THERMODYNAMIC PROPERTIES OF AIR AT 12,000-25,000°K

AND 0.1-100 ATMOSPHERES, ALLOWING

FOR THE REDUCTION IN THE IONIZATION POTENTIAL

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The composition of air is calculated for pressures of 0.1, 1, 10, and 100 atm and temperatures of 12,000-25,000°K, allowing for the Coulomb interaction, which yields a considerable increase in the electron component as compared with earlier treatments [1]. Physically justified analytical expressions describing the resultant composition and thermodynamic properties to a satisfactory accuracy are selected. These approximations are convenient for solving applied problems, since no iterations are required.

1. The influence of Coulomb interaction is chiefly felt in the temperature range corresponding to intensive ionization ($T \geq 12,000°K$). When ionization is practically complete, the role of the Coulomb corrections to the composition and thermodynamic properties diminishes. The electron concentration is then not very sensitive to the ionization constant, while the atomic concentrations are small and have little effect on the thermodynamic properties.

For processes sensitive to the concentration of the atoms (such as radiation transfer in an ionized continuum and resonance lines) the effect of the Coulomb interaction is felt at any temperature.

The most comprehensive data relating to the composition and thermodynamic properties of air at 12,000-20,000°K are presented in the tables of [1]. However, the Coulomb interaction was only partly taken into account when compiling these.

2. Setting up the equations for the free energy of a mixture of ions and electrons, with due allowance for the Coulomb interaction energy, and executing a variation with respect to the number of particles at constant temperature and volume, we obtain the conditions for ionization equilibrium [2]

$$\frac{N_e N_{i+1}}{N_i} = \frac{Q_e Q_{i+1}}{Q_i} \exp\left[-\left(\frac{\delta F}{\delta N_e}\right)_{V,\,T} \Big/ kT\right] \tag{2.1}$$

where N is the number of particles in the volume, Q is the statistical sum allowing for all forms of motion, F is that part of the free energy which is associated with the Coulomb interaction, k is the Boltzmann constant, T is the temperature, the index e corresponds to the electrons, the index i denotes i-fold ionization, and $i = 0$ corresponds to neutral atoms.

If we separate out the values of the progressive statistical sums in Q and allow for spin degeneracy, we obtain

$$\frac{Q_e Q_{i+1}}{Q_i} = 2V \left(\frac{2\pi mkT}{h^2}\right)^{3/2} \frac{Z_{i+1}^*}{Z_i^*} \tag{2.2}$$

where Z is the statistical sum over the electron states, V is the volume, m is the mass of an electron, and h is Planck's constant.
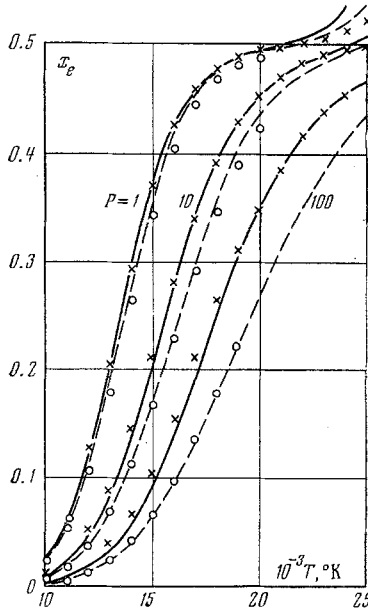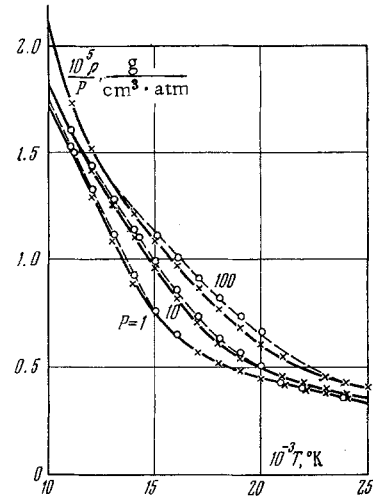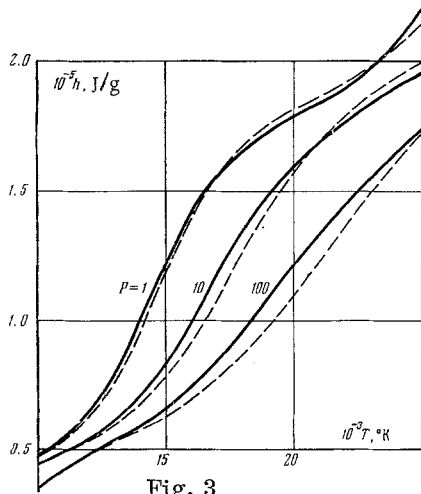
Fig. 1

