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.

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Analytical Approximations of Thermodynamic Functions of Air

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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.

where $R = k/2m_A$ is the gas constant per unit mass of the original diatomic gas.

Making use of (4), we can transform (3) as follows:

$$\frac{\gamma^2}{1-\gamma^2} = B \cdot \frac{T^{5/2}}{P} e^{-I/T}$$
$$B = 2Rm_A \text{ const} \frac{Z_A{}^+}{Z_A} \tag{5}$$

If $X_O{}^+$, $X_N{}^+$, $X_{Ar}{}^+$ are molar fractions (relative numbers) of oxygen, nitrogen, and argon ions, N is the total number of particles, and γ is the total degree of ionization, then

$$\gamma = \frac{n_O{}^+ + n_N{}^+ + n_{Ar}{}^+}{N - n_O{}^+ - n_N{}^+ - n_{Ar}{}^+} = \frac{X_O{}^+ + X_N{}^+ + X_{Ar}{}^+}{1 - X_O{}^+ - X_N{}^+ - X_{Ar}{}^+} \tag{6}$$

On computing γ with the aid of (6) and tables and the quantity B from Eq. (5), we obtain the results shown in Table 1.

It is evident from these figures that in the most important, from our point of view, region of ionization, in which γ is not very close to 1 or 0, the value of B is approximately constant. In order to make the most rational choice of B = const, we shall find the value of γ, for which the error in γ for a given error in B is a maximum. From Eq. (5) it follows that

$$\frac{\partial\gamma}{\partial B} = \frac{1}{2B}\gamma(1-\gamma^2)$$
$$\frac{\partial}{\partial\gamma}\left(\frac{\partial\gamma}{\partial B}\right)_{B=\text{const}} = \frac{1}{2B}(1-3\gamma^2)$$

Equating $(\partial/\partial\gamma)(\partial\gamma/\partial B)_{B=\text{const}}$ to zero, we get $\gamma \approx 0.6$.

Thus, we see that the essential thing is to obtain a good approximation of B in the region where $\gamma \approx 0.6$. Let us find values of B for $\gamma \approx 0.6$ at different pressures and temperatures.

When $P = 0.001$ atm and $T = 10{,}000°$, $\gamma \approx 0.6$ and $B = 9.5 \cdot 10^{-7}$. When $P = 1$ atm and $T = 15{,}400°$, $\gamma \approx 0.6$ and $B = 9 \cdot 10^{-7}$. For $P = 1000$, $\gamma = 0.6$ is attained when $T > 20{,}000°$, and we cannot evaluate B, since data have not been tabulated for such high temperatures. Accordingly, we shall assume B constant and equal to $9 \cdot 10^{-7}$.

Now, basing ourselves on this approximate equation of the law of mass action, we can obtain the corresponding thermodynamic functions for air in the region of single ionization.

If f_A, f_{A+}, f_e are the total statistical sums for an atom, an ion, and an electron, respectively, then the internal energy of a certain quantity of gas, consisting of n_A atoms, $n_A{}^+$ ions, and n_e electrons, can be represented in the form

$$U = kT^2 \left] n_A \frac{\partial}{\partial T} \ln f_A + n_A{}^+ \frac{\partial}{\partial T} \ln f_{A+} + n_e \frac{\partial}{\partial T} \ln f_e \right] + Ikn_e$$

The statistical sums f have the form

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

where Z are the statistical sums of the particles with respect to electronic energy levels.

For electrons Z_e = const. For ions and atoms, in accordance with the foregoing assumptions, $Z_A{}^+/Z_A$ = const (i.e., B = const).

If, for the sake of simplicity, we consider that Z_A and $Z_A{}^+$ are themselves constant,* then the equation for U assumes the following form:

$U = \frac{3}{2} kT(n_A + n_A{}^+ + n_e) + Ikn_e = kN \left[\frac{3}{2} T(1+\gamma) + I\gamma\right]$

Whence the internal energy per unit mass will be

$$u/R = 3(1+\gamma)T + 2I\gamma \tag{7}$$

From Eqs. (4) and (7) it is easy to obtain the enthalpy per unit mass:

$$\frac{h}{R} = \frac{u}{R} + \frac{P}{R\rho} = 5(1+\gamma)T + 2I\gamma$$

In computing the entropy, the specific heat capacities, and the velocity, of sound, we make use of the relations

$$\frac{S}{R} = \int \frac{du + Pd(1/\rho)}{RT} \qquad \frac{C_v}{R} = \frac{1}{R}\left(\frac{\partial u}{\partial T}\right)_{\rho=\text{const}}$$
$$\frac{C_P}{R} = \frac{1}{R}\left(\frac{\partial h}{\partial T}\right)_{P=\text{const}} \qquad a^2 = \left(\frac{\partial P}{\partial \rho}\right)_{S=\text{const}}$$

