DETERMINATION OF ZERO COMPONENTS IN THE COMPOSITION OF A SYSTEM

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A method is proposed for determining components whose concentration in a system of chemically reacting components is zero without necessity of computing the composition of the entire system. Theoretical considerations are applied to the case of the equilibrium composition of combustion products of hydrocarbons with air and an ionization additive, K_2CO_3.

In research and technical practice, the investigation and practical utilization of processes proceeding at high temperatures and accompanied by chemical changes of their components are of great importance. Combustion products of hydrocarbons containing an ionization additive and oxidized by air enriched to a varying degree by oxygen may serve as an example. Combustion products produce high-temperature multicomponent chemically reacting mixtures, whose thermodynamic and transport properties are determined, *e.g.*, by their composition. The only available possibility of determining the composition of a multicomponent mixture at a high temperature is its calculation. Of many components whose presence in the mixture may be assumed in such a calculation, only those are of some importance which occur in nonnegligible amounts. Other possible compounds are zero components, which need not be considered during the calculation. The determination of zero components in multicomponent mixtures at high temperatures only from experience is considerably dubious. In our contribution we propose a method for determing these zero components.

The System of Components

Let us have a set $E = \{e_1, e_2, \ldots, e_M\}$ of chemical elements, which can also contain e^-. This set E creates a system of components $S(E)$ with the following properties:

$$s_i \in S(E) \Rightarrow s_i = \left[\sum_{j=1}^{M} a_{ij} e_j \right] (p) , \tag{1}$$

where a_{ij}'s are integers and p denotes the phase. For an arbitrary $e_k \in E$ there is a component $s_i \in S(E)$ such that $a_{ik} \neq 0$, *i.e.*, each element from E is present in at least one component from $S(E)$.

The system cannot include all components (1), but only those which really exist and whose concentrations can be calculated from available data; such components make up a system $S_r(E)$. In calculations of composition, the concentration of a component is taken as zero if its mole fraction x_i is lower than z. The number z is always greater than zero and its magnitude depends on the type of computer used for the computation as well as on the manner in which the results are further employed; it is determined with a certain reserve. Thus, at given temperature and pressure, the mole fraction of some components in $S(E)$ is lower than z; these components create a system of zero components, $Z(S, z)$.

The calculation of composition of the system $S_r(E)$ is often lengthy and in some cases it cannot be accomplished due to enormous requirements on the computer time and memory. It is optimum to consider only the system $S(E) = S_r(E) - Z(S_r, z)$ and to this purpose it is desirable to find a method for determining $Z(S_r, z)$, or at least a subset of $Z(S_r, z)$, without the necessity of calculating the composition of the entire system $S_r(E)$.

The system $S_1(E_1)$ is a subsystem of the system $S_2(E_2)$ if $E_1 \subset E_2$ and $S_1(E_1) \subset$ $\subset S_2(E_2)$. Since the relation $E_1 \subset E_2$ includes also the case $E_1 = E_2$, either we can have $E_1 \neq E_2$ or both the system and its subsystem are created by the same set of elements. Subsystems to a given system can be created without taking into account the possibility of real existence of such isolated systems. Let $S_1(E_1)$ be a subsystem to $S_2(E_2)$; we shall call this subsystem a dependent one if there is at least one pair of components s_1, s_2, $s_1 \in S_1(E_1)$, $s_2 \in S_2(E_2) - S_1(E_1)$ such that it holds $x_1 < z$ in the system $S_1(E_1)$ and $x_1 \geq z$ in $\{s_2\} \cup S_1(E_1)$. In the opposite case, $S_1(E_1)$ is an independent subsystem.

An example of a dependent subsystem in a system containing positive and negative ions is an electrically neutral subsystem containing either only positive or only negative ions. To enable the existence of negative ions, this subsystem must contain a sufficient amount of e^- as well as components which can be ionized and give rise to positive ions, *e.g.*, K, K^+. If we assume in our subsystem the existence of some component both in a condensed, $s(c)$, and in the gaseous, $s(g)$, phase at a temperature lower than is the boiling point temperature, then in an equilibrium we can observe $x_{s(c)} \geq z$ only if the subsystem contains also other components than $s(g)$ in its gaseous phase[1,2].