Fig. 2

Fig. 3

In the expressions for the statistical sums of the ions taken over the electron states, we allow for the fact that some of the upper excited levels are not actually realized in the plasma, since interaction converts the upper discrete levels into a continuous spectrum. The influence of this effect is indicated in the nomenclature of the statistical sums by an asterisk.

Substituting (2.2) into (2.1), expressing the result in terms of concentrations, and making the origin for reckoning the energy of all the ions coincide with their ground states, we obtain

$$\frac{n_e n_{i+1}}{n_i} = 2 \left(\frac{2\pi mkT}{h^2} \right)^{3/2} \frac{Z_{i+1}^*}{Z_i^*} \exp\left(-\frac{I_i - \Delta I_i}{kT} \right)$$

where n is the concentration of the particles, I_i is the ionization potential of an i-fold ionized ion, and

$$\Delta I_i = -(\delta F / \delta N_e)_{V,\,T}$$

Allowing for the equation of state

$$P = nkT + \Delta P$$

where P is the pressure, $\Delta P = (-\delta F/\delta V)_{T,N_i}$ is the correction to the pressure arising from the Coulomb interaction, and converting to molar proportions, we finally obtain

$$\frac{x_e x_{i+1}}{x_i} = \frac{2}{P - \Delta P} \left(\frac{2\pi mkT}{h^2} \right)^{3/2} \frac{Z_{i+1}^*}{Z_i^*} \exp\left(-\frac{I_i - \Delta I_i}{kT} \right) \tag{2.3}$$

where x is a molar proportion.

Thus in the ionization equilibrium equation (2.3) we must allow for Coulomb corrections to the three quantities Z_i^*, ΔI_i, ΔP. A number of theories have been proposed for calculating the reduction in the ionization potential ΔI_i, which is also required for calculating Z_i^* and Z_{i+1}^*. In the calculations of [1], the Debye—Hückel theory [3] was used, giving a small value of ΔI. In the present investigation we used the more rigorously-based Ecker—Weizel data [4]. The Ecker—Weizel theory [4] would appear to be one of the most reliable at the present time. A numerical solution of the Shrödinger equation for the hydrogen atom in a screened Coulomb field [5] gave results similar to the calculations of [4]. We therefore treated [4] as a basis for the present investigation. We note that the higher values of the drop in ionization potential obtained elsewhere [6] may be associated with making a double allowance for the polarization effect. A comparison of various theories was also presented in [7].