If we now take into account the energy entering into the dissociation of the molecules,[1] we finally obtain the following expressions for air in the region of single equilibrium ionization:

$$\frac{u}{R} = 3(1+\gamma)T + 2\gamma I + \sum_1^2 \eta_i D_i$$
$$\frac{h}{R} = 5(1+\gamma)T + 2\gamma I + \sum_1^2 \eta_i D_i$$
$$\frac{S}{R} = (1+\gamma)(3\ln T - 2\ln\rho) - 2(1-\gamma)\ln(1-\gamma) - 4\gamma \ln\left(\gamma \cdot \sqrt{\frac{2R}{e^{5/2} \cdot B}}\right) + \text{const}$$

or

$$\frac{S}{R} = (1+\gamma)(5\ln T - 2\ln P) - 2(1-\gamma)\ln(1-\gamma) + 2(1+\gamma)\ln(1+\gamma) - 4\gamma \ln \frac{\gamma}{\sqrt{e^{5/2}B}} + \text{const}$$
$$\frac{C_v}{R} = 3(1+\gamma) + \left(3 + 2\frac{I}{T}\right)^2 \frac{\gamma(1-\gamma)}{2(2-\gamma)}$$
$$\frac{C_P}{R} = 5(1+\gamma) + \left(5 + 2\frac{I}{T}\right)^2 \frac{\gamma(1-\gamma^2)}{4}$$
$$\frac{a^2}{R} = \frac{2}{3} T(1+\gamma) \left\{ 5 - \frac{2\gamma(1-\gamma)\left(\frac{I}{T}\right)^2}{3 + \gamma(1-\gamma)\left[\frac{15}{4} + 3\frac{I}{T} + \left(\frac{I}{T}\right)^2\right]} \right\}$$
$$\frac{P}{R} = 2\rho T(1+\gamma)$$
$$\gamma = \frac{2}{1 + \sqrt{1 + \frac{8R}{B}\frac{\rho}{T^{3/2}} e^{I/T}}} = \frac{1}{\sqrt{1 + \frac{P}{BT^{5/2}} e^{I/T}}}$$

The expressions obtained hold true only in the region of temperatures and pressures, within which air is completely dissociated.

Table 1

	$P = 0.001$ atm			$P = 1$ atm	
T, deg	γ	B	T, deg	γ	B
6000	$1.55 \cdot 10^{-3}$	$9.7 \cdot 10^{-7}$	6000	$7.7 \cdot 10^{-6}$	$2.4 \cdot 10^{-8}$
9000	0.254	$9.8 \cdot 10^{-7}$	9000	$8.19 \cdot 10^{-3}$	$9.4 \cdot 10^{-7}$
12,000	0.964	$8.8 \cdot 10^{-7}$	12,000	0.110	$8.2 \cdot 10^{-7}$
15,000	0.993	$1.6 \cdot 10^{-7}$	15,000	0.525	$9.1 \cdot 10^{-7}$

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* Without complicating the final formulas, we can assume also that Z_A and $Z_A{}^+$ depend on the temperature in accordance with a power law.

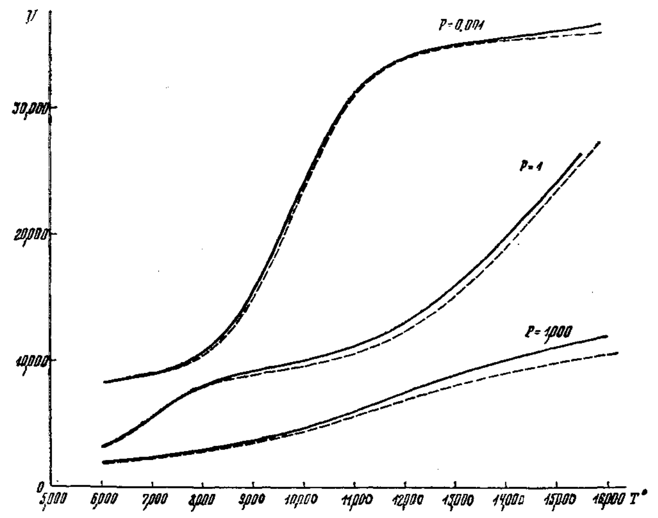

Fig. 1.

