Analysis of equilibrium states of reacting carbon-oxygen thermodynamic system

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Abstract. The problem of determining the equilibrium states of reacting thermodynamic system that is the molecules of substances consisting of only oxygen and carbon atoms has been numerically solved basing on given external parameters (pressure and temperature). Here it has been assumed that the shift of system chemical equilibrium resulting from the chemical reaction can imply the presence of condensed carbon as suspended ultradispersed graphite particles among the gaseous products of reaction. In computations, the values of pressure, temperature and the relation of concentration of oxygen and carbon atoms have been varied. The conditions, under which carbon condensate appears in the reaction products and homogeneous thermodynamic system becomes heterogeneous one, have been determined.

1. Introduction
When solving a series of scientific and applied problems in the field of combustion physics and detonation of gases, methods [1, 2] developed to compute the equilibrium flows of combustion products of hydrocarbon fuel have been successfully used for a long time. When describing such flows, one often assumes that the rate of chemical equilibrating is much higher than that of changing the external parameters, i.e., a chemical reaction can be considered as an instantaneous one. However, the factors stated in [1, 2] do not cover the cases so important for practice when due to the lack of oxygen, combustion products may contain not only gaseous but condensed carbon. Note that such a way of obtaining condensed carbon has been lately of heightened interest because this makes it possible to obtain special forms of nano-scale carbon particles [3], which are highly demanded in different branches of industry.

In [4], the computer program “Safety” was first mentioned. In the authors’ opinion, this program is able to describe chemical equilibrium for condensed components in detonation products. Here, it is assumed that their computational algorithm partially coincides with calculation methods presented in [2] for gaseous chemically reacting system. At the same time nothing is mentioned about assumptions used for interfacial equilibrium in heterogeneous medium (it is also relevant to the later publication of the same authors [5]). In [3], the experiment is compared to computations of detonation velocity depending on mole fraction of fuel in acetylene-oxygen and acetylene-air mixtures obtained by using [4, 5]. The computations are carried out for two limiting cases: the first case is when detonation products contain only gaseous carbon, the second one is when detonation products contain only condensed carbon. It is established that in both cases for the range of fuel concentrations, when according to computations, the shift of chemical equilibrium results in appearance of carbon behind the detonation front, the numerical solution essentially differs from experimental data. Experimental
points are located roughly in the middle between computation curves in the graph when acetylene \( C_2H_2 \) concentration in the initial mixture exceeds oxygen \( O_2 \) concentration. This may denote that the detonation products contain both gaseous and condensed phases of carbon and special approaches to the computation of chemical equilibrium in such thermodynamic systems are required. Therefore, the computed parameters of detonation for mixtures over enriched by hydrocarbon fuel in [3] should be regarded as an estimate.

The problem of equilibrium computation is to determine the chemical composition (mole fractures of components) of reaction products at two fixed external parameters which are typically pressure \( p \) and temperature \( T \). If only one external parameter is changed, both equilibrium shift and change of chemical composition take place. The reaction products are the mixture of molecules of different substances. Knowing the chemical composition of such a mixture, it is possible to determine for it average molar mass, density, specific (per unit mass) internal energy, and thermal effect of chemical reaction that is necessary for theoretical description of many stationary and nonstationary gas-dynamic processes.

In this work the problem on computation of equilibrium states of reacting thermodynamic system is solved with allowance for the fact that among the chemical reaction components one part of free carbon can be in gaseous state and another one can be in condensed state. Here, it is assumed that condensed carbon is graphite whose thermophysical properties for a sufficiently wide range of values \( p \) and \( T \) are known [6]. To simplify a theoretical analysis, we consider the case when all molecules of substances being the part of closed thermodynamic system consist of only oxygen and carbon atoms.

