Reconstruction of the Combustion Efficiency of Hydrogen Air Mixtures from Experimental Data

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1 Introduction

Studying the combustion efficiency, the heat release of chemical reactions, and the molecular weight of products in hydrogen combustion in a scramjet and other devices is an important and difficult problem. The only well-measurable quantity at the moment is the pressure. Measuring the temperature of the medium in combustion chambers of scramjet models by contact methods is impeded, in particular, by the short test regimes in short-duration wind tunnels. Methods that involve probing of the flow (including probes for mass spectrometry) give distorted information about the composition of combustion products. Probes and various samplers introduce perturbations into the flow and distort the velocity field.

A promising direction in solving this problem is the use of non-intrusive optical methods for measuring the concentration of reaction products. Appropriate laser equipment and methods for non-intrusive optical measurements of the concentration of OH radicals and the temperature of reaction products are now under development at the Institute of Thermophysics of the Siberian Division of the Russian Academy of Sciences [1]. Concerning the remaining species in combustion products, there are almost insuperable difficulties in obtaining reliable information necessary for determining the enthalpy and molecular weight. Hence, there arises an urgent problem of creating methods for reconstruction of the mixture enthalpy and combustion efficiency from limited information obtained by optical methods. Note that gas-dynamic problems associated with cost efficiency of the engines do not require accurate and complete reconstruction of the chemical composition. It is sufficient to know the molecular weight and enthalpy (heat release) of combustion products within accuracy provided by thermodynamic tables.

2 System of Reactions

Let us consider combustion of a $b_{H2}^{0}H_2+b_{O2}^{0}O_2+b_{N2}^{0}N_2$.mixture. The stoichiometric coefficients b_i^{0} correspond to the initial state. The amount of molecules in reaction products, such as HO₂, H₂O₂, and O₃, is so small that their effect on the molecular weight and the enthalpy of reaction products is obviously lower than the influence of the error in thermodynamic tables [2]. We assume N₂ to be an inert gas, as the mole fraction of NO in hydrogen–air reaction products is fractions of a percent and the mole portion of atomic nitrogen stays within thousandths of a percent. Therefore the basic reaction products are H₂O, O₂, H₂, O, H, OH, and N₂.

The number of moles of the species in the reacting medium b_i obeys three equations of atomic balance for hydrogen, oxygen, and nitrogen or inert additive:

$$2b_{\text{H}_2\text{O}} + 2b_{\text{H}_2} + b_{\text{H}} + b_{\text{OH}} = 2b_{\text{H}_2}^0$$
, $b_{\text{H}_2\text{O}} + 2b_{\text{O}_2} + b_{\text{O}} + b_{\text{OH}} = 2b_{\text{O}_2}^0$ and $2b_{\text{N}_2} = 2b_{\text{N}_2}^0$.

Following [3, 4], we introduce $n=2\Sigma b_{i}^{0}$, which is the total number of all atoms involved into the reaction (*n* remains unchanged in the course of the reaction) and the "mole fraction" of all atoms:

$$y_0=2\Sigma b_i^0/\Sigma b_i=n/\Sigma b_i$$

In the calculation, y_0 becomes an additional unknown, and its initial value is determined by the formula $y_{00} = n / \Sigma b_i^0$. If the initial composition contains only diatomic molecules, then we have $y_{00} = 2$. It can be easily demonstrated that the ratio y_0/y_{00} equals the inverse ratio of molecular weights μ_0/μ .

