real factor for stoichiometric combustion gas from Equation (1).

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Table 1: Approximation equations for the thermodynamic properties of combustion gases.

1 Realfaktor

$$Z(\theta;\pi;r) = \frac{PV}{R_0T} = \frac{\pi}{\theta}\left[B_0 - \frac{A}{\theta}e^{D/\theta^2}\right] + 1 + \frac{(0{,}420 + 0{,}193\,r)\,\pi^{+0{,}007}}{1 + \frac{1}{\theta}e^{1/1}} + \frac{0{,}774 + 0{,}198\,r + (0{,}0126 + 0{,}0059\,r)\ln\pi}{1 + \frac{1}{\theta}e^{1/2}} \qquad (I)$$

2 Enthalpie:

$$\frac{H(\theta;\pi;r)}{R_0T} = \frac{\pi}{\theta}\left[B_0 - \frac{2A}{\theta}e^{D/\theta^2}\cdot\left(1 + \frac{D}{\theta^2}\right)\right] + \sum_{j=0}^{5} a_j\theta^j + \frac{(25{,}9 - 11{,}0\,r)\,\pi^{+0{,}0115}}{\theta\left(1 + \frac{1}{\theta}e^{1/1}\right)} + \frac{86{,}50 - 3{,}065\ln\pi - 1{,}435\,r}{\theta\left(1 + \frac{1}{\theta}e^{1/2}\right)} \qquad (II)$$

$$\begin{aligned}
a_0 &= +3{,}514956 - 0{,}005026\cdot r\\
a_1 &= +0{,}131438 + 0{,}383504\cdot r\\
a_2 &= +0{,}477182 + 0{,}185214\cdot r\\
a_3 &= -0{,}287367 - 0{,}694862\cdot 10^{-1}\cdot r\\
a_4 &= +0{,}742561\cdot 10^{-1} + 0{,}164041\cdot 10^{-1}\cdot r\\
a_5 &= +0{,}916344\cdot 10^{-2} + 0{,}204537\cdot 10^{-2}\cdot r\\
a_6 &= +0{,}439896\cdot 10^{-3} + 0{,}101610\cdot 10^{-3}\cdot r
\end{aligned}$$

3 Entropie

$$\frac{S(\theta;\pi;r)}{R_0} = \frac{\pi}{\theta}\left[-\frac{A}{\theta}e^{D/\theta^2}\cdot\left(1 + \frac{D}{\theta^2}\right)\right] + (3{,}5566 - 0{,}0659\,r)\ln 1000\theta + \sum_{j=0}^{6} b_j\theta^j - \ln\pi - \sum_{k=0}^{3} c_k r^k +$$

$$+ \frac{(8{,}279 - 3{,}726\,r)\,\pi^{-0{,}03453}}{1 + \frac{1}{\theta}e^{1/1}} + \frac{14{,}512\,\pi^{-0{,}05648} - 2{,}434\,r}{1 + \frac{1}{\theta}e^{1/2}} \qquad (III)$$

$$\begin{aligned}
b_0 &= +2{,}972979 + 0{,}553140\cdot r & c_0 &= +0{,}805214\\
b_1 &= +0{,}583837\cdot 10^{-1} + 0{,}485001\cdot r & c_1 &= +0{,}400581\\
b_2 &= -0{,}871349 + 0{,}632183\cdot 10^{-1}\cdot r & c_2 &= +0{,}576989\\
b_3 &= -0{,}451556 - 0{,}287210\cdot 10^{-2}\cdot r & c_3 &= +0{,}060056\\
b_4 &= +0{,}109164 - 0{,}693661\cdot 10^{-3}\cdot r\\
b_5 &= -0{,}129754\cdot 10^{-1} + 0{,}920231\cdot 10^{-4}\cdot r\\
b_6 &= +0{,}608234\cdot 10^{-3} - 0{,}299679\cdot 10^{-5}\cdot r
\end{aligned}$$

4 mit

$$y_1 = 15\left(\frac{\theta}{1{,}65}\right)^{\left[-0{,}51\,\pi^{-0{,}103} - 0{,}14 + (0{,}12 - 0{,}29\,\pi^{-1{,}127})\ln\frac{\theta}{1{,}65}\right]} - 6{,}9076 - \left\{(1 - r) - (1 - r)^{0{,}2772}\right\}0{,}9088\,\pi^{-0{,}212} +$$

$$+ (0{,}573 + 0{,}083\ln\pi)\,e^{-0{,}306\theta}$$

$$y_2 = 18{,}0972 - 2{,}43\cdot\theta\cdot\pi^{-0{,}045}$$

$$A = 2{,}77105\cdot 10^{-4} - 0{,}900711\cdot 10^{-4}\,r\,;\quad B_0 = 6{,}42217\cdot 10^{-4} - 0{,}98367\cdot 10^{-4}\,r\,;\quad D = 0{,}8868\cdot 10^{-2} - 0{,}613\cdot 10^{-2}\,r$$

5 Temperatur: θ

$$\theta = \frac{T\ K}{1000\ K} = \frac{T\ °R\,(Rankine)}{1000\cdot(5/9)\ °R}$$

6 Druck:

$$\pi = \frac{P\ ata}{1\ ata} = \frac{P\ bar}{0{,}980665\ bar} = \frac{P\ atm}{0{,}967841\ atm}$$