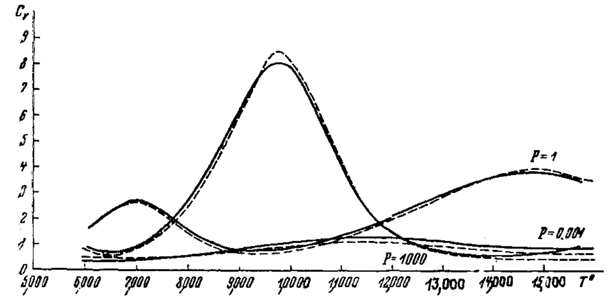

Fig. 2.

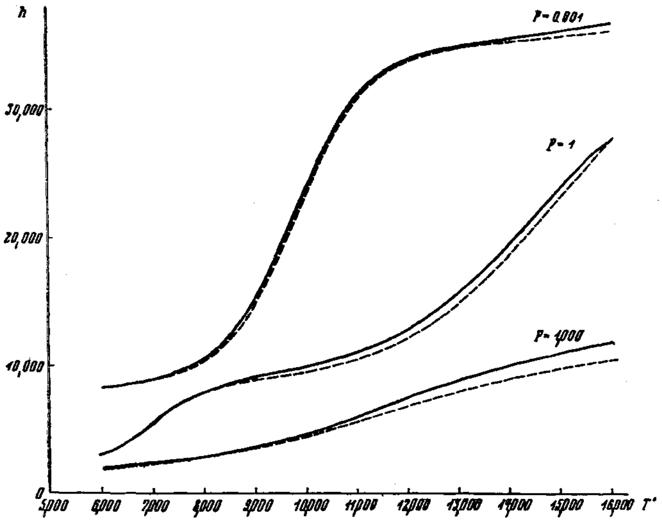

Fig. 3.

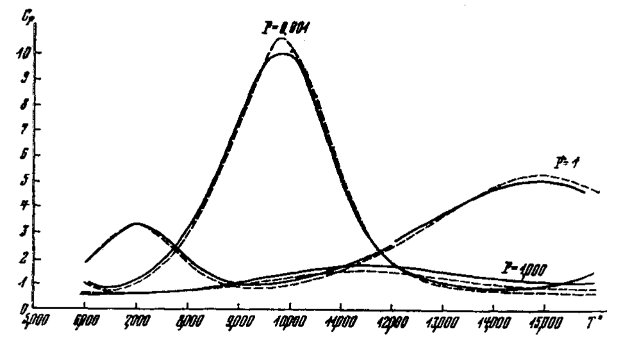

Fig. 4.

In order to obtain more general expressions, applicable to both the region of single ionization and the region of dissociation, we shall combine our own results with the results of Ref. 1, so that as $\gamma \to 0$ we get formulas for dissociating air, and as $\alpha_1 \to \eta_1$ and $\alpha_2 \to \eta_2$, the expressions given in Ref. 1.

Combining results in this way enables us to write

$$\frac{u}{R} = 3(1+\gamma)T + \sum_1^2 \alpha_i \cdot D_i + 2\gamma I$$

$$\frac{h}{R} = (4+\alpha+5\gamma)T + \sum_1^2 \alpha_i D_i + 2\gamma I$$

$$\frac{S}{R} = 3(1+\gamma)\ln T - (1+\alpha+2\gamma)\ln\rho - \sum_1^2 (\eta_i - \alpha_i)\ln(\eta_i - \alpha_i) - \sum_1^2 2\alpha_i \cdot \ln 0.0513\alpha_i - 2(1-\gamma)\ln(1-\gamma) - 4\gamma \ln 719\gamma + \text{const}$$

or

$$\frac{S}{R} = (4+\alpha+5\gamma)\ln T - (1+\alpha+2\gamma)\ln P - \sum_1^2 (\eta_i - \alpha_i)\ln(\eta_i - \alpha_i) - \sum_1^2 2\alpha_i \ln 0.0304\alpha_i + (1+\alpha+2\gamma)\ln(1+\alpha+2\gamma) - 2(1-\gamma)\ln(1-\gamma) - 4\gamma\ln 427\gamma + \text{const}$$

