AIAA Journal

RUSSIAN SUPPLEMENT

Igor Jurkevich, Editor

Published under National Science Foundation Grant-in-Aid. The Russian Supplement will appear monthly in 1963.

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

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

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

Translated from Inzhenernyi Sbornik (Engineering Collection) 28, 36–43 (1960). Translated by Faraday Translations, New York.

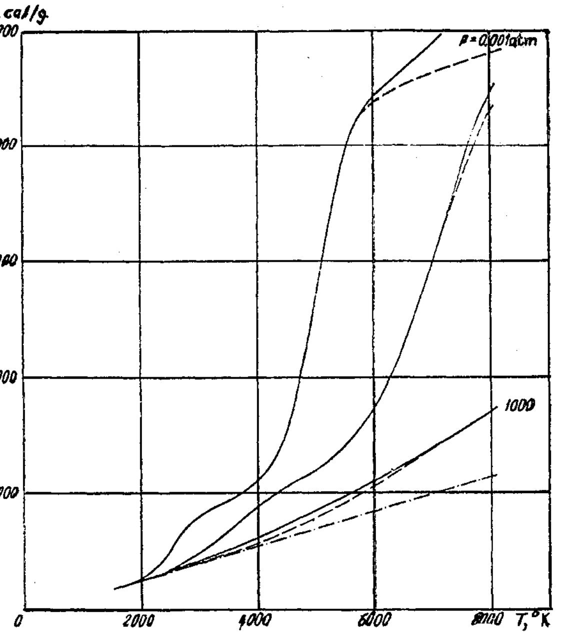

Fig. 1.

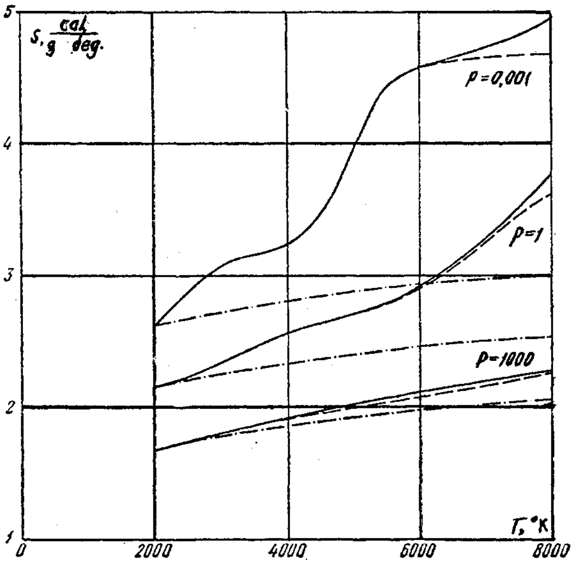

Fig. 2.

It is known that the translational energy levels do not depend on the internal levels. In the temperature range in question (2000°–8000°K) the internal levels—rotational, vibrational, and electronic—may also be considered independent, at least to within a few percent. Then the statistical sum of a particle in all its states may be represented as the product

$$f = f_T \cdot f_R \cdot f_v \cdot f_e$$

where f_T, f_R, f_v, f_e are the statistical sums for the translational, rotational, vibrational, and electronic energy levels, taken separately. The translational part f_T of the statistical sum has the form

$$f_T = \text{const} \cdot T^{3/2} \cdot V$$

With our assumptions the rotational part f_R will be

$$f_R = \text{const} \cdot T$$

The vibrational part of the statistical sum is approximated by the power function

$$f_v = \text{const} \cdot T^{\lambda}$$

An f_v in this form will be characteristic of a gas, for which the degree of excitation of vibrational levels is constant and equal to λ, i.e., the vibrational degrees of freedom of the molecule correspond to an energy λkT.

The electronic levels of particles taking part in dissociation reactions have the following properties: some of them lie very low and in the required range of temperatures are completely excited, whereas others lie higher and are hardly excited at all. Accordingly, the electronic part of the statistical sum can be well approximated by the equality

$$f_e = m$$

where m is the number of excited levels.