TABLE 1

$$P = 0.1$$

T	n_e	n_N	n_{N+}	n_{N++}	n_O
12000	1.688(16)	2.087(16)	1.409(16)	1.662(9)	6.678(15)
13000	2.139(16)	1.022(16)	1.754(16)	1.647(10)	3.710(15)
14000	2.328(16)	4.382(15)	1.873(16)	1.163(11)	1.777(15)
15000	2.330(16)	1.826(15)	1.851(16)	6.344(11)	7.902(14)
16000	2.249(16)	7.917(14)	1.775(16)	2.824(12)	3.518(14)
17000	2.144(16)	3.655(14)	1.685(16)	1.063(13)	1.632(14)
18000	2.037(16)	1.800(14)	1.595(16)	3.478(13)	7.992(13)
19000	1.939(16)	9.384(13)	1.504(16)	1.007(14)	4.131(13)
20000	1.854(16)	5.073(13)	1.406(16)	2.640(14)	2.222(13)
21000	1.785(16)	2.889(13)	1.290(16)	6.000(14)	1.273(13)
22000	1.740(16)	1.651(13)	1.140(16)	1.224(15)	7.480(12)
23000	1.718(16)	9.336(12)	9.496(15)	2.158(15)	4.503(12)
24000	1.715(16)	5.116(12)	7.348(15)	3.295(15)	2.736(12)
25000	1.717(16)	2.684(12)	5.270(15)	4.397(15)	1.647(12)

T	n_{O+}	n_{O++}	n_{Ar}	n_{Ar+}	n_{Ar++}
12000	2.702(15)	5.111(6)	1.337(14)	8.439(13)	1.844(8)
13000	3.739(15)	8.457(7)	6.140(13)	1.118(14)	1.723(9)
14000	4.425(15)	9.344(8)	2.373(13)	1.205(14)	1.109(10)
15000	4.667(15)	7.317(9)	8.868(12)	1.179(14)	5.504(10)
16000	4.624(15)	4.348(10)	3.483(12)	1.120(14)	2.253(11)
17000	4.459(15)	2.079(11)	1.470(12)	1.052(14)	7.877(11)
18000	4.255(15)	8.345(11)	6.631(11)	9.775(13)	2.392(12)
19000	4.043(15)	2.839(12)	3.120(11)	8.840(13)	6.313(12)
20000	3.826(15)	8.957(12)	1.456(11)	7.513(13)	1.440(13)
21000	3.593(15)	2.390(13)	6.676(10)	5.793(13)	2.640(13)
22000	3.325(15)	5.759(13)	2.820(10)	3.917(13)	3.961(13)
23000	3.002(15)	1.233(14)	1.126(10)	2.367(13)	4.907(13)
24000	2.619(15)	2.347(14)	4.426(9)	1.338(13)	5.304(13)
25000	2.192(15)	4.004(14)	1.769(9)	7.392(12)	5.293(13)

$$P = 1$$

T	n_e	n_N	n_{N+}	n_{N++}	n_O
12000	7.466(16)	3.599(17)	6.343(16)	2.163(9)	1.027(17)
13000	1.153(17)	2.580(17)	9.735(16)	2.267(10)	7.805(16)
14000	1.543(17)	1.652(17)	1.288(17)	1.667(11)	5.423(16)
15000	1.824(17)	9.496(16)	1.499(17)	9.200(11)	3.424(16)
16000	1.965(17)	5.091(16)	1.590(17)	4.046(12)	1.990(16)
17000	1.995(17)	2.666(16)	1.595(17)	1.490(13)	1.099(16)
18000	1.961(17)	1.414(16)	1.554(17)	4.763(13)	5.983(15)
19000	1.897(17)	7.725(15)	1.495(17)	1.357(14)	3.294(15)
20000	1.823(17)	4.378(15)	1.429(17)	3.506(14)	1.861(15)
21000	1.750(17)	2.573(15)	1.360(17)	8.303(14)	1.086(15)
22000	1.681(17)	1.561(15)	1.287(17)	1.816(15)	6.537(14)
23000	1.622(17)	9.712(14)	1.205(17)	3.676(15)	4.058(14)
24000	1.576(17)	6.062(17)	1.107(17)	6.998(15)	2.554(14)
25000	1.541(17)	3.918(14)	9.915(16)	1.174(16)	1.687(14)

