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A STUDY OF THE THERMODYNAMIC FUNCTIONS OF THE COMBUSTION PRODUCTS OF COMPOSITE PROPELLANTS

Sixth–order polynomials were determined to approximate the values of the standard state molar enthalpies of the gaseous combustion products of composite propellants over two temperature ranges (from 298.15 to 1000K, and from 1000 to 5000K) and fourth–order polynomials for the condensed products over specified temperature ranges. The polynomial coefficients were tabulated for 47 chemical species. From their relations with the molar enthalpy expressions for the heat capacity and entropy were derived. The accuracy of the approximation was estimated and compared with other available reference data. It has shown that the approximation accuracy was improved.

Thermochemical tables containing data at discrete values of temperature are unsuitable for direct use in computer calculations. To enable that the consistent data published in the JANAF tables [1] can be used in computer studies of combustion systems, such as composite rocket propellants, a continuous representation of the standard state molar enthalpy of each combustion product as a function of temperature was derived by fitting the tabulated data, and it was shown that these approximations, combined with standard entropies and specific heats, were sufficient to determine all the remaining thermochemical properties. These approximations gave a consistent set of data, of which the accuracy had to be comparable to the number of significant figures given in the tabulated values.

A typical composite rocket propellant contains C, H, N, O, Cl and Al as constitutive chemical elements. Hence, the combustion products consist of the given six elements or contain them in a bounded form. Gaseous atomic species, gaseous complex chemical species (some of them can simultaneously exist in the condensed phase) and condensed chemical species can then coexist in the combustion products of composite propellants. There may be more than 70 species in this reactive mixture [2–4]. The most probable chemical species which can be formed from the atoms of the propellants and which can exist under the conditions of combustion must be known or postulated.

Although there is no serious difficulty to analyze such a reactive system with, for example, more than 70 chemical species, except, perhaps the availability of thermodynamic data for some mixture components, it was assumed in this paper that the combustion products consist of 47 components, which are presented in Table 1.

In this case all the products are gaseous except Al_2O_3 (the chamber reaction gases contain liquid aluminum oxide and the colder gases in the nozzle exhaust contain solid, condensed aluminum oxide particles).

For each combustion product the thermochemical data, required in studies of combustion systems, are its standard enthalpy of formation at the reference temperature and its enthalpy change, heat capacity and entropy as functions of temperature over a wide range (at least 500–4000 K). Fortunately, there is virtually no problem in obtaining these data for the combustion products because the JANAF tables contain a critically evaluated and internally consistent set. The data are presented in tabular form.

The numerous data for the combustion products fitted to the empirical equations are available from different sources [5–8]. However, the published empirical equations, of different degrees of accuracy, are commonly related to specific combustion systems and can be incomplete for some applications.

The aim of this study was to find equations with a higher degree of accuracy for the considered combustion products.

Polynomials are most commonly used for data fitting by least squares methods. A single polynomial, however, can be insufficient to fit the whole range of temperature to the required accuracy. In references, different suggestions appear for polynomial degrees and/or temperature intervals of their validity, for example, fourth–order polynomial regression for the molar heat capacity data over two ranges 298.15K to 1000K and 1000K to 5000K [5] or 298.15 to 1500 and 1500 to 5000K [9], or sixth–order polynomial regression for these data over two ranges 298.15K to 2000K and 2000K to 6000K [6], or seventh–order polynomial regression for molar total enthalpy data over the single range of temperature 298.15 to 6000 [7], or fourth–order polynomial regression for the enthalpy change data over the single temperature range 1100 to 5000K [8].

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Table 1. Components of the combustion products of composite propellants

H_2	H_2O	H	OH	O	O_2	N_2	NO	N	NH	NH_2	NH_3
N_2O	NO_2	CO_2	CO	C	HCO	HCN	CH	CH_2	CH_3	CH_4	C_2H_2
HCl	Cl	Cl_2	ClO	ClO_2	Cl_2O	CClO	CCl	CCl_2	CCl_3	CCl_4	$Al_2O_{3(l)}$
$Al_2O_{3(s)}$	Al	AlO	Al_2O	AlO_2	AlOCl	AlCl	$AlCl_2$	$AlCl_3$	AlH	AlOH	AlO_2H

In this paper, for each combustion product (subscript *j*), the thermodynamic function, – standard state molar enthalpy, defined as the sum of two measurable values – the standard molar enthalpy of formation at the reference temperature and the enthalpy change from the reference temperature to the observed temperature: $h_j^o = \Delta_f h^o_{To,j} + h^o_{T,j} - h^o_{To,j}$, is given in the form of least squares coefficients as follows:

$$h_j^o(T) = a_{o,j} + \sum_{i=1}^{m} a_{i,j}\left(\frac{T}{1000}\right)^{i} \qquad (1)$$

where a_o and a_i are the least squares coefficients, i denotes the degree of the polynomial, m is the optimal degree of the polynomial with respect to the accuracy of approximation, and T is the absolute temperature.

Sixth–order polynomials were determined to approximate the data for gaseous species over two temperature ranges (from 298.15 to 1000K, and from 1000 to 5000K), and fourth–order polynomials for condensed species over a specified temperature range. Due to the phase transformation points, various polynomials were determined in different temperature ranges for condensed chemical species.

From their relations with the molar enthalpy, the standard state heat capacity and the entropy were derived.

