DETERMINATION OF THE EQUILIBRIUM COMPOSITION OF GAS IN REACTING MIXTURES AT HIGH TEMPERATURE

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An iterative method, which is quite convenient for calculations on small computers, is proposed for finding the equilibrium state of gas in reacting mixtures with few components. Examples of calculations of the equilibrium composition and gas dynamic quantities in pure carbon dioxide and in the mixture $CO-N_2-Ar$ behind a shock wave are given.

When solving many problems related with the propagation of shock waves in reacting mixtures, with a jet stream in plasmotrons, chemical reactors, etc., it is necessary to know the composition and thermodynamic properties of the gas in a state of partial or complete statistical equilibrium. In a number of cases (shock waves in air, etc.) such information can be found in available monographs and articles (see, for example, [1-3] . However, such data are insufficient when setting up experiments with other mixtures.

General methods of solving the problem of the equilibrium composition of gas behind a shock wave have been known for a long time; sufficiently general programs have been compiled for computer calculation of the composition and thermodynamics of mixtures of practically any arbitrarily complex composition [4].

However, in many cases the research must have on hand considerably simpler methods of solving these problems as applied to mixtures with few reacting components without resorting to cumbersome computer calculations. Such examples are indicated in [5], where cases of equilibrium after exciting oscillations of molecules in a nondissociating gas and equilibrium upon dissociation and ionization of a one-component gas are investigated. The method proposed in [5], however, is unjustifiably complex, since it is based on multiple graphic interpolation.

We will indicate here a simpler method and give concrete relations which permit in many cases finding without great effort the equilibrium composition and thermodynamics of gas for given temperature and pressure values.

The law of mass action, Dalton's law, and equation of state are used as the initial premises. The concrete calculation of the equilibrium state and gas dynamic quantities are given here for the case of a shock wave. To determine the velocity of the shock wave and pressure and density drops at the front, we use the relations of the laws of conservation of energy, momentum, and mass from which, after certain unessential simplifications, it is easy to obtain the expressions (see [6])

$$V=\sqrt{\frac{\sum\limits_i h_i x_i}{116\sum\limits_i \mu_i x_i}-\frac{H_0}{116\mu_0}}, \tag{1}$$

$$\frac{\rho_2}{\rho_1}=\frac{60V^2\Sigma\mu_i x_i}{T_2}\left(1+\sqrt{1-\frac{0{,}03327T_2}{V^2\sum\limits_i \mu_i x_i}}\right), \tag{2}$$

$$\frac{p_2}{p_1}=\frac{\rho_2}{\rho_1}\cdot\frac{T_2\mu_0}{T_1\sum\limits_i \mu_i x_i}. \tag{3}$$

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Here V is the velocity of the shock wave, km/sec; h_i is the total molar enthalpy of the i-th component at temperature T_2 behind the shock wave; x_i, μ_i are the mole fraction and molecular weight of the i-th component, respectively; H_0, μ_0 are the molar enthalpy and molecular weight of the initial composition of the mixture of gases at temperature T_1 ahead of the shock wave front; p_2/p_1 is the ratio of the pressure behind the shock wave front to the pressure ahead of the front; ρ_2/ρ_1 is the analogous ratio for density.

1. Equilibrium with Respect to Internal Degrees of Freedom of Molecules in Mixture. When the chemical composition of a gas does not change in the system it is sufficient to determine the conditions of equilibrium with respect to the internal degrees of freedom of the molecules in the gas. It is of interest to calculate the partial equilibrium with respect to internal degrees of freedom for the case of a shock wave when it is necessary to know the gas composition before the start of processes related with chemical transformations. For a mixture of any composition the ratio of the values of the gas density on the shock wave can be written in the form*

$$\frac{\rho_2}{\rho_1} = b\,\{1+\sqrt{1+T_1 b^{-2} T_2^{-1}}\}, \tag{4}$$

where

$$b = \left(\frac{H_2}{RT_2} - \frac{1}{2}\right) - \frac{T_1}{T_2}\left(\frac{H_1}{RT_1} - \frac{1}{2}\right).$$

Here R is the gas constant. The value of the enthalpy of the mixture is equal to the sum $H = \sum_i H_i x_i$, where H_i is the molar enthalpy of the i-th component.† The values of $H_i(T)$ (and also of h_i) can be found in thermodynamics handbooks, for example, in [7].

