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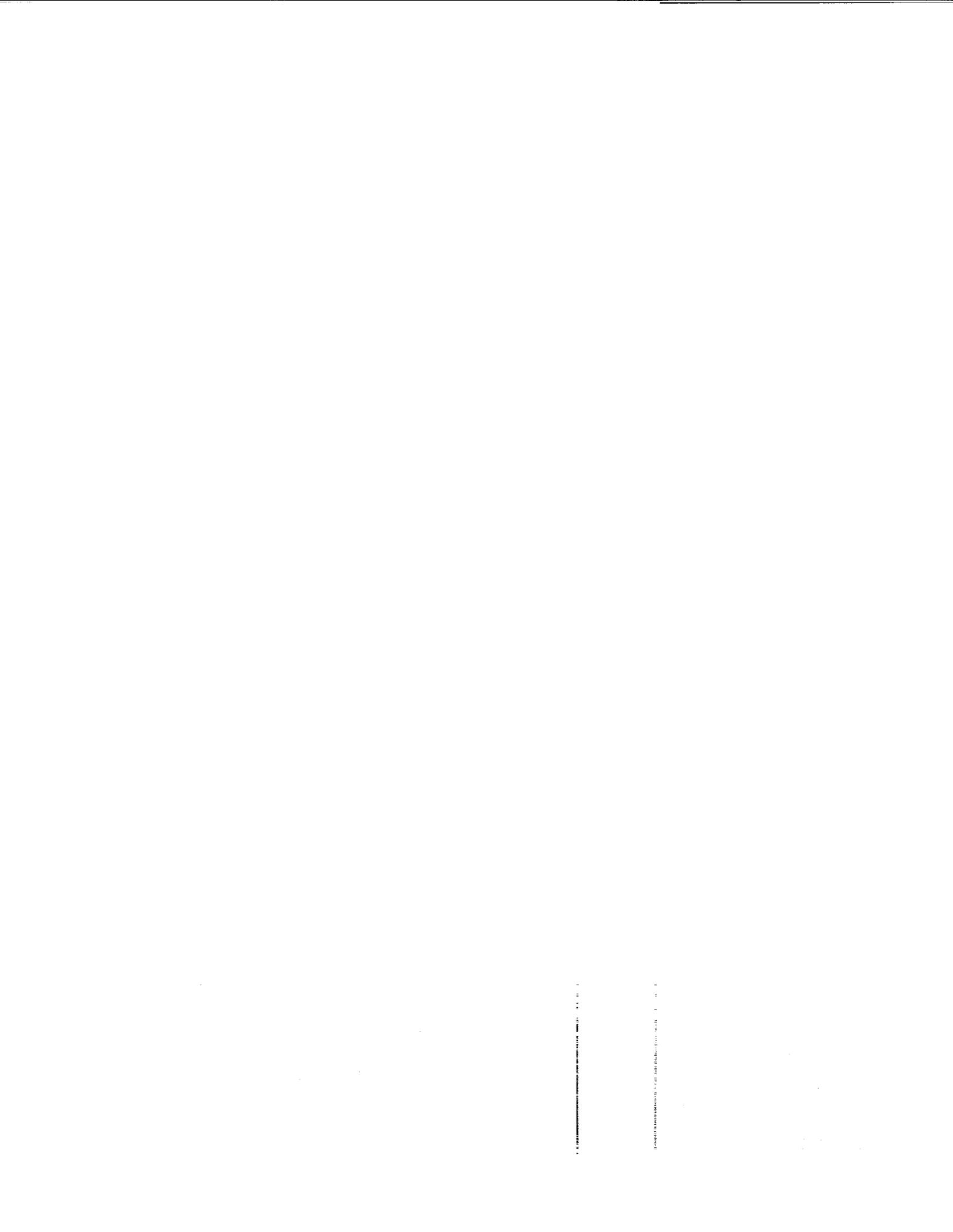
PLANETARY AERONOMY II:
NO₂ IN THE MARTIAN ATMOSPHERE

By P. Warneck and F. F. Marmo

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ABSTRACT

The transmission curve of the Martian atmosphere derived by Öpik is compared with transmission curves of an atmosphere containing various amounts of nitrogen dioxide. It is found that the amount of 6×10^{18} cm²-column NO₂ (or even less) given by Sinton as an upper limit for the Martian NO₂ content could adequately explain the phenomenon of the blue haze. This finding made it worthwhile to investigate the effect of the temperature and pressure sensitive equilibrium $2 \text{NO}_2 \rightleftharpoons \text{N}_2\text{O}_4$ upon the total NO₂ content and the altitude-number density distributions of NO₂ and N₂O₄. Computations were carried out for surface temperatures of 273°K, 243°K, 213°K, and 183°K and for three different temperature distributions. The discussion of the results leads to the suggestion of several important new experiments.