The heat capacity was determined as:

$$c^o_{p,j}(T) = 0.001\sum_{i=1}^{m} i a_{i,j}\left(\frac{T}{1000}\right)^{i-1} \qquad (2)$$

The molar entropy was determined as:

$$s_j^o\,(T) = a_{s,j} + \\ + 0.001\left[a_{1,j}\,1n\left(\frac{T}{1000}\right) + \sum_{i=1}^{m}\frac{i}{i-1}a_{i,j}\left(\frac{T}{1000}\right)^{i-1}\right] \qquad (3)$$

where the integration constant $a_{s,j}$ was determined as the mean arithmetic value of all $a_{s,j,T}$:

$$a_{s,j,T} = s_j^o\,(T_{tab}) - \\ - 0.001\left[a_{1,j}\ln\left(\frac{T_{tab}}{1000}\right) + \sum_{i=1}^{m}\frac{i}{i-1}a_{i,j}\left(\frac{T_{tab}}{1000}\right)^{i-1}\right] \qquad (4)$$

where T_{tab} and s_j^o (T_{tab}) are the tabulated thermochemical data [1].

The molar enthalpy, heat capacity and entropy are sufficient to determine all the remaining properties, such as the free energy, the heat of reaction and the equilibrium constant.

The polynomial coefficients, temperature ranges (initial T_i and final T_f temperatures), standard deviations for the molar enthalpy approximations h_{SD} and for other thermodynamic functions calculated from the molar enthalpy polynomials (s_{SD} for entropy, cp_{SD} for heat capacity), and absolute errors of temperature ΔT are presented in Table 2 for selected combustion products.

The sixth–order was chosen because it gives excellent agreement between tabulated and calculated values. The obtained R–squared values for polynomial regression are very high, between 0.999–1.

The following equation was used to estimate the absolute errors of temperature, i.e. the accuracy of the approximation:

$$\Delta T = \frac{\Delta h_j^o}{c^o_{p,j}} \qquad (5)$$

where ΔT is the error of the argument, i.e. the difference between the observed and calculated temperature, Δh_j^o is the error of the function, i.e. the difference between the tabulated and calculated value (by polynomial) of the molar enthalpy for species j, and $c^o_{p,j}$ is the tabulated value of the molar heat capacity at the observed temperature.

The accuracy of the approximation defined by Eq.(5) allows the estimation of the error magnitude and the prediction of the influence of that error on the calculation of the combustion temperature.

As can be seen from Table 2, the standard deviations of the computed data from JANAF data range from 0.0009 to 0.0173 kJ/mol for the molar enthalpies, 0.0012 to 0.5367 J/molK for the entropies and 0.0064 to 0.3547 for the heat capacities. That means that these approximations give a consistent set of data, of which the accuracy is comparable to the number of significant figures given in the tabulated values. Furthermore, it can be seen from the given table, that the absolute errors of temperature are always lower than 0.5K for each combustion product. These absolute errors of temperature are much lower than the acceptance criterion defined as $\Delta T \leq 3$ [7].

The accuracy of the method was compared briefly with other approximations for one of the most important combustion product – CO. The results of our calculations and the corresponding comparative analysis are presented in Table 3. It is obvious that the accuracy of the applied method is better than those presented in the available references.

Table 2. Polynomial coefficients, temperature ranges, standard deviations of computed data from JANAF data and absolute errors of temperature

