

Thermodynamic Property Models for Unburned Mixtures and Combustion Gases

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Abstract

New mathematical functions, with the functional form of a fifth order logarithmic polynomial, have been developed. These polynomials have been used to describe gases' thermodynamic properties, and have been utilized for combustion processes, with "frozen composition" and "shifting equilibrium composition" evaluation. The logarithmic polynomials present the advantage of covering a wide range of temperatures with only a single mathematical function. The logarithmic polynomial coefficients have been evaluated through the least squares fit on the basis of experimental measurements (taken from scientific literature). The set of logarithmic polynomials gives the possibility of studying the combustion phenomena and allows for the description of specific heat at constant pressure, enthalpy, entropy and equilibrium constants for gases' dissociation.

Keywords: Combustion, thermochemical dissociation, gases thermodynamic properties, fifth order logarithmic polynomials, internal combustion engine.

1. Introduction

Fifth order logarithmic polynomials have been implemented for the determination of gases' thermodynamic properties. These functions have been used to evaluate "frozen composition", "shifting equilibrium composition" and the dissociation equilibrium constants.

The polynomials have been calculated for isobaric specific heat, enthalpy, entropy and equilibrium constants. The polynomial coefficients for the isobaric specific heat have been computed for each single gas through the least squares method, and the coefficients for enthalpy and entropy are expressed as a combination of the previous ones.

The polynomial functions can be used in temperature ranges of practical interest (ICE applications, gas turbine applications, etc).

Logarithmic polynomial coefficients have been obtained by matching the thermodynamic properties data taken from the JANAF

Thermochemical Tables (1971), Chase (1998), Gordon and McBride (1999), Gurvich et al. (1978) and Gurvich et al. (1989).

The isobaric specific heats have been calculated depending on temperature, and they have been compared with the experimental ones in order to evaluate the relative errors.

The logarithmic polynomials pointed out an elevate interpolation accuracy, the possibility of utilizing a single logarithmic polynomial for a wide temperature range.

Utilizing the logarithmic polynomials for the equilibrium constants, it is possible to evaluate the molar fraction of the gases constituting the products of combustion and the thermodynamic properties of the mixture.

In this formulation the mixing entropy has been taken into account for a correct evaluation of the mixture entropy. It is also possible to take into account the heat occulted during the dissociation phenomenon and the great influence

of thermochemical dissociation on mixture specific heat.

2. Thermodynamic Properties for a Single Gas

Logarithmic polynomials can be evaluated through the least squares method in order to reduce the percentage relative error, and to maximize the correlation factor (Milton, 1995).

The logarithmic polynomial specific heat at constant pressure is reported in Equation (1):

$$\tilde{c}_p(T^*) = \sum_{i=0}^5 a_i (\ln T^*)^i \quad (1)$$

Integrating Equation (1) with respect to the temperature yields the enthalpy (Equation (2)).

$$\int_{h_0}^{\tilde{h}} d\tilde{h} = \int_1^{T^*} \tilde{c}_p(T^*) dT^* \quad (2)$$

Substituting Equation (1) into Equation (2) and developing the integrals of Equation (2), it is possible to obtain the expression for the sensible enthalpy:

$$\begin{aligned} \tilde{h}(T^*) - \Delta\tilde{h}_f^0 &= \\ &= T_0 \left\{ T^* \left[\sum_{i=0}^5 b_i (\ln T^*)^i \right] + b_0 \right\} = \tilde{h}_s(T^*) \quad (3) \end{aligned}$$

where $\Delta\tilde{h}_f^0$ is the enthalpy of formation at $T = T_0$ ($T^*=1$), and $\tilde{h}(T^*) - \Delta\tilde{h}_f^0$ is equal to zero at the reference temperature $T = T_0 = 298.15$ K.

All the b_i coefficients are expressed in Equation (4):

$$b_i = \sum_{j=0}^5 (-1)^j \frac{(i+j)!}{i!} a_{i+j} \quad (4)$$

with $a_{i+j} = 0$ if $(i+j) > 5$.