2. Formulation of the problem

Let us characterize the atomic composition of reacting thermodynamic system, which does not exchange the substance with the environment, as relative concentrations of atoms of oxygen \( n_O \) and carbon \( n_C \) connected by the following relation:

\[
n_O + n_C = 1. \tag{1}
\]

Assume that the products of chemical reaction occurring in such a system can have only the following equilibrium composition (the fraction of other substances is minimal):

\[
b_{CO_2} CO_2 + b_{CO} CO + b_{O_2} O_2 + b_O O + b_C C + b_{c_g} C_g, \tag{2}
\]

where \( b_s \) is a stoichiometric coefficient of substance \( s = \{CO_2, CO, O_2, O, C, C_g\} \). By \( C_g \) we denote a condensed carbon, which in our case can be represented as suspension (ultradisperse dust) of graphite particles whose size can be ignored. The rest of substances are gaseous and can be described by the model of ideal gas.

The comparison of (1) and (2) yields two equations of atomic balance: one is for oxygen

\[
n_O = 2b_{CO_2} + b_{CO} + 2b_{O_2} + b_O, \tag{3}
\]

and another one is for carbon

\[
n_C - b_{c_g} = b_{CO_2} + b_{CO} + b_C. \tag{4}
\]

Let us define the total number of moles of gaseous substances taking part in chemical reaction at equilibrium point

\[
b = b_{CO_2} + b_{CO} + b_{O_2} + b_O + b_C. \tag{5}
\]

Then equations (3) - (5) can be represented as

\[
n_O/b = 2y_{CO_2} + y_{CO} + 2y_{O_2} + y_O, \tag{6}
\]

\[
(n_C - b_{c_g})/b = y_{CO_2} + y_{CO} + y_C, \tag{7}
\]
\[ y_{CO_2} + y_{CO} + y_{O_2} + y_O + y_C = 1, \]  

where \( y_s = b_s/b \) is a mole fraction of gaseous component \( s \), whose partial pressure can now be defined as \( p_s = p y_s \). Note that for condensed carbon the partial pressure is assumed to equal zero.

Let us supplement these relations by the three equations of chemical equilibrium

\[ K_{CO_2} y_{CO_2} = p^2 y_C y_O^2, \quad K_{CO} y_{CO} = p y_C y_O, \quad K_{O_2} y_{O_2} = p y_O^2, \]  

where equilibrium constants \( K_{CO_2} = K_{CO_2}(T) \), \( K_{CO} = K_{CO}(T) \), and \( K_{O_2} = K_{O_2}(T) \) are known functions of temperature [6].

At given values of pressure \( p \), temperature \( T \), and relative concentration of oxygen atoms \( n_O \) (or carbon atoms \( n_C \) with allowance for (1)), system (7) – (9) for computation of equilibrium state of thermodynamic system contains 6 equations for 7 unknowns: \( b, y_{CO_2}, y_{CO}, y_{O_2}, y_O, y_C, b_{Cg} \). To close the system, an additional condition defining the value of a variable is needed.

3. The method of solution

For numerical solution of nonlinear system of equations (7)-(9), Newton’s method was used. At first, the computations of mole fractions of gaseous components \( y_s \) and \( b \) were performed assuming that the whole free carbon is concentrated only in gaseous phase, i.e., \( b_{Cg} = 0 \). Then the partial pressure \( p_C = p y_C \) was compared to the pressure of saturated vapor for graphite \( p_* \) at the same temperature. To this end we used reference data for the dependence \( p_* = p_*(T) \), i.e., the curve of equilibrium of gaseous and condensed graphite phases [6].

If \( p_C \) was less than \( p_* \), it was a confirmation of the fact that at given initial parameters \( (n_O, p, T) \) the equilibrium composition of reaction products did not contain condensed carbon \( (b_{Cg} = 0) \) and further solution of the problem was finished. In the contrary case when \( p_C > p_* \) and the condensed carbon \( (b_{Cg} \neq 0) \) is available, it is necessary to solve the system of equations (7)-(9) once more under the following condition: \( y_C = p_*(T)/p \), i.e., the equality \( p_C = p_* \) is assumed to be satisfied at equilibrium. Knowing now the value \( y_C \), it is possible to define unambiguously the other unknown variables including \( b_{Cg} \).