Label	M g/mol	Δ_{fh} kJ/mol	a_s J/molK	a_o kJ/mol	a_1 kJ/molK	a_2 kJ/molK^2	a_3 kJ/molK^3	a_4 kJ/molK^4	a_5 kJ/molK^5	a_6 kJ/molK^6	T_i K	T_f K	h_{SD} kJ/mol	s_{DV} J/molK	c_{pSD} J/molK	ΔT K
Al	26.982	326.539	$2.001363*10^{2}$	$3.197321*10^{2}$	$2.513723*10^{1}$	$-1.180909*10^{1}$	$1.691993*10^{1}$	$-1.221023*10^{1}$	3.488612	$1.144409*10^{-5}$	298	1000				
Al	26.982	326.539	$1.904439*10^{2}$	$3.202866*10^{2}$	$2.117849*10^{1}$	$-3.213343*10^{-1}$	$1.469291*10^{-1}$	$-3.541376*10^{-2}$	$3.849366*10^{-3}$	$-9.838006*10^{-5}$	1000	5000	0.0010	0.0016	0.0097	0.1138
Al_2O	69.962	–131.453	$2.854846*10^{2}$	$-1.431566*10^{2}$	$3.251241*10^{1}$	$1.991089*10^{1}$	$2.400992*10^{1}$	$-6.424964*10^{1}$	$5.118949*10^{1}$	$-1.453612*10^{1}$	298	1000				
Al_2O	69.962	–131.453	$3.142805*10^{2}$	$-1.482407*10^{2}$	$5.032159*10^{1}$	5.156563	–1.932630	$4.173803*10^{-1}$	$-4.823949*10^{-2}$	$2.309248*10^{-3}$	1000	5000	0.0016	0.0015	0.0202	0.0696
Al_2O_3(s)	101.960	–1676.3947	$-7.229168*10^{1}$	$-1.688460*10^{3}$	$-1.070485*10^{1}$	$2.211339*10^{2}$	$-1.770128*10^{2}$	$5.708727*10^{1}$			298	900				
Al_2O_3(s)	101.960	–1676.395	$1.579137*10^{2}$	$-1.713017*10^{3}$	$1.039042*10^{2}$	$1.205908*10^{1}$	–1.111035	$-1.984557*10^{-2}$			901	2315				
Al_2O_3(l)	101.960	–1563.020	$2.172891*10^{2}$	$-1.635533*10^{3}$	$1.398256*10^{2}$	2.626548	$-5.953707*10^{-1}$	$5.031731*10^{-2}$			2316	4000	0.0073	0.0115	0.2451	0.1765
AlCl	62.435	–51.493	$2.673859*10^{2}$	$-6.144203*10^{1}$	$3.283300*10^{1}$	–4.443984	$3.469882*10^{1}$	$-5.785373*10^{1}$	$4.213236*10^{1}$	$-1.162889*10^{1}$	298	1000				
AlCl	62.435	–51.493	$2.710950*10^{2}$	$-6.281483*10^{1}$	$3.660237*10^{1}$	$5.092418*10^{-1}$	$3.669088*10^{-2}$	$-4.735313*10^{-2}$	$1.013048*10^{-2}$	$-5.681439*10^{-4}$	1000	5000	0.0009	0.0017	0.0202	0.0533
$AlCl_2$	97.894	–313.980	$2.863622*10^{2}$	$-3.266310*10^{2}$	$2.706480*10^{1}$	$7.923779*10^{1}$	$-1.211445*10^{2}$	$1.101836*10^{2}$	$-5.501354*10^{1}$	$1.162888*10^{1}$	298	1000				
$AlCl_2$	97.894	–313.980	$3.521085*10^{2}$	$-3.313138*10^{2}$	$5.523020*10^{1}$	2.046113	$-7.951993*10^{-1}$	$1.768324*10^{-1}$	$-2.091211*10^{-2}$	$1.018934*10^{-3}$	1000	5000	0.0012	0.0013	0.0076	0.0490
$AlCl_3$	133.341	–584.840	$3.021518*10^{2}$	$-6.019606*10^{2}$	$3.369168*10^{1}$	$1.212103*10^{2}$	$-1.816088*10^{2}$	$1.639672*10^{2}$	$-8.198356*10^{1}$	$1.744331*10^{1}$	298	1000				
$AlCl_3$	133.341	–584.840	$4.037385*10^{2}$	$-6.095639*10^{2}$	$7.783127*10^{1}$	3.605825	–1.389538	$3.072889*10^{-1}$	$-3.622130*10^{-2}$	$1.761822*10^{-3}$	1000	5000	0.0014	0.0013	0.0095	0.0364
AlH	27.988	259.557	$2.430709*10^{2}$	$2.502801*10^{2}$	$3.596717*10^{1}$	$-3.101100*10^{1}$	$6.576070*10^{1}$	$-6.337739*10^{1}$	$3.045872*10^{1}$	–5.814440	298	1000				
AlH	27.988	259.557	$2.150587*10^{2}$	$2.506940*10^{2}$	$2.642243*10^{1}$	7.155321	–2.479298	$5.248740*10^{-1}$	$-5.979638*10^{-2}$	$2.829573*10^{-3}$	1000	5000	0.0016	0.0017	0.0153	0.1230
AlO	42.981	83.728	$2.465935*10^{2}$	$7.527112*10^{1}$	$2.632308*10^{1}$	3.228668	$2.080694*10^{1}$	$-3.546808*10^{1}$	$2.374975*10^{1}$	–5.814439	298	1000				
AlO	42.981	83.728	$2.695259*10^{2}$	$7.255346*10^{1}$	$3.895210*10^{1}$	$-1.029439*10^{1}$	9.537445	–3.039747	$4.322618*10^{-1}$	$-2.334651*10^{-2}$	1000	5000	0.0103	0.0048	0.0774	0.4921
AlO_2	58.980	–184.219	$2.510014*10^{2}$	$-1.957753*10^{2}$	$2.627530*10^{1}$	$5.219287*10^{1}$	$-3.477502*10^{1}$	–1.453650	$1.489395*10^{1}$	–5.814449	298	1000				
AlO_2	58.980	–184.219	$3.044926*10^{2}$	$-2.022468*10^{2}$	$5.395384*10^{1}$	5.477521	–2.023263	$4.235572*10^{-1}$	$-4.662450*10^{-2}$	$2.149147*10^{-3}$	1000	5000	0.0015	0.0016	0.0204	0.0600