All the b_i constants depend on the a_i coefficients. So the least squares method is applied only once to the experimental data on specific heat at constant pressure.

Managing the expressions of each b_i it is possible to obtain:

$$\begin{aligned} b_0 &= a_0 - a_1 + 2a_2 - 6a_3 + 24a_4 - 120a_5 \\ b_1 &= a_1 - 2a_2 + 6a_3 - 24a_4 + 120a_5 \\ b_2 &= a_2 - 3a_3 + 12a_4 - 60a_5 \\ b_3 &= a_3 - 4a_4 + 20a_5 \\ b_4 &= a_4 - 5a_5 \\ b_5 &= a_5 \end{aligned}$$

Starting from the specific heat at constant pressure, it is possible to evaluate the entropy for each gas:

$$\int_{\tilde{s}_0}^{\tilde{s}} d\tilde{s} = \int_1^{T^*} \frac{\tilde{c}_p(T^*)}{T^*} dT^* - \tilde{R} \int_1^{p^*} \frac{dp^*}{p^*} \quad (5)$$

The integration yields:

$$\tilde{s}(T^*, p^*) - \tilde{s}(1, 1) = \sum_{i=1}^6 c_i (\ln T^*)^i - \tilde{R} \ln p^* \quad (6)$$

where $\tilde{s}(T^*, p^*) - \tilde{s}(1, 1)$ is equal to zero at $T = T_0 = 298.15$ K and $p = p_0 = 101325$ Pa; while the constants c_i for $1 \leq i \leq 6$ are given in Equation (7)

$$c_i = \frac{a_{i-1}}{i} \quad (7)$$

also the c_i constants are expressed in function of the a_i coefficients.

The three mathematical formulations for specific heat at constant pressure [$\tilde{c}_p(T^*)$], enthalpy [$\tilde{h}(T^*)$] and entropy [$\tilde{s}(T^*, p^*)$] are given in Equations (8), (9) and (10).

$$\begin{aligned} \tilde{c}_p(T^*) &= a_0 + a_1 \ln(T^*) + a_2 [\ln(T^*)]^2 + \\ &+ \dots + a_5 [\ln(T^*)]^5 \quad (8) \end{aligned}$$

$$\tilde{h}(T^*) = T_0 \left\{ T^* \left\{ \begin{aligned} &b_0 + b_1 \ln(T^*) + \\ &b_2 [\ln(T^*)]^2 + \\ &+ \dots + b_5 [\ln(T^*)]^5 \end{aligned} \right\} + b_0 \right\} + \Delta\tilde{h}_f^0 \quad (9)$$

$$\begin{aligned} \tilde{s}(T^*, p^*) &= c_1 \ln(T^*) + c_2 [\ln(T^*)]^2 + \\ &+ \dots + c_6 [\ln(T^*)]^6 - \tilde{R} \ln p^* + \tilde{s}(1, 1) \quad (10) \end{aligned}$$

3. Evaluation of the Logarithmic Polynomials Performance

By using the least squares method on the experimental measurements of gases' \tilde{c}_p , for each gas, it is possible to determine the six coefficients a_i of Equation (8). The following gases were considered as the main components of typical ICE products of combustion: O₂, O, N₂, N, H₂, H, Ar, H₂O, OH, CO₂, CO, and NO. The six coefficients a_i for all the gases are reported in TABLE I.

The fifth order logarithmic polynomial for the twelve gases is able to cover, with only one mathematical formulation, the temperature range from 100 K to 5000 K with a correlation factor R² always greater than 0.99 (Lanzafame and Messina, 2000) (see TABLE I). The correlation

factor compares the predicted data from mathematical functions with the experimental ones, and it varies from 0 to 1. If it is equal to 1, it means that a perfect correlation between preview data and experimental data exists (Milton, 1995). The relative errors (shown in Equation (11)), between experimental and simulated data, are very low (see *Figure 1*), especially considering the wide temperature range of interpolation (see *Figure 1*).

$$\frac{\tilde{c}_p|_{\text{simulated}} - \tilde{c}_p|_{\text{experimental}}}{\tilde{c}_p|_{\text{experimental}}} \quad (11)$$

If the range of temperatures is restricted to one of more practical interest (for example from 273 K to 3500 K for application inside ICE), the errors are notably reduced (see *Figure 2*).

