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TEMPERATURE DEPENDENCE OF THE RATE CONSTANTS FOR THE REACTIONS $O^+ + O_2 \rightarrow O_2^+ + O$ AND $O^+ + N_2 \rightarrow NO^+ + N$

PETER STUBBE

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Laboratory for Space Sciences

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ABSTRACT

The dependency of the rate constant k_r for the reactions

$$O^+ + O_2 \rightarrow O_2^+ + O \qquad k_1 \tag{1}$$

$$O^+ + N_2 \rightarrow NO^+ + N \qquad k_2 \tag{2}$$

on the gas temperature T, the vibrational temperature T_v of the molecular reactant, and the relative flow velocity v_s between the gases, is studied theoretically by means of a collision theory approach. The resulting expression for k_r contains the two unknown parameters A (activation energy) and P_0 (scaling factor) which have to be determined empirically. k_1 (T) is found to have a minimum at about 650°K and a nearly linear increase for temperatures above 750°K. For reaction (2), the rate constant is presented as a function of T and A, since uncertainties in the experimental results do not allow a reliable determination of A. The increase rate of k_2 with $T_v(N_2)$, the vibrational temperature of N_2, falls off strongly with increasing gas temperature.

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CONTENTS

TEMPERATURE DEPENDENCE OF THE RATE CONSTANTS FOR THE REACTIONS $O^+ + O_2 \rightarrow O_2^+ + O$ AND $O^+ + N_2 \rightarrow NO^+ + N$

1. INTRODUCTION

The chemical reactions of O^+ with O_2 and N_2,

$$O^+ + O_2 \rightarrow O_2^+ + O \qquad k_1 \tag{1}$$

$$O^+ + N_2 \rightarrow NO^+ + N \qquad k_2 \ , \tag{2}$$

provide the main electron-ion loss mechanism in the ionospheric F-region. A great number of laboratory measurements of the reaction rates k_1 and k_2 at a temperature of 300°K (summarized by Ferguson, 1967) yielded ionospheric loss coefficients which led to serious difficulties in explaining some observed F-layer phenomena, mainly the maintenance of the nighttime F-layer. Therefore, it would be highly desirable to find a negative temperature dependence of k_1 and k_2 as claimed by Donahue (1966) and Hanson and Cohen (1968).

Recent measurements of k_1 and k_2 as a function of temperature between 77°K and 600°K (Nakshbandi and Hasted, 1967; Smith and Fouracre, 1968; Dunkin, Fehsenfeld, Schmeltekopf, and Ferguson, 1968) showed very consistently that k_1 is indeed decreasing with increasing temperature. For k_2, on the other hand, the situation is not as clear. Nakashbandi and Hasted (1967) report a slight increase of k_2 with temperature, while after Dunkin et al. (1968) k_2 clearly shows a negative temperature dependence. According to Warneck (1967), finally, k_2 is constant between 700°K and 1400°K.

The temperature dependence of k_1 and k_2 described so far applies to a system in thermal equilibrium, i.e. with a distribution of excited states as given by Boltzmann's law. According to Thomas and Norton (1966), k_2 may be appreciably higher when the vibrational states of N_2 are excessively excited. This effect was measured quantitatively by Schmeltekopf, Fehsenfeld, Gilman, and Ferguson (1967) with the result that for a gas temperature of 300°K k_2 strongly increases with the vibrational temperature T_v. As pointed out by Thomas and Norton (1966), this process may be of importance for the ionosphere during magnetic storms.

The purpose of this paper is to present a theoretical model which is capable of reproducing the above cited experimental results as well as making predictions for physical conditions and temperature ranges which are not covered by the experiments. In the light of recent ideas about large scale horizontal neutral gas motions (King and Kohl, 1965) it appears that a considerable amount of kinetic energy is stored in the atmosphere. It seems worthwhile to study how this could influence the rate of an ion-molecule reaction or, in other words, how the reaction rate depends on the relative velocity between the ion and neutral gas. We will include this question in our considerations.

Our theory is based on a collision theory approach which is essentially a manifold modification of the Gioumousis-Stevenson theory (Gioumousis and Stevenson, 1958) that was successfully applied to some ion-molecule reactions involving hydrogen. Additional information concerning the temperature dependence of the steric factor will be taken from the transition-state theory.