7 Luftgehalt r:

$$r = \frac{\lambda - 1}{1{,}0698 + \lambda - 1}\ \frac{mol\ Luft\ 9}{mol\ VG_{undissoziert}\ 10}$$

8 Gaskonstante: R_0 – ; Gaskonstante des idealen Gases 11

12 Molmasse d. idealen VG $M_0 = 28{,}89758 + 0{,}06021\cdot r$ [kg/kmol].

Table 1

1 Real factor

2 Enthalpy

3 Entropy

4 with

5 Temperature

6 Pressure

7 Air content

8 Gas constant

9 Air

10 Combustion $gas_{undissociated}$

11 Gas constant for the ideal gas

12 Molecular weight of the ideal combustion gas:

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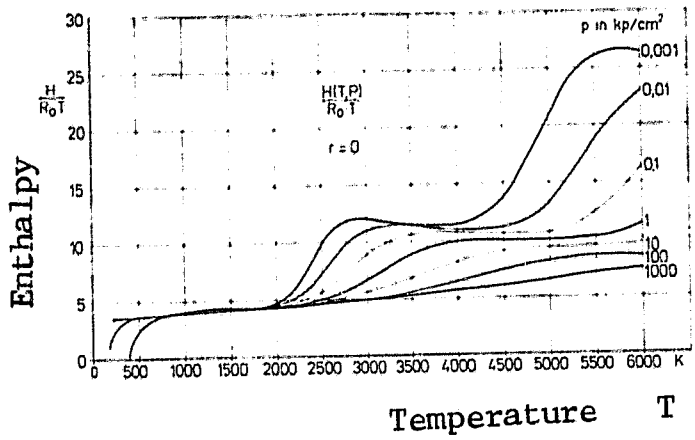

Figure 4. Reduced enthalpy for stoichiometric combustion gas according to Equation (2).

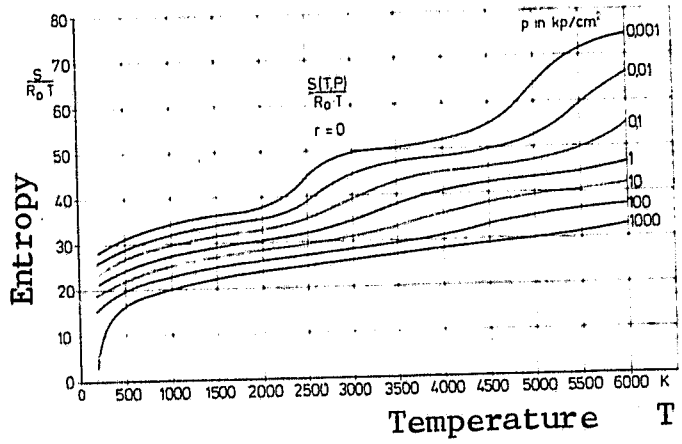

Figure 5. Reduced entropy for stoichiometric combustion gas according to Equation (3).

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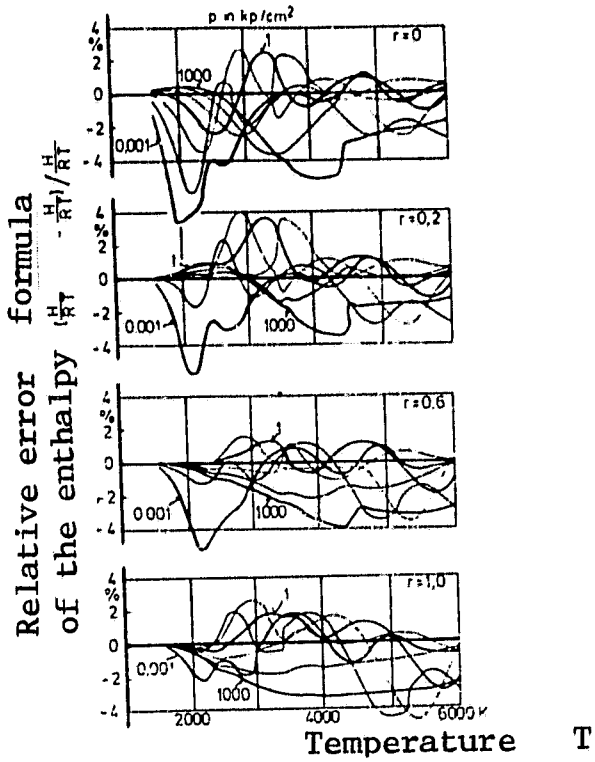

Figure 6. Error curves for enthalpy.