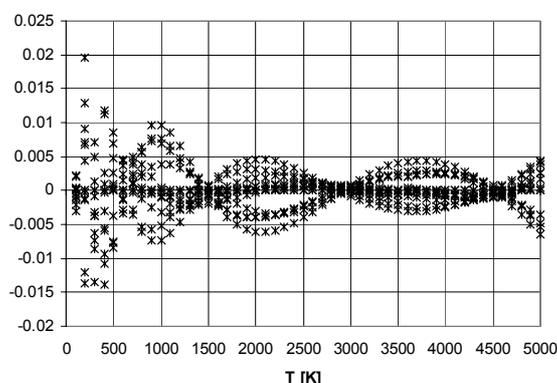


Figure 1. Oscillation of the relative errors for all the gases (temperature range of interpolation $100 \leq T \leq 5000$ K).

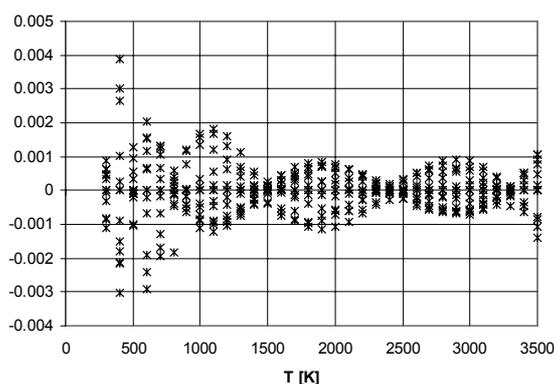


Figure 2. Oscillation of the relative errors for all the gases (temperature range of interpolation $300 \leq T \leq 3500$ K).

For a complete description of all logarithmic polynomials, in TABLE II the enthalpy of formation and the entropy at the standard conditions (JANAF Thermochemical Tables, 1971) are reported.

Fifth order logarithmic polynomials have evidenced the possibility of utilizing a single

polynomial to cover a wide range of temperatures, furnishing great accuracy. In *Figure 3* an example is shown for hydrogen. In this figure a comparison between a traditional

fifth order polynomial ($\tilde{c}_p(T) = \sum_{i=0}^5 a_i T^i$) and a

fifth order logarithmic polynomial ($\tilde{c}_p(T) = \sum_{i=0}^5 a_i (\ln T)^i$) has been performed. The

comparison shows that a logarithmic polynomial represents the best fit. The fifth order logarithmic polynomial covers with good accuracy the experimental data on the entire temperature range, while the traditional fifth order polynomial does not fit well the experimental data after $T=1500$ K.

The same trend shown for this gas is also valid for all the other gases considered in this paper, and for this reason, they are not exposed.

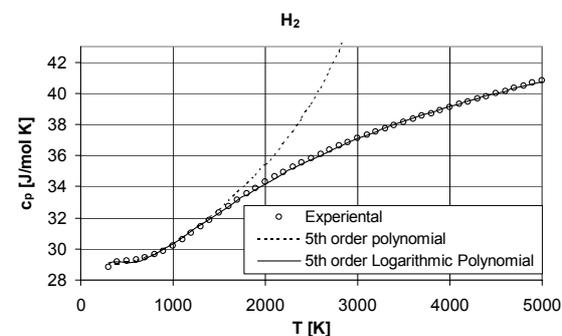


Figure 3. Comparison between a fifth order polynomial and a fifth order logarithmic polynomial.