T	n_{O+}	n_{O++}	n_{Ar}	n_{Ar+}	n_{Ar++}
12000	1.085(16)	5.932(6)	2.267(15)	3.735(14)	2.360(8)
13000	1.730(16)	9.704(7)	1.583(15)	6.338(14)	2.423(9)
14000	2.463(16)	1.085(9)	9.522(14)	8.814(14)	1.693(10)
15000	3.147(16)	8.838(9)	4.975(14)	1.030(15)	8.608(10)
16000	3.642(16)	5.479(10)	2.389(14)	1.070(15)	3.445(11)
17000	3.895(16)	2.690(11)	1.128(14)	1.047(15)	1.161(12)
18000	3.953(16)	1.089(12)	5.466(13)	1.000(15)	3.437(12)
19000	3.893(16)	3.778(12)	2.762(13)	9.450(14)	9.155(12)
20000	3.775(16)	1.154(13)	1.456(13)	8.845(14)	2.243(13)
21000	3.629(16)	3.168(13)	7.914(12)	8.133(14)	4.864(13)
22000	3.471(16)	7.922(13)	4.358(12)	7.233(14)	9.636(13)
23000	3.300(16)	1.819(14)	2.375(12)	6.090(14)	1.695(14)
24000	3.110(16)	3.928(14)	1.230(12)	4.727(14)	2.641(14)
25000	2.894(16)	7.500(14)	6.387(11)	3.440(14)	3.495(14)

TABLE 1 (continued)

$$P = 10$$

T	n_e	n_N	n_{N+}	n_{N++}	n_O
12000	2.893(17)	4.341(18)	2.472(17)	3.205(9)	1.190(18)
13000	4.921(17)	3.648(18)	4.202(17)	3.622(10)	1.022(18)
14000	7.490(17)	2.925(18)	6.369(17)	2.876(11)	8.481(17)
15000	1.029(18)	2.212(18)	8.687(17)	1.701(12)	6.726(17)
16000	1.289(18)	1.574(18)	1.077(18)	7.859(12)	5.067(17)
17000	1.490(18)	1.055(18)	1.231(18)	2.952(13)	3.625(17)
18000	1.619(18)	6.790(17)	1.320(18)	9.413(13)	2.474(17)
19000	1.679(18)	4.277(17)	1.354(18)	2.627(14)	1.630(17)
20000	1.689(18)	2.683(17)	1.350(18)	6.596(14)	1.052(17)
21000	1.668(18)	1.696(17)	1.323(18)	1.519(15)	6.755(16)
22000	1.628(18)	1.089(17)	1.283(18)	3.257(15)	4.356(16)
23000	1.581(18)	7.134(16)	1.235(18)	6.539(15)	2.848(16)
24000	1.532(18)	4.749(16)	1.183(18)	1.247(16)	1.888(16)
25000	1.484(18)	3.216(16)	1.126(18)	2.253(16)	1.274(16)

T	n_{O+}	n_{O++}	n_{Ar}	n_{Ar+}	n_{Ar++}
12000	4.062(16)	8.444(6)	2.718(16)	1.447(15)	3.475(8)
13000	6.917(16)	1.436(8)	2.261(16)	2.764(15)	3.912(9)
14000	1.076(17)	1.653(9)	1.765(16)	4.564(15)	3.058(10)
15000	1.539(17)	1.379(10)	1.268(16)	6.535(15)	1.742(11)
16000	2.037(17)	8.787(10)	8.327(15)	8.190(15)	7.559(11)
17000	2.507(17)	4.444(11)	5.070(15)	9.183(15)	2.614(12)
18000	2.890(17)	1.853(12)	2.943(15)	9.520(15)	7.615(12)
19000	3.151(17)	6.537(12)	1.683(15)	9.415(15)	1.950(13)
20000	3.291(17)	2.005(13)	9.699(14)	9.083(15)	4.529(13)
21000	3.332(17)	5.474(13)	5.709(14)	8.650(15)	9.736(13)
22000	3.305(17)	1.358(14)	3.444(14)	8.161(15)	1.957(14)
23000	2.235(17)	3.095(14)	2.427(14)	7.611(15)	3.676(14)
24000	3.140(17)	6.611(14)	1.330(14)	6.972(15)	6.494(14)
25000	3.027(17)	1.326(15)	8.339(13)	6.243(15)	1.067(15)