The following two lemmas are valid; the first one is a consequence of the independence of a subsystem. The second one, which may be denoted as a lemma about the extension of a subsystem, follows from the first one and it offers a method for determining $Z(S, z)$.

1. Let $S_1(E_1)$ be an independent subsystem to $S_2(E_2)$; then $Z(S_1, z) \subset Z(S_2, z)$.

2. Let

$$S(E) = \bigcup_{i=1}^{n} S_i(E_i), \quad E = \bigcup_{i=1}^{n} E_i$$

and the subsystems

$$\bar{S}_1(E_1) = S_1(E_1),$$

$$\bar{S}_k(\bigcup_{i=1}^{k} E_i) = \bigcup_{i=1}^{k} S_i(E_i) - \bigcup_{i=1}^{k-1} Z(\bar{S}_i, z) \quad k = 2, 3, \dots, n$$

are independent; then it holds

$$Z(S, z) = \bigcup_{i=1}^{n} Z(\bar{S}_i, z).$$

The System of Hydrocarbon Combustion Products

The theory was applied to a system of combustion products of CH_4 or a hypothetic CH fuel with air and K_2CO_3 (K forms 1% of the mass of the combustion products). These products can be encountered in magnetohydrodynamic generators of the electrical energy. The equilibrium composition is to be calculated at $T = 1\ 500$, $2\ 000, 2\ 500, 3\ 000, 3\ 500$ K and $p = 0{\cdot}1, 0{\cdot}2, \dots, 1{\cdot}0$ MPa by minimizing the Gibbs free energy. Both the minimization method and the computation algorithm written in Algol 60 has been published elsewhere[2].

The system of products is created by the set $E = \{Ar, C, H, K, N, O, e^-\}$ and it contains all possible compounds enumerated in[3], which amounts to 112 compounds creating the system $S_r(E)$. A direct computation of composition at the given temperatures and pressures allows to divide compounds in the system $S_r(E)$ into two groups. This separation into groups is identical for CH_4 and for the CH fuel. The first group contains 52 compounds with the maximum value of the mole fraction m greater or equal than $z = 10^{-9}$. In brackets we report temperatures and pressures for which the mole fraction of preceding compound is greater or equal than z. The hyphen denotes all temperatures and pressures considered, *e.g.*, the notation e^-, K^+ ($T = 1\ 500, p < 0{\cdot}3; T > 1\ 500$) means that $x_{e^-}, x_{K^+} \geqq z$ at $0{\cdot}1$ or $0{\cdot}2$ MPa and $1\ 500$ K, or at all pressures considered and $2\ 000, 2\ 500, 3\ 000, 3\ 500$ K. The second group consists of 60 compounds which make up the set $Z(S_r, 10^{-9})$, since it holds $x < z$ at all temperatures and pressures considered.

1. Group $(m \geqq z)$

a) $10^{-3} \leqq m < 1$;
Ar, CO, CO_2, H, H_2, H_2O, K, KOH, N_2, NO, O, O_2, OH$(-)$;

b) $10^{-6} \leqq m < 10^{-3}$;
HO_2, KNO_2, KO, NO_2, $N_2O(-)$,
e^-, K^+ ($T = 1\ 500, p < 0{\cdot}3; T > 1\ 500$),
HNO ($T = 1\ 500, p > 0{\cdot}5; T > 1\ 500$),

$(KOH)_2$ $(T < 3\,000;\ T = 3\,000,\ p > 0 \cdot 1;\ T = 3\,500,\ p > 0 \cdot 4)$,

H_2O_2, KH, OH^- $(T > 1\,500)$,

HCO, N, NH, NH_2, H^-, O^-, O_2^- $(T > 2\,000)$,

K_2CO_3 $(T < 2\,500;\ T = 2\,500,\ p > 0 \cdot 1)$;

c) $10^{-9} \leqq m < 10^{-6}$:

K_2O $(T = 1\,500,\ p < 0 \cdot 4;\ T > 1\,500)$,

KNO_3 $(T = 1\,500,\ p > 0 \cdot 9;\ T = 2\,000,\ p > 0 \cdot 6;\ T = 2\,500,\ p > 0 \cdot 6)$,