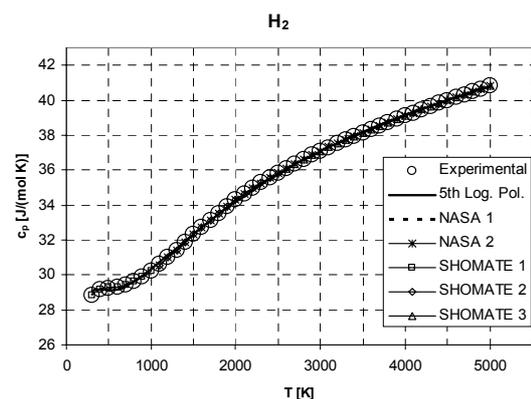


Figure 4. Comparison for hydrogen between mathematical functions and experimental data.

In *Figure 4* the comparison is performed between the logarithmic polynomial (six terms), other mathematical functions (Gordon and McBride, 1971, Chase, 1998) and experimental data (Gurvich et al., 1978). In Gordon and McBride (1971) two polynomials (the functional

form is $c_p(T) = \sum_{i=-2}^4 a_i T^i$ - seven terms) have

been used to cover the temperature range from 100 K to 5000 K (one from 100 K to 1000 K, and another from 1100 K to 5000 K), while, as reported by Chase (1998), three Shomate polynomials (the functional form is

$$c_p(T) = \left\{ \left[\sum_{i=0}^3 a_i (T/1000)^i \right] + a_4 / (T/1000)^2 \right\} -$$

five terms) have been used to cover the temperature range from 298 K to 5000 K (one from 298 K to 1000 K, another from 1100 K to 2500 K, and the last from 2600 K to 5000 K). Although only one logarithmic polynomial has been used to cover the entire temperature range, the interpolation furnishes a very low error (see *Figure 1*), comparable with the errors from the other two interpolations. A direct comparison between the different polynomials used in *Figure 4* doesn't represent a significant confrontation. In fact, starting from the same experimental data, a correct comparison between different polynomials must be effected between polynomials with the same numbers of order (fifth order with fifth order, sixth order with sixth order, etc.), and the same number of terms, because the precision of the fit depends on the order of the polynomial and on the number of terms.

4. Thermodynamic Models for an Unburned Mixture

In order to obtain the thermodynamic properties of the mixture for an unburned gas (Heywood, 1998), a summation of the thermodynamic properties of the gases constituting the mixture must be carried out, as shown (Bucker et al., 2003) in Equations (12) – (14):

$$\tilde{c}_{p,mix}(T^*) = \sum_{k=1}^{n.gases} x_k \tilde{c}_{p,k}(T^*) \quad (12)$$

$$\tilde{h}_{mix}(T^*) = \sum_{k=1}^{n.gases} x_k \tilde{h}_k(T^*) \quad (13)$$

$$\tilde{s}_{mix}(T^*, p^*) = \sum_{k=1}^{n.gases} x_k \tilde{s}_k(T^*, p^*) + \Delta \tilde{s}_{mix} \quad (14)$$

with the entropy of mixing

$$\Delta \tilde{s}_{mix} = -\tilde{R} \sum_{k=1}^{n.gases} x_k \ln x_k \quad (15)$$

In Equations (12) – (15) the subscript k denotes the single gas and x_k indicates the molar fraction of the single gas.

5. Dissociation and Equilibrium Constants

The natural logarithm of the equilibrium constant ($\ln K_p$) of a thermochemical dissociation reaction is defined as (Strehlow, 1985)

$$\ln K_p = -\frac{1}{T_0 \tilde{R}} \frac{1}{T^*} \sum_{i=1}^s v_i \tilde{g}_i(T^*, p^*) \quad (16)$$

the subscript “ i ” refers to the i^{th} specie of the dissociation reaction, with the convention that v_i is negative for the dissociation reaction reactant species (the species that appears on the left in the reactions of TABLE III). The Gibbs function $\tilde{g}(T^*, p^*)$ is expressed in Equation (17).

$$\tilde{g}(T^*, p^*) = \tilde{h}(T^*) - T_0 T^* \tilde{s}(T^*, p^*) \quad (17)$$

Substituting Equations (9) and (10) in Equation (17) the Gibbs function assumes the functional form of Equation (18).