AlO_2H	59.988	–460.504	$2.349705*10^{2}$	$-4.711694*10^{2}$	$1.697529*10^{1}$	$7.974614*10^{1}$	$-6.285779*10^{1}$	$2.238547*10^{1}$	2.348224	–2.907240	298	1000				
AlO_2H	59.988	–460.504	$3.020410*10^{2}$	$-4.785103*10^{2}$	$5.039436*10^{1}$	$1.726211*10^{1}$	–5.617200	1.101437	$-1.188688*10^{-1}$	$5.409263*10^{-3}$	1000	5000	0.0015	0.0017	0.0171	0.0491
AlOCl	78.437	101.269	$2.130471*10^{2}$	$-3.589987*10^{2}$	$1.283194*10^{1}$	$1.172198*10^{2}$	$-1.750181*10^{2}$	$1.596064*10^{2}$	$-8.091016*10^{1}$	$1.744332*10^{1}$	298	1000				
AlOCl	78.437	101.269	$3.104854*10^{2}$	$-3.665211*10^{2}$	$5.548703*10^{1}$	4.639409	–1.783707	$3.931968*10^{-1}$	$-4.616316*10^{-2}$	$2.235249*10^{-3}$	1000	5000	0.0014	0.0015	0.0152	0.0604
AlOH	43.989	–180.015	$2.932776*10^{2}$	$-1.897330*10^{2}$	$4.232040*10^{1}$	$-8.023184*10^{1}$	$2.289182*10^{2}$	$-2.788027*10^{2}$	$1.681269*10^{2}$	$-4.070112*10^{1}$	298	1000				
AlOH	43.989	–180.015	$2.375305*10^{2}$	$-1.908893*10^{2}$	$2.774903*10^{1}$	$1.767887*10^{1}$	–5.615312	1.081139	$-1.151405*10^{-1}$	$5.192050*10^{-3}$	1000	5000	0.0016	0.0017	0.0259	0.0606
C	12.011	715.482	$2.104822*10^{2}$	$7.083193*10^{2}$	$3.037015*10^{1}$	$-4.124928*10^{1}$	$9.169012*10^{1}$	$-1.107649*10^{2}$	$6.910226*10^{1}$	$-1.744329*10^{1}$	298	1000				
C	12.011	715.482	$1.831439*10^{2}$	$7.091531*10^{2}$	$2.083651*10^{1}$	$2.023435*10^{-1}$	$-2.817401*10^{-1}$	$1.319622*10^{-1}$	$-2.211064*10^{-2}$	$1.296376*10^{-3}$	1000	5000	0.0013	0.0017	0.0201	0.1335
C_2H_2	26.038	226.883	$6.362939*10^{1}$	$2.215814*10^{2}$	$-2.786798*10^{1}$	$2.467093*10^{2}$	$-4.285331*10^{2}$	$4.535267*10^{2}$	$-2.583626*10^{2}$	$6.105167*10^{1}$	298	1000				
C_2H_2	26.038	226.883	$2.262549*10^{2}$	$2.145130*10^{2}$	$3.359160*10^{1}$	$2.640702*10^{1}$	–7.662560	1.388049	$-1.398672*10^{-1}$	$6.003772*10^{-3}$	1000	5000	0.0013	0.0021	0.0689	0.0391
CCl	47.464	502.416	$2.421785*10^{2}$	$4.937765*10^{2}$	$2.380145*10^{1}$	$2.407655*10^{1}$	$-3.269416*10^{1}$	$3.372389*10^{1}$	$-2.133460*10^{1}$	5.814457	298	1000				
CCl	47.464	502.416	$2.625579*10^{2}$	$4.915593*10^{2}$	$3.369183*10^{1}$	2.638842	$-8.908839*10^{-1}$	$1.802493*10^{-1}$	$-1.860241*10^{-2}$	$8.026216*10^{-4}$	1000	5000	0.0012	0.1698	0.0132	0.0648
CCl_2	82.917	238.648	$2.471140*10^{2}$	$2.283020*10^{2}$	$1.696607*10^{1}$	$8.453436*10^{1}$	$-1.049824*10^{2}$	$7.442497*10^{1}$	$-2.542706*10^{1}$	2.907234	298	1000				
CCl_2	82.917	238.648	$2.791916*10^{2}$	$2.335777*10^{2}$	$2.012485*10^{1}$	$3.239901*10^{1}$	$-1.116884*10^{1}$	1.989489	$-1.788913*10^{-1}$	$6.355894*10^{-3}$	1000	5000	0.0073	0.0048	0.0504	0.3474
CCl_3	118.370	79.549	$2.532190*10^{2}$	$6.614843*10^{1}$	$1.624242*10^{1}$	$1.399588*10^{2}$	$-1.869807*10^{2}$	$1.549550*10^{2}$	$-7.238984*10^{1}$	$1.453611*10^{1}$	298	1000				
CCl_3	118.370	79.549	$3.746875*10^{2}$	$5.542103*10^{1}$	$7.181155*10^{1}$	7.546136	–2.872423	$6.283242*10^{-1}$	$-7.333725*10^{-2}$	$3.535338*10^{-3}$	1000	5000	0.0018	0.0017	0.0164	0.0564
CCl_4	153.823	–96.045	$2.122391*10^{2}$	$-1.122723*10^{2}$	7.049860	$2.432604*10^{2}$	$-3.713557*10^{2}$	$3.485759*10^{2}$	$-1.826183*10^{2}$	$4.070111*10^{1}$	298	1000				
CCl_4	153.823	–96.045	$4.137768*10^{2}$	$-1.277429*10^{2}$	$9.501384*10^{1}$	8.757476	–3.344605	$7.332475*10^{-1}$	$-8.573406*10^{-2}$	$4.139540*10^{-3}$	1000	5000	0.0023	0.5367	0.0736	0.0467
CClO	63.464	–62.796	$3.278503*10^{2}$	$-7.595891*10^{1}$	$4.608634*10^{1}$	$-2.374495*10^{1}$	$8.643325*10^{1}$	$-1.171611*10^{2}$	$7.735448*10^{1}$	$-2.035056*10^{1}$	298	1000				
CClO	63.464	–62.796	$3.118756*10^{2}$	$-7.712962*10^{1}$	$4.331221*10^{1}$	9.155120	–3.304209	$6.955337*10^{-1}$	$-7.887956*10^{-2}$	$3.719526*10^{-3}$	1000	5000	0.0018	0.0017	0.0379	0.0655
