

A computational thermodynamic evaluation of the altitude profiles of $(\text{N}_2)_2$, $\text{N}_2\text{-O}_2$ and $(\text{O}_2)_2$ in the Earth's atmosphere¹

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Abstract

The equilibrium constants of formation of the gas phase species $(\text{N}_2)_2$, $\text{N}_2\text{-O}_2$ and $(\text{O}_2)_2$ are used for evaluation of the altitude population profiles in the Earth's atmosphere. The equilibrium constants are derived from recently computed quantum-chemical data. Estimates of the lower bounds of the interaction energies are employed so that the reported data should also represent a lower bound of the populations. The mole fractions of each of the dimers, computed for their equilibrium mixture with N_2 and O_2 under atmospheric conditions, decrease with altitude. The mole fractions decrease in the order $(\text{N}_2)_2$, $\text{N}_2\text{-O}_2$, and $(\text{O}_2)_2$. The $(\text{N}_2)_2$ mole fraction close to the surface is found to be $8 \times 10^{-4}\%$, i.e. comparable with other minor components of the Earth's atmosphere currently being vigorously studied.

INTRODUCTION

In a series of our previous articles we evaluated structure, energetics, vibrations and thermodynamics of formation of the gas phase $(\text{N}_2)_2$ [1, 2], $\text{N}_2\text{-O}_2$ [3], and $(\text{O}_2)_2$ [4, 5] species. Those species are of a clear interest to atmospheric science. Although some of their properties have been investigated in the past [6–21] their thermodynamic stabilities have not been systematically studied. Our interest in the three dimers pertinent to the Earth's atmosphere can be placed in the broader context of molecular

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complexes in planetary atmospheres [22–31]. The complexes are relevant to atmospheric spectroscopy and could also play a role in atmospheric-chemistry processes.

The present paper completes our series [1–5]. The computed dimerization equilibrium constants are used for evaluation of the altitude concentration profile of $(\text{N}_2)_2$, $\text{N}_2\text{-O}_2$, and $(\text{O}_2)_2$ in the Earth's atmosphere.

COMPUTATIONS

We shall deal with three dimerization processes



described by the dimerization equilibrium constants

$$K_{\text{p},\text{N}_2} = \frac{x_{(\text{N}_2)_2}}{x_{\text{N}_2}^2 P} \quad (4)$$

$$K_{\text{p},\text{N}_2/\text{O}_2} = \frac{x_{\text{N}_2\text{-O}_2}}{x_{\text{N}_2} x_{\text{O}_2} P} \quad (5)$$

$$K_{\text{p},\text{O}_2} = \frac{x_{(\text{O}_2)_2}}{x_{\text{O}_2}^2 P} \quad (6)$$

The equilibrium constants (4)–(6) are expressed in the terms of the equilibrium mole fractions of the components x_i , and the total pressure of the mixture P . No other atmospheric species are considered so that for the mole fractions

$$x_{\text{N}_2} + x_{\text{O}_2} + x_{(\text{N}_2)_2} + x_{\text{N}_2\text{-O}_2} + x_{(\text{O}_2)_2} = 1 \quad (7)$$

Finally, the known nitrogen to oxygen atmospheric ratio r should be fulfilled

$$\frac{x_{\text{N}_2} + 2x_{(\text{N}_2)_2} + x_{\text{N}_2\text{-O}_2}}{x_{\text{O}_2} + 2x_{(\text{O}_2)_2} + x_{\text{N}_2\text{-O}_2}} = r \quad (8)$$

Equations (4)–(8) allow for determination of the equilibrium mole fractions, supposing that the equilibrium constants and P , r parameters are known.

The equilibrium constants were evaluated by means of partition functions supplied with parameters from our ab initio computations [1–5]. With respect to the amount of computed information available, the partition functions were of the usual rigid-rotor and harmonic-oscillator

(RRHO) quality. The dimerization energetics were treated at two different levels, regarding the basis set superposition error (BSSE). The term was either ignored or estimated by the counterpoise method [32]. Although the latter method is an approximation [33, 34], these approaches should generally yield upper and lower limits for the well depth [35]. In fact, the results presented in this paper are entirely based on the energetics with the BSSE correction.

Finally, the observed profiles [36] of temperature and pressure in the region of the altitude $z = 0\text{--}90$ km were used (in fact, the so called geopotential altitude was employed). The nitrogen/oxygen ratio r [36] was supposed to be constant over the region.

RESULTS AND DISCUSSION

Table 1 presents the temperatures T and total pressures P for selected altitudes z , extracted from published data [36]. For each T, P pair the equilibrium dimerization constants (4)–(6) were computed and the equilibrium mixture composition evaluated. As discussed in detail in our previous papers [1–5], the dimers are in fact represented by equilibrium mixtures of several isomeric structural forms. Hence, the dimerization equilibrium constants have a complex, convoluted nature.