After approximating the statistical sum in the foregoing manner and introducing the notation

$$\alpha_1 = n_0/2N \qquad \alpha_2 = n_N/2N \qquad \beta = n_{N_0}/N$$

where N is the number of air molecules in the starting, undissociated mixture, Eqs. (1) assume the form:

$$\begin{aligned} \frac{\alpha_1^2}{\eta_1 - \alpha_1 - (\beta/2)} &= \frac{A_1}{\rho T^{\nu}} \cdot e^{-T_1/T} \\ \frac{\alpha_2^2}{\eta_2 - \alpha_2 - (\beta/2)} &= \frac{A_2}{\rho T^{\nu}} \cdot e^{-T_2/T} \qquad (2) \\ \frac{\alpha_i \alpha_2}{\beta} &= \frac{A_3}{\rho T^{\nu}} \cdot e^{-T_3/T} \end{aligned}$$

where

η_1, η_2 = volume fractions of O_2 and N_2 in the starting mixture
A_i = constants
ν = $\lambda - \frac{1}{2}$
T_i = D_i/k
ρ = mN/V, density (m = mass of air molecule)

In obtaining Eqs. (2) the following conditions of constant proportions were employed:

$$\begin{aligned} 2\eta_1 N &= n_0 + n_{N_0} + 2n_{O_2} \\ 2\eta_2 N &= n_N + n_{N_0} + 2n_{N_2} \end{aligned}$$

The presence in air of 1% argon has been neglected. The internal energy of a certain volume of dissociating air is expressed by the known equation

$$U = kT^2 \sum_i n_i \frac{\partial}{\partial T} \ln f_i + \tfrac{1}{2} D_i n_0 + \tfrac{1}{2} D_2 n_N - D_3 n_{N_0}$$

The sum $\sum_i$ is taken with respect to particles of all kinds within a volume V.

In the case in question this equation, written for a unit mass of gas, becomes

$$\frac{u}{R} = [3 + (1 - \alpha)\nu]T + \alpha_1 T_1 + \alpha_2 T_2 + \left(\frac{T_1 + T_2}{2} - T_3\right)\beta \qquad (3)$$

where R is the gas constant of unit mass of starting mixture and $\alpha = \alpha_1 + \alpha_2$, the total degree of dissociation.

The equation of state of a dissociating gas is given by

$$p/R = \rho T(1 + \alpha) \qquad (4)$$

Hence, the equation for the enthalpy of dissociating air may be written in the form

$$\frac{H}{R} = \frac{1}{R}\left(u + \frac{p}{\rho}\right) = [4 + \nu + \alpha(1 - \nu)]T + \alpha_1 T_1 + \alpha_2 T_2 + \left(\frac{T_1 + T_2}{2} - T_3\right)\beta \qquad (5)$$

In order that, when $T = 2000°\mathrm{K}$, the values of U and H, calculated from these equations, may coincide with their true values, we shall add to the right-hand sides of Eqs. (3) and (5) the quantity -2600ν. Finally, for U and H we get

$$\frac{U}{R} = [3 + (1 - \alpha)\nu]T + \alpha_1 T_1 + \alpha_2 T_2 + \left(\frac{T_1 + T_2}{2} - T_3\right)\beta - 2600\,\nu \quad (6)$$

$$\frac{H}{R} = [4 + \nu + \alpha(1 - \nu)]T + \alpha_1 T_1 + \alpha_2 T_2 + \left(\frac{T_1 + T_2}{2} - T_3\right)\beta - 2600\,\nu \quad (7)$$