Knowing the value of the ratio of the gas density on the shock wave, we can determine the ratio of pressures

$$\frac{p_2}{p_1} = \frac{\rho_2}{\rho_1}\cdot\frac{T_2}{T_1} \tag{5}$$

and the velocity of the shock wave

$$V = \left\{\frac{IR}{\mu}\left(\frac{\rho_2}{\rho_1}T_2 - T_1\right)\left(1-\frac{\rho_1}{\rho_2}\right)^{-1}\right\}^{1/2}, \tag{6}$$

where I is the mechanical equivalent of heat.

Thus to solve the problem in this case we must assign a set of values of T_1 and T_2 and, finding the values of enthalpy H_2 for a mixture of a given composition by means of tables [7], we must determine p_2/p_1, ρ_2/ρ_1, and V, and then plot graphs of T_2, p_2/p_1, ρ_2/ρ_1 against the shock wave velocity. We note that the procedure of calculating is equally simple for a mixture of any composition. The states of equilibrium with respect to individual degrees of freedom of the molecule (rotational, vibrational, electronic) can be determined by changing the values of the molar enthalpy.

2. Dissociating Gas. Change of a Diatomic Component (in Inert Gas) Consisting of Identical Atoms. In the simplest case, viz., dissociation of diatomic gas consisting of identical atoms, having used Dalton's law and the law of mass action, we obtain a quadratic equation for the mole fraction of the atomic component, the solution of which is the expression

$$x_A = \sqrt{\frac{\alpha_0^2}{4}\left(\frac{K_{A_2}}{p}\right)^2 + \left(\frac{K_{A_2}}{p}\right)\frac{1}{(1+2\beta_0)}} - \frac{\alpha_0}{2}\left(\frac{K_{A_2}}{p}\right). \tag{7}$$

For the mole fraction of molecules we have

$$x_{A_2} = \left(\frac{p}{K_{A_2}}\right)x_A^2.$$

Here $K_{A_2}(T)$ is the equilibrium constant of dissociation of molecules A_2, atm; x_A, x_{A_2} are the equilibrium values of the mole fractions of atoms and molecules at temperature T and pressure p of the gas;

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*This expression can be found, for example, from Eqs. (9.1)-(9.5) in [5].

†The total enthalpy of the component is $h_i = H_i + \Delta H_f^0$, where ΔH_f^0 is the heat of formation of the component from elements in standard states.

$\alpha_0 = (1 + \beta_0)/(1 + 2\beta_0)$, where $\beta_0 = \gamma_0\mu_A/(\mu_0 - 40\gamma_0)$, where γ_0 and μ_0 are the mole fraction of inert gas (argon) and molecular weight of the initial composition of the mixture; μ_A is the molecular weight of the atom A.

Assigning the table values of the equilibrium constants K_{A_2} at different temperatures T and values of the gas pressure p for different compositions of the mixture, we can obtain the temperature and pressure dependences of the concentration of components. Having such an array of equilibrium values, we can determine the necessary thermodynamic quantities in each concrete case.

3. Chemical Equilibrium in a Complex Mixture of Gases. When determining the equilibrium values in a mixture of chemically reacting gases (at a high temperature) the problem is divided into two stages: determination of the equilibrium composition of the gas and calculations of the thermodynamic and gas dynamic quantities. The first part of the problem is most laborious.