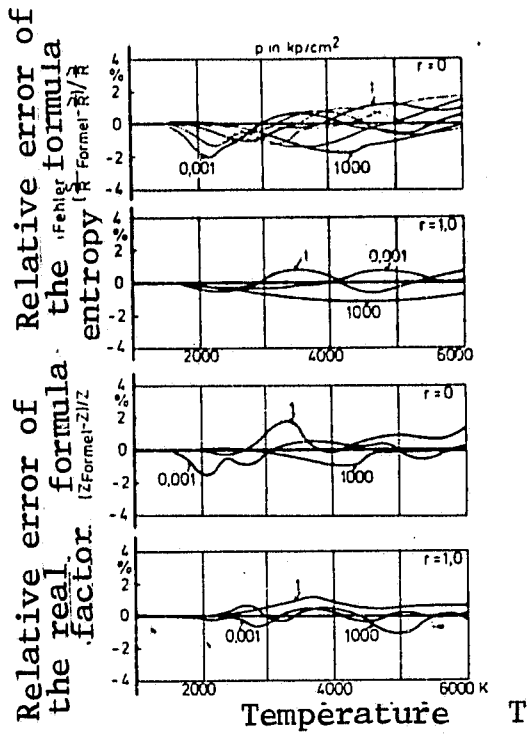

Figure 7. Error curves for entropy and realfactor.