From Eqs. (6) and (7), making use of Eq. (2), it is easy to obtain an expression for the entropy

$$S = \int \frac{dU + pd\,(1/\rho)}{T}$$

$$\frac{S}{R} = [3 + (1 - \alpha)\nu]\ln T - (1 + \alpha)\ln\rho + \sum_1^2 \alpha \ln \frac{A_i e^{1-\nu}}{\alpha_i^2} - \sum_1^2 \left(\eta_i - \alpha_i - \frac{\beta}{2}\right)\ln\left(\eta_i - \alpha_i - \frac{\beta}{2}\right) + \beta \ln \frac{\sqrt{A_1 A_2 l}}{A_3 \beta} + \text{const} \quad (8)$$

Equations (2), (4), (6), (7), and (8) constitute a solution of our problem, i.e., they are analytic expressions of the thermodynamic functions of dissociating air. It is easy to see that, written for a single gas with $\nu = 0$, these equations go over into the known expressions for an "ideal dissociating gas," derived by Lighthill.[2]

There is a certain inconvenience attached to the use of the expressions obtained, since Eqs. (2) are not accurately solvable with respect to the quantities α_i, α_2, β. However, it is easy to obtain an approximate solution of these equations by taking into account the fact that under ordinary conditions the nitric oxide content of air (i.e., the quantity β) is small.

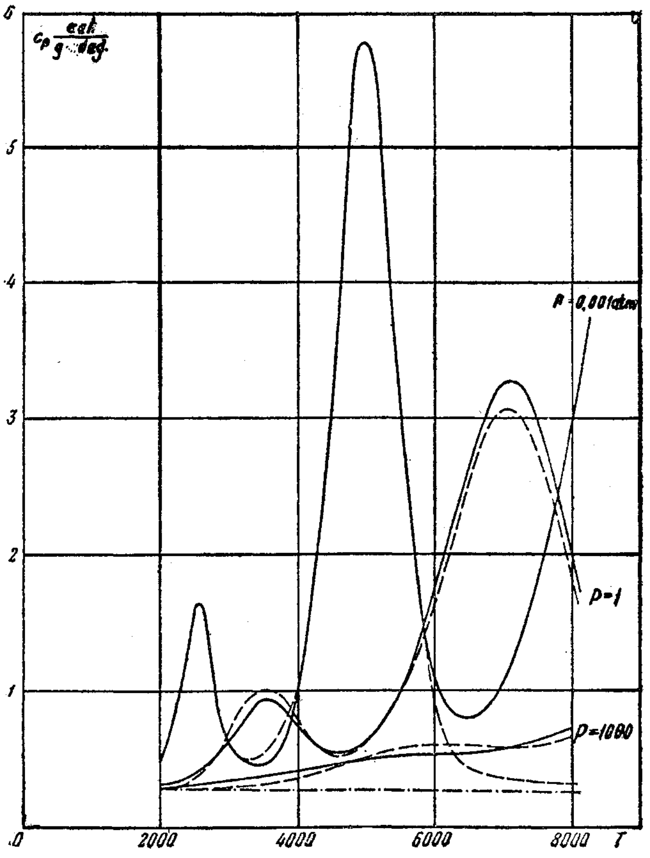

Fig. 3.

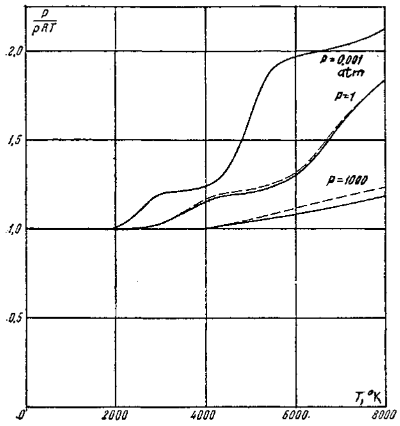

Fig. 4.