We will consider a gas mixture whose components at high temperature are atoms and diatomic molecules, whereby three kinds of atoms i, j, k participate pairwise in the formation of the molecules. In a more general case we can, of course, consider a mixture of gases which includes also triatomic components and a greater number of kinds of atoms. However, our purpose is to show a general approach to the solution of problems of the equilibrium composition in gas mixtures, the number of components in which makes possible calculations on small computers or even manually. By means of the relations of the law of mass action for molecular components we can represent the concentrations (mole fractions) of diatomic components in terms of concentrations of atomic components

$$\begin{gathered} x_{ii} = \beta_{ii}x_i^2; \quad x_{jj} = \beta_{jj}x_j^2; \quad x_{kk} = \beta_{kk}x_k^2; \\ x_{ij} = \beta_{ij}x_ix_j; \quad x_{ik} = \beta_{ik}x_ix_k; \quad x_{jk} = \beta_{jk}x_jx_k. \end{gathered} \tag{8}$$

Then from Dalton's law and the two conditions of constancy of the ratio of the number of atoms of kind i (and j) to the number of atoms of kind k we obtain directly a system of three (according to the number of kinds of elementary components) nonlinear algebraic equations for three unknowns x_i, x_j, x_k:

$$\beta_{ii}x_i^2 + \beta_{jj}x_j^2 + \beta_{kk}x_k^2 + \beta_{ij}x_ix_j + \beta_{ik}x_ix_k + \beta_{jk}x_jx_k + x_i + x_j + x_k + x_0 - 1 = 0, \tag{9}$$

$$2\beta_{ii}x_i^2 + \beta_{ij}x_ix_j + \beta_{ik}x_ix_k + x_i - \alpha_{ik}(2\beta_{kk}x_k^2 + \beta_{jk}x_jx_k + \beta_{ik}x_ix_k + x_k) = 0, \tag{10}$$

$$2\beta_{jj}x_j^2 + \beta_{ij}x_ix_j + \beta_{jk}x_jx_k + x_j - \alpha_{jk}(2\beta_{kk}x_k^2 + \beta_{jk}x_jx_k + \beta_{ik}x_ix_k + x_k) = 0. \tag{11}$$

Here x_0 is the mole fraction of inert gas; α_{ik} and α_{jk} are the values of the ratios of the number of atoms of one kind to the number of atoms of another kind, calculated from the initial composition of the mixture; coefficient $\beta_m = pK_m^{-1}$, where p is the equilibrium value of pressure, atm; K_m is the equilibrium constant of dissociation of molecules of kind m, atm.

An iterative method is proposed for solving this system. When considering mixtures of concrete gases having known values of the equilibrium constants $K_m(T)$ at different temperatures T (cf. [7]), among the coefficients β_m there is always one or several which exceed the others by an order or more. This condition should be used for finding the iterative expressions for atomic components.

Since the mole fraction of the component is always less than unity it is necessary to represent the iterative relations for x_a* so that the largest of the coefficients β_m is in the denominator and the entire fraction is less than unity in each step of the calculations. If nevertheless the iterative expression for some x_a, found by means of one of Eqs. (9)-(11) does not meet this condition, we can always bring it to the necessary form by adding the term $\sum\limits_{a \neq a'} \beta_{\max}x_a$ to the right and left sides of the equation. After performing such a procedure for each of the quantities x_a the iterative relations for x_i, x_j, x_k obtained by Eqs. (9)-(11) have the form

$$\begin{aligned} x_i &= f_i(\beta_m, x_i, x_j, x_k), \\ x_j &= f_j(\beta_m, x_i, x_j, x_k), \\ x_k &= f_k(\beta_m, x_i, x_j, x_k). \end{aligned} \tag{12}$$

The selection of the values of the atomic components for the initial step of iteration in each specific case is done, as will be shown below, from concrete physical considerations.

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*The subscript *a* denotes atomic components and m molecular.