$$P = 100$$

T	n_e	n_N	n_{N+}	n_{N++}	n_O
12000	1.144(18)	4.625(19)	9.791(17)	6.288(9)	1.251(19)
13000	2.075(18)	4.109(19)	1.778(18)	8.129(10)	1.122(19)
14000	3.413(18)	3.584(19)	2.920(18)	7.374(11)	9.929(18)
15000	5.139(18)	3.044(19)	4.382(18)	4.962(12)	8.619(18)
16000	7.129(18)	2.499(19)	6.044(18)	2.576(13)	7.292(18)
17000	9.168(18)	1.979(19)	7.715(18)	1.066(14)	5.992(18)
18000	1.102(19)	1.513(19)	9.195(18)	3.623(14)	4.776(18)
19000	1.251(19)	1.125(19)	1.033(19)	1.038(15)	3.704(18)
20000	1.358(19)	8.179(18)	1.111(19)	2.615(15)	2.799(18)
21000	1.424(19)	5.864(18)	1.154(19)	5.906(15)	2.074(18)
22000	1.456(19)	4.186(18)	1.170(19)	1.224(16)	1.515(18)
23000	1.462(19)	2.989(18)	1.165(19)	2.365(16)	1.095(18)
24000	1.450(19)	2.151(18)	1.146(19)	4.287(16)	7.926(17)
25000	1.427(19)	1.553(18)	1.118(19)	7.479(16)	5.723(17)

T	n_{O+}	n_{O++}	n_{Ar}	n_{Ar+}	n_{Ar++}
12000	1.588(17)	1.635(7)	2.889(17)	5.717(15)	6.792(8)
13000	2.851(17)	3.140(8)	2.557(17)	1.174(16)	8.812(9)
14000	4.713(17)	4.049(9)	2.205(17)	2.133(16)	7.990(10)
15000	7.232(17)	3.748(10)	1.827(17)	3.452(16)	5.323(11)
16000	1.035(18)	2.608(11)	1.437(17)	4.992(16)	2.692(12)
17000	1.387(18)	1.416(11)	1.068(17)	6.480(16)	1.062(13)
18000	1.750(18)	6.200(12)	7.523(16)	7.648(16)	3.380(13)
19000	2.087(18)	2.244(13)	5.101(16)	8.353(16)	8.954(13)
20000	2.376(18)	6.974(13)	3.362(16)	8.650(16)	2.077(14)
21000	2.598(18)	1.901(14)	2.200(16)	8.648(16)	4.321(14)
22000	2.749(18)	4.653(14)	1.438(16)	8.395(16)	8.292(14)
23000	2.838(18)	1.041(15)	9.467(15)	8.051(16)	1.491(15)
24000	2.868(18)	2.144(15)	6.338(15)	7.630(16)	2.524(15)
25000	2.859(18)	4.188(15)	4.160(15)	7.161(16)	4.111(15)

The correction to the pressure ΔP is usually calculated in accordance with the method of [3].

3. In the present investigation we calculated the composition of hot air with due allowance for all the foregoing effects over the temperature range $T = 12,000-25,000°K$, for pressures of $P = 0.1-100$ atm. Over this range of parameters the concentration of the molecules is low (except for the lowest temperature and $P = 100$ atm). On the other hand, triply-charged ions are practically absent.

The original system of equations consists of six equations of the type (2.3) for nitrogen, oxygen, and argon atoms and singly and doubly charged ions, the equation of state, and the conservation equation for the nuclei of the interacting particles

$$\frac{n_N + n_{N+} + n_{N++}}{0.7808} = \frac{n_O + n_{O+} + n_{O++}}{0.2095} = \frac{n_{Ar} + n_{Ar+} + n_{Ar++}}{0.0097}$$

where the indices N, N^+, N^{++} relate to neutral nitrogen atoms and singly-charged and doubly-charged nitrogen ions, and similarly for oxygen (O, O^+, O^{++}) and argon (Ar, Ar^+, Ar^{++}).