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Table 3. THERMOBIBL subprogram system.

```
      SUBROUTINE  VATP
      REAL  J, K1, K2, K3, LP, MS
      COMMON  T, P, V, H, S, R, NA
      COMMON  AB,AC,G,J,V1,LP,PI,TETA
      COMMON B2(7),B3(7),C(8),K3(4),Q3(8)
      COMMON  Y1Q, Y2Q, Y3, Y4
      NA = 0
      CALL  ANF
      TETA = T * .001
      CALL  PPI
      IF  (NA)  1,10,1
   10 CALL  VA
      IF  (NA)  1,11,1
   11 V = AD
    1 RETURN
      END


      SUBROUTINE  HATP
      REAL  J, K1, K2, K3, LP, MS
      COMMON  T, P, V, H, S, R, NA
      COMMON  AB,AD,G,J,V1,LP,PI,TETA
      COMMON B2(7),B3(7),C(8),K3(4),Q3(8)
      COMMON  Y1Q, Y2Q, Y3, Y4
      NA = 0
      CALL  ANF
      TETA = T * .001
      CALL  PPI
      IF  (NA)  1,9,1
    9 CALL  CMISCH
      CALL  HA
      IF  (NA)  1,11,1
   11 H = AD
    1 RETURN
      END


      SUBROUTINE  SATP
      REAL  J, K1, K2, K3, LP, MS
      COMMON  T, P, V, H, S, R, NA
      COMMON  AB,AC,G,J,V1,LP,PI,TETA
      COMMON B2(7),B3(7),C(8),K3(4),Q3(8)
      COMMON  Y1Q, Y2Q, Y3, Y4
      NA = 0
      CALL  ANF
      TETA = T * .001
      CALL  PPI
      IF  (NA)  1,12,1
   12 CALL  CMISCH
      CALL  SA
      IF  (NA)  1,11,1
   11 S = AD
    1 RETURN
      END


      SUBROUTINE  TAPV
      REAL  J, K1, K2, K3, LP, MS
      COMMON  T, P, V, H, S, R, NA
      COMMON  AB,AD,G,J,V1,LP,PI,TETA
      COMMON B2(7),B3(7),C(8),K3(4),Q3(8)
      COMMON  Y1Q, Y2Q, Y3, Y4
      EXTERNAL  VA
      NA = 0
      G = V
      CALL  TZUM(VA)
      RETURN
      END


      SUBROUTINE  TAPH
      REAL  J, K1, K2, K3, LP, MS
      COMMON  T, P, V, H, S, R, NA
      COMMON  AB,AC,G,J,V1,LP,PI,TETA
      COMMON B2(7),B3(7),C(8),K3(4),Q3(8)
      COMMON  Y1Q, Y2Q, Y3, Y4
      EXTERNAL  HA
      NA = 0
      G = H
      CALL  TZUM(HA)
      RETURN
      END


      SUBROUTINE  TAPS
      REAL  J, K1, K2, K3, LP, MS
      COMMON  T, P, V, H, S, R, NA
      COMMON  AB,AC,G,J,V1,LP,PI,TETA
      COMMON B2(7),B3(7),C(8),K3(4),Q3(8)
      COMMON  Y1Q, Y2Q, Y3, Y4
      EXTERNAL  SA
      NA = 0
      G = S
      CALL  TZUM(SA)
      RETURN
      END


      SUBROUTINE  PATV
      REAL  J, K1, K2, K3, LP, MS
      COMMON  T, P, V, H, S, R, NA
      COMMON  AB,AC,G,J,V1,LP,PI,TETA
      COMMON B2(7),B3(7),C(8),K3(4),Q3(8)
      COMMON  Y1Q, Y2Q, Y3, Y4
      EXTERNAL   VA
      NA = 0
      IF  (V)    1, 1, 3
    3 G = ALOG(V)
      CALL  PZUM(VA)
      IF  (NA)  1,2,2
    1 NA = 1
    2 RETURN
      END
```

```
      SUBROUTINE  PATS
      REAL  J, K1, K2, K3, LP, MS
      COMMON  T, P, V, H, S, R, NA
      COMMON  AB,AC,G,J,V1,LP,PI,TETA
      COMMON B2(7),B3(7),C(8),K3(4),Q3(8)
      COMMON  Y1Q, Y2Q, Y3, Y4
      EXTERNAL  SA
      NA = 0
      IF  (S)    1, 1, 3
    3 G = ALOG(S)
      CALL  PZUM(SA)
      IF  (NA)  1,2,2
    1 NA = 1
    2 RETURN
      END


      SUBROUTINE   TPAVH
      REAL  J, K1, K2, K3, LP, MS
      COMMON  T, P, V, H, S, R, NA
      COMMON  AB,AD,G,J,V1,LP,PI,TETA
      COMMON B2(7),B3(7),C(8),K3(4),Q3(8)
      COMMON  Y1Q, Y2Q, Y3, Y4
      EXTERNAL  HA
      NA = 0
      J = H
      CALL  TPZUM(HA)
      RETURN
      END


      SUBROUTINE  TPAVS
      REAL  J, K1, K2, K3, LP, MS
      COMMON  T, P, V, H, S, R, NA
      COMMON  AB,AD,G,J,V1,LP,PI,TETA
      COMMON B2(7),B3(7),C(8),K3(4),Q3(8)
      COMMON  Y1Q, Y2Q, Y3, Y4
      EXTERNAL  SA
      NA = 0
      J = S
      CALL  TPZUM(SA)
      RETURN
      END


      FUNCTION  UFTGEH(E)
      COMMON  T, P, V, H, S, R, NA
      NA = .0
      IF  (E-1.)  1,2,2
    2 IF  (E - 1000.)  3,4,4
    3 R = (E-1.)/(.C698*E)
      UFTGEH = R
      GO  TO  5
    4 R=1.
      UFTGEH=R
      GO TO 5
    1 NA = 1
    5 RETURN
      END


      SUBROUTINE VA
      REAL  J, K1, K2, K3, LP, MS
      COMMON  T, P, V, H, S, R, NA
      COMMON  AB,AC,G,J,V1,LP,PI,TETA
      COMMON B2(7),B3(7),C(8),K3(4),Q3(8)
      COMMON  Y1Q, Y2Q, Y3, Y4
      RO = 8314.38
      CALL  GR
      IF  (NA)  1,10,1
   10 A = Q3(1)*PI**.007/Y1Q+(Q3(2)+Q3(3)
     1*LP)/Y2Q+1. + (K3(2)-Y4)*PI/TETA
      AD = A*RO*T/(P*K3(4))
    1 RETURN
      END


      SUBROUTINE  HA
      REAL  J, K1, K2, K3, LP, MS
      COMMON  T, P, V, H, S, R, NA
      COMMON  AB,AD,G,J,V1,LP,PI,TETA
      COMMON B2(7),B3(7),C(8),K3(4),Q3(8)
      COMMON  Y1Q, Y2Q, Y3, Y4
      RO = 8314.38
      CALL  GR
      IF  (NA)  1,10,1
   10 P = HRN(B2,TETA,7)+(Q3(4)*PI**.0115/
     1Y1Q+(Q3(5)-3.065*LPI/Y2Q+(K3(2)-2.
     2*Y4*(1.+Y3))*PI)/TETA
      AD = RO*T*B/K3(4)
    1 RETURN
      END


      SUBROUTINE  SA
      REAL  J, K1, K2, K3, LP, MS
      COMMON  T, P, V, H, S, R, NA
      COMMON  AB,AD,G,J,V1,LP,PI,TETA
      COMMON B2(7),B3(7),C(8),K3(4),Q3(8)
      COMMON  Y1Q, Y2Q, Y3, Y4
      RO = 8314.38
      CALL  GR
      IF  (NA)  1,3,1
    3 IF (T)  2, 2, 4
    4 IF  (PI)2, 2, 5
    5 AD = (Q3(6)*ALOG(T)+HRN(B3,TETA,7)+
     1(C3(7)*PI**(-.03453))/Y1Q-LP+(Q3(8)
     2*14.512*PI**(-.05648))/Y2Q-(Y4*PI*
     3(1.+Y3))/TETA)*RO/K3(4)
      GO TO 1
    2 NA = 1
    1 RETURN
      END
```

```
      SUBROUTINE  ANF
      REAL  J, K1, K2, K3, LP, MS
      COMMON  T, P, V, H, S, R, NA
      COMMON  AB,AD,G,J,V1,LP,PI,TETA
      COMMON B2(7),B3(7),C(8),K3(4),Q3(8)
      COMMON  Y1Q, Y2Q, Y3, Y4
      DIMENSION  K1(4), K2(4), Q1(8), Q2(8)
      K1(1) = 2.771C5E-
      K1(2) = 6.422171
      K1(3) = 0.8868E-
      K1(4) = 28.89758
      K2(1) = -.900711E-4
      K2(2) = -.98367E-4
      K2(3) = -.6131E-2
      K2(4) = 0.06021
      CALL  KOMB(4, K1, K2)
      DO  10   I = 1, 4
   10 K3(I) = C(I)
      Q1(1) = 0.42C
      Q1(2) = 0.774
      Q1(3) = -0.0128
      Q1(4) = 25.9
      Q1(5) = 86.5
      Q1(6) = 3.5566
      Q1(7) = 8.179
      Q1(8) = 0.
      Q2(1) = -0.193
      Q2(2) = -0.119
      Q2(3) = -0.005
      Q2(4) = -11.0
      Q2(5) = -14.35
      Q2(6) = -0.0659
      Q2(7) = -3.726
      Q2(8) = -2.434
      CALL  KOMB(8, Q1, Q2)
      DO  11  I = 1, 8
   11 Q3(I) = C(I)
      V1 = 1.-R
      AB = -0.9088 * (-.2772 * V1**4 + V1)
      RETURN
      END


      SUBROUTINE  KOMB(N, A, B)
      REAL  J, K1, K2, K3, LP , MS
      COMMON  T, P, V, H, S, R, NA
      COMMON  AB,AC,G,J,V1,LP,PI,TETA
      COMMON B2(7),B3(7),C(8),K3(4),Q3(8)
      COMMON  Y1Q, Y2Q, Y3, Y4
      DIMENSION  A(8), B(8)
      DO  10  I = 1, N
   10 C(I) = A(I) + B(I)*R
      RETURN
      END


      SUBROUTINE   PPI
      REAL J, K1, K2, K3, LP, MS
      COMMON  T, P, V, H, S, R, NA
      COMMON  AB,AD,G,J,V1,LP,PI,TETA
      COMMON B2(7),B3(7),C(8),K3(4),Q3(8)
      COMMON  Y1Q, Y2Q, Y3, Y4
      IF  (P)  1,1,3
    3 PI = P*1.C1972E-5
      LP = ALOG(PI)
      GO TO 2
    1 NA = 1
    2 RETURN
      END


      SUBROUTINE  GR
      REAL J, K1, K2, K3, LP, MS
      COMMON  T, P, V, H, S, R, NA
      COMMON  AB,AC,G,J,V1,LP,PI,TETA
      COMMON B2(7),B3(7),C(8),K3(4),Q3(8)
      COMMON  Y1Q, Y2Q, Y3, Y4
      IF  (TETA)  1, 1, 1C
   10 B = ALOG(TETA/1.65)
      A = -.51*PI**(-.1C3)-.14 + B*(.12-
     1.25*PI**(-.127))
      A = 15.*EXP(A*B)+(.573+.083*LP)*
     1EXP(-.3C6*TETA)-6.9078
      Y1 = AB*PI**(-.02121)+A
      Y2 = 18.0972-2.43*TETA*PI**(-.045)
      Y1Q = 1.+EXP(Y1)/TETA
      Y2C = 1.+EXP(Y2)/TETA
      Y3 = K3(3)/(TETA*TETA)
      Y4 = EXP(Y3)*K3(1)/TETA
      GO TO 2
    1 NA = 1
    2 RETURN
      END


      SUBROUTINE  CMISCH
      REAL  J, K1, K2, K3, LP, MS
      COMMON  T, P, V, H, S, R, NA
      COMMON  AB,AD,G,J,V1,LP,PI,TETA
      COMMON B2(7),B3(7),C(8),K3(4),Q3(8)
      COMMON  Y1Q, Y2Q, Y3, Y4
      DIMENSION  H1(7), H2(7), S1(7), S2(7), MS(4)
      H1(1) = 3.514956
      H1(2) = 0.131438
      H1(3) = 0.477182
      H1(4) = -.287367
      H1(5) = 0.742561E-1
      H1(6) = -.916344E-2
      H1(7) = 0.439896E-3
      H2(1) = -.005C26
      H2(2) = -.383504
```

