Computation of equilibrium states for products of hydrocarbon combustion under oxygen lack

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Abstract. A unified approach to the computation of equilibrium in combustion products of oxygen mixtures overriched with hydrocarbon fuel, when both gaseous and condensed carbon phases may appear simultaneously among the components of chemical reaction, has been formulated. Within the framework of this approach, the problem of determining the equilibrium parameters (pressure, density, temperature, etc) of chemical reaction products produced at explosion of acetylene-oxygen mixture in a closed volume as the values of molar fraction of fuel (acetylene) vary up to the values when oxygen in the mixture is almost absent has been solved.

1. Introduction
The computation of equilibrium is the determination of chemical composition of reaction products at two fixed external parameters (for example, pressure $p$ and temperature $T$). Knowing chemical composition, it is possible to find average values of molar mass $\mu$, density $\rho$, specific (per unit mass) internal energy $U$ of the reaction products that is necessary for theoretical description of many stationary and non-stationary gas-dynamic processes.

In the present work, a unified approach to the computation of equilibrium in combustion products of oxygen mixtures overriched with hydrocarbon fuel, when both gaseous and condensed carbon phases may appear simultaneously among the components of chemical reaction, has been formulated. This approach is based on the analysis of regularities established in [1, 2].

Thus, on the one side, according to [1], the lack of oxygen in combustion products implies that almost all oxygen is “taken” by carbon forming the molecules of carbon oxide CO which do not almost dissociate into atoms at temperature of up to 5000 K (characteristic for combustion processes). The concentrations of other oxygen compounds can be neglected. In the combustion products, only two chemical reactions are admitted: $2\text{H}_2 \rightleftharpoons \text{H}+\text{H}$ (hydrogen dissociation) and $\text{C} \rightleftharpoons \text{C}^\prime$ (carbon condensation), where $\text{C}^\prime$ denotes carbon condensate (graphite). This causes a significant reduction of solvable equations for determination of chemical composition of reaction products.

On the opposite side, in [2], a high efficiency of the method of “large molecules” for the computation of equilibrium in complex heterogeneous systems has been shown. This method essentially simplifies a computational algorithm providing its uniformity for different components of chemical reaction and makes it possible to obtain the solutions for those cases which defy a standard method of calculation of heterogeneous mixtures. Thus, it is proposed in the computations that the particles of a condensed substance are “large molecules” which consist of $k$ conventional molecules (as a rule $k=100\div1000$). Then the reaction of forming the particle of condensed phase (in our case it is graphite) can be
conditionally presented as $k C \rightleftharpoons C^*_s$. The equilibrium equation for this reaction is of the following form: $p_C = p_{C^*_s}^{sat}(p_{C^*_s})^{1/k}$, where $p_{C^*_s}^{sat}$ is the pressure of saturated carbon vapor over a plane surface. As $k \to \infty$, partial pressure $p_C$ of gas phase of condensed substance tends to the pressure of its saturated vapor.

The above-mentioned approach can be described by the following mathematical model.

2. Mathematical model

Let us characterize the atomic composition of reacting thermodynamic system consisting of products of hydrocarbon fuel combustion as relative concentrations of oxygen $z_o$, carbon $z_c$ and hydrogen $z_h$, which are related by the following relation

$$z_o + z_c + z_h = 1. \quad (1)$$

We assume that the components of chemical reaction taking place in such a system under the lack of oxygen may have the following equilibrium composition only (the proportion of the rest of substances is insignificant):

$$b_{CO}CO + b_{C}C + b_{C^*_s}C^*_s + b_{H_2}H_2 + b_{H}H, \quad (2)$$

where $b_s$ is a stoichiometric coefficient of substance $s = \{CO, C, C^*_s, H_2, H\}$. All substances are gaseous and can be described by the model of ideal gas.

The comparison of (1) and (2) may yield three equations of atomic balance:

for oxygen

$$z_o = b_{CO}, \quad (3)$$

for carbon

$$z_c = b_{CO} + b_{C} + kb_{C^*_s} \quad (4)$$

for hydrogen

$$z_h = 2b_{H_2} + b_{H}. \quad (5)$$

Denote the total number of moles taking part in the chemical reaction at equilibrium point

$$b = b_{CO} + b_{C} + b_{C^*_s} + b_{H_2} + b_{H}. \quad (6)$$

Then Eqs. (3)-(6) can be represented as

$$z_o / b = y_{CO}, \quad (7)$$

$$z_c / b = y_{CO} + y_{C} + ky_{C^*_s}, \quad (8)$$

$$z_h / b = 2y_{H_2} + y_{H}, \quad (9)$$

$$y_{CO} + y_{C} + y_{C^*_s} + y_{H_2} + y_{H} = 1. \quad (10)$$

where $y_s = b_s / b$ is the molar fraction of the component $s$ whose partial pressure can be now determined as $p_s = py_s$. 


These relations can be added by two equations of chemical equilibrium
\[(y_{c_1})^{1/k} p_{c_1}^{1/1-k} = y_{c} p^{1/1-k}, \quad K_{H_1} y_{H_2} = y_{H}^{2} p, \quad (11)\]
where variables \(p_{c_1} = p_{c}^{1/1-k}(T), \quad K_{H_1} = K_{H}^{2}(T)\) are the known functions of temperature [3].