2. THEORY

A collision between two particles can lead to a chemical reaction when two conditions are fulfilled. First, the relative kinetic energy at the moment of the impact must exceed the activation energy A. Second, the particles must be so oriented relative to each other that the reacting groups come close to each other during the collision. The fraction of collisions with a proper orientation of the particles is represented by the steric factor P. The determination of the chemical reaction rate k_r by means of collision theory simply amounts to a count of the number of collisions that satisfy the above conditions. A theoretical prediction of the constant activation energy A and the temperature dependent steric factor P(T) lies beyond the scope of this theory. There is, however, another theoretical approach to the problem, provided by the transition-state theory. This theory enables a description of the temperature dependence of P. Thus, adding this information to our collision theory derivation of k_r, we are left with only two unknown parameters, namely the activation energy A and the constant P_0 in the steric factor P. A and P_0 must be determined empirically.

According to these preliminary remarks, k_r is defined by

$$dk_r = P\,Q(g)\,g\,\frac{\overline{dN_i\,dN_n}}{N_i\,N_n} \tag{3}$$

where g is the relative velocity between an ion and a neutral particle. Q(g) is the effective cross section for collisions with relative kinetic energies greater than A. N_i and N_n are the numbers of ions and neutral particles per cm^3, respectively. $\overline{dN_i\, dN_n}/N_i \cdot N_n$ is the number of ion-neutral pairs with a relative velocity between g and g + dg, related to the total number of ion-neutral pairs. $\overline{dN_i\, dN_n}/N_i \cdot N_n$ can be obtained by integration over θ in Equation (47) of Stubbe (1968) as

$$\frac{\overline{dN_i\, dN_n}}{N_i\, N_n} = 4\pi\left(\frac{R}{\pi}\right)^{3/2} e^{-Rv_s^2}\, e^{-Rg^2}\, g^2\, dg \sum_{n=0}^{\infty} \frac{1}{(2n+1)!} \left(2Rv_s\, g\right)^{2n} \tag{4}$$

This expression is based on the assumption that both gases possess Maxwellian velocity distributions which are displaced by the macroscopic drift velocities $\underline{v}_i$ and $\underline{v}_n$, respectively (see Stubbe, 1968, Equations (44a, b)). v_s and R are defined by

$$v_s = \left|\underline{v}_i - \underline{v}_n\right| , \tag{5}$$

$$R = \frac{\mu_{in}}{2k\, T_R} , \tag{6}$$

with

$$T_R = \mu_{in}\left(\frac{T_i}{m_i} + \frac{T_n}{m_n}\right) \tag{7}$$

the reduced temperature, and

$$\mu_{in} = \frac{m_i m_n}{m_i + m_n} \tag{8}$$

the reduced mass; T_i, T_n, m_i, m_n are the ion temperature, neutral gas temperature, ion mass, and neutral particle mass, respectively. Q(g) is given by Stubbe (1966) as

$$\left.\begin{aligned} Q(g) &= 0 && \text{for } 0 \leq g \leq v_1 \\ Q(g) &= Q_0\left(1 - \frac{v_1^2}{g^2}\right) && \text{for } v_1 \leq g \leq \infty \end{aligned}\right\} \text{ for } A \geq \frac{\mu_{in}}{2} v_0^2 \tag{9a}$$

$$\left.\begin{aligned} Q(g) &= \frac{k_0}{g} && \text{for } 0 \leq g \leq v_2 \\ Q(g) &= Q_0\left(1 - \frac{v_1^2}{g^2}\right) && \text{for } v_2 \leq g \leq \infty \end{aligned}\right\} \text{ for } A \leq \frac{\mu_{in}}{2} v_0^2 \tag{9b}$$

where v_0, v_1, v_2, Q_0, and k_0 are defined by

$$v_0 = \frac{e}{\sigma^2}\sqrt{\frac{\eta}{\mu_{in}}} \tag{10}$$

$$v_1 = \sqrt{\frac{2A}{\mu_{in}} - v_0^2} \tag{11}$$

$$v_2 = v_0 - \sqrt{\frac{2A}{\mu_{in}}} \tag{12}$$

$$Q_0 = \pi \sigma^2 \tag{13}$$

$$k_0 = 2 Q_0 v_0 = 2\pi e \sqrt{\frac{\eta}{\mu_{in}}} \tag{14}$$

e is the ion charge, η the neutral particle polarizability, and σ the sum of the gas-kinetic radii of the ions and the neutral particles. For $A = 0$ and $\sigma = 0$, the cross section of (9a) and (9b) becomes identical to the orbiting cross section in Langevin's ion mobility theory for an attractive inverse fourth power potential (Langevin, 1905). The orbiting cross section was taken as the chemical reaction cross section by Gioumousis and Stevenson (1958) in their theory. Introducing the further abbreviations