CH	13.019	594.526	$2.411414*10^{2}$	$5.849924*10^{2}$	$3.728513*10^{1}$	$-3.365593*10^{1}$	$7.190208*10^{1}$	$-8.518146*10^{1}$	$5.494642*10^{1}$	$-1.453609*10^{1}$	298	1000				
CH	13.019	594.526	$2.031832*10^{2}$	$5.898057*10^{2}$	$1.820273*10^{1}$	9.084051	–1.300899	$-6.521027*10^{-2}$	$3.682541*10^{-2}$	$-2.754436*10^{-3}$	1000	5000	0.0031	0.0022	0.0330	0.2303
CH_2	14.027	385.479	$2.145545*10^{2}$	$3.770235*10^{2}$	$2.749398*10^{1}$	$-1.029853*10^{1}$	$6.396722*10^{1}$	$-8.605366*10^{1}$	$5.601987*10^{1}$	$-1.453610*10^{1}$	298	1000				
CH_2	14.027	385.479	$1.877787*10^{2}$	$3.790126*10^{2}$	$1.619447*10^{1}$	$2.515155*10^{1}$	–8.182920	1.602366	$-1.723454*10^{-1}$	$7.801010*10^{-3}$	1000	5000	0.0020	0.0119	0.0179	0.0767
CH_3	15.035	145.784	$2.504754*10^{2}$	$1.347323*10^{2}$	$3.966478*10^{1}$	$-3.224139*10^{1}$	$1.132816*10^{2}$	$-1.418724*10^{2}$	$9.016859*10^{1}$	$-2.325777*10^{1}$	298	1000				
CH_3	15.035	145.784	$1.993298*10^{2}$	$1.389381*10^{2}$	$1.735424*10^{1}$	$3.241731*10^{1}$	–9.881646	1.825646	$-1.870250*10^{-1}$	$8.140019*10^{-3}$	1000	5000	0.0014	0.0015	0.0312	0.0495
CH_4	16.043	–74.916	$2.795763*10^{2}$	$-8.601985*10^{1}$	$5.004938*10^{1}$	$-9.688554*10^{1}$	$2.468473*10^{2}$	$-2.604871*10^{2}$	$1.417606*10^{2}$	$-3.197945*10^{1}$	298	1000				
CH_4	16.043	–74.916	$1.578952*10^{2}$	$-7.966828*10^{1}$	1.629843	$5.642420*10^{1}$	$-1.830929*10^{1}$	3.564722	$-3.814133*10^{-1}$	$1.720779*10^{-2}$	1000	5000	0.0042	0.0024	0.0328	0.1064
Cl	35.457	121.079	$1.602422*10^{2}$	$1.157829*10^{2}$	$1.023265*10^{1}$	$4.223894*10^{1}$	$-7.748625*10^{1}$	$8.227443*10^{1}$	$-4.776792*10^{1}$	$1.162889*10^{1}$	298	1000				
Cl	35.457	121.079	$1.958493*10^{2}$	$1.135574*10^{2}$	$2.492141*10^{1}$	–2.139982	$6.845102*10^{-1}$	$-1.319148*10^{-1}$	$1.402017*10^{-2}$	$-6.300979*10^{-4}$	1000	5000	0.0010	0.0015	0.0151	0.1006
Cl_2	70.914	0.000	$2.415275*10^{2}$	–9.088849	$2.507481*10^{1}$	$2.610154*10^{1}$	$-3.397577*10^{1}$	$2.820006*10^{1}$	$-1.361922*10^{1}$	2.907223	298	1000				
Cl_3	70.914	0.000	$2.610559*10^{2}$	$-1.039277*10^{1}$	$3.343885*10^{1}$	4.030039	–1.934327	$5.242096*10^{-1}$	$-6.857414*10^{-2}$	$3.437961*10^{-3}$	1000	5000	0.0011	0.0015	0.0170	0.0643
Cl_2O	86.905	87.923	$3.274220*10^{2}$	$7.071270*10^{1}$	$5.293273*10^{1}$	3.519939	–1.336871	$2.914265*10^{-1}$	$-3.389352*10^{-2}$	$1.628878*10^{-3}$	1000	5000				
Cl_2O	86.905	87.923	$2.356120*10^{2}$	$7.749266*10^{1}$	$1.336934*10^{1}$	$1.127868*10^{2}$	$-1.805641*10^{2}$	$1.785035*10^{2}$	$-9.875612*10^{1}$	$2.325778*10^{1}$	298	1000	0.0013	0.0014	0.0208	0.0508
ClO	51.457	101.279	$2.376485*10^{2}$	$9.325170*10^{1}$	$2.049224*10^{1}$	$2.877755*10^{1}$	$-2.911941*10^{1}$	$1.657119*10^{1}$	–4.025399	$3.337860*10^{-6}$	298	1000				
ClO	51.457	101.279	$2.643166*10^{2}$	$9.037213*10^{1}$	$3.361208*10^{1}$	2.705407	$-9.144524*10^{-1}$	$1.935448*10^{-1}$	$-2.181994*10^{-2}$	$1.015496*10^{-3}$	1000	5000	0.0021	0.0014	0.0145	0.2883
ClO_2	67.457	104.670	$7.681500*10^{2}$	$7.845193*10^{1}$	$1.997488*10^{2}$	$-7.252748*10^{2}$	$1.679883*10^{3}$	$-2.047644*10^{3}$	$1.276080*10^{3}$	$-3.206666*10^{2}$	298	1000				
ClO_2	67.457	104.670	$3.046047*10^{2}$	$8.855680*10^{1}$	$4.612040*10^{1}$	8.322578	–3.007887	$6.539366*10^{-1}$	$-7.588707*10^{-2}$	$3.638394*10^{-3}$	1000	5000	0.0033	0.0120	0.3547	0.2207
CO	28.011	–110.605	$2.338206*10^{2}$	$-1.193469*10^{2}$	$2.955904*10^{1}$	$2.045005*10^{-1}$	–8.671022	$2.325775*10^{1}$	$-1.972437*10^{1}$	5.814442	298	1000				
CO	28.011	–110.605	$2.233795*10^{2}$	$-1.185322*10^{2}$	$2.445455*10^{1}$	6.955992	–2.144340	$3.899236*10^{-1}$	$-3.807016*10^{-2}$	$1.541897*10^{-3}$	1000	6000	0.0023	0.0016	0.0146	0.1513