Let us pass to partial pressures using the relation $p_i = p \cdot b_i / \Sigma b_i$:

 $2p_{\rm H2O} + 2p_{\rm H2} + p_{\rm H} + p_{\rm OH} = 2b^{0}_{\rm H2} \cdot p / \Sigma b_{i} = 2b^{0}_{\rm H2} p y_{0} / n = C_{\rm H} y_{0} \cdot p, \text{ where } C_{H} = 2b^{0}_{\rm H2} / n, \tag{1}$

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(3) (4)

 $p_{\rm H2O} + 2p_{\rm O2} + p_{\rm OH} = (2b^0_{\rm O2}/n) \cdot py_0 = C_{\rm O} \cdot y_0 \cdot p, \text{ where } C_{\rm O} = 2b^0_{\rm O2}/n,$ (2)

$$2p_{N2} = (2b_{N2}^{0}/n) \cdot p \cdot y_{0} = C_{N} \cdot y_{0} \cdot p$$
, where $C_{N} = 2b_{N2}^{0}/n$.

$$\sum p_i = p$$

These equations (atomic balance and Dalton's law) are *exactly satisfied* within the entire zone of the chemical reaction and outside this zone, because they reflect the law of conservation of matter and the equation of state of an ideal gas.

Let us write a slightly modified system of reactions used in [5], which may contain the aboveindicated substances, and the reaction heats calculated from [2]:

$H_2O+O \Longrightarrow OH+OH - 17001 \text{ cal/mole}$	(I)
O_2 +H \leftrightarrows OH+O + 16613 cal/mole	(II)
$H_2+O \Longrightarrow OH+H-1904 \text{ cal/mole}$	(III)
$H+O+M \Longrightarrow OH+M + 101360 \text{ cal/mole}$	(IV)
H+OH+M \Leftrightarrow H ₂ O+M + 117731 cal/mole	(V)
$H_2+O+M \Longrightarrow H_2O+M + 116097 \text{ cal/mole}$	(VI)
H+H+M $⇔$ H ₂ +M + 103264 cal/mole	(VII)

$$O+O+M \leftrightarrows O_2+M + 117973 \text{ cal/mole}$$
(VIII)

Experimental and theoretical studies [6-8] show that the rates of exchange reactions (I)–(III) in combustible mixtures with sufficiently high temperatures are much greater than the rates of recombination reactions (IV)–(VIII) proceeding only with participation of the third bodies, and it is these reactions that are mainly responsible for energy release. The absolute value of the total heat release of reactions (I)–(III) is lower than that of recombination reactions by an order of magnitude and can be even endothermic [9] because of partial dissociation of the original mixture. Exchange reactions do not alter the molecular weight of the mixture. This fact allows us to assume that reactions (I)–(III) are quasi-equilibrium after the induction period [5]. Such an assumption was also used in other studies (see, e.g., [10]). In this case, the following relations have to be satisfied for the partial pressures of the reagents:

$$\frac{p_{\rm H_2O} \cdot p_{\rm O}}{p_{\rm OH}^2} = \frac{k_{p\rm OH}^2}{k_{p\rm H_2O}} = k_1(T), \quad \frac{p_{\rm O_2} \cdot p_{\rm H}}{p_{\rm O} \cdot p_{\rm OH}} = \frac{k_{p\rm OH}}{k_{p\rm O_2}} = k_2(T) \text{ and } \frac{p_{\rm H_2} \cdot p_{\rm O}}{p_{\rm H} \cdot p_{\rm OH}} = \frac{k_{p\rm OH}}{k_{p\rm H_2}} = k_3(T), \dots$$
(5)

where the equilibrium constants $k_{pH_2} = \frac{p_{\rm H} \cdot p_{\rm H}}{p_{\rm H_2}}$, $k_{pO_2} = \frac{p_{\rm O} \cdot p_{\rm O}}{p_{\rm O_2}}$ and $k_{pOH} = \frac{p_{\rm O} \cdot p_{\rm H}}{p_{\rm OH}}$, are calculated exactly

with help of thermodynamic tables.

Thus, we obtained seven expressions relating seven partial pressures of the species and the "mole fraction" of all atoms y_0 . If the temperature and the partial pressure of one species (e.g., OH radical) are measured in experiments, these algebraic equations make it possible to reconstruct the remaining composition of the mixture at the measurement point.