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```
      H2(3) = 0.185214
      H2(4) = -.654863E-1
      H2(5) = 0.164641E-1
      H2(6) = -.204537E-2
      H2(7) = 0.101616E-3
      CALL  KCMB(7, H1, H2)
      CC 10   I = 1, 7
   10 B2(I) = C(I)
      S1(1) = 2.572975
      S1(2) = 0.583837E-1
      S1(3) = 0.871345
      S1(4) = -.451556
      S1(5) = 0.109164
      S1(6) = -.129754E-1
      S1(7) = 0.608234E-3
      S2(1) = 0.553140
      S2(2) = -.485001
      S2(3) = 0.698183E-1
      S2(4) = -.287720E-2
      S2(5) = -.693663E-3
      S2(6) = 0.920771E-4
      S2(7) = -.299679E-5
      CALL  KCMB(7, S1, S2)
      CC 11   I = 1, 7
   11 B3(I) = C(I)
      MS(1) = -.805214
      MS(2) = -.400981
      MS(3) = 0.576989
      MS(4) = 0.060056
      B3(1) = B3(1)+HRN(MS, R, 4)
      RETURN
      END


      FUNCTION  HRN(BI, X, N)
      REAL  J, K1, K3, K2, LP, MS
      COMMON  T, P, V, H, S, R, NA
      COMMON  AB,AC,G,J,V1,LP,PI,TETA
      COMMON B2(7),B3(7),C(8),K3(4),Q3(8)
      COMMON  Y1Q, Y2Q, Y3, Y4
      DIMENSION  BI(7)
      HRN = 0.
      I = N+1
    1 I = I-1
      HRN = HRN * X + BI(I)
      IF  (I-1)   2, 2, 1
    2 RETURN
      END