$$\tilde{g}(T^*, p^*) = T_0 T^* \left\{ \left[\sum_{j=0}^6 g_j (\ln T^*)^j \right] + g_7 \right\} + g_8 \quad (18)$$

where g_j (for $0 \leq j \leq 8$) are the Gibbs function coefficients, defined below;

$$g_j = b_j - c_j \quad (\text{for } 0 \leq j \leq 5; c_0=0)$$

$$g_6 = -c_6$$

$$g_7 = \tilde{R} \ln p^* - \tilde{s}(1, 1) \quad (19)$$

$$g_8 = b_0 + \Delta \tilde{h}_f^0$$

Considering Equations (4) and (7) the g_j coefficients are valuable directly from the a_i coefficients and from thermodynamic data at reference conditions.

Evaluating the g_j coefficients, Equation (16) has been applied for the reaction in TABLE III, and a comparison has been effected with the data present in JANAF Thermochemical Tables (1971), and shown in *Figure 5*.

The comparison has evidenced the perfect matching between the logarithmic polynomial simulation and the data found in scientific literature (JANAF Thermochemical Tables, 1971).

6. Lean and Rich Combustion Applications

In the combustion process, the x_k can be evaluated applying the equilibrium thermodynamics equations (Olikara and Borman, 1975), based on atomic balance and equilibrium constants.

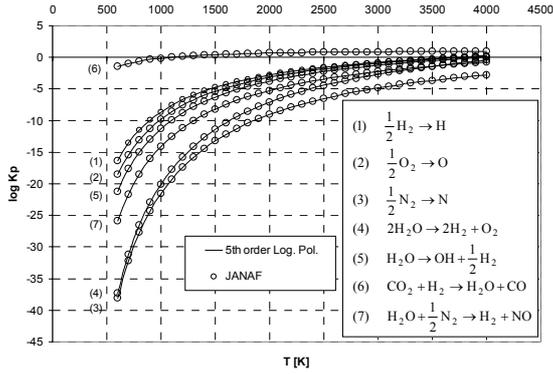


Figure 5. Comparison between $\log_{10} K_p$ evaluated with the 5th order logarithmic polynomial and the data present in scientific literature [1].

As an example of combustion phenomena, the oxidation of methane with technical air, with the following equivalence ratio $\Phi = 0.8, 1.0, 1.2$, has been considered. Furthermore the following combustion pressures $p = 1, 10$ and 100 bar have been considered.

The simulation results have been compared with those carried out from the CEA program (Chemical Equilibrium with Application), furnished by NASA (Gordon and McBride, 1994).

The enthalpy of mixture has been evaluated in Equation (20):

$$h_{\text{mix}}(T^*) = \frac{\sum_{k=1}^{\text{n.gases}} x_k(T^*) \tilde{h}_k(T^*)}{\sum_{k=1}^{\text{n.gases}} x_k(T^*) M_k} \quad (20)$$

The molar fractions vary significantly with temperature (when it reaches high values about greater than 1500 K) and with pressure.

In Figures 6 and 7 the comparison between the simulation with the logarithmic polynomials and the data carried out from the CEA-NASA program is shown. In these figures the mixture enthalpy is evaluated, and it is possible to notice the good agreement with the CEA-NASA results. For the evaluation of mixture isobaric specific heat, it is necessary to take into account the variability with the temperature of the molar fractions. Applying the specific heat at constant pressure definition, it is possible to obtain:

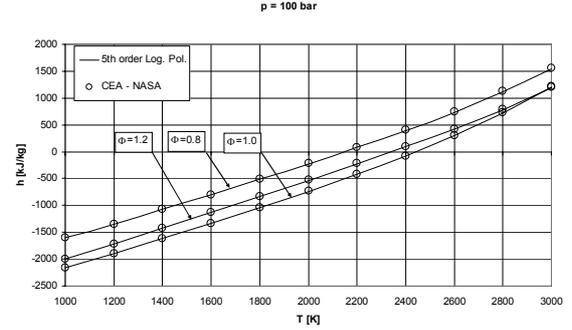


Figure 6. Mixture enthalpy at $p = 100$ bar and $\Phi = 0.8, 1.0$ and 1.2 .