$$u_0 = \sqrt{R}\, v_2 \tag{15}$$

and

$$A_0 = \frac{\mu_{in}}{2} v_0^2 , \tag{16}$$

lumping together Equations (3), (4), (9a), (9b) and integrating over g, we obtain for the reaction rate constant

$$k_r = P k_0 \Bigg\{ \frac{e^{-R\left(v_s^2 + v_1^2\right)}}{v_0 \sqrt{\pi R}} \sum_{n=1}^{\infty} \frac{\left(4R\, v_s^2\right)^{n-1} n!}{(2n-1)!} \sum_{\nu=0}^{n} \frac{\left(R\, v_1^2\right)^{\nu}}{\nu!}$$

$$- \frac{v_1^2}{v_0} \sqrt{\frac{R}{\pi}}\, e^{-R\left(v_s^2 + v_1^2\right)} \sum_{n=0}^{\infty} \frac{\left(4R\, v_s^2\right)^{n} n!}{(2n+1)!} \sum_{\nu=0}^{n} \frac{\left(R\, v_1^2\right)^{\nu}}{\nu!} \Bigg\} \quad \text{for} \quad A \geq A_0 \tag{17a}$$

$$k_r = P k_0 \Bigg\{ \frac{2}{\sqrt{\pi}} \int_0^{u_0} e^{-u^2}\, du - 2v_2 \sqrt{\frac{R}{\pi}}\, e^{-R\left(v_s^{\,2}+v_2^{\,2}\right)} \sum_{n=1}^{\infty} \frac{\left(R\, v_s^{\,2}\right)^{n-1}}{(n-1)!}$$

$$\sum_{\nu=1}^{n} \frac{\left(4R\, v_2^{\,2}\right)^{\nu-1} (\nu-1)!}{(2\nu-1)!} + \frac{e^{-R\left(v_s^{\,2}+v_2^{\,2}\right)}}{v_0 \sqrt{\pi R}} \sum_{n=1}^{\infty} \frac{\left(4R\, v_s^{\,2}\right)^{n-1} n!}{(2n-1)!} \sum_{\nu=0}^{n} \frac{\left(R\, v_2^{\,2}\right)^{\nu}}{\nu!}$$

$$- \frac{v_1^{\,2}}{v_0} \sqrt{\frac{R}{\pi}}\, e^{-R\left(v_s^{\,2}+v_2^{\,2}\right)} \sum_{n=0}^{\infty} \frac{\left(4R\, v_s^{\,2}\right)^{n} n!}{(2n+1)!} \sum_{\nu=0}^{n} \frac{\left(R\, v_2^{\,2}\right)^{\nu}}{\nu!} \Bigg\} \qquad \text{for} \quad A \leq A_0 \qquad (17b)$$

For $A = A_0$, (17a) and (17b) become identical. When the relative flow velocity v_s is negligibly small, (17a) and (17b) reduce to

$$k_r = P k_0 \frac{1}{v_0 \sqrt{\pi R}}\, e^{-R v_1^{\,2}} \qquad \text{for} \quad A \geq A_0 \qquad (18a)$$

$$k_r = P k_0 \left\{ \frac{2}{\sqrt{\pi}} \int_0^{u_0} e^{-u^2}\, du + \frac{1}{v_0 \sqrt{\pi R}}\, e^{-R v_2^{\,2}} \right\} \qquad \text{for} \quad A \leq A_0 \qquad (18b)$$

So far we have considered only the conversion of kinetic energy into activation energy. There is evidence, however, that energy belonging to the internal degrees of freedom can also contribute to the activation of molecules (e.g. Hinshelwood, 1955; Kontrat'ev, 1964). According to recent studies (Thomas and Norton, 1966; Schmeltekopf et al., 1967), especially the effect of a vibrational energy contribution should be important, and we will, therefore, include it in our derivation.