      SUBROUTINE  TZUM(TK)
      REAL  J, K1, K2, K3, LP, MS
      COMMON  T, P, V, H, S, R, NA
      COMMON  AB,AC,G,J,V1,LP,PI,TETA
      COMMON B2(7),B3(7),C(8),K3(4),Q3(8)
      COMMON  Y1Q, Y2Q, Y3, Y4
      EXTERNAL  TP
      CALL  CMISCH
      CALL  ANF
      CALL  PPI
      IF  (NA)  1,12,1
   12 T = ULL1(249.,6000.,TP,TK)
      NA = ABS(NA)
    1 RETURN
      END


      SUBROUTINE  PZUM(PK)
      REAL  J, K1, K2, K3, LP, MS
      COMMON  T, P, V, H, S, R, NA
      COMMON  AB,AC,G,J,V1,LP,PI,TETA
      COMMON B2(7),B3(7),C(8),K3(4),Q3(8)
      COMMON  Y1Q, Y2Q, Y3, Y4
      EXTERNAL  CP
      RC = 8314.38
      CALL  CMISCH
      CALL  ANF
      TETA = T * .001
      IF  (T-400.)  4,4,3
    4 Y4=EXP(K3(3)/(TETA*TETA))*K3(1)/TETA
      P = RO*T/((V-(K3(2)-Y4)*84.783C8/
     1K3(4))*K3(4))
      IF  (P)  5,5,6
    6 PI = P*1.01972E-5
      LP = ALOG(PI)
      GO  TO  1
    5 NA = 1
      GO  TO  1
    3 LP = ULL1(3.,16.91,DP,PK)-10.
      IF  (NA)  1,2,1
    2 PI = EXP(LP)
      P = PI*.980665E5
    1 RETURN
      END


      SUBROUTINE  TPZUM(W)
      REAL  J, K1, K2, K3, LP, MS
      COMMON  T, P, V, H, S, R, NA
      COMMON  AB,AD,G,J,V1,LP,PI,TETA
      COMMON B2(7),B3(7),C(8),K3(4),Q3(8)
      COMMON  Y1Q, Y2Q, Y3, Y4
      EXTERNAL   FIF
      IF  (V)   1, 1, 3
    3 G = ALOG(V)
      CALL  ANF
      CALL  CMISCH
      T = ULL1(249.,700.,FIF,W)
      IF  (NA)  4,2,2
    4 T = ULL1(700.,2000.,FIF,W)
      IF  (NA)  5,2,2
    5 T = ULL1(2000.,6000.,FIF,W)
      IF  (NA)  1,2,2
    1 NA = 1
    2 RETURN
      END


      FUNCTION  CP(X, E)
      REAL  J, K1, K2, K3, LP, MS
      COMMON  T, P, V, H, S, R, NA
      COMMON  AB,AC,G,J,V1,LP,PI,TETA
      COMMON B2(7),B3(7),C(8),K3(4),Q3(8)
      COMMON  Y1Q, Y2Q, Y3, Y4
      LP = X-10.
      PI = EXP(LP)
      P = PI * .980665E5
      CALL  E
      IF  (NA)  2,3,2
    3 IF  (AC)   1, 1, 4
    4 CP = ALOG(AC) - G
      GO TO 2
    1 NA = 1
    2 RETURN
      END


      FUNCTION  TP(X, E)
      REAL  J, K1, K2, K3, LP, MS
      COMMON  T, P, V, H, S, R, NA
      COMMON  AB,AC,G,J,V1,LP,PI,TETA
      COMMON B2(7),B3(7),C(8),K3(4),Q3(8)
      COMMON  Y1Q, Y2Q, Y3, Y4
      T = X
      TETA = T * .001
      CALL  E
      IF  (NA)  1,2,1
    2 TP = AD - G
    1 RETURN
      END


      FUNCTION   FIF(X,E)
      REAL  J, K1, K2, K3, LP, MS
      COMMON  T, P, V, H, S, R, NA
      COMMON  AB,AC,G,J,V1,LP,PI,TETA
      COMMON B2(7),B3(7),C(8),K3(4),Q3(8)
      COMMON  Y1Q, Y2Q, Y3, Y4
      EXTERNAL  DP, VA
      RC = 8314.3E
      T = X
      TETA = T * .001
      IF  (T-400.)  5,5,1
    5 Y4=EXP(K3(3)/(TETA*TETA))*K3(1)/TETA
      P = RO*T/((V-(K3(2)-Y4)*84.783C8/
     1K3(4))*K3(4))
      IF  (P)  2,3,6
    6 PI = P*1.01972E-5
      LP = ALOG(PI)
      GO  TO  7
    1 ARG = RO*T/(V*.980665E5*K3(4))
      IF  (ARG)  3,3,2
    2 AA = 9.55+ALOG(ARG)
      EP = AA*.E4
      LP = ULL2(AA,BB,DP,VA)-10.
      IF  (NA)  4,E,4
    8 PI = EXP(LP)
      P = PI*.980665E5
    7 CALL  E
      IF  (NA)  4,9,4
    9 FIF = AD-J
      GO TO 4
    3 NA = 1
    4 RETURN
      END