$$\frac{C_v}{R} = 3(1+\gamma) + \sum_1^2 L_i M_i^2 + \left(3 + 2\frac{I}{T}\right)^2 \cdot \frac{\gamma(1-\gamma)}{2(2-\gamma)}$$

$$\frac{C_P}{R} = 4+\alpha+5\gamma + \sum_1^2 L_i(M_i+1) \times \left(M_i + \frac{1+\alpha+\sum_1^2 L_i M_i}{1+\alpha-\sum_1^2 L_i}\right) + \left(5+2\frac{I}{T}\right)^2 \frac{\gamma(1-\gamma^2)}{4}$$

$$\frac{a^2}{R} = T\left\{1+\alpha-\sum_1^2 L_i + \frac{\left(1+\alpha+\sum_1^2 L_i M_i\right)^2}{3+\sum_1^2 L_i M_i^2} + \frac{10}{3}\gamma - \frac{\frac{4}{3}\gamma(1-\gamma^2)\left(\frac{I}{T}\right)^2}{3+\gamma(1-\gamma)\left[\frac{15}{4}+3\frac{I}{T}+\left(\frac{I}{T}\right)^2\right]}\right\}$$

$$P/R = \rho T(1+\alpha+2\gamma)$$

$$\alpha_i = \frac{2\eta_i}{1+\sqrt{1+0.0286\eta_i\rho e^{Di/T}}}$$

$$\gamma = \frac{2}{1+\sqrt{1+2.52\cdot 10^7 \frac{\rho}{T^{3/2}} e^{I/T}}} = \frac{1}{\sqrt{1+1.11\cdot 10^6 \frac{P}{T^{5/2}} e^{I/T}}}$$

In order to obtain the dependence on pressure and temperature in explicit form, we shall assume, without much loss of accuracy, that oxygen and nitrogen dissociate successively. We then have

$$\alpha_1 = \frac{2\eta_1}{\eta^2 + \sqrt{(1+\eta_1)^2 + 0.0101\eta_1 \frac{P}{T} e^{D_1/T}}}$$

$$\alpha_2 = \frac{1-\eta_1^2}{\eta_1 + \sqrt{1+0.00252(1-\eta_1^2)\frac{P}{T} e^{D_2/T}}}$$

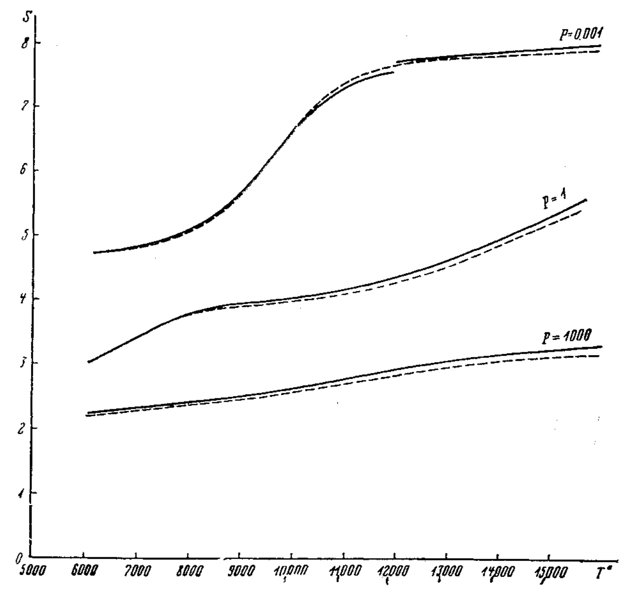

Fig. 5.

In the foregoing expressions

$$\alpha = \alpha_1 + \alpha_2$$

$$L_i = \frac{\alpha_i(\eta_i - \alpha_i)}{2\eta_i - \alpha_i}$$

$$M_i = D^i/T \qquad i = 1; 2$$

where P is expressed in physical atmospheres.