For convenient treatment of the computation results, normalize stoichiometric coefficients in (2). To this end, divide them into the total number of all substances (not only gaseous) \( b + b_{Cg} \). Then the distribution of substance in 1 mole of the reacting mixture at equilibrium can be represented as

\[ v_{CO_2} CO_2 + v_{CO} CO + v_{O_2} O_2 + v_O O + v_C C + v_{Cg} C_g, \]

where \( v_s \) is a mole fraction of substance \( s \) \( \{CO_2, CO, O_2, O, C, C_g\} \). Here, always \( \sum v_s = 1 \).

4. The analysis of computation results

The preliminary computations of equilibrium states of reacting carbon-oxygen thermodynamic system are carried out at pressure \( p = 1 \) atm for temperature range 2000 ÷ 5000 K typical for the products of hydrocarbon combustion [2]. A relative oxygen concentration in the system was varied within the following limits: \( 0 < n_O < 1 \).

Basing on these data, it is possible to make the following conclusions. Thus, free carbon in a noticeable amount appears among the products of chemical reaction when oxygen in thermodynamic system is insufficient to oxidize \( C \) to carbon oxide \( CO \) (when the relation \( n_O/n_C < 1 \)). Therefore, in this case, we always have \( v_{CO_2} = v_{O_2} = v_O = 0 \). At \( T = 2000K \), the chemical composition of products is close to ultimate-recombined state when the process of dissociation of molecules into atoms can be neglected. Note that at \( n_O/n_C = 1 \) \( n_O = n_C = 0.5 \) the reaction products consist of 100 % \( CO \).

At temperature rise up to 3000 K, the probability of decomposition reactions for molecules of carbon dioxide \( CO_2 \) \( (CO_2 \rightarrow CO + O) \) and oxygen \( O_2 \) \( (O_2 \rightarrow O + O) \) increases. As a result for the region of values \( n_O/n_C > 1 \) in thermodynamic system, one can observe the increase of concentrations...
of atomic oxygen $O$ and molecules of $CO$ for which such a temperature is insufficient yet for dissociation into atoms according to the scheme: $CO \rightarrow C + O$.

Taking into account the fact that at relatively moderate temperatures free carbon is in condensed state, at $T = 4000$ K the process of graphite sublimation starts and the part of $C_g$ is graphitized, and at $T = 5000$ K the whole condensed carbon turns into gaseous phase. Note that at higher temperatures due to dissociation of $CO$ molecules into atoms, it is possible to find $C$ in the reaction products but in very low concentrations, even in the case $n_O/n_C = 3/2 > 1$ ($n_O = 0.6$ and $n_C = 0.4$).

Figure 1 shows changes of mole fractions of condensed $v_{C_g}$ (solid lines) and gaseous $v_C$ (dashed lines) carbon at temperature rise in detail. The computation results for the case $n_O/n_C = 3/7 < 1$ ($n_O = 0.3$ and $n_C = 0.7$) are presented as an example in the figure. It is seen that at fixed pressure $p$ there is a wide temperature range (up to 1000 K) inside which both carbon phases are simultaneously present at equilibrium in thermodynamic system. At the point of intersection of solid and dashed lines plotted at one value $p$, the equality $v_{C_g} = v_C$ holds.

Quantitative information on mole fractions $v_{C_g}$ and $v_C$ is fundamentally essential for a correct computation of the total thermal effect of chemical reaction since the energy released in the reaction of carbon condensation $C \rightarrow C_g$ is 711.185 kJ/mol (at $T = 0$ K) and is comparable to the energy of carbon dioxide $CO$ formation (1071.78 kJ/mol at $T = 0$ K) [6]. Therefore, the values of detonation parameters in [3] computed for two limiting cases when: 1) the reaction products do not contain condensed carbon and 2) the reaction products do not contain gaseous carbon, are considerably different.