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION



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I. INTRODUCTION

It is well known that the Martian atmosphere becomes increasingly optically dense in going from the red to the blue portion of the visible spectrum. The extent to which this occurs cannot be ascribed solely to Rayleigh scattering. In fact, it appears that the observations can be better explained in terms of some absorption process in addition to the effect of Rayleigh scattering. This fact was pointed out by Öpik⁽¹⁾ who used results from recent observations for comparing the relative roles of absorption and scattering in the spectral transmission characteristics of the Martian atmosphere. Öpik concluded that at least in the blue, absorption could account for the dominant part of the observed decline in transmissivity for decreasing wavelengths. Kiess et al.⁽²⁾ recently pointed out that the decline of the spectral intensity of Mars relative to that of the moon closely resembles the absorption curve of nitrogen dioxide, thus implying the presence of NO₂ in the atmosphere of Mars. More recently, Sinton⁽³⁾ observed an infrared absorption band in the 3.43 micron region in the atmosphere of Mars and established an upper limit NO₂-content of 6×10^{18} cm²-column if it is assumed that NO₂ is the sole contributor to the observed absorption band. In this paper, an NO₂-content upper limit is established by applying the absorption cross sections reported by Dixon⁽⁴⁾ and by Hall and Blacet.⁽⁵⁾ In addition,

with this limit considered, the physical-chemical behavior of the $2 \text{NO}_2 \rightleftharpoons \text{N}_2\text{O}_4$ system is given some detailed attention to derive the variation of NO_2 -content with respect to temperature and pressure. Finally, on the basis of this preliminary study, some definitive experiments are suggested.

II. COMPUTATIONS OF NO₂, N₂O₄ NUMBER DENSITIES WITH ALTITUDE

Any study of the present system must consider that at equilibrium, the monomer and dimer coexist:



It has been well established that this system exists in both the condensed and gaseous forms and that the partitioning of the monomer and dimer varies with temperature and pressure. Accordingly, over large temperature or pressure intervals, significant variation can occur in the absorption characteristics and physical states of this system. On this basis, Kiess et al.⁽²⁾ attempted to explain the various haze, cloud formations, and seasonal color changes observed on Mars. However, their theory requires that the combined number density of NO₂ and N₂O₄ must be greater than 10²⁴ cm²-column. For Martian surface temperatures between 180° and 270°, the corresponding NO₂ contents would vary from about 5x10²¹ to 10²⁴ cm²-column, respectively. Such high NO₂-contents are not compatible with experimental observations since the data of Hall and Blacet⁽⁵⁾ indicate an average cross section value of about 10⁻¹⁹ cm² for the visible region around 5000 Å.

Although the theory of Kiess et al.⁽²⁾ is untenable, one cannot dismiss NO₂ as being unimportant on the grounds that it is only a minor constituent. This can be conveniently demonstrated by means of Figure 1 where the percent transmission is plotted versus wavelength for a Martian