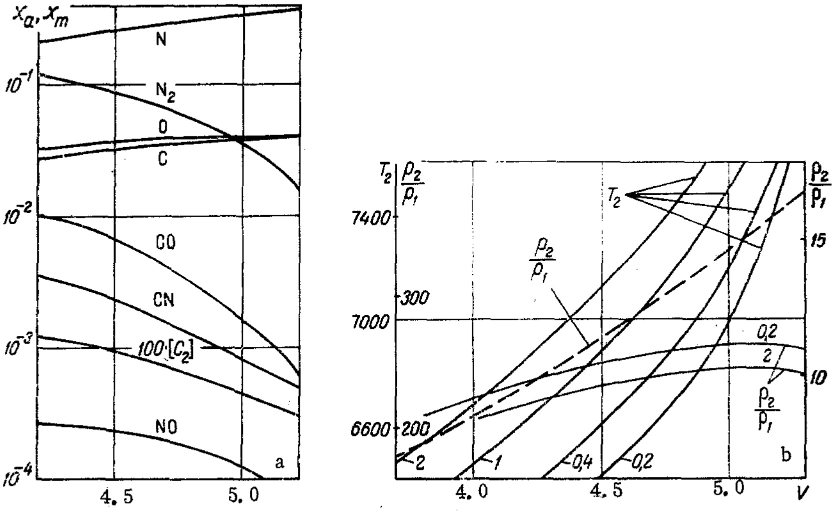

Fig. 1. Equilibrium values of mole fractions of components behind the shock wave in a mixture of 5% CO–25% N_2–70% Ar (p_2 = 1 atm) (a) and equilibrium values of T_2, p_2/p_1, ρ_2/ρ_1 in a mixture of 5% CO–25% N_2–70% Ar (the numbers near the curves are the equilibrium values of p_2, atm) (b) as a function of the shock wave velocity. V, km/sec; T, °K.

In the general case, for the values of x_i, x_j, x_k in the initial step we have

$$x_i^{(0)} = f_i^{(0)}, \quad x_j^{(0)} = f_j^{(0)}, \quad x_k^{(0)} = f_k^{(0)},$$

where $f_i^{(0)}$, $f_j^{(0)}$, $f_k^{(0)}$ are functions of the assigned T and p and initial composition, or simply numbers less than unity.

In conformity with (12), for the first step the values of x_i, x_j, x_k will have the form

$$x_i^{(1)} = f_i(x_i^{(0)}, x_j^{(0)}, x_k^{(0)}),$$
$$x_j^{(1)} = f_j(x_i^{(1)}, x_j^{(0)}, x_k^{(0)}),$$
$$x_k^{(1)} = f_k(x_i^{(1)}, x_j^{(1)}, x_k^{(0)}).$$

Hence we see that the values of x_i, x_j, x_k obtained in this step are used for calculating x_j and x_k.

In the second step the values of x_a have the form

$$x_i^{(2)} = f_i(x_i^{(1)}, x_j^{(1)}, x_k^{(1)}),$$
$$x_j^{(2)} = f_j(x_i^{(2)}, x_j^{(1)}, x_k^{(1)}),$$
$$x_k^{(2)} = f_k(x_i^{(2)}, x_j^{(2)}, x_k^{(1)}).$$

These calculations must be repeated until the iterations converge (with a prescribed accuracy) to the unknown values of x_i, x_j, x_k, which are the roots of system of Eqs. (9)-(11). The procedure of solving the problem of the equilibrium composition can be presented concretely by the following examples.

a) Mixture of Diatomic Gases with an Inert Gas (CO–N_2–Ar). Suppose that at high temperatures (up to T = 10,000°K) the mixture of gases CO–N_2–Ar contains only neutral components: C (1), N (2), O (3), CO (4), N_2 (5), NO (6), CN (7), C_2 (8), O_2 (9), Ar (10). For coefficients β_m the following inequality exists in this mixture:

$$\beta_4 \gg \beta_5 > \beta_7 > \beta_6 > \beta_8 > \beta_9. \tag{13}$$

With consideration of (13) the iterative expressions for the mole fractions of carbon, nitrogen, and oxygen atoms (x_1, x_2, x_3) have the form

$$x_1 = \frac{2\beta_9 x_3^2 + \beta_6 x_2 x_3 + x_3}{1 + 2\beta_8 x_1 + \beta_7 x_2};$$

$$x_2 = \frac{1 - c\xi - x_1(1 + \beta_8 x_1 - \beta_4 x_2 + \beta_7 x_2) - x_3(1 + \beta_4 x_1 + \beta_9 x_3)}{1 + \beta_4 x_1 + (1 + c)\beta_5 x_2 + (1 + 1{,}07c)\beta_6 x_3 + 0{,}5c},$$