For comparison, figure 1 also presents analogous computation dependences for $v_{C_g}$ and $v_C$ obtained at higher $p = 10 \div 40$ atm. At such pressures, detonation processes in fuel gas mixtures basing on hydrocarbon fuel usually take place under standard conditions (with initial $p_0 = 1$ atm and $T_0 = 298.15$ K) [2]. It is obvious that for each $p$ there is some value of threshold temperature $T_g$ of thermodynamic system (i.e., the intersection point of solid line and abscissa) above which the system contains only gaseous products of reaction, i.e., the system is homogeneous. At $T < T_g$, condensed particles appear in the system and it turns heterogeneous.

For all cases under consideration, the threshold temperature value $T_g$ rises monotonically at $n_O/n_C = const < 1$ and increase of pressure $p$. Figure 2 presents the dependency graphs, where $T_g = T_g(p)$ are the curves of threshold temperature of thermodynamic system, the dashed line indicates computations at $n_O/n_C \rightarrow 1$below (to put it more exactly, at $n_O/n_C = 0.999$). For this limiting case, mole fractions $v_C$ and $v_{C_g}$ do not exceed $10^{-3}$ any more.

![Figure 1. Computation dependences of mole fractions $v_C$ (dashed lines) and $v_{C_g}$ (solid lines) versus temperature $T$ (for $n_O/n_C = 3/7 < 1$) at different pressure values: $p = 1$ atm (1), 10 atm (2), 20 atm (3), 40 atm (4).](image-url)
Figure 2. The curves of threshold temperature \( T_g = T_g(p) \) for different relations of concentrations of oxygen atoms \( n_O \) and carbon atoms \( n_C \) in thermodynamic system:

- \( n_O/n_C = 0.1 \) (1), 0.4 (2), 0.7 (3), 0.9 (4), 0.99 (5);
- the dashed line (curve 6) indicates computations at \( n_O/n_C = 0.999 \).

By analysing our results and calculation data [2], it is possible to make the following regular conclusion. Namely, under hydrocarbon combustion and lack of oxygen \( (n_O < n_C) \), the thermodynamic system consisting of products of chemical reaction can be conditionally divided into 2 subsystems. The first one is carbon-oxygen system described above which can include only such components as \( CO, C \) and \( C_g \). The second subsystem includes all other feasible components. They can be molecular \( H_2 \) and atomic \( H \) hydrogen, nitrogen \( N_2 \) and other monoatomic inert substances such as argon \( Ar \) and helium \( He \). Note that such components as \( H_2O, OH, NO \) are absent. They are assumed to be present when oxygen is in excess [2]. Due to the lack of oxygen in the system, carbon “takes” it all turning into molecules of CO. Moreover, at moderate temperatures (up to 5000 K), typical for the processes of combustion and detonation, such substances as \( N_2 \) and \( CO \) almost do not dissociate into atoms. Then it is possible to assume that these two subsystems do not exchange the substance at identical (common) external parameters \( p \) and \( T \). Therefore, with regard to the first subsystem, the second one is an inert medium with some partial pressure and vice versa. Note that taking into consideration of inert medium does not change the value of relation of concentration \( n_O/n_C \) (although the values \( n_O \) and \( n_C \) themselves change). Such an approach makes the computation of equilibrium states in combustion products maximally simple, since for the first and second subsystems it is possible to restrict ourselves to only one reaction of the following type: \( C \rightleftharpoons C_g \) and \( H+H \rightleftharpoons H_2 \), respectively. In other words, it is much easier to compute an equilibrium composition of hydrocarbon combustion products under the lack of oxygen than under its excess. Previously, such regularity was not discussed.

5. Conclusion

Thus, a unified technique for calculation of equilibrium states of reacting thermodynamic system with different concentration of oxygen and carbon which can be the part of molecules of different substances is proposed. When the concentration of carbon atoms exceeds that of oxygen atoms, one can observe the appearance of both gaseous and condensed carbon phases among the products of chemical reaction occurring in the system. The numerical analysis is carried out assuming that condensed carbon is a suspension of graphite particles. The \((p,T)\) – diagram of states of thermodynamic system shows the curves of threshold temperature, above which all the products of chemical reaction are only gaseous.

References

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