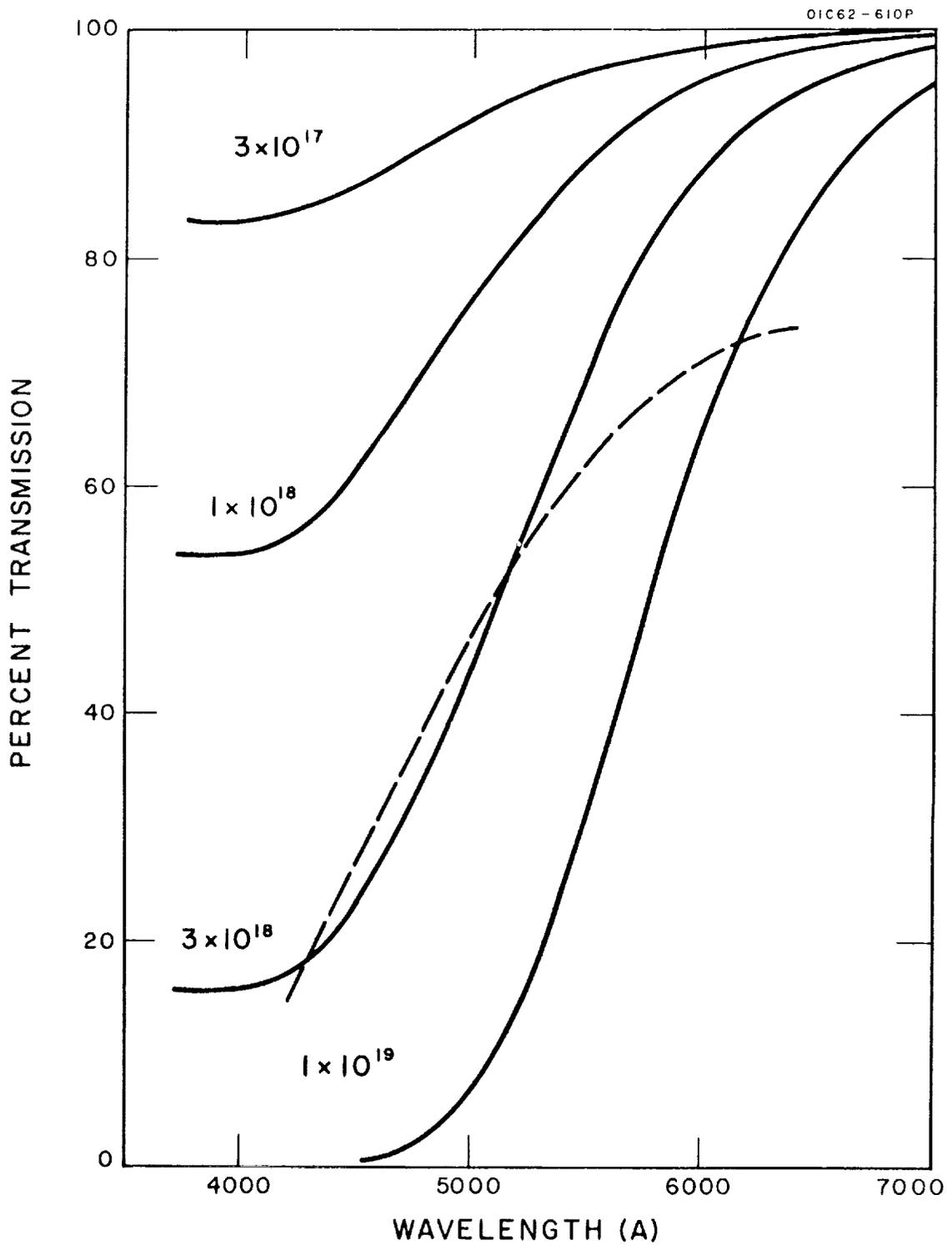


Figure 1. Solid Curves: Transmission coefficients of an atmosphere containing between 3×10^{17} and 1×10^{19} cm^2 -column NO_2 . Broken Curve: Transmission coefficients of Martian atmosphere derived by Öpik.

atmosphere with NO_2 contents varying from only 3×10^{17} to $1 \times 10^{19} \text{ cm}^2$ -column. The dashed curve represents the transmission coefficients of the Martian atmosphere as derived by Öpik⁽¹⁾ from experimental observations. It can be noted that Öpik's findings are not incompatible with the upper limit NO_2 content suggested by Sinton.⁽³⁾ Figure 1 can also serve to demonstrate that a variation of NO_2 content between the limits cited could adequately explain the phenomena of the blue haze and possibly provide a clue for the source of the occasional blue clearings.⁽⁶⁾ A considerable variation of NO_2 content with temperature and pressure could occur owing to the sensitivity of the $\text{NO}_2 \rightleftharpoons \text{N}_2\text{O}_4$ system to these parameters. Herein lies the value of examining the extent to which the NO_2 content can vary in the Martian atmosphere.

Despite a number of objections⁽⁷⁾ which can be raised against this interpretation, the temperature and pressure dependence of the system $\text{NO}_2 \cdot \text{N}_2\text{O}_4$ provides the simplest among several conceivable mechanisms for a temporary NO_2 depletion. Accordingly, this aspect of the problem was investigated in some detail.

The amount of NO_2 on Mars and the distribution of $\text{NO}_2 - \text{N}_2\text{O}_4$ with altitude depends strongly on the assumed thermal structure of the Martian atmosphere, thus, computations were carried out considering three cases:

- (a) an isothermal atmosphere
- (b) a linear temperature decrease according to an adiabatic lapse rate of $3.7^\circ\text{K}/\text{km}$ up to a tropopause at 12 km and an isothermal atmosphere above that level
- (c) a similar structure with a tropopause at 24 km altitude.

For the system depicted in Eq. (1), the partial pressures, p , and the number densities, n , of the nitrogen oxides are governed by the relations

$$K p_2 = p_1^2 \quad (2a)$$

$$p = n k T \quad (2b)$$

$$K n_2 = k T n_1^2 \quad (2c)$$

where k is the Boltzmann constant, T the absolute temperature, and the subscripts 1 and 2 refer to NO_2 and N_2O_4 , respectively. Employing the data of Giaque and Kemp⁽⁸⁾ the following expression was derived for the temperature variation of the equilibrium constant, $K(T)$:

$$K = 1.58 \times 10^9 \times 10^{-13693/4.576 \times T} \quad (3)$$

Further, it was assumed that Expression (3) is valid below 273°K . The integrated amount of NO_2 , whether occurring free or in its combined form, remains constant so that

$$\int_0^\infty n_1 dz + 2 \int_0^\infty n_2 dz = C \quad (4)$$

where

$$C = 6 \times 10^{18} \text{ cm}^2\text{-column} .$$

For the combined densities of NO_2 and N_2O_4

$$\rho = m_1 (n_1 + 2n_2) = m_1 n \quad , \quad (5)$$

m_1 being the molecular mass of NO_2 .

Consequently,

$$C = \int_0^{\infty} n \, dz = n_0 H_0 \quad (6)$$

n_0 is the combined density at the surface of the planet and H_0 the scale height at the same level. This last formula permits the evaluation of n_0 from C and H_0 . Since the nitrogen oxides are minor constituents in the Martian atmosphere, properties like the scale height, H , and the adiabatic lapse rate, β , are determined by the major atmospheric constituent, which is probably nitrogen. Accordingly, the following values were employed: $H_0 = 0.0796 \times T$ kilometers and $\beta = 3.7$ degrees/km.