At pressures of less than 10 atm it is generally possible to neglect the presence in air of nitric oxide (i.e., to put $\beta = 0$), without detracting from the accuracy of the expressions obtained. In this case Eqs. (2) are solvable with respect to α_1 and α_2 and the system as a whole assumes the following form:

$$U/R = [3 + (1 - \alpha)\nu]T + \alpha_1 T_1 + \alpha_2 T_2 - 2600\,\nu$$

$$H/R = [4 + \nu + \alpha(1 - \nu)]T + \alpha_1 T_1 + \alpha_2 T_2 - 2600\,\nu$$

$$S/R = [3 + (1 - \alpha)\nu]\ln T - (1 + \alpha)\ln\rho + \sum_1^2 \alpha_i \ln(A_i e^{1-\nu}/\alpha_i^2) - \sum_1^2 (\eta_i - \alpha_i)\ln(\eta_i - \alpha_i) + \text{const}$$

$$p/R = \rho T(1 + \alpha)$$

$$\alpha_i = \frac{2\eta_i}{\sqrt{1 + \nu + 4\eta_i(\rho T^\nu/A_i)\, e^{T_i/T}}} \quad (9)$$

From these expressions it is easy to obtain equations for the velocity of sound and the specific heats of dissociating air:

$$a^2 = \left(\frac{\partial p}{\partial \rho}\right)_{s\,=\,\text{const}} = RT\left\{1 + \alpha - \sum_1^2 L_i + \frac{\left(1 + \alpha + \sum_1^2 L_i M_i\right)^2}{3 + (1 - \alpha)\nu + \sum_1^2 L_i M_i^2}\right\}$$

$$\frac{c_p}{R} = \frac{1}{R}\left(\frac{\partial H}{\partial T}\right)_{p\,=\,\text{const}} = 4 + \nu + \alpha(1 - \nu) + \sum_1^2 L_i(M + 1)\left(M_i + \frac{1 + \alpha + \sum_1^2 L_i M_i}{1 + \alpha - \sum L_i}\right)$$

$$\frac{c_V}{R} = \frac{1}{R}\left(\frac{\partial U}{\partial T}\right)_{V\,=\,\text{const}} = 3 + (1 - \alpha)\nu + \sum_1^2 L_i M_i (M_i + \nu) \quad (10)$$

where

$$L_i = \frac{\alpha_i(\eta_i - \alpha_i)}{2\eta_i - \alpha_i} \qquad M_i = \frac{T_i}{T} - \nu$$

Figures 1–4 show the results of calculations based on Eqs. (9) and (10). The solid lines indicate accurate values of the thermodynamic functions of dissociating air, obtained at the Energetics Institute of the Academy of Sciences of the USSR.[1] The broken-line curves were obtained from Eqs. (9) and (10); the dot-dash curves relate to nondissociating air with an adiabatic exponent $\gamma = 1.308$. This value of γ corresponds to the value $\nu = 0.25$ used in our calculations.

It is clear from the graphs that the accuracy of expressions (9) and (10) falls with increase in pressure. This is due, on the one hand, to the increase in the nitric oxide content of the air, and, on the other, to a displacement of the region of dissociation toward higher temperatures, i.e., to an increase in the part played by processes of excitation of new energy levels of the particles. The difference between the calculated and accurate curves at temperatures of 6000°–8000° is mainly due to ionization of the air.

Note that calculation based on Eqs. (2), (7), and (8) somewhat improves the accuracy of the curves corresponding to $p = 1000$ technical atm.

In conclusion we shall give values of the constants entering into the expressions written out in the foregoing:

$$\eta_1 = 0.21 \qquad \eta_2 = 0.79$$

$$T_1 = 59{,}000°\text{K} \qquad T_2 = 113{,}000°\text{K} \qquad T_3 = 75{,}000°\text{K}$$

$$R = 0.0687 \text{ cal/g. degree} = 2.83 \text{ atm}\cdot\text{cc/g}\cdot\text{degree}$$

The value $\nu = 0.25$, used in the calculations, corresponds to the following values of the constants A_i:

$$A_1 = A_2 = 1100 \qquad A_3 = 240$$

When $\nu = 0$:

$$A_1 = A_2 = 140 \qquad A_3 = 30$$

The curves corresponding to constant pressure were calculated by the method of successive approximations, since the equations given do not permit the substitution of the parameters PT for the parameters ρT.