TABLE 1

Altitude z profiles^a of temperature T and pressure P in the Earth's atmosphere

z /km	T /K	P /atm ^b
0	288	1.0
1	282	0.89
3	269	0.69
5	256	0.53
7	243	0.41
10	223	0.26
15	217	0.12
20	217	0.054
25	222	0.025
30	227	0.012
40	251	0.0027
50	271	0.00075
60	255	0.00021
70	217	0.000048
80	181	0.0000085
90	185	0.0000013

^a Geopotential height [36]. ^b 1 atm = 101 325 Pa.

TABLE 2

Altitude z profiles of the dimeric mole fractions ^a $x_{(\text{N}_2)_2}$, $x_{\text{N}_2\text{-O}_2}$, $x_{(\text{O}_2)_2}$

z/km	$x_{(\text{N}_2)_2}/\%$	$x_{\text{N}_2\text{-O}_2}/\%$	$x_{(\text{O}_2)_2}/\%$
0	7.6×10^{-4}	8.1×10^{-5}	2.5×10^{-5}
1	7.3×10^{-4}	7.7×10^{-5}	2.4×10^{-5}
3	6.6×10^{-4}	7.0×10^{-5}	2.2×10^{-5}
5	6.0×10^{-4}	6.3×10^{-5}	2.0×10^{-5}
7	5.4×10^{-4}	5.7×10^{-5}	1.8×10^{-5}
10	4.5×10^{-4}	4.8×10^{-5}	1.5×10^{-5}
15	2.3×10^{-4}	2.4×10^{-5}	7.6×10^{-6}
20	1.0×10^{-4}	1.1×10^{-5}	3.5×10^{-6}
25	4.4×10^{-5}	4.7×10^{-6}	1.5×10^{-6}
30	1.9×10^{-5}	2.0×10^{-6}	6.4×10^{-7}
40	3.2×10^{-6}	3.5×10^{-7}	1.1×10^{-7}
50	7.0×10^{-7}	7.4×10^{-8}	2.3×10^{-8}
60	2.3×10^{-7}	2.5×10^{-8}	7.8×10^{-9}
70	9.2×10^{-8}	9.8×10^{-9}	3.1×10^{-9}
80	2.9×10^{-8}	3.1×10^{-9}	9.9×10^{-10}
90	4.1×10^{-9}	4.4×10^{-10}	1.4×10^{-10}

^a $x_{\text{N}_2} + x_{\text{O}_2} + x_{(\text{N}_2)_2} + x_{\text{N}_2\text{-O}_2} + x_{(\text{O}_2)_2} = 100\%$.

Table 2 presents the computed dimeric mole fractions at the selected altitudes z . It turns out that in all three cases the dimeric mole fractions decrease with the increasing altitude. This may be surprising as the temperature decreases in lower parts of the atmosphere which should stabilize the dimers; however, the pressure decreases which helps dissociation processes. The competition between temperature and pressure effects creates the final altitude decrease. There is also a uniform order in the populations of the dimers. The most populated N_2 dimer is followed by the heterodimer $\text{N}_2\text{-O}_2$ and finally, the O_2 dimer is the least populated species.

The results in Table 2 are based on the interaction energies corrected for the BSSE error, which should rather represent a lower bound of the well depth [35]. Moreover, as discussed in refs. 2, 3 and 5 the vibrational part of the RRHO partition functions had to be neglected in the approach. Hence, it can be expected that the values in Table 2 represent a lower bound of the dimeric populations. The interaction energy without the BSSE correction is an upper bound; however, it yields dimeric populations which are apparently too high. For example, at a temperature of 298 K and 1 atm pressure, the dimeric mole fractions for nitrogen and oxygen would read 8.6 and 1.6%, respectively. Thus, we do not present the results for the other evaluation of the equilibrium constants [2, 3, 5].

In the treatment, other components of the Earth's atmosphere were ignored. This is reasonable as they form less than 1% of the total. Nevertheless, it should be realized that molecular complexes of N_2 and O_2

with those minor atmospheric components can also be formed. Although the nitrogen/oxygen ratio r is considered as a constant here, this is not necessarily true at a high altitude. It is interesting to note that the computed dimeric mole fractions can be comparable with the mole fractions of some minor atmospheric components such as He, CH₄ or SO₂.

This is the first, purely computational evaluation of the altitude profiles of the three molecular complexes especially pertinent to the Earth's atmosphere. Although various improvements of the computational treatment could be suggested, the conclusion that the dimeric mole fractions decrease with increasing altitude should not be changed. The improvements of the treatment should concern both the quality of partition functions and interaction energies. A final solution of the problem would however be possible only within sophisticated potential hypersurface, which is a very remote target.

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