Label	M g/mol	Δ_{fh} kJ/mol	a_s J/molK	a_o kJ/mol	a_1 kJ/molK	a_2 kJ/molK^2	a_3 kJ/molK^3	a_4 kJ/molK^4	a_5 kJ/molK^5	a_6 kJ/molK^6	T_i K	T_f K	h_{SD} kJ/mol	s_{DV} J/molK	c_{pSD} J/molK	ΔT K
CO_2	44.010	–393.748	$2.099781*10^{2}$	$-4.021944*10^{2}$	$1.689833*10^{1}$	$4.846865*10^{1}$	$-4.026840*10^{1}$	$2.267624*10^{1}$	–5.903848	$-1.430511*10^{-5}$	298	1000				
CO_2	44.010	–393.748	$2.471522*10^{2}$	$-4.077258*10^{2}$	$3.713708*10^{1}$	$1.387855*10^{1}$	–4.362022	$8.089478*10^{-1}$	$-8.049165*10^{-2}$	$3.327156*10^{-3}$	1000	6000	0.0051	0.0031	0.0353	0.2193
H	1.008	218.111	$1.360583*10^{2}$	$2.120544*10^{2}$	$1.940247*10^{1}$	5.068098	–8.646081	6.977381	–2.146897	$4.768372*10^{-6}$	298	1000				
H	1.008	218.111	$1.398263*10^{2}$	$2.119195*10^{2}$	$2.078197*10^{1}$	$1.242432*10^{-2}$	$-5.066339*10^{-3}$	$1.198200*10^{-3}$	$-1.529686*10^{-4}$	$8.051840*10^{-6}$	1000	6000	0.0011	0.0013	0.0070	0.0935
H_2	2.016	0.000	$1.411283*10^{2}$	–7.698092	$1.992449*10^{1}$	$3.353000*10^{1}$	$-6.171220*10^{1}$	$6.076095*10^{1}$	$-2.992203*10^{1}$	5.814445	298	1000				
H_2	2.016	0.000	$1.585824*10^{2}$	–5.888031	$2.290067*10^{1}$	4.188385	$-4.954111*10^{-1}$	$6.573860*10^{-3}$	$6.021466*10^{-3}$	$-4.752492*10^{-4}$	1000	6000	0.0059	0.0029	0.0347	0.4701
H_2O	18.016	–241.965	$2.732766*10^{2}$	$-2.532341*10^{2}$	$4.849935*10^{1}$	$-6.919984*10^{1}$	$1.575018*10^{2}$	$-1.851901*10^{2}$	$1.147235*10^{2}$	$-2.907223*10^{1}$	298	1000				
H_2O	18.016	–241.965	$2.072350*10^{2}$	$-2.475261*10^{2}$	$1.952491*10^{1}$	$1.502932*10^{1}$	–3.437288	$4.857704*10^{-1}$	$-3.842940*10^{-2}$	$1.308463*10^{-3}$	298	6000	0.0027	0.0021	0.0713	0.2054
HCl	36.465	–92.365	$2.293977*10^{2}$	$-1.013344*10^{2}$	$3.181666*10^{1}$	–9.765077	$1.768152*10^{1}$	$-1.773408*10^{1}$	$1.093564*10^{1}$	–2.907226	298	1000				
HCl	36.465	–92.365	$2.108164*10^{2}$	$-9.867979*10^{1}$	$2.171557*10^{1}$	7.343993	–1.986651	$3.295004*10^{-1}$	$-2.995451*10^{-2}$	$1.146000*10^{-3}$	1000	6000	0.0013	0.0012	0.0105	0.0814
HCN	27.026	135.221	$1.411083*10^{2}$	$1.287077*10^{2}$	–3.077385	$1.379209*10^{2}$	$-2.523301*10^{2}$	$2.814192*10^{2}$	$-1.670535*10^{2}$	$4.070112*10^{1}$	298	1000				
HCN	27.026	135.221	$2.250376*10^{2}$	$1.255505*10^{2}$	$2.746882*10^{1}$	$1.782442*10^{1}$	–5.489565	1.036481	$-1.084957*10^{-1}$	$4.802740*10^{-3}$	1000	5000	0.0011	0.0016	0.0356	0.0445
HCO	29.019	224.739	$2.669483*10^{2}$	$-2.201183*10^{1}$	$3.341877*10^{1}$	–9.689717	$3.985679*10^{1}$	$-4.331761*10^{1}$	$2.428649*10^{1}$	–5.814444	298	1000				
HCO	29.019	224.739	$2.436203*10^{2}$	$-2.090576*10^{1}$	$2.413418*10^{1}$	$1.856026*10^{1}$	–6.157525	1.220388	$-1.324441*10^{-1}$	$6.042895*10^{-3}$	1000	5000	0.0020	0.0016	0.0176	0.0798
N	14.008	473.063	$1.746663*10^{2}$	$4.670062*10^{2}$	$1.940246*10^{1}$	5.068131	–8.646152	6.977456	–2.146942	$1.907349*10^{-5}$	298	1000				
N	14.008	473.063	$1.786964*10^{2}$	$4.668474*10^{2}$	$2.090944*10^{1}$	$-2.222092*10^{-1}$	$1.973235*10^{-1}$	$-8.628327*10^{-2}$	$1.739607*10^{-2}$	$-1.133121*10^{-3}$	1000	5000	0.0011	0.0012	0.0075	0.1074
N_2	28.013	0.000	$2.006568*10^{2}$	–7.910203	$2.017653*10^{1}$	$4.213178*10^{1}$	$-1.031913*10^{2}$	$1.366394*10^{2}$	$-8.963190*10^{1}$	$2.325778*10^{1}$	298	1000				
N_2	28.013	0.000	$2.164157*10^{2}$	–7.407111	$2.342541*10^{1}$	7.299757	–2.210188	$3.959814*10^{-1}$	$-3.824724*10^{-2}$	$1.539184*10^{-3}$	1000	6000	0.0020	0.0120	0.0220	0.1155