The numbers in the denominators reflect the initial air composition.

The system of equilibrium equations was solved by successive approximations in an electronic computer. The results appear in Table 1.

A comparison between the results of these calculations (crosses), and the data presented in the tables of [1] (circles) is given in Figs. 1 and 2. We see that at 100 atm the values of x_e are considerably greater than those of [1].

4. In solving problems with a computer it is sometimes inconvenient to use tabulated values. In this case we require analytical expressions approximating the tabulated data to an acceptable accuracy. Approximations of three types are used in the literature:

1) Formal approximations representing the tabulated data by arbitrary mathematical expressions. These approximations are cumbersome and only suitable for the particular parameters for which they are chosen;

2) Physical approximations requiring iterations. These are extremely accurate, since they constitute a slightly simplified system of equilibrium equations. The use of these approximations for applied purposes is inconvenient owing to the need for iterations;

3) Physical approximations not requiring any iterations. These are obtained by further simplifying the original system of equations, and they are therefore less accurate than those of the second group. However, they have the merit of simplicity and allow corrections improving the accuracy to be introduced.

In the present investigation we chose the physical approximations of A. N. Kraiko as initial approximating expressions [8]. The errors in the approximating system of equations given in [8] arise mainly from three causes:

1) the splitting of the original system of equations of equilibrium by virtue of a number of simplifying assumptions listed in [6];

2) the neglect of the influence of Coulomb interaction on the pressure;

3) the neglect of the drop in the ionization potential.

This latter factor creates the greatest error in the range of parameters under consideration. For this reason, and also in order to avoid unduly complicating the system of equations given in [8], all three sources of error are approximately eliminated by making two corrections to the ionization potentials of the atoms and singly-charged ions. These "effective reductions in ionization temperature" ΔT_0^* and ΔT_i^* are chosen in such a way as to ensure adequate accuracy in the results of the calculations.

The complete system of analytical expressions approximating the composition and thermodynamic properties of hot air are presented below. In this system the particle concentration n has the dimensions cm^{-3}, the pressure P is measured in physical atmospheres (1 atm $= 1.013 \cdot 10^6$ dyn/cm^2), the temperature T in degrees Kelvin, the density ρ in g/cm^3, the enthalpy H and the Coulomb correction to the enthalpy ΔH in J/cm^3, and the remaining quantities are dimensionless:

$$x_O = \frac{2\varepsilon_1 - 0.42\varepsilon_3}{\alpha}, \quad x_N = \frac{2\varepsilon_2 - 1.58\varepsilon_3}{\alpha}, \quad x_{O_2} = \frac{0.21 - \varepsilon_1}{\alpha}$$

$$x_{N_2} = \frac{0.79 - \varepsilon_2}{\alpha}, \quad x_{N+} + x_{O+} = \frac{2\varepsilon_3}{\alpha}$$

$$x_{N++} + x_{O++} = \frac{2\varepsilon_4}{\alpha}, \quad x_e = \frac{2(\varepsilon_3 + 2\varepsilon_4)}{\alpha}$$

$$\bar{n}_i = 0.734 \cdot 10^{22} \frac{P - \Delta P}{T} x_i, \quad \rho = 0.3565 \frac{P - \Delta P}{\alpha T}$$

$$H = 0.2843 \{ T [(0.21 - \varepsilon_1) H_{O_2} + (0.79 - \varepsilon_2) H_{N_2} + 2(\varepsilon_1 - 0.21\varepsilon_3) H_O +$$

$$+ 2(\varepsilon_2 - 0.79\varepsilon_3) H_N + 2\varepsilon_3 H_i + 5(\varepsilon_3 + \varepsilon_4)] + 59\,000\varepsilon_1 + 113\,000\varepsilon_2 +$$