COOH, HNO_2, K_2 $(T > 1\,500)$,

NH_3 $(T = 2\,000,\ p > 0 \cdot 1;\ T > 2\,000)$,

NO_2^-, K_2^+ $(T > 2\,000)$,

HCOOH $(T = 2\,500;\ T = 3\,000;\ T = 3\,500,\ p > 0 \cdot 1)$,

HCN, O_3 $(T > 2\,500)$,

HO_2^-, K_2O^+ $(T > 2\,500,\ p > 0 \cdot 1)$,

H_2CO $(T = 3\,000,\ p > 0 \cdot 1;\ T = 3\,500)$,

NCO $(T = 3\,000,\ p > 0 \cdot 5;\ T = 3\,500)$,

CN, CN^- $(T > 3\,000)$,

NCN $(T = 3\,500,\ p > 0 \cdot 2)$,

C $(T = 3\,500,\ p < 0 \cdot 2)$;

2. *Group* $(x < z)$

a) $10^{-12} \leqq m < 10^{-9}$:

K_2O_2, HNO_3, NH_2OH, NO_3^-, N_2H_2, HNC, N_3, CNN, HN_3, N_2O_3, NO^+, CH, CH_2, CH_3, C_2O, CH_2OH, H_3O^+;

b) $m < 10^{-12}$:

C_2, C_3, C_4, C_5, CCN, CH_3O, CH_3OH, CH_4, CNC, C_2H, C_2H_2, C_2H_3, C_2H_4, C_2H_5, C_2H_6, C_2H_5OH, C_2N_2, C_3O_2, HCCN, NH_2NO_2, N_2H_4, N_2O_4, N_2O_5, C^-, C_2^-, Ar^+, C^+, C_2^+, CH^+, CN^+, CO^+, CO_2^+, H^+, H_2^+, H_3^+, H_2O^+, N^+, N_2^+, NH^+, NH_4^+, O^+, O_2^+, OH^+.

The first lemma in the preceding paragraph was verified for subsystems $S_i(E_i)$ of the system $S_r(E)$ for $E_i \subset E$, $E_i \neq E$, $i = 1, 2, \ldots, 5$

$$E_1 = \{Ar, N, O, e^-\},$$
$$E_2 = \{H, O, e^-\},$$
$$E_3 = \{C, O, e^-\},$$
$$E_4 = \{C, H, N\},$$
$$E_5 = \{C, H, O\}.$$

The lemma about the extension of a subsystem was verified with the help of subsystems created by the sets E_1, E_2, $\ldots$, E_5 and further with the help of subsystems

$\bar{S}_i(E)$, $i = 1, 2, \ldots, 5$ of the system $S_r(E)$. The subsystems $\bar{S}_i(E)$ are created by the set E, just like the system $S_r(E)$. The subsystem $\bar{S}_1(E)$ contains 8 components: Ar, C, H_2, K, N_2, O_2, e^-, K^+. The order of the remaining 104 components corresponds to that in which these components were searched for in the tables[3] and therefore it is rather arbitrary. With the help of a random number generator, these components were divided into 4 groups, S_2, S_3, S_4, S_5, each containing 26 components. A computation of composition in the set $\bar{S}_1(E)$ showed that $Z(\bar{S}_1, 10^{-9})$ is an empty set. Further, the set $\bar{S}_1(E)$ was extended to $\bar{S}_2(E) = \bar{S}_1(E) + S_2$ and a computation of its composition yielded the set $Z(\bar{S}_2, 10^{-9})$. In accordance with the second lemma of the preceding paragraph, we determined subsequently the composition in the systems

$$\bar{S}_k(E) = \bar{S}_{k-1}(E) + S_k - Z(\bar{S}_{k-1}, 10^{-9}), \quad k = 3, 4, 5$$

as well as the sets $Z(\bar{S}_i, 10^{-9})$, $i = 3, 4, 5$. It holds

$$Z(S_r, 10^{-9}) = \bigcup_{k=1}^{5} Z(\bar{S}_k, 10^{-9}).$$

The set $Z(S_r, 10^{-9})$ was determined for $T = 3\,500$ K and all pressures considered, when it contains 62 components, and it was determined without computing the composition in the $S_r(E)$ system, which contains 112 components. The systems $\bar{S}_i(E)$, $i = 1, 2, \ldots, 5$ possess subsequently 8, 34, 49, 60, 66 components.