N_2O	44.016	34.213	$2.023705*10^{2}$	$7.365255*10^{1}$	$1.310524*10^{1}$	$7.374712*10^{1}$	$-1.019304*10^{2}$	$1.026250*10^{2}$	$-5.950862*10^{1}$	$1.453612*10^{1}$	298	1000				
N_2O	44.016	34.213	$2.520256*10^{2}$	$6.875377*10^{1}$	$3.614132*10^{1}$	$1.602457*10^{1}$	–5.792747	1.226129	$-1.401164*10^{-1}$	$6.663583*10^{-3}$	1000	5000	0.0026	0.0018	0.0232	0.1107
NH	15.015	339.131	$2.183595*10^{2}$	$3.303452*10^{2}$	$2.979918*10^{1}$	–2.802763	6.704311	–9.884453	8.788696	–2.907212	298	1000				
NH	15.015	339.131	$2.059482*10^{2}$	$3.329323*10^{2}$	$2.184614*10^{1}$	6.633162	–1.579599	$2.307593*10^{-1}$	$-1.807999*10^{-2}$	$5.740862*10^{-4}$	1000	5000	0.0012	0.0015	0.0064	0.0949
NH_2	16.023	167.891	$2.311432*10^{2}$	$1.581478*10^{2}$	$3.173734*10^{1}$	4.162578	–9.318805	$2.325782*10^{1}$	$-1.945605*10^{1}$	5.814446	298	1000				
NH_2	16.023	167.891	$2.082743*10^{2}$	$1.623450*10^{2}$	$1.764419*10^{1}$	$1.897263*10^{1}$	–5.487439	$9.628491*10^{-1}$	$-9.385759*10^{-2}$	$3.896891*10^{-3}$	1000	5000	0.0011	0.0014	0.0223	0.0557
NH_3	17.031	–45.925	$2.421232*10^{2}$	$-5.600216*10^{1}$	$3.570660*10^{1}$	$-2.452205*10^{1}$	$8.400124*10^{1}$	$-9.186822*10^{1}$	$5.098821*10^{1}$	$-1.162889*10^{1}$	298	1000				
NH_3	17.031	–45.925	$1.879003*10^{2}$	$-5.104336*10^{1}$	$1.082809*10^{1}$	$3.703806*10^{1}$	$-1.256815*10^{1}$	2.707227	$-3.211912*10^{-1}$	$1.601372*10^{-2}$	1000	5000	0.0173	0.0078	0.1082	0.4560
NO	30.008	90.343	$2.996746*10^{2}$	$7.967417*10^{1}$	$4.857267*10^{1}$	$-7.723411*10^{1}$	$1.581366*10^{2}$	$-1.715261*10^{2}$	$9.821937*10^{1}$	$-2.325778*10^{1}$	298	1000				
NO	30.008	90.343	$2.367869*10^{2}$	$8.217171*10^{1}$	$2.501834*10^{1}$	7.549394	–2.653140	$5.546471*10^{-1}$	$-6.275609*10^{-2}$	$2.962036*10^{-3}$	1000	5000	0.0015	0.0018	0.0302	0.0908
NO_2	45.998	82.103	$2.941155*10^{2}$	$2.259400*10^{1}$	$3.789948*10^{1}$	$-3.156196*10^{1}$	$1.089336*10^{2}$	$-1.299528*10^{2}$	$7.500632*10^{1}$	$-1.744333*10^{1}$	298	1000				
NO_2	45.998	82.103	$2.724274*10^{2}$	$1.956524*10^{1}$	$3.610851*10^{1}$	$1.394597*10^{1}$	–5.126208	1.093539	$-1.253061*10^{-1}$	$5.958788*10^{-3}$	1000	5000	0.0027	0.0022	0.0240	0.1292
O	15.999	249.338	$2.203333*10^{2}$	$2.416352*10^{2}$	$3.373582*10^{1}$	$-4.685419*10^{1}$	$9.593765*10^{1}$	$-1.116373*10^{2}$	$6.883402*10^{1}$	$-1.744332*10^{1}$	298	1000				
O	15.999	249.338	$1.869040*10^{2}$	$2.432426*10^{2}$	$2.102164*10^{1}$	$-5.297924*10^{-2}$	$-3.457758*10^{-3}$	$-1.593056*10^{-3}$	$2.029129*10^{-3}$	$-2.125538*10^{-4}$	1000	5000	0.0010	0.0016	0.0242	0.1289
O_2	31.999	0.000	$2.542479*10^{2}$	–9.092337	$3.384895*10^{1}$	$-2.184140*10^{1}$	$4.634955*10^{1}$	$-4.128255*10^{1}$	$1.764460*10^{1}$	–2.907221	298	1000				
O_2	31.999	0.000	$2.364987*10^{2}$	–9.912852	$2.933944*10^{1}$	4.460848	–1.516870	$3.948768*10^{-1}$	$-5.479249*10^{-2}$	$2.996896*10^{-3}$	1000	5000	0.0024	0.0019	0.0196	0.1770
OH	17.007	39.486	$2.349998*10^{2}$	$2.995997*10^{1}$	$3.555108*10^{1}$	$-2.015254*10^{1}$	$3.696583*10^{1}$	$-3.982893*10^{1}$	$2.374976*10^{1}$	–5.814442	298	1000				
OH	17.007	39.486	$2.123812*10^{2}$	$3.299069*10^{1}$	$2.386282*10^{1}$	3.982669	$-3.502739*10^{-1}$	$-6.846898*10^{-2}$	$1.912693*10^{-2}$	$-1.296978*10^{-3}$	1000	5000	0.0017	0.0015	0.0111	0.1144