ρ = g/cm^3

T = °K

D_1 = 59,369°K,† the dissociation energy of a molecule of oxygen, referred to Boltzmann's constant (using 5.1155 ev/molecule)

D_2 = 113,262,† the dissociation energy of a molecule of nitrogen referred to Boltzmann's constant (k = 1.38042 × 10^{-16} erg deg^{-1}, using 9.7592 ev/molecule)

I = 169,924°K

η_1 = 0.21, the molecular fraction of oxygen in air under normal conditions

η_2 = 0.79, the molecular fraction of nitrogen in air under normal conditions. B is assumed equal to $9 \cdot 10^{-1}$

$$R = 0.06874 \frac{\text{g} \cdot \text{cal}}{\text{g} \cdot \text{deg}} = 2.838 \frac{\text{atm} \cdot \text{cm}^3}{\text{g} \cdot \text{deg}} = 287.5 \frac{m^2}{\text{sec}^2 \cdot \text{deg}}$$

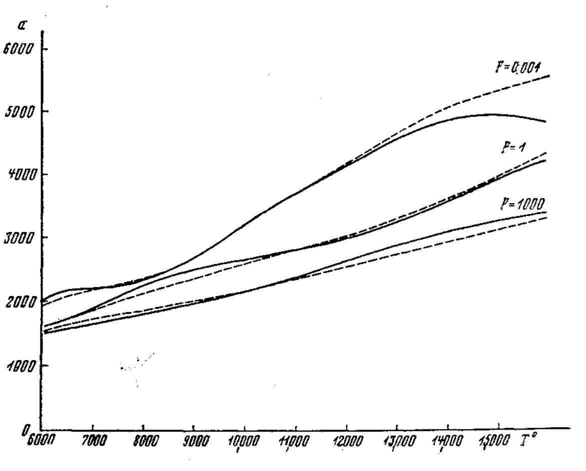

Fig. 6.

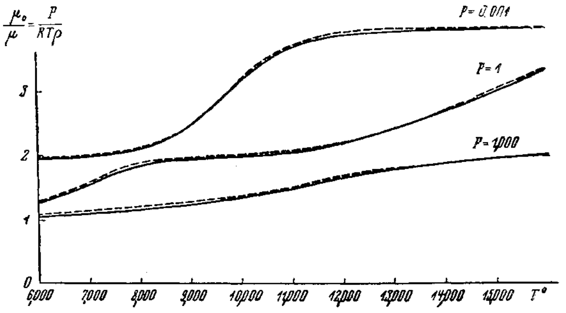

Fig. 7.

The parameter ν entering into the expressions in Ref. 1 is put equal to zero.

The results of computations based on the combined formulas are shown in Figs. 1–7. The solid lines represent exact values of the thermodynamic functions, the broken lines those obtained by means of the approximate formulas.

—*Received January 11, 1960*

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[1] Mikhailov, V. V., "Analytical representation of the thermodynamic functions of dissociating air," *Inzhenernii Sbornik* (*Engineering Collection*) **28**, 36–43 (1960); translated in AIAA J. **1**, 2689–2692 (1963).

[2] Predvoditelev, A. S., et al., *Tables of Thermodynamic Functions of Air* (Academy of Sciences Press USSR, 1957).

[3] "Thermodynamic functions and composition of air, thermodynamic functions of the components of air in the interval of temperatures from 12,000 to 20,000°K and pressures from 0.001 to 1000 atm," Sci. Rept., Inst. Power Eng. and Acad. Sci. USSR.

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† The values for D_1 and D_2 appearing in the text have been recommended by the reviewer. The values used in the original Russian paper are: D_1 = 59,400; D_2 = 113,300—Editor.

Reviewer's Comment

The thermodynamic data presented by the author were computed on the assumptions that the gases are ideal and that the mixture is in chemical equilibrium. Standard thermodynamic procedures have been used in computing the data.

The substitution of the average energy (expressed in °K) of a singly ionized particle for the principal ions in air, represents an interesting feature. This is permissible because of closeness of the ionization potentials of nitrogen and oxygen atoms (14.5482 and 13.6173 ev, respectively).[1] Hansen[2] discussed this possibility earlier.

Using the accepted values for the ionization energy for oxygen atoms, the corresponding temperature was found to be 158,038°K instead of 157,036°K as reported by the author. The temperatures corresponding to the ionization energies of nitrogen and argon were found to be almost identical to the values reported (168,842°K and 182,891.9°K, respectively). The average value of $I = i_A/k$ in degrees K turns out to be 169,924 and not 166,500 as reported. These minor errors apparently do not affect the data significantly. A comparison of the specific heat data with similar data published by American scientists[2–4] show reasonably good agreement.

It should be pointed out that in the investigations of hypersonic phenomena, the specific heat and other thermodynamic quantities of the pure species are the most useful. Much data of this type, which covers a wide range of temperatures, are available.[1,2,5–7]

The author does not list the following input data: a) electronic degeneracy of the states, b) the number of electronic states used, and c) the standard density or the standard