—Received April 1, 1959

References

[1] Predvoditelev, A. S., et al., *Tablitsy Termodinamicheskikh Funktsii Vozdukha* (*Tables of Thermodynamic Functions of Air*) (Acad. Sci. USSR Press, Moscow, 1957).

[2] Lighthill, M. J., "Dynamics of dissociating gas," part I, "Equilibrium Flow," J. Fluid Mech. **2**, pt. I (1957).

NOVEMBER 1963 AIAA JOURNAL VOL. 1, NO. 11

Analytical Approximations of Thermodynamic Functions of Air

V. V. Mikhailov

This paper is a continuation of Ref. 1, the purpose of which was to obtain sufficiently simple analytical expressions for the thermodynamic characteristics of air in the high-temperature region. Formulas are obtained that are analogous to those of Ref. 1 but applicable to a wider range of temperatures.

LET us consider the region of single ionization of air, in which the process of dissociation may be regarded as having ended and the process of double ionization as not having begun. This division into regions of dissociation and single and double ionization is possible because the processes in question take place successively, with hardly any overlap, owing to the large differences in the energies involved. The results of Ref. 1 make it clear that in the region of dissociation air cannot be regarded as a single-component dissociating gas. The same paper shows, however, that in this region the presence of nitric oxide generally can be neglected, i.e., each component of the dissociating air can be considered independently and its interaction with other components ignored.

In the region of single ionization the situation is different. Here the interaction between oxygen and nitrogen cannot be neglected, since free electrons mainly are involved. On the other hand, in this region air can be regarded as a single-component gas, since the energies of singly ionized oxygen and nitrogen are close (approximately 1 ev difference). Consequently, the question of interaction can be dismissed.

Thus, we shall replace air with a monatomic single-component gas A with the same molecular weight and a certain average ionization energy i_A, which we shall choose so that the ionization energy of a gram molecule of air is the same as that of a gram molecule of gas A:

$$i_A = 0.21 i_0 + 0.78 i_N + 0.01 i_{Ar}$$

The values of i/k, where k is Boltzmann's constant for oxygen, nitrogen, and argon, are 158,038°, 168,842°, 182,892°, respectively. Hence it follows that $I = i_A/k = 169{,}924°$. The equation of the law of mass action for an ionization reaction of the type

$$A + i_A \rightleftarrows A^+ + e \tag{1}$$

is written in the form

$$\frac{n_{A^+}\, n_e}{n_A} = \text{const}\,\frac{Z_{A^+}}{Z_A}\cdot V\cdot T^{3/2}\cdot e^{-I/T} \tag{2}$$

Here $n_{A^+}\cdot n_e\cdot n_A$ are, respectively, the numbers of ions, electrons, and neutral atoms in volume V, and Z_{A^+}, Z_A are the statistical sums with respect to the electronic states of an ion and an atom, respectively.

Taking into account the condition of charge conservation ($n_e = n_{A^+}$) and introducing the degree of ionization

$$\gamma = n_{A^+}/(n_A + n_{A^+})$$

from Eq. (2) we obtain

$$\frac{\gamma^2}{1-\gamma} = m_A\cdot\text{const}\,\frac{Z_{A^+}}{Z_A}\,\frac{T^{3/2}}{\rho}\cdot e^{-I/T} \tag{3}$$

where m_A is the atomic mass and ρ the density of the gas.

In the notation that we have adopted, the equation of state of an ideal ionizing gas assumes the form

$$P = 2R\rho T(1 + \gamma) \tag{4}$$

Translated from Institut Mekhaniki Akademii Nauk SSSR, Inzhenernii Sbornik (Institute of Mechanics of the Academy of Sciences of the USSR, Engineering **31**, 206–216 (1961). Translated by Faraday Translations, New York.