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Analytical Representation of the Thermodynamic Functions of Dissociating Air

V. V. Mikhailov
Institute of Mechanics, Academy of Sciences of the USSR, Moscow

ANALYTIC expressions for the thermodynamic functions of dissociating air are obtained on the basis of an approximation of the statistical sums of the gas particles.

As is known, at temperatures of the order of 200°C and above there is a marked excitation of vibrational degrees of freedom of air molecules, whereas at a temperature of the order of 2000° the molecules begin to break down into atoms or dissociate. This dissociation is paralleled, however, by continuing processes of excitation of new vibrational and electronic levels, as well as by the process of excitation of those rotational levels that depend on the rigidity of the atomic bond in the molecule.

When all these phenomena are taken into account, the expressions for the thermodynamic functions of dissociating air become very cumbersome. This makes it practically impossible to use them directly in flow computations.

We can, however, obtain relatively simple and accurate expressions for the thermodynamic functions of dissociating air, provided we neglect processes of additional excitation of degrees of freedom of the particles.

Let us consider the equations of the chemical reactions proceeding in air at high temperatures:

$$O_2 + 5.11\ \text{ev} \rightleftarrows O + O$$
$$N_2 + 9.76\ \text{ev} \rightleftarrows N + N$$
$$N + O \rightleftarrows NO + 6.49\ \text{ev}$$

The equilibrium conditions for these reactions have the form

$$\begin{aligned} \frac{n_O{}^2}{n_{O_2}} &= \frac{f_O{}^2}{f_{O_2}} \cdot e^{-D_1/kT} \\ \frac{n_N{}^2}{n_{N_2}} &= \frac{f_N{}^2}{f_{N_2}} \cdot e^{-D_2/kT} \\ \frac{n_O n_N}{n_{NO}} &= \frac{f_O f_N}{f_{NO}} \cdot e^{-D_2/kT} \end{aligned} \qquad (1)$$

where

f = statistical sums of particles, i.e., sums of the form $\sum_i g_i e^{-\epsilon_i/kT}$
g_i = statistical weight of the state with energy ϵ_i
n = number of particles of a given kind in volume V
D_i = dissociation energies of molecules
k = Boltzmann's constant

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