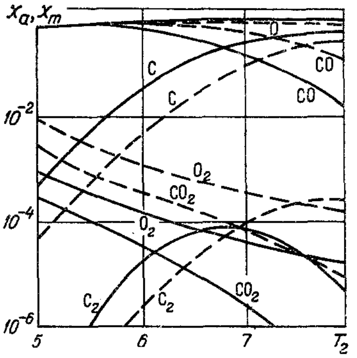

Fig. 2

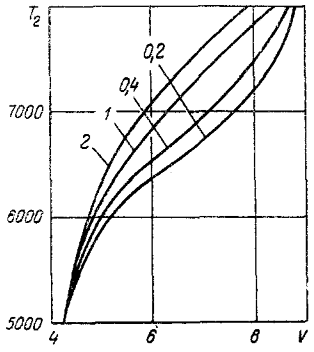

Fig. 3

Fig. 2. Equilibrium values of the molar fractions of components in pure carbon dioxide behind the shock wave as a function of T_2 (thousands of degrees K). Solid line: $p_2 = 0.2$ atm; dashed line: $p_2 = 2$ atm.

Fig. 3. Equilibrium values of T_2 (°K) vs V (km/sec) in pure CO_2. The equilibrium values of p_2, atm (numbers by curves) are the parameter.

where

$$c = \frac{\gamma_0}{1-\gamma_0};$$

$$\xi = 0.43x_1 + 0.57x_3 + 0{,}93\beta_7 x_1 x_2 + 0.86\beta_8 x_1^2 + \beta_4 x_1 x_3,$$

$$x_3 = \frac{x_2(2\beta_5 x_2 + \beta_6 x_3 + \beta_7 x_1 + 1)}{\alpha_{23}(\beta_4 x_1 + 2\beta_9 x_3 + \beta_6 x_2 + 1)}.$$

On comparing the iterative expression for x_2 from an equation analogous to (9) we take into account that the equilibrium value of the mole fraction of the inert gas is equal to

$$x_0 = \gamma_0 \frac{\mu}{\mu_0},$$

where

$$\mu = \sum_i \mu_i x_i \quad (i = 0, \ldots, 9).$$

The value of $x_2^{(0)}$ for the initial step is found on the assumption that in the zeroth approximation the dissociation of nitrogen molecules is the only reaction affecting the loss of N_2 molecules. Then, according to (7)

$$x_2^{(0)} = \frac{1}{\beta_5}\left(\sqrt{0.25\alpha_0^2 + \beta_5(1+2\beta_0)^{-1}} - 0.5\alpha_0\right).$$

Taking into account the condition of the constant ratio of the number of N atoms to the number of O atoms for a concrete initial composition of the mixture, we will consider that in the zeroth approximation $x_3^{(0)} \approx x_2^{(0)}\alpha_{23}^{-1}$. We can set the value of $x_1^{(0)}$ equal to zero.

The equilibrium composition and thermodynamic and gas dynamic quantities in the mixture $CO-N_2-Ar$ were calculated for the case of a shock wave.* The results of the calculations can be presented in the form of x_m, x_a, T_2, p_2/p_1, ρ_2/ρ_1 as a function of the shock wave velocity V and initial pressure p_1, in which case the assigned equilibrium values of T_2 and p_2 serve as parameters. Figure 1a and b shows the mole fractions, equilibrium values of temperature behind the shock wave front T_2, pressure drop p_2/p_1, and density drop ρ_2/ρ_1 plotted against the shock wave velocity V. The values of the equilibrium pressure p_2 (0.2-2 atm) serve as parameters in both figures. The curve of p_2/p_1 (dashed line) vs V is the same for all temperatures. Assigning the values of p_1 and V (always known in the experiment or calculation), from the array of values of Fig. 1 we can find all equilibrium quantities of interest for calculating shock waves.

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*The calculations were made on the "Nairi" computer.

In the case of mixture $CO-N_2-Ar$ rapid convergence of iterations was observed only for $T \geq 6000$°K; the iterations diverged when $\alpha_{23} \leq 2$.

b) Mixture of Triatomic Gases (CO_2, H_2O) with an Inert Diluent. Analogous calculations for mixtures of the type CO_2-Ar and H_2O-Ar do not differ fundamentally from each other. As an example we will select a mixture of carbon dioxide with argon. The gas dynamic quantities are calculated by (1)-(3).