Table 3. Comparative analyses of the approximation errors for CO

	Temperature ranges	Absolute errors of temperature	Standard deviations		
	$T_i - T_f$ K	ΔT K	h_{SD} kJ/mol	s_{SD} J/molK	c_{pSD} J/molK
This paper	298.15 – 6000	0.1513	0.0023	0.0016	0.0146
Ref. 7	298.15 – 6000	1.5770	0.0031	0.0195	0.0418
Ref. 9	298.15 – 5000	2.6349	0.0368		0.0354
Ref. 6	500 – 6000	3.2210			0.0012
Ref. 8	1100 – 5000	2.9458	0.0608	0.0177	0.0953

A similar conclusion may be derived by analyses of the diagrams represented in Figure 1.

CONCLUSION

To enable that the consistent data published in the JANAF tables can be used in computer studies of combustion systems, such as composite rocket propellants, a continuous representation of the standard state molar enthalpy of each combustion product as a function of temperature was derived by fitting the tabulated data. It is shown that these approximations, combined with standard entropies and specific heats, are sufficient to determine all the remaining thermochemical properties. These approximations give

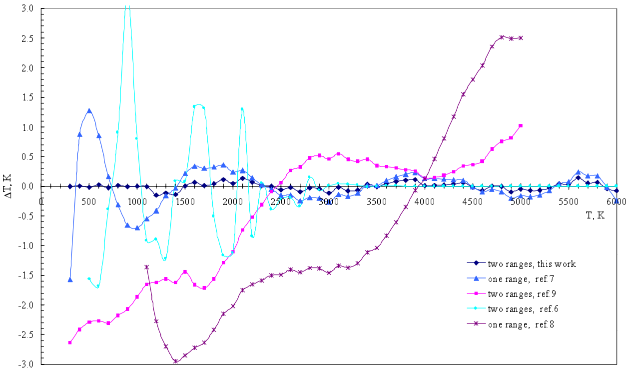

Figure 1. Comparative analyses of the absolute errors of temperature for CO obtained by various approximation methods

a consistent set of data, of which the accuracy must be comparable to the number of significant figures given in the tabulated values. Sixth–order polynomials were determined to approximate values of the standard state total molar enthalpy for gaseous combustion products over two temperature ranges (from 298.15 to 1000K, and from 1000 to 5000K) and fourth–order polynomials for condensed species over a specified temperature range. The polynomial coefficients were tabulated. The accuracy of the approximation was estimated and compared with other available reference data. It was shown that the accuracy of approximation was improved.

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IZVOD

STUDIJA TERMODINAMIČKIH FUNKCIJA PRODUKATA SAGOREVANJA KOMPOZITNIH RAKETNIH GORIVA

(Naučni rad)

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Određeni su koeficijenti polinoma šestog stepena koji aproksimiraju standardne molarne entalpije gasovitih produkata sagorevanja kompozitnih raketnih goriva u dva temperaturna opsega (od 298.15 do 1000 i od 1000 do 5000K) i koeficijenti polinoma četvrtog stepena za kondenzovane produkte u specificiranim temperaturnim intervalima. Koeficijenti polinoma dati su tabelarno za 47 hemijskih vrsta. Izvedeni su izrazi za toplotni koeficijent i entropiju. Tačnost aproksimacije procenjena je i komparativno analizirana u odnosu na druge raspoložive literaturne podatke. Pokazano je da je tačnost aproksimacije u odnosu na njih poboljšana.

Ključne reči: Kompozitna raketna goriva • Proizvodi sagorevanja • Termodinamičke funkcije • Koeficijenti polinoma •
Key words: Composite propellants • Combustion products • Thermodynamic functions • Polynomial coefficients •