Notes

We defined here the following terms: component, zero component, system, subsystem, dependent and independent subsystem. All these terms refer to the composition in a system of chemically reacting substances without making any difference between equilibrium and nonequilibrium cases. We gave examples of dependent subsystems which basically include all possibilities in the case of an equilibrium composition. In a nonequilibrium case, the situation will be more complicated due to the effect of catalysts, intermediate products, *etc.*

The criterion for determining the zero component, *i.e.*, $x_i < z$, may be replaced with another one, *e.g.*, with the requirement that the product of the concentration of a component and its collision cross-section with another particle be lower than z. However, the use of any criterion different from $x_i < z$ may cause that mole fractions of components considered in the calculation will be loaded with error.

A special case of the independent subsystem in a system is the subsystem $S(E_1)$ which may be denoted as a totally independent subsystem of $S(E)$ and for which it holds

$$E_1 \subset E, \quad E_1 \neq E, \quad S(E) = S(E_1) \cup S(E - E_1).$$

The composition of the system $S(E)$ is in this case determined directly by the composition of the subsystems $S(E_1)$, $S(E - E_1)$.

The concept of the independent subsystem enables not only to determine zero components without calculating the composition of the entire system, but it also possesses the following meaning. Let a set $Z(S_1, z)$ be defined in a system $S_1(E_1)$ and let $S_1(E_1)$ be an independent subsystem of $S_2(E_2)$, then it holds $Z(S_1, z) \subset Z(S_2, z)$, *i.e.*, component of $Z(S_1, z)$ need not be considered in calculations of composition in the system $S_2(E_2)$. Our system of hydrocarbon combustion products is an independent subsystem, *e.g.*, in a system of combustion products of sulphur-containing hydrocarbons or in a system of coal combustion products containing an ionizing additive or in systems of combustion products of hydrocarbons, possibly also coal, when we assume the presence of a condensed phase. If we take into account that the concentration of the ionizing additive in combustion products is relatively low, then our results are valid rather exactly (when the number z is selected with a sufficient reserve) also for combustion products without any ionizing additive. This is one of the reasons for selecting the above example.

The lemma about the extension of a subsystem when both the system $S(E)$ and its possible subsystems are created by the same set E may be applied also in the following manner. Let $S_i(E)$ be an arbitrary subsystem of $S(E)$ for which we must find $Z(S, z)$. A component $s \in S_i(E)$ depends on a component $s' \in S(E)$ when it holds $x_s < z$ for $s' \notin S_i(E)$ and $x_s \geqq z$ for $s' \in S_i(E)$. The component s depends on components which create the set $M(s)$. The s is an independent component if $M(s) = \emptyset$. Let

$$S_0 = \bigcup_{k=1}^{N} M(s_k) \, ,$$

where N is the number of components in the system $S(E)$. Thus, the set S_0 consists of some components of the system $S(E)$. If all elements from E are present in components of S_0, then let us select a subsystem $S_1(E) = S_0$, $S_1(E) \subset S(E)$. In the opposite case we add to S_0 other components so that $S_1(E)$ would contain all elements from E. The subsystem $S_1(E)$ selected in this manner as well as all subsystems $S_i(E)$ which satisfy the relation $S_1(E) \subset S_i(E) \subset S(E)$ are independent in $S(E)$. We may assume that the number of components N_1 of $S_1(E)$ is substantially lower than N and that it is also lower than the number of nonzero components of $S(E)$, N_z. Then, if the system $S_1(E)$ is being subsequently expanded, each time by one component only, the set $Z(S, z)$ may be found by calculating the composition of subsystems $S_i(E)$ whose number of components does not exceed $N_z + 1$. An analogous method has been employed and described in the preceding paragraph for a system of hydrocarbon combustion products.

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