If complete mixing exists in the investigated portion of the atmosphere, ρ and also n will remain at constant fractions of the corresponding quantities for the bulk atmospheric constituent. Thus, for that portion of the atmosphere in which the temperature decreases linearly with the altitude,

$$n = n_0 \left(\frac{H_0}{H} \right)^{\frac{1-B}{B}} \quad (7)$$

where

$$B = h \beta / T \quad ;$$

and for the isothermal part of the atmosphere,

$$n = n^* \exp(-z/H^*) \quad , \quad (8)$$

where the asterisk indicates the tropopause level. For a completely isothermal atmosphere, $n^* = n_0$ and $H^* = H_0$.

Combining Equations (2c), (4), (7) and (8), the variation of the number density of NO₂ can be expressed by:

$$n_1 = \frac{K}{4kT} \left[\sqrt{1 + \frac{8kTn_o}{K} \left(\frac{H}{H_o}\right)^{\frac{1-B}{B}}} - 1 \right] \quad (9)$$

for that portion of the atmosphere with a linear temperature decrease; whereas for the isothermal part, one can write

$$n_1 = \frac{K}{4kT} \left[\sqrt{1 + \frac{8kTn^*}{K} \exp(-z/H^*)} - 1 \right] \quad (10)$$

Equations (9) and (10) were employed for two types of computations:

(a) the total NO₂-contents were obtained by integration over the appropriate altitude regimes (see Figure 2); and (b) the number density-altitude behavior was obtained by direct computation (see Figs. 3 - 6).

In each case, a C-value of 6×10^{18} cm²-column was employed. (3)

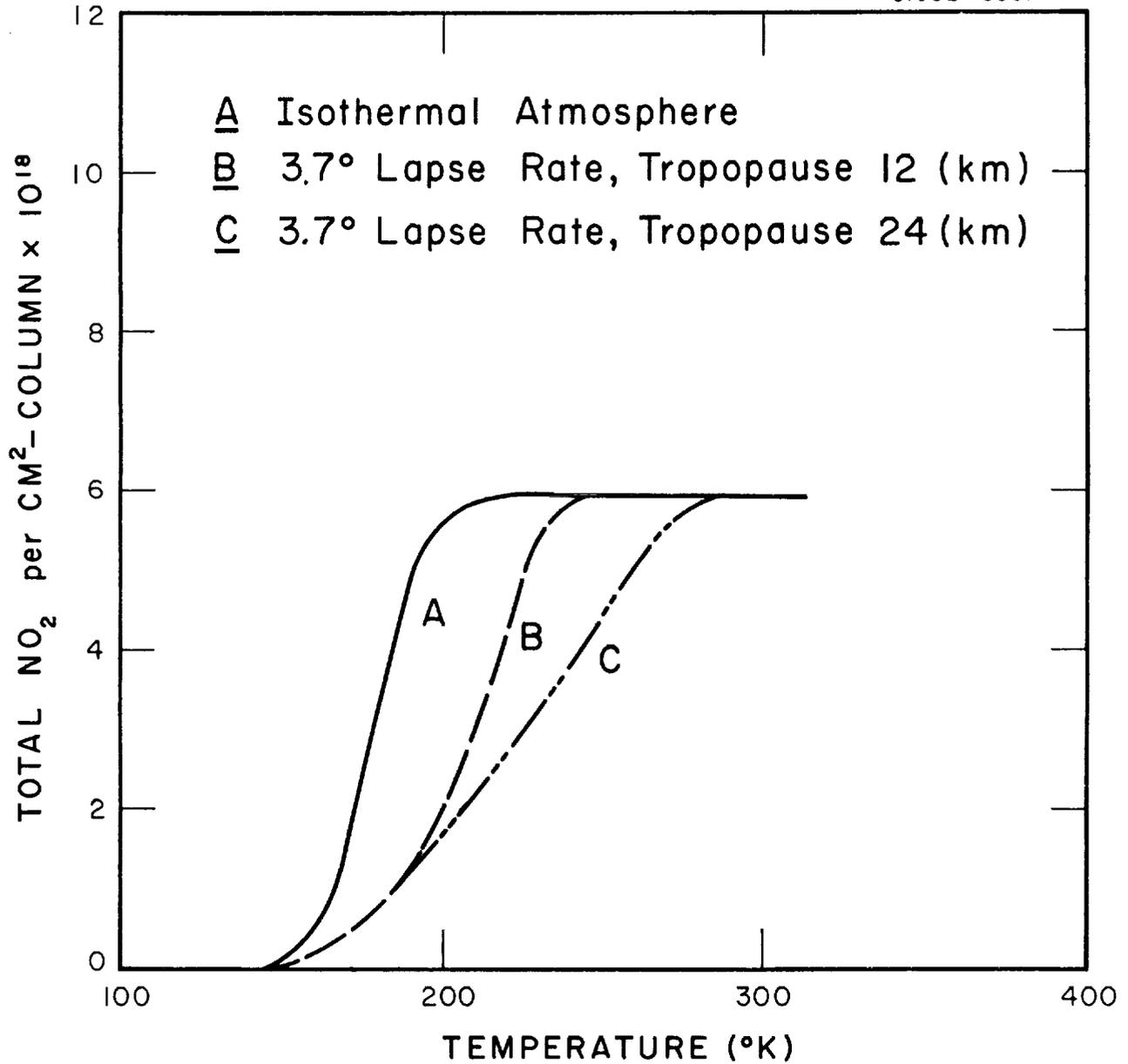


Figure 2. Variation of Total NO₂ Content of Mars with Surface Temperature.