      FUNCTION  ULL1(A, B, F, E)
      REAL  J, K1, K2, K3, LP, MS
      COMMON  T, P, V, H, S, R, NA
      COMMON  AB,AC,G,J,V1,LP,PI,TETA
      COMMON B2(7),B3(7),C(8),K3(4),Q3(8)
      COMMON  Y1Q, Y2Q, Y3, Y4
      NA = 0
      NZ = 200
      EPS = 0.005
      XON = A
      X4N = 0.
      YON = F(XON, E)
      IF  (NA)  14,15,14
   15 X2N = B
      Y2N = F(X2N, E)
      IF  (NA)  14,29,14
   29 IF  (Y2N)  27,25,26
   26 IF  (YON)  12,28,30
   27 IF  (YON)  30,28,12
   12 NZ = NZ - 1
      IF  (NZ)  13,13,16
   16 X1N = (XON+X2N)*.5
      Y1N = F(X1N, E)
      IF  (NA)  14,17,14
   17 DN = Y2N - Y1N
      EN = Y1N-YON
      CN = DN-EN
      DN = (DN+EN)*.5
      GN = 2.*Y1N*CN
      IF  (GN)  18,1,18
   18 ARG = CN*DN - GN
      IF (ARG)  13,19,19
   19 HN = SQRT(ARG)
      EN = (HN-DN)/CN
      IF (ABS(EN)-1.1)   2,2,20
   20 EN = -(EN+HN)/CN
      GO TO 2
    1 EN = -Y1N/DN
    2 X3N = EN*(X1N-XON)+X1N
      Y3N = F(X3N, E)
      IF  (NA)  14,21,14
   21 IF  (Y1N)   3, 22, 22
   22 IF  (Y2N)   4, 5, 5
    3 IF  (Y2N)   5, 4, 4
    5 Y2N = Y1N
      X2N = X1N
      GO TO 6
    4 YON = Y1N
      XON = X1N
    6 IF  (Y3N)   7, 23, 23
   23 IF (YON)   8, 9, 9
    7 IF(YON)   9, 8, 8
    9 YON = Y3N
      XON = X3N
      GO TO 10
    8 Y2N = Y3N
      X2N = X3N
   10 IF (ABS(X3N-X4N)-EPS)  11, 24, 24
   24 X4N = X3N
      GO TO 12
   11 ULL1 = X3N
      GO TO 14
   25 ULL1 = X2N
      GO  TO  14
   28 ULL1 = XON
      GO  TO  14
   30 NA = -1
      GO  TO  14
   13 NA = 1
   14 RETURN
      END