The iterative relations for the mole fractions of atoms of oxygen (x_3) and carbon (x_1) have the form

$$x_1 = \frac{0.5x_3 + \beta_9 x_3^2 - 2\beta_8 x_1}{1+0.5\beta_4 x_3},$$

$$x_3 = \frac{1-\beta_8 x_1^2(1+0.54c) - \beta_9 x_3^2(1+0.73c) - \beta_{10} x_1 x_3^2(1+c) - x_1(1+c)}{1+\beta_4 x_1(1+0.64c) + 0.36c}.$$

Here we used the notations of example a): $\beta_{10} = p^2 K_{10}^{-1}$, where K_{10} is the equilibrium constant of the reaction $CO_2 = 2O + C$.

The expressions for $x_1^{(0)}$ and $x_3^{(0)}$ for the initial step of the iterations are found from the condition that in the zeroth approximation the decomposition of CO_2 proceeds incompletely and according to the reaction $CO_2 = CO + O$ with an equilibrium constant $K'_{10} = K_{10} K_4^{-1}$. In this case $x_4 \approx x_3$, but $x_4 \simeq \beta_4 x_1 x_3$, and then $x_1^{(0)} \approx \beta_4^{-1}$. We note that according to the law of mass action the mole fraction CO_2 $x_{10} = \beta'_{10} x_4 x_3$; here $\beta'_{10} = p(K'_{10})^{-1}$. Having written the relation for Dalton's law with consideration of decomposition of CO_2 molecules into CO molecules and O atoms, we obtain a quadratic equation for finding the initial condition for $x_3^{(0)}$, the solution of which is the following expression:

$$x_3^{(0)} = \frac{1}{\beta'_{10}(1+c)} \left\{ \sqrt{0.25(2+c)^2 + \beta'_{10}(1+c)} - 1 - \frac{c}{2} \right\}.$$

For mole fractions of the molecular components we have

$$x_{10} = \beta_{10} x_1 x_3^2; \quad x_4 = \beta_4 x_1 x_3;$$

$$x_9 = \beta_9 x_3^2; \quad x_8 = \beta_8 x_1^2.$$

Figure 2 shows the concentrations of components as a function of the equilibrium temperature T_2 calculated for pure carbon dioxide behind the shock wave front, and Fig. 3 shows the equilibrium values of temperature as a function of the shock wave velocity for different pressures p_2.

The use of the iterative method for finding the equilibrium composition of gases in reacting mixtures with few components permits rather quick and simple equilibrium calculations. The method, which was tried in a concrete case (reacting gas behind a shock wave) and gave good results, deserves attention in a number of other applications.

NOTATION

T	is the gas temperature, °K;
x_a and x_m	are the mole fraction of atomic and molecular components, respectively;
H	is the enthalpy of gas;
H_i	is the enthalpy of i-th component;
H_0	is the enthalpy of gas or mixture of gases at T = 298°K;
μ	is the molecular weight of mixture of gases;
μ_0	is the molecular weight of gas at T = 298°K;
x_1	is the mole fraction of carbon atoms;
x_2	is the mole fraction of nitrogen atoms;
x_3	is the mole fraction of oxygen atoms;
x_4	is the mole fraction of carbon monoxide molecules;
x_5	is the mole fraction of nitrogen molecules;
x_6	is the mole fraction of nitric oxide molecules;
x_7	is the mole fraction of cyan molecules;
x_8	is the mole fraction of molecular carbon C_2;
x_9	is the mole fraction of oxygen molecules;
x_{10}	is the mole fraction of carbon dioxide molecules;
γ_0	is the mole fraction of inert gas (argon) in initial composition of mixture;

$\beta_0 = \gamma_0 \mu_A/(\mu_0 - 40\gamma_0)$;
$\alpha_0 = (1 + \beta_0)/(1 + 2\beta)$;
$c = \gamma_0/(1 - \gamma_0)$.

Subscripts

1 denotes gas parameters ahead of the shock wave front;
2 denotes gas parameters behind the shock wave front.

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