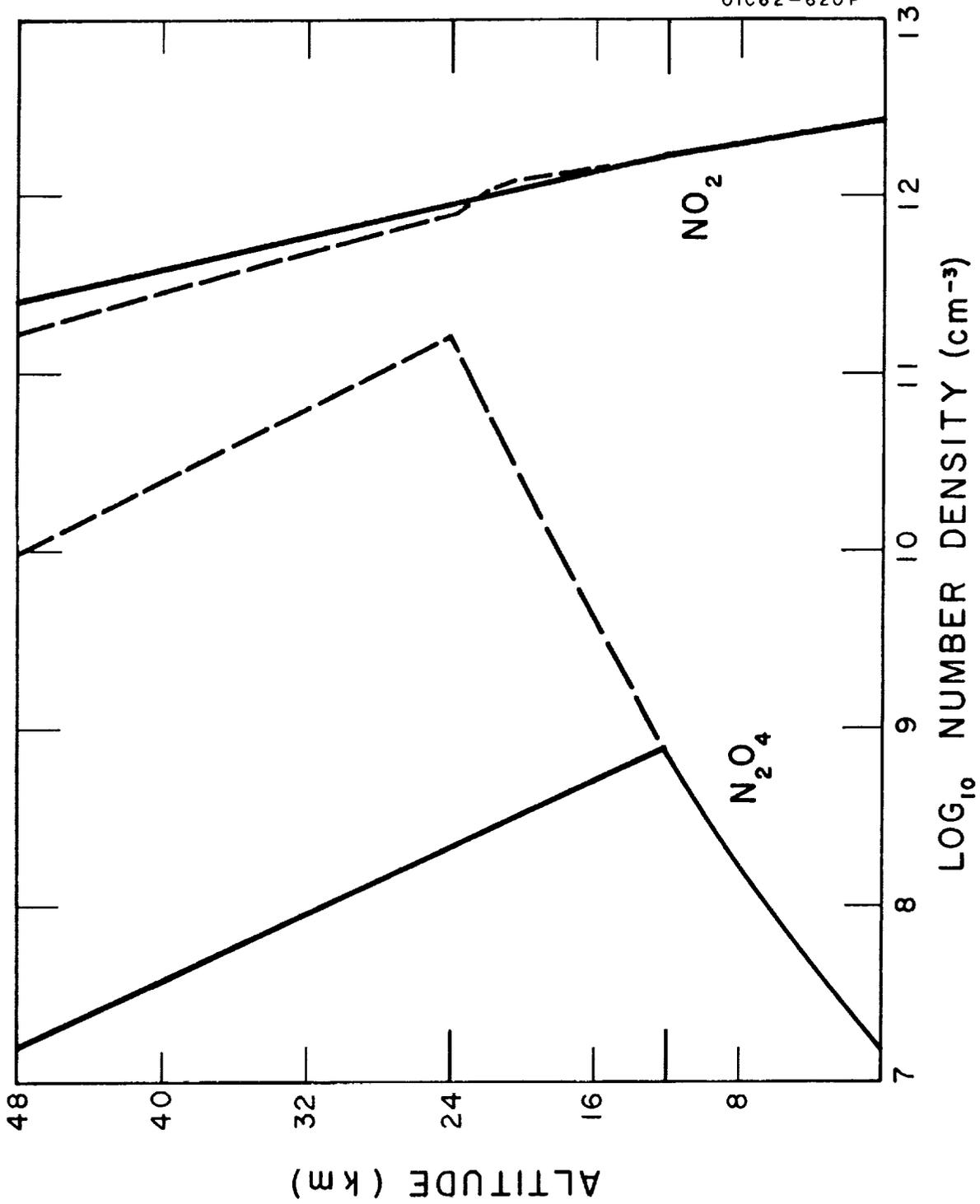


Figure 3. Distribution of NO_2 - N_2O_4 with Altitude for $T_0 = 273^\circ\text{K}$.
Solid Curves: Tropopause at 12 km. Broken Curves: Tropopause at 24 km.