The number of molecules being in the j-th vibrational state for a gas in thermal equilibrium is given by

$$N_j = N_n \left(1 - e^{-h\nu/kT_n}\right) e^{-j(h\nu/kT_n)} \tag{19}$$

with ν the vibration frequency and $jh\nu$ the energy of the j-th state. Thus, if instead of the kinetic energy alone the sum of kinetic and vibrational energy is available for an activation of the molecule, the reaction rate k_r is given by

$$k_r = \left(1 - e^{-h\nu/kT_n}\right) \sum_{j=0}^{\infty} e^{-j(h\nu/kT_n)} k_{rj} \left(A_j\right) \tag{20}$$

$k_{rj}\left(A_j\right)$ is the reaction rate after (17a), (17b) or (18a), (18b) calculated for an effective activation energy

$$A_j = \text{Max}\,(A - jh\nu,\ 0) \tag{21}$$

instead of A. The vibration frequencies are 4.74 10^{13} sec^{-1} for O_2 and 7.08 10^{13} sec^{-1} for N_2 (Syrkin and Dyatkina, 1964).

We have not yet specified the steric factor, in particular not its temperature dependence. In order to do so, we have to leave our collision theory considerations and engage the more elaborate transition-state theory. The steric factor P, as predicted by the transition-state theory, depends on the configuration of the activated complex which is formed at the moment the reaction occurs (e.g. Frost and Pearson, 1963). We may expect that for both reactions (1) and

(2) the activated complex is nonlinear since no valence electrons in the s-state are involved. For a nonlinear complex, P is given by

$$P = P_0 \frac{T_c^{7/2}}{T_i^{3/2}\, T_n^{5/2}} \frac{\left(1 - e^{-h\nu/kT_n}\right)}{\left(1 - e^{-h\nu/kT_c}\right)^2} \tag{22}$$

with T_c the temperature of the activated complex. A reliable determination of T_c can be made only when T_i and T_n are equal. In this case we have, of course, $T_c = T_i = T_n$. Thus, we obtain for the steric factor

$$P = P_0\, T^{-1/2} \frac{1}{1 - e^{-h\nu/kT}} \tag{23}$$

A combination of Equations (20) and (23) with either (17a), (17b) or (18a), (18b) gives the final result for k_r as a function of the temperature T and, when Equations (17a), (17b) are employed, of the relative flow velocity v_s.

The unknown parameters A and P_0 can be determined only empirically by selecting them so that the agreement between the theoretical and the experimental results is optimum.

It must be emphasized that the theory developed so far holds true only for a system in thermal equilibrium. An attempt to generalize it in order to describe the effect of excessively excited vibrational states (Thomas and Norton, 1966; Schmeltekopf et al., 1967) will be made in section 5. An attempt will not be made, however, to extend the theory to the case $T_i \neq T_n$, because this would create many complex problems concerning the partition function and the temperature of the activated complex. Another limitation of our theory is set by the fact that for energies above about 0.2 eV (see Hasted, 1964, Chapter 14) some of our assumptions will begin to fail. These assumptions are: Applicability of classical mechanics, constant gas kinetic radius, pure inverse fourth power interaction potential, and well defined geometry of the activated complex.

The unfortunate consequence of these restrictions is that we cannot make use of several valuable experimental works (Bohme, Ong, and Hasted, 1967; Giese, 1966; Paulson, Dale, and Murad, 1967; Stebbings, Turner, and Rutherford, 1966), at least not quantitatively. We can learn from these works, however, that despite the possible decrease of k_1 and k_2 with temperature for low energies there is a distinct increase at higher energies. Therefore, our theory must be capable of producing a minimum for k_r at temperatures in the vicinity of 1000°K.

3. THE REACTION $O^+ + O_2 \rightarrow O_2^+ + O$

In this and in the following sections we will present numerical evaluations of k_r as a function of temperature. For reaction (1), the polarizability η and the gas kinetic radius σ are taken as $1.60 \quad 10^{-24}$ cm³ and $2.50 \quad 10^{-8}$ cm, respectively. Thus, the energy A_0 is $4.72 \quad 10^{-13}$ erg or 6.80 kcal/mole.

Figure 1 shows k_1 as a function of T for four activation energies between $0.86A_0$ and $0.98A_0$ together with the experimental results of Nakshbandi and Hasted (1967) and Smith and Fouracre (1968). The data point for T = 375°K in Table 1 of Nakshbandi and Hasted (1967) is disregarded since, as stated by the authors themselves, it may be subject to an error. At the time Figure 1 was prepared, the author had no knowledge of the work of Dunkin et al. (1968) so that their data points are not included in Figure 1. A redrawing, however, was not deemed necessary because of the good agreement between all three experimental works.

The theoretical curves are adjusted to a value of $k_1 = 1.9 \ 10^{-11} \text{ cm}^3 \text{ sec}^{-1}$ for T = 300°K through a proper choice of P_