At given values of relative concentrations of atoms of substances (\(z_{o}, z_{c}, z_{H}\)), pressure \(p\), temperature \(T\), and parameter \(k\) for the determination of structure of “large molecules”, system (7)-(11) is closed. Its numerical solution, for example, by using Newton method, makes it possible to find the sought variables \(b, y_{CO}, y_{c}, y_{c_1}, y_{H_2}, y_{H}\) which may be further used for the computation of other parameters characterizing thermodynamic system in a state of chemical equilibrium.

For example, for the combustion products, it is possible to find average molar mass \(\mu = \sum \mu_{x} y_{x}\), specific internal (with allowance for potential chemical energy) energy \(U = (\sum y_{x} U_{x}) / \mu\) and density \(\rho = \mu / RT\) \((R\) is the absolute gas constant). Note that according to [2], we assume \(\mu_{c_1} = k\mu_{c}\) and \(U_{c_1} = kU_{c}\) for “large molecules”. To determine \(U_{c}\), reference data [3] can be used.

3. The problem of explosion in a volume
To illustrate the availability of formulated approach, the problem on computation of equilibrium parameters of combustion products produced at explosion of acetylene-oxygen mixture \(nC_{2}H_{2} + (1-n)O_{2}\) in a closed volume for the values of relative molar fuel concentration \(n \geq 0.5\), i.e., under the lack of \(O_{2}\). In this connection, for this mixture we have the following values of relative atom concentrations in the combustion products:
\[z_{c} = z_{H} = \frac{n}{1+n}, \quad z_{o} = \frac{1-n}{1+n}.\]

In the chemical reaction, at constant volume, the following conditions are hold:
\[U = U_{0} = \text{const}, \quad \rho = \rho_{0} = \text{const}, \quad (12)\]
where the values for internal energy \(U_{0}\) and density \(\rho_{0}\) of the mixture before the explosion were given at initial pressure \(p_{0} = 1\) atm and temperature \(T_{0} = 298.15\) K. Solving systems (7)-(11) in combination with (12), it is possible to find pressure \(p\) and temperature \(T\) of the combustion products after the explosion simultaneously with determination of chemical composition.

Within the framework of this problem statement for limiting value \(n = 0.5\) when the oxygen amount suffices for oxidation of \(C\) into \(CO\), the following values of equilibrium parameters of combustion products are obtained: \(p = 23.24\) atm, \(T = 4167\) K, \(\mu = 17.45\) g/mole, \(\rho = 1.186\) kg/m\(^3\). These values can be used to non-dimensionalize analogous parameters (\(\tilde{p}, \tilde{T}, \tilde{\mu}, \tilde{\rho}\)), obtained in computations at variation of molar concentration of fuel \(n\).

The results of corresponding computations at \(k = 100\) are presented (solid lines) in Fig. 1. In the same figure, a dashed line corresponds to the increase in mass fraction of the condensed phase \(\rho_{c^*}/\rho\) in a heterogeneous mixture as \(n\) rises, where \(\rho_{c^*} = \mu_{c_1} p_{c_1}/RT\) is a volume density of carbon condensate in the mixture.
Figure 1. Dimensionless values of equilibrium parameters of the combustion products of the mixture $nC_{n}H_{2} + (1-n)O_{2}$ versus molar fraction of fuel $n$:

$\mu_0$ (curve 1), $\rho_0$ (2), $T_0$ (3), $p_0$ (4); the dashed line corresponds to $\rho_C/\rho$.

The additional computations performed at $k=1000$ do not almost differ (the divergence is not more than 2%) from the results presented in Fig. 1. This means that at values $k>100$, the partial pressure $p_{C}$ produced by “large molecules” in the mixture of combustion products can be neglected, i.e., their influence is analogous to that of condensed ultrafine (nanosize) particles in a gaseous medium.

Conclusion

Thus, the approach to the computation of equilibrium states of hydrocarbon combustion products under the lack of oxygen is formulated. It is based on two principals: 1) exceeding the concentration of carbon atoms in comparison to oxygen ones may cause the appearance of both gaseous and condensed carbon phases simultaneously in the products of chemical reaction; 2) the particles of condensed substance are “large molecules” consisting of a large number of conventional molecules. To describe thermophysical properties of the condensed phase, the reference data for graphite were used.

This approach shows both simplicity and versatility since it is available for the wide range of hydrocarbon fuel types. It may be easily generalized to the case when air is used instead of oxygen. It makes possible to evaluate the mass of condensed carbon in detonation combustion of hydrocarbon fuel. Note that such a way to obtain hydrocarbon condensate heightens the interest considerably since it allows obtaining the special forms of nanosize carbon particles [4].

References

[1] Prokhorov E S 2018 J. Phys.: Conf. Ser. 1105 012032
[2] Glusko V P (ed) 1973 Thermodynamic and thermophysical properties of combustion products: Handbook vol. 3 (Moscow: Viniti Press)
[3] Glusko V P (ed) 1978 Thermodynamic Properties of Individual Substances: Handbook vols.1, 2 book 2 (Moscow: Nauka Press)
[4] Vasil'ev A A, Pinaev A V 2008 Combust. Explos. Shock Waves 44 317