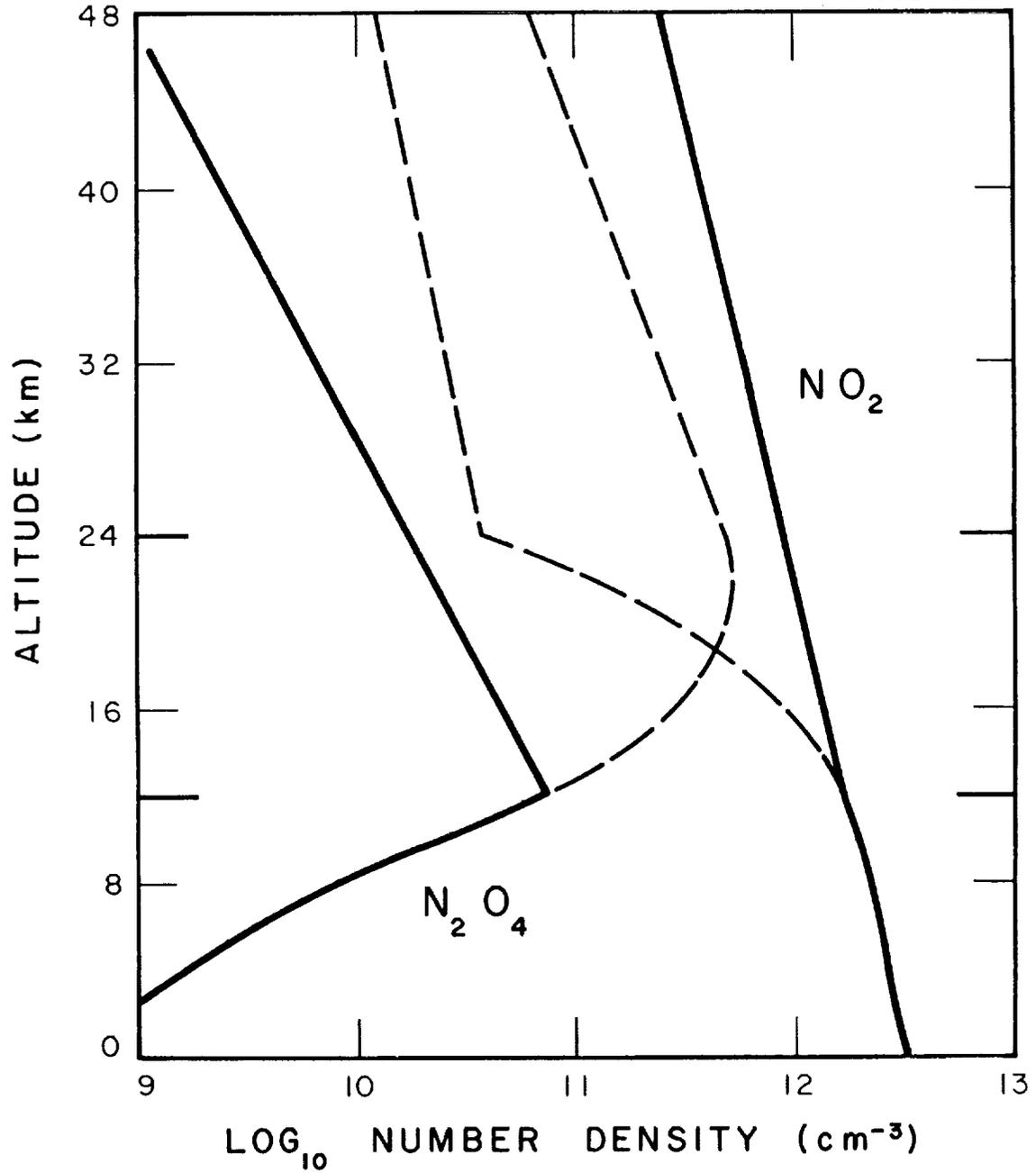


Figure 4. Distribution of $\text{NO}_2 - \text{N}_2\text{O}_4$ with Altitude for $T_0 = 243^\circ\text{K}$. Solid Curves: Tropopause at 12 km. Broken Curves: Tropopause at 24 km.