3 Equations for Calculating the Chemical Composition of Hydrogen–Air Mixtures with Given Temperature and Concentration of OH Radicals

The ratio of oxygen, nitrogen, and other gases (primarily, argon) in air is determined by the atmosphere composition; hence, the ratio between the constants $C_{\rm H}$, $C_{\rm O}$, and $C_{\rm N}$ can be presented in terms of one parameter: oxidizer-to-fuel ratio α . In the rich mixtures, $\alpha < 1$; in lean ones, $\alpha > 1$. The initial composition of the combustible mixture corresponds to the chemical formula $2H_2 + \alpha \cdot (O_2 + 3.728N_2 + 0.0444Ar)$. Within the approximation of the problem considered, we may assume that nitrogen is an inert gas and unite nitrogen with argon. This new species is described as nitrogen with the number of moles $b_{N2}^0 = 3.7724$ and molecular weight $\mu_{N2} = 28.1564$.

As all gases considered are diatomic at the initial state, we have

 $n = 2\Sigma b_{i}^{0} = 4 + 2\alpha(1 + b_{N2}^{0}) = 4 + 9{,}5448\alpha,$

and the constants C_i are determined by the formulas:

 $C_{H}=2b^{0}_{H2}/n=4/[4+2\alpha(1+b^{0}_{N2})]; C_{O}=2b^{0}_{O2}/n=2\alpha/[4+2\alpha(1+b^{0}_{N2})]; C_{N}=b^{0}_{N2}/n=7,5448\alpha/[4+2\alpha(1+b^{0}_{N2})].$ Thus, we consider a reaction of the form:

 $b_1H_2O + b_2O_2 + b_3H_2 + b_4O + b_5H + b_6OH + b_7N_2 \leftrightarrow \alpha \cdot b_2^0O_2 + b_3^0H_2 + \alpha \cdot b_7^0N_2.$

As the partial pressure of OH radicals is assumed to be known (found from experiments) $p_6 = p_{OH}$ it is transferred to the right side of the equations, which acquire the following form after passing to mole fractions by the relation $y_i = p_i/p$:

3 equations of atomic balance:

hydrogen -
$$2y_1+2y_3+y_5-C_Hy_0 = -y_{OH};$$

oxygen - $y_1+2y_2+y_4-C_Oy_0 = -y_{OH};$ (6)
nitrogen - $2y_7-C_Ny_0 = 0;$

Dalton's law –
$$\sum_{i\neq 6}^{\prime} y_i = 1 - y_{OH}$$
. (7)

Equations of chemical equilibrium of exchange reactions:

$$y_{1} = \frac{k_{1}(T) \cdot y_{6(\text{OH})}}{y_{4}} = \frac{K_{1}}{y_{4}}, \quad y_{2} = k_{2}(T) \frac{y_{6(\text{OH})} \cdot y_{4}}{y_{5}} = K_{2} \frac{y_{4}}{y_{5}}, \text{ and } \quad y_{3} = k_{3}(T) \frac{y_{6(\text{OH})} \cdot y_{5}}{y_{4}} = K_{3} \frac{y_{5}}{y}, \quad (8)$$

where $K_1 = k_1(T)y_{\text{OH}}^2$, $K_2 = k_2(T)y_{\text{OH}}$, $K_3 = k_3(T)y_{\text{OH}}$.

As a result, we obtain a closed system of seven equations for seven unknowns y_i (i= 0,...6). The pressure of the medium p, temperature T, and mole fraction of OH radicals are assumed to be known from experiments and are used as constants of the problem, as well as the oxidizer-to-fuel ratio α determined by test conditions. All variables expressed in mole fractions (except y_0) lie inside the interval [0, 1], which facilitates monitoring of convergence in numerical calculations.