      FUNCTION  ULL2(A, B, F, E)
      REAL  J, K1, K2, K3, LP, MS
      COMMON  T, P, V, H, S, R, NA
      COMMON  AB,AC,G,J,V1,LP,PI,TETA
      COMMON B2(7),B3(7),C(8),K3(4),Q3(8)
      COMMON  Y1Q, Y2Q, Y3, Y4
      NA = 0
      NZ = 200
      EPS = .005
      XON = A
      X4N = 0.
      YON = F(XON, E)
      IF  (NA)  14,15,14
   15 X2N = B
      Y2N = F(X2N, E)
      IF  (NA)  14,29,14
   29 IF  (Y2N)  27,25,26
   26 IF  (YON)  12,28,30
   27 IF  (YON)  30,28,12
   12 NZ = NZ - 1
      IF  (NZ)  13,13,16
   16 X1N = (XON+X2N)*.5
      Y1N = F(X1N, E)
      IF  (NA)  14,17,14
   17 CN = Y2N-Y1N
      EN = Y1N-YON
      CN = CN-EN
      DN = (DN+EN)*.5
      CN = 2.*Y1N*CN
      IF  (GN)   18, 1, 18
   18 ARG = DN*CN-GN
      IF  (ARG)   13, 19, 19
   19 HN = SQRT(ARG)
      EN = (HN-CN)/CN
      IF  (ABS(EN)-1.1)   2, 2, 20
   20 EN = -(DN+HN)/CN
      GO TO 2
    1 EN = -Y1N/DN
    2 X3N = EN*(X1N-XON)+X1N
      Y3N = F(X3N, E)
      IF  (NA)  14,21,14
   21 IF  (Y1N)   3, 22, 22
   22 IF  (Y2N)   4, 5, 5
    3 IF  (Y2N)   5, 4, 4
    5 Y2N = Y1N
      X2N = X1N
      GO TO 6
    4 YON = Y1N
      XON = X1N
    6 IF  (Y3N)   7, 23, 23
   23 IF  (YON)   8, 9, 9
    7 IF (YON)   9, 8, 8
    9 YON = Y3N
      XON = X3N
      GO TO 10
    8 Y2N = Y3N
      X2N = X3N
   10 IF  (ABS(X3N-X4N)-EPS)   11, 24, 24
   24 X4N = X3N
      GO TO 12
   11 ULL2 = X3N
      GO TO 14
   25 ULL2 = X2N
      GO  TO  14
   28 ULL2 = XON
      GO  TO  14
   30 NA = -1
      GO  TO  14
   13 NA = 1
   14 RETURN
      END
```

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Table 2. Organization of the THERMOBIBL subprogram system.

Serial No.	Subprogram name	Independent variable	Dependent variable	Approximation Equation used according to Table 1
			from:	
1	VATP	V	T,P,r	indirectly from I
2	HATP	H	T,P,r	indirectly from II
3	SATP	S	T,P,r	indirectly from III
4	TAPV	T	P,V,r	iteratively from I
5	TAPH	T	P,H,r	iteratively from II
6	TAPS	T	P,S,r	iteratively from III
7	PATV	P	T,V,r	iteratively from I
8	PATS	P	T,S,r	iteratively from III
9	TPAVH	T and P	V,H,r	iteratively from I and II
10	TPAVS	T and P	V,S,r	iteratively from I and III
11	UFTGEH (λ)	r	air λ ratio	-

By comparing the values from the approximation equations with the base data previously obtained pointwise, one gets the errors of the approximation. These are shown in Figures 6 and 7 for the real factor, the enthalpy, and the entropy. The errors are greater than in the usual approximations of simpler functions, corresponding to the complexity of the functions to be represented and the difficulty of the three-fold dependence of T, P and r. In selecting types of approximation functions and the number of free constants in them, one must make a compromise between the accuracy of the approximation and the computing cost and storage capacity of the computer. From the diffuse course of the error curves, it is also apparent that the equations established represent a certain optimum between smoothness and the exact reproduction of the already scattered basis data determined point-wise by iteration.

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Comparison of the thermodynamic data computed from the equations of Table 1 with those from the Mollier I,S diagrams of Pflaum [2] shows only errors of less than 2% in the entire range presented by [2]. The diagrams [2] themselves have been compared with other modern thermal diagrams in [12] with very good results.

5. Application of the Approximation Equations in Programmed Computer Systems

By means of the approximation equations, Table 1, a system of subprograms was established (THERMOBIBL). It provides for computing the explicit variables V, H, and S from T, P and r, as well as computation of the inverse functions; e. g., T from P, S and r. Solution of the inverse functions is possible only iteratively. In these subprograms, one of the variables T, P, V, H, or S can be calculated from any three of the others, as the scheme of Table 2 shows. The air content, r, is always used as an independent parameter, corresponding to the general usage of the I,S diagram.

"Quadratic bracketing" according to Zurmühl [13] was used as the iteration procedure to solve the inverse functions. The Newtonian iteration procedure failed because of the wavy form of the approximation functions, Figures 3, 4, and 5.

The subprogram system which provides for computing the dependences according to Table 2 with call of the particular subprogram desired is summarized by the name "THERMOBIBL" and was written in FORTRAN (DOS basic FORTRAN IV). It has been listed in Table 2 for immediate use. This program system is a further development of that published in [14].

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All the variables appearing here have units from the international MKSA system: T(K); P(N/m^2); V(m^3/kg); H(J/kg); S(J/kg K); r (dimensionless). The ideal gas constant used is:

$$R_o = 8314.38/28.898 + 0.06\ r) \quad \text{in J/kg K}$$

With respect to behavior of the equations at low temperatures and high pressures, the state range, which is represented by the iteratively obtained inverse functions (Table 2, No. 4 - 10) is limited to the following boundaries:

T = 250 - 6,000 K
P = 0.001 - 300 kp/cm^2 98.0665 - 29.4 · 10^6 N/m^2

There is an additional pressure limit for TPAVH and TPAVS: Maximum pressure 200 kp/cm^2 in the range 250 - 400 K.

The following details are mentioned for setting up a computer program using the THERMOBIBL subprogram system.

1. The following COMMON region must be specified in the main program:

```
REAL        J, K1, K2, K3, LP, MS
COMMON      T, P, V, H, S, R, NA
COMMON      AB, AD, G, J, V1, LP, PI, TETA
COMMON      B2(7), B3(7), C(8), K3(4), Q3(8)
COMMON      Y1Q, Y2Q, Y3, Y4
```

   Here only the first seven quantities of the COMMON are outside the subprogram of interest.
2. The variables established in the COMMON region have the dimensions specified above and are REAL quantities except for the INTEGER quantity NA.
3. The entire subprogram system, THERMOBIBL, should always be stored in the computer.

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4. There should be no new definition of the following names in the main program, because they appear as program names in the subprogram system: aside from those listed in Table 2, the names VA, HA, SA, ANF, KOMB, PPI, GR, CMISCH, HRN, TZUM, PZUM, DP, TP, FIF, ULL1, ULL2.

5. Before the call of one of the subprograms listed in Table 2 (e. g., CALL TPAVH) the input parameters (independent parameters, e. g., V, H, r) must be placed in the COMMON region. After running the subprogram the corresponding dependent variable (e. g., T and P) must be fetched from the COMMON region.

6. After running one of the subprograms listed in Table 2 it is possible to test for the correct course of the computation via the quantity NA:
   a) NA = 0 correct course of computation
   b) NA = 1 computation erroneous because the range of presentation has been exceeded

   By means of this control quantity it is possible to branch or terminate the main program corresponding to certain requirements without destroying the computation.

This subprogram system makes it possible to compute all the thermodynamic quantities with combustion gases rapidly and accurately on a computer. The simple and general applicability of the subprograms makes research and design work easier for combustion machines.

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