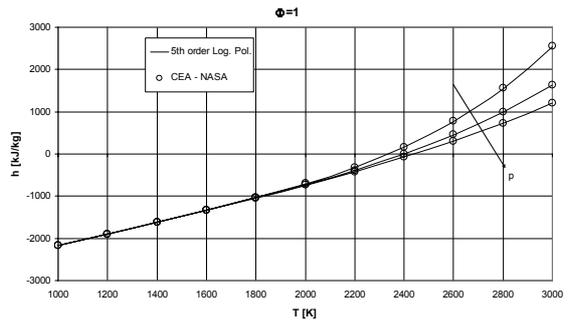


Figure 7. Mixture enthalpy at $\Phi = 1.0$ and $p = 1$ bar, 10 bar and 100 bar.

$$\tilde{c}_{p, \text{mix}}(T^*) = \frac{d\tilde{h}_{\text{mix}}}{dT^*} = \quad (21)$$

$$= \sum_{k=1}^{\text{n.gases}} x_k \tilde{c}_{p, k}(T^*) + \sum_{k=1}^{\text{n.gases}} \frac{dx_k}{dT^*} \tilde{h}_k(T^*)$$

The shifting equilibrium value of $\tilde{c}_{p, \text{mix}, e}$ may be expressed as the sum of a “frozen” contribution, $\tilde{c}_{p, \text{mix}, f}$, and a “reaction” contribution $\tilde{c}_{p, \text{mix}, r}$ as follows:

$$\tilde{c}_{p, \text{mix}}(T^*) = \tilde{c}_{p, \text{mix}, e} = \tilde{c}_{p, \text{mix}, f} + \tilde{c}_{p, \text{mix}, r} \quad (22)$$

with

$$\tilde{c}_{p, \text{mix}, f} = \sum_{k=1}^{\text{n.gases}} x_k \tilde{c}_{p, k}(T^*)$$

$$\tilde{c}_{p, \text{mix}, r} = \sum_{k=1}^{\text{n.gases}} \frac{dx_k}{dT^*} \tilde{h}_k(T^*)$$

The isobaric specific heat, represented in Figures 9 and 10, is shown in Equation (23)

$$c_{p, \text{mix}}(T^*) = \frac{\sum_{k=1}^{\text{n.gases}} x_k \tilde{c}_{p, k}(T^*) + \sum_{k=1}^{\text{n.gases}} \frac{dx_k}{dT^*} \tilde{h}_k(T^*)}{\sum_{k=1}^{\text{n.gases}} x_k(T^*) M_k} \quad (23)$$

The last term in Equations (21) and (22) is always equal to zero for frozen composition

($dx_k/dT^* = 0$). The results are shown in Figures 8 and 9.

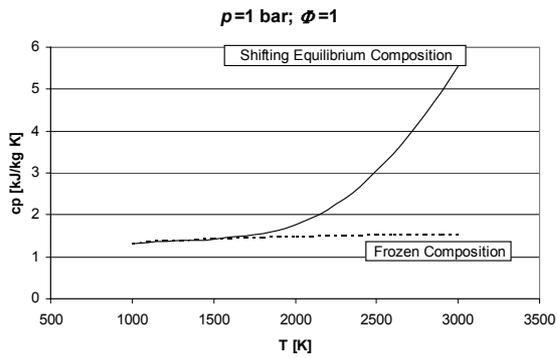


Figure 8. Mixture c_p at $p = 1$ bar and $\Phi=1.0$ – frozen and shifting equilibrium composition.

In Figure 8 the difference between the isobaric specific heat for frozen composition and for shifting equilibrium composition is shown. In Figure 9 a comparison has been performed between logarithmic polynomial and CEA-NASA results.