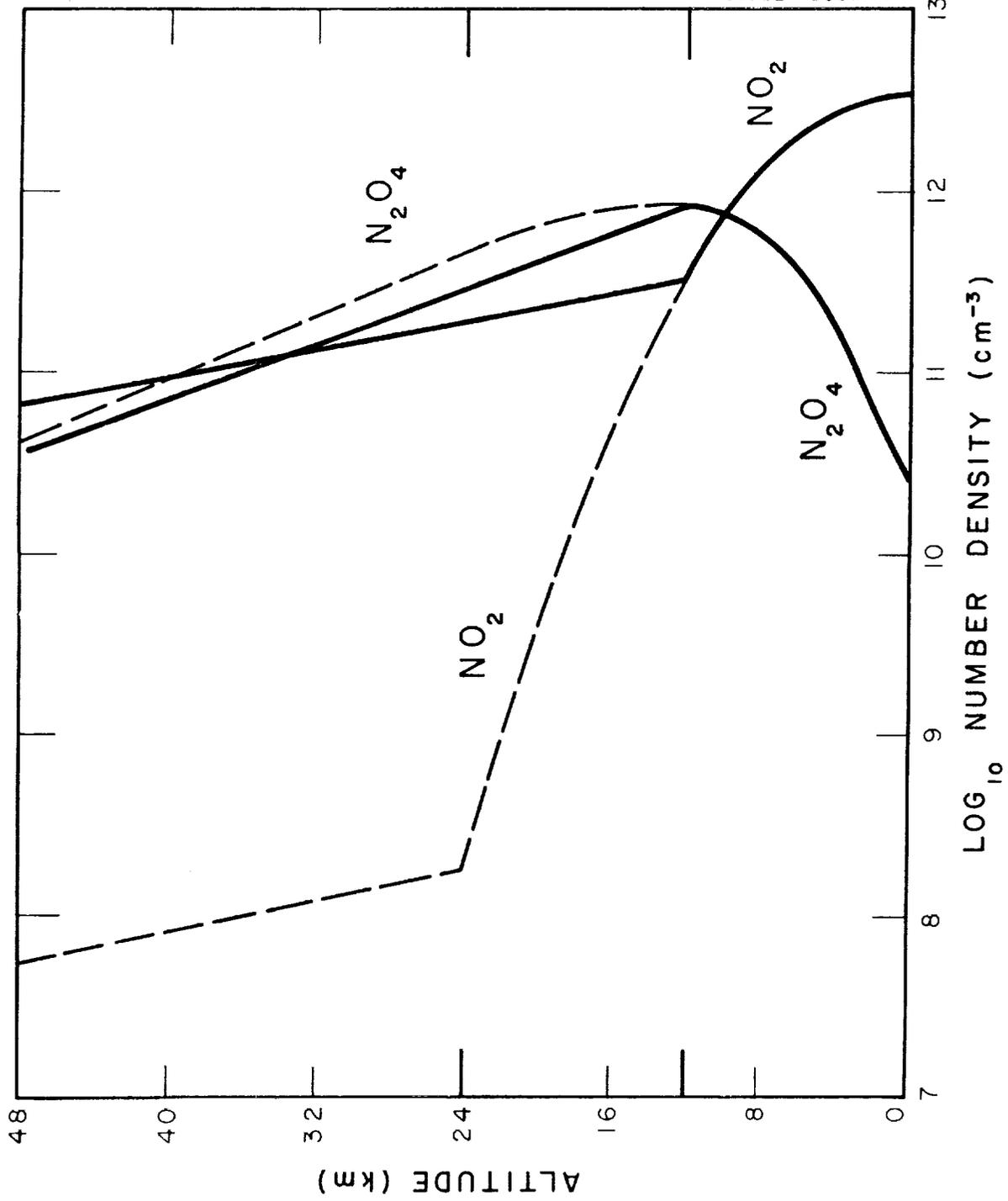


Figure 5, Distribution of NO_2 - N_2O_4 with Altitude for $T_0 = 213^\circ\text{K}$.
Solid Curve: Tropopause at 12 km. Broken Curves: Tropopause at 24 km.