$$+ (333\,100 - \Delta T_0)\varepsilon_3 + (714\,440 - \Delta T_1)\varepsilon_4 \} + \Delta H$$

$$\varepsilon_1 = \left[1.88 + \sqrt{8.3 + \frac{P}{T} \exp\left(\frac{57800}{T} - 4.02 + 1.32 \cdot 10^{-4} T\right)} \right]^{-1}$$

$$\varepsilon_2 = \left[0.22 + \sqrt{1.096 + \frac{P}{T} \exp\left(\frac{113\,300}{T} - 5.94\right)} \right]^{-1}$$

$$\varepsilon_3 = \left[1 + P\left(\frac{10\,000}{T}\right)^{5/2} \exp\left(\frac{161\,620 - \Delta T_0^*}{T} - 8.73\right) \right]^{-1/2}$$

$$\varepsilon_4 = -0.5 + \sqrt{0.25 + \left[1 + P\left(\frac{10\,000}{T}\right)^{5/2} \exp\left(\frac{357\,220 - \Delta T_1^*}{T} - 8.44\right) \right]^{-1}}$$

$$\Delta T_0^* = 8170 \sqrt[3]{P \cdot 10\,000/T} \,[1 + P^{1/4}(10\,000/T)^{5/4}\exp(16\,9000/T - 10)]^{-1/4}$$

$$\Delta T_1^* = 96\,000 \sqrt[3]{P} \,(10\,000/T)^2 \,[1 + \sqrt{P}\exp(343\,400/T - 14.87)]^{-1/4}$$

$$\alpha = 1 + \varepsilon_1 + \varepsilon_2 + 2\varepsilon_3 + 2\varepsilon_4$$

$$\Delta P = -0.276 \,(10\,000/T)^2 \left(P\,\frac{\varepsilon_3 + 3\varepsilon_4}{\alpha}\right)^{3/4}$$

$$\Delta T_0 = 8950 \sqrt[3]{\frac{P}{\alpha}\left(\frac{10\,000}{T}\right)} (\sqrt[3]{\varepsilon_3} + 1.28 \sqrt[3]{\varepsilon_4}) + 4125 \left(\frac{10\,000}{T}\right) \sqrt{P\frac{(\varepsilon_3 + 3\varepsilon_4)}{\alpha}}$$

$$\Delta T_1 = 14\,400 \sqrt[3]{\frac{P}{\alpha}\frac{10\,000}{T}} (\sqrt[3]{\varepsilon_3} + 1.24 \sqrt[3]{\varepsilon_4}) + 8300 \left(\frac{10\,000}{T}\right) \sqrt{P\frac{\varepsilon_3 + 3\varepsilon_4}{\alpha}}$$

$$\Delta H = -3140 \,(10\,000/T) \sqrt{P} \,(\varepsilon_3 + 3\varepsilon_4)^{3/2} \alpha^{-1/2}$$

$$H_{O_2} = 3.076 + 1.19 \cdot 10^{-3} T - 9 \cdot 10^{-8} T^2$$

$$H_{N_2} = 3.415 + 2.17 \cdot 10^{-4} T - 1.2 \cdot 10^{-8} T^2$$

$$H_O = 2.514 + 10^{-5} T + 1.2 \cdot 10^{-10} T^2$$

$$H_N = 2.117 + 10^{-1} T - 1.97 \cdot 10^{-9} T^2$$

$$H_{i+} = 2.46 + 2 \cdot 10^{-5} T$$

A comparison of the approximations (continuous lines) with the exact calculations (crosses) and the approximations of [8] (broken lines) is presented in Figs. 1, 2, and 3 for pressures of 1, 10, and 100 atm.

The proposed approximations are valid for pressures up to P = 100 atm and temperatures up to T = 25,000°K. For higher temperatures and pressures the error may increase.

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