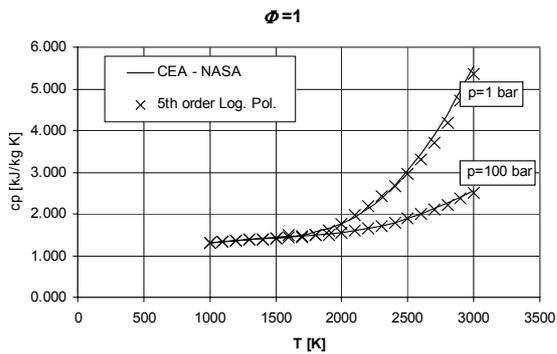


Figure 9. Mixture c_p at $p = 1$ and 100 bar; $\Phi = 1.0$.

The comparisons are relative to CH_4 combustion at the pressure of 1 bar and 100 bar at the equivalence ratio $\Phi=1$. For the evaluation of mixture entropy, the relationship in Equation (24) has been implemented.

$$s_{\text{mix}}(T^*, p^*) = \frac{\sum_{k=1}^{n.\text{gases}} x_k(T^*) \tilde{s}_k(T^*, p^*) + \Delta \tilde{s}_{\text{mix}}}{\sum_{k=1}^{n.\text{gases}} x_k(T^*) M_k} \quad (24)$$

In Figures 10 and 11 the entropy of the mixture has been evaluated, and it is possible to notice the good agreement between the fifth order logarithmic polynomial and the CEA – NASA program.

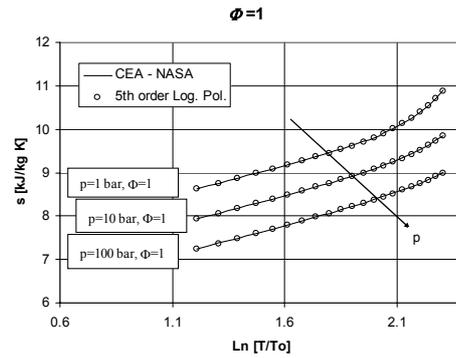


Figure 10. Mixture entropy at $p = 1, 10$ and 100 bar and $\Phi=1.0$.

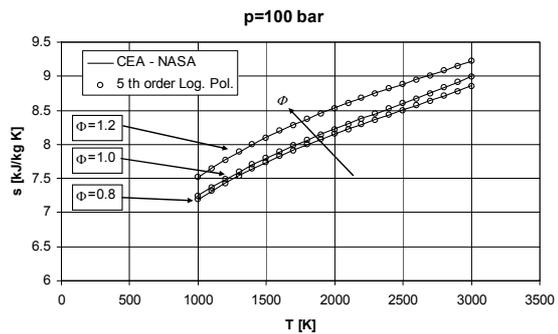


Figure 11. Mixture entropy at $p = 100$ bar and $\Phi = 0.8, 1.0, 1.2$.

7. Conclusion

Fifth order logarithmic polynomials have been implemented to study thermodynamic properties for unburned and burned mixtures. These polynomials have several advantages with respect to other models utilized in scientific literature. With one single polynomial it is possible to cover a wide range of temperatures; the logarithmic polynomial has very low errors in respect to experimental data. The logarithmic polynomials have been utilized to describe thermodynamic properties of gases, mixtures and equilibrium constants of practical interest for ICE combustion phenomena. The coefficients of the logarithmic polynomials have been evaluated through the least squares fit, on the basis of experimental data found in scientific literature. A comparison has been carried out between the simulated results and the most accredited CEA-NASA equilibrium code. The comparison has shown a perfect matching between the CEA-NASA program and the logarithmic polynomial simulation, and it has been implemented in the calculation of thermodynamic properties of the products of combustion of methane with technical air, at different fuel-to-air equivalence ratio and for different combustion pressures.