4 Calculation Results and Verification of the Method

When y_i satisfying these equations are calculated, the molecular weight is found from the relation $\mu = \mu_0 y_0 / y_{00}$, (the latter follows from the definition of y_0). With the use of thermodynamic tables, the molar enthalpy was calculated on the basis of reconstructed mole fractions by the conventional formula:

$$I = \Sigma I_i y_i$$

As there are no available publications with reliable experimental and numerical data on changes in the chemical composition in the course of the combustion reaction, the tests were based on the calculations of the Chapman-Jouguet state and (for extending the range) overdriven waves for a stoichiometric hydrogen-air mixture and for hydrogen-oxygen mixtures (including strongly enriched and diluted mixtures). For this purpose, the temperature and the mole fraction of OH radicals obtained in exact thermodynamic calculations [3,4] (upper rows of Table 1) were substituted into the above-given formulas (6-8), and the equilibrium composition of the mixture was calculated. The factors compared were (see Tables 1) the mole fractions y_i , molecular weights μ , total specific enthalpies $e=I/\mu$ (MJ/kg).

Comparison both for a stoichiometric H_2 -air mixture and for H_2 - O_2 mixtures of different compositions ($\alpha = 0.5, 1.0, 6.0$) showed that the supposition about the equilibrium of exchange reactions

Table 1. Verification of the Method with Calculations of Equilibrium in Waves of Gas Detonation.

<i>Т</i> , К	p, atm	µ, g/mol	e, MJ/kg	Δe/e %	H ₂ O	O ₂	H_2	0	Н	OH	N_2	NO	Ν
2568.6	0.1340	23.467	3.9012	0.15	0.26107	0.01537	0.04648	0.00677	0.01978	0.02499	0.61184	0.00636	0.0511
		23.558	3.9069		0.26675	0.01664	0.04291	0.00663	0.01786		0.62450	_	—
3189.8	1620.0	24.413	4.9608	0.23	0.32561	0.00227	0.01364	0.00025	0.00079	0.00719	0.63697	0.00566	0.069
		24.643	4.9720		0.33026	0.00315	0.00983	0.00024	0.00056		0.64878	_	-
3503.0	8.7965	21.73	5.6470	0.26	0.16073	0.01947	0.08289	0.02620	0.06533	0.05844	0.55892	0.02099	0.0464
		22.28	5.6321		0.18842	0.02267	0.07119	0.02252	0.04785		0.58990	_	_

Stoichiometric Hydrogen–Air Mixtures

Explosions, Detonations, and Reactive Systems

2 2)										
Т, К	p, atm	μ, g/mole	e, MJ/kg	Δ <i>e/e</i> %	H ₂ O	O ₂	H_2	0	Н	ОН
3248.0	9.5092	9.500	13.042	0.06	0.44324	0.00090	0.45699	0.00240	0.06967	0.02680
		9.509	13.034		0.44378	0.00090	0.45678	0.00239	0.06955	
3433.4 17.91	17.010	9.399	13.960	0.07	0.42951	0.00125	0.45200	0.00344	0.08003	0.03375
	17.910	9.412	13.950	0.07	0.43029	0.00125	0.45173	0.00344	0.07983	
<i>Mixture</i> $2H_2 + O_2$,										
3506.6	9.6837	14.71	9.5635	0.66	0.56004	0.04786	0.15575	0.03500	0.07564	0.12571
		14.95	9.5003		0.57193	0.04929	0.15119	0.03426	0.07189	
3682.1 18.791	18 701	14.52	10.158	0.73	0.53621	0.04791	0.16149	0.03827	0.08066	0 13546
	10.791	14.78	10.084	0.75	0.54977	0.04943	0.15647	0.03732	0.07622	0.13340
<i>Mixture</i> $H_2 + 3O_2$,										
2651.7	13.762	27.71	3.5827	0.03	0.26837	0.69747	0.00101	0.00655	0.00040	0.02619
		27.75	3.5816		0.26837	0.69888	0.00101	0.00655	0.00040	
2462.2	7.3005	27.82	3.2853	0.02	0.27428	0.70357	0.00059	0.00370	0.00019	0.01768
		27.84	3.2847		0.27428	0.70437	0.00059	0.00369	0.00019	

Mixture $4H_2 + O_2$.

within the range of pressures from 0.2 to 500 atm and temperatures from 2500 to 3500 K allows the specific enthalpy to be reconstructed with accuracy better than 1%.

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