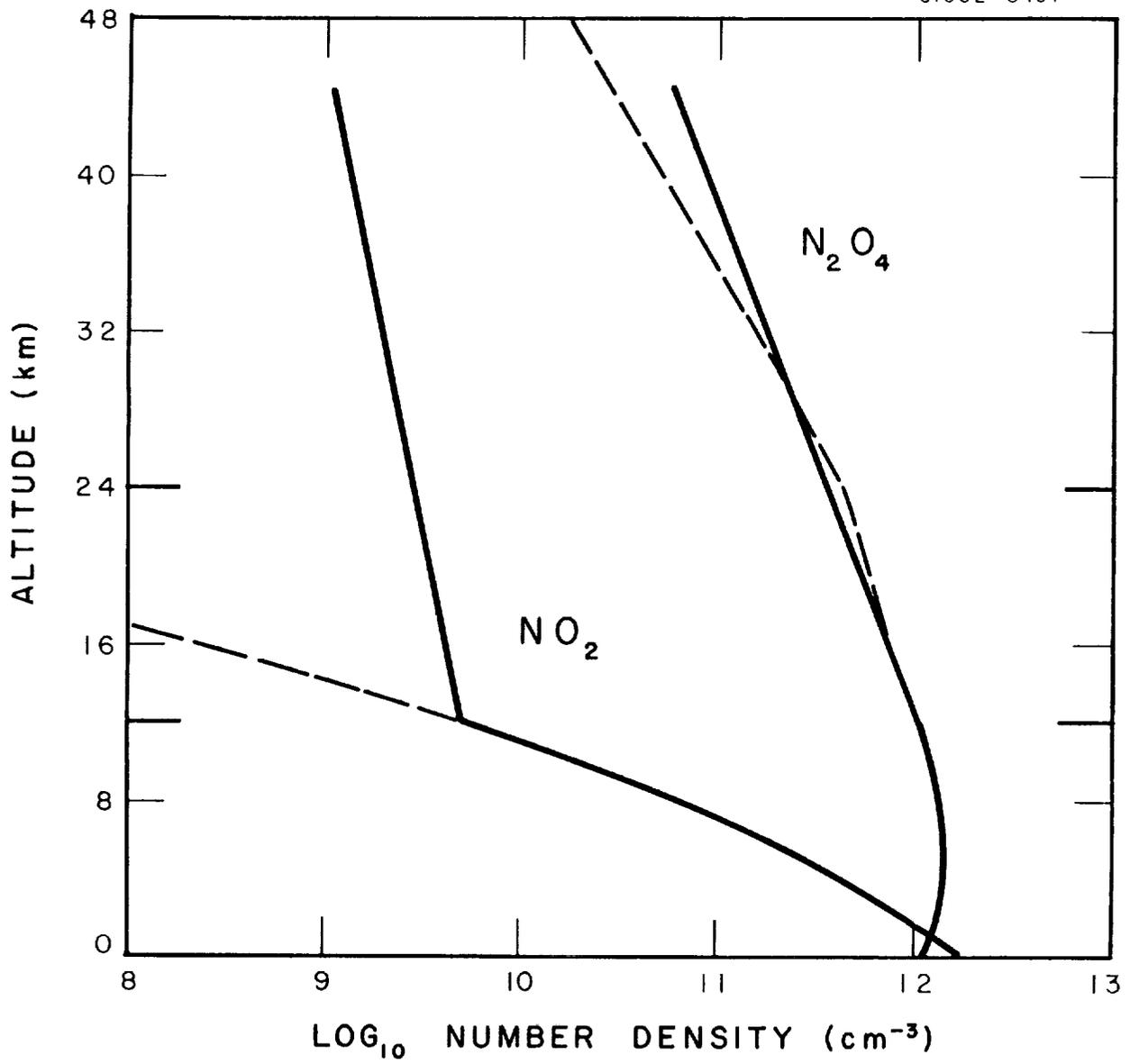


Figure 6. Distribution of NO_2 - N_2O_4 with Altitude for $T_0 = 183^\circ\text{K}$.
Solid Curves: Tropopause at 12 km.
Broken Curves: Tropopause at 24 km.

III. RESULTS AND DISCUSSION

It is clear that an interpretation of these data requires a knowledge of the temperature variation on Mars, which at the present time is not available. A crude average of the observed daytime surface temperatures over the entire planet is about 240°K , although Mintz⁽⁹⁾ points out that only a few meters above the ground, the temperature may decrease by as much as 50°K ; this behavior is analogous to terrestrial desert regions. The variation of temperature for a given region during daylight hours appears to be of the order of 80°K , while seasonal changes at the equator may produce a difference of 40°K . Accordingly, it seems unlikely that the equatorial temperatures at midday assume values much less than 210°K , although it could conceivably occur for a brief period of time. With a C-value of $6 \times 10^{18} \text{ cm}^2$ -column used in this study, Fig. 2 shows that in the case of an isothermal atmosphere, no depletion of the NO_2 content occurs for temperatures above 210°K ; but the introduction of the adiabatic lapse rate can produce a pronounced change. Even in this case the NO_2 content varies not more than a factor or two for reasonable temperatures. If the amount of NO_2 is required to change by a factor of ten in order to produce a blue clearing, the expected surface temperature changes are not great enough to cause such an event. On the other hand, it can be gleaned from Fig. 1 that a NO_2 variation by a factor of two causes the transmission coefficient to change from $p = 0.05$ to $p = 0.22$ at 4450 \AA , which amounts to a decrease in opacity by a factor of four. These findings are of interest, but it should be made clear that it is necessary to investigate the influence

of other possible depletion mechanisms (for instance, solar photodecomposition, chemical reactivity, heterogeneous surface reactions, etc.) before definite conclusions can be reached concerning the role of NO_2 in the blue clearings.

The number density-altitude distributions of the NO_2 and N_2O_4 were computed for assumed surface temperatures of 273° , 243° , 213° and 183°K and an adiabatic lapse rate of $3.7^\circ\text{K}/\text{km}$. The results of these calculations are displayed in Figures 3 through 6 where the solid curves are used for a 12-km tropopause, and the broken curves for a 24-km tropopause. It is interesting to note that the distributions of N_2O_4 exhibit maxima owing to the influence of temperature and pressure upon the $\text{NO}_2 - \text{N}_2\text{O}_4$ equilibrium, while the NO_2 number densities show a monotonically decreasing number density with height. As expected, at the lower temperatures, crossings occur which depend on the assumed height of the tropopause. A not-immediately obvious point is the possibility of condensation of N_2O_4 in the atmosphere at sufficiently low temperatures. While NO_2 would probably not freeze out in the temperature-concentration range explored here, the vapor pressures of N_2O_4 are such that condensation could occur above 18 km for a surface temperature of 213°K , and above 9 km for a temperature of 183°K at the surface, provided the lapse rate is 3.7 degrees per kilometer up to 12 km. However, these conclusions are based upon a rather severe extrapolation of the measured range of the published vapor pressure curves⁽¹⁰⁾ towards lower temperatures which could give rise to considerable inaccuracies. Accordingly, in the present calculations, the role of condensation was not taken into consideration. However, it is only the upper portions of the distribution curves

is negligible.

On the basis of the findings reported here, the following experiments can be suggested:

- (a) The absorption strength of the 3.43 micron band should be monitored before, during, and after a blue clearing to determine whether or not this event can be associated with Martian NO_2 depletion.
- (b) If no variation is observed, then it appears that the NO_2 hypothesis must be rejected.
- (c) On the other hand, an observed variation would then make it worthwhile to search for additional absorption bands due to N_2O_4 .
- (d) If such bands are discovered, it would be worthwhile to compare the absorption intensity ratios.
- (e) To make simultaneous, independent measurements of the Martian atmosphere to check and find out if the observed NO_2 depletion can be due to temperature variations.
- (f) If the measurements in (d) and (e) are found to be not self-consistent, it is evident that the NO_2 depletion cannot be ascribed solely to temperature variations but rather are caused by other depletion mechanisms; i.e., solar photodecomposition.

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