Nomenclature

p_0	reference pressure 101325 Pa
P	pressure [Pa]
p^*	p/p_0
T_0	reference temperature 298.15 K
T	temperature [K]
T^*	T/T_0
a_i	coefficients of $\tilde{c}_p(T^*)$
b_i	$\tilde{h}(T^*)$ coefficients
c_i	$\tilde{s}(T^*, p^*)$ coefficients
\tilde{c}_p	molar specific heat at constant pressure [J mol ⁻¹ K ⁻¹]
c_p	specific heat at constant pressure [J kg ⁻¹ K ⁻¹]
\tilde{g}	Gibbs function [J mol ⁻¹]
g_j	Gibbs function coefficients
h_0	molar enthalpy at $T=T_0$
\tilde{h}	molar enthalpy [J mol ⁻¹]
h	enthalpy [J kg ⁻¹]
ICE	internal combustion engine
K_p	equilibrium constant
n.gases	number of gases present in the mixture
M	molecular weight
\tilde{R}	universal gas constant 8.314472 [J mol ⁻¹ K ⁻¹]
R^2	correlation factor
\tilde{s}_0	molar entropy for $p=p_0$ and $T=T_0$
\tilde{s}	molar entropy [J mol ⁻¹ K ⁻¹]
s	entropy [J kg ⁻¹ K ⁻¹]
x	molar fraction
Φ	fuel to air equivalence ratio
v_i	dissociation reaction stoichiometric coefficient
$\Delta\tilde{s}_{mix}$	entropy of mixing

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TABLE I: LOGARITHMIC POLYNOMIAL COEFFICIENTS FOR $\tilde{c}_p(T^*)$ ($\tilde{c}_p = [J/(mol K)]$) ($100 \leq T \leq 5000 K$).

Species	a ₅	a ₄	a ₃	a ₂	a ₁	a ₀	R ²
O ₂	0.06180721	-0.15731959	-0.46630845	1.94145005	2.70119522	29.51785250	0.99864
O	0.07027490	-0.31136053	0.28282306	0.69409831	-1.70433174	21.93889086	0.99943
N ₂	0.21448719	-1.19546050	1.08309312	2.86102669	-0.21824417	28.87396814	0.99941
N	0.14239267	-0.47731848	0.14265183	0.65286173	-0.32933464	20.71144423	0.99447
H ₂	-0.15719883	0.59756168	0.01975705	-0.16827168	1.14285222	28.45084504	0.99786
H	0.00000000	0.00000000	0.00000000	0.00000000	0.00000000	20.78600000	1.00000
Ar	0.00000000	0.00000000	0.00000000	0.00000000	0.00000000	20.78600000	1.00000
H ₂ O	0.14904476	-1.35853914	2.19675399	4.39059147	0.30777852	33.36570240	0.99957
OH	0.03478011	-0.50597218	1.13636273	1.96908941	-2.38685363	29.88074938	0.99849
CO ₂	0.09995132	0.00042527	-2.46535403	3.28070636	13.60436265	37.10227658	0.99997
CO	0.22518502	-1.18879042	0.88803413	2.99191804	0.18922297	28.92502641	0.99955
NO	0.22148616	-1.05253689	0.26215865	3.81009255	-0.18819240	29.74540076	0.99931

TABLE II. ENTHALPY OF FORMATION AND ENTROPY AT STANDARD TEMPERATURE AND PRESSURE (T₀=298.15 K; P₀=101325 Pa), FOR ALL THE 12 GASES.

Species	$\tilde{\Delta h}_f^o$ [J/mol]	$\tilde{s}(1,1)$ [J/(mol K)]
CO	-110530	197.54
CO ₂	-393520	213.69
H ₂ O	-241830	188.72
H ₂	0	130.57
OH	38990	183.6
O ₂	0	205.04
O	249170	160.95
H	218000	114.61
N ₂	0	191.5
NO	90290	210.65
N	472690	153.19
Ar	0	154.74

TABLE III. THERMOCHEMICAL DISSOCIATION REACTIONS.

- (1) $\frac{1}{2}H_2 \rightarrow H$
- (2) $\frac{1}{2}O_2 \rightarrow O$
- (3) $\frac{1}{2}N_2 \rightarrow N$
- (4) $2H_2O \rightarrow 2H_2 + O_2$
- (5) $H_2O \rightarrow OH + \frac{1}{2}H_2$
- (6) $CO_2 + H_2 \rightarrow H_2O + CO$
- (7) $H_2O + \frac{1}{2}N_2 \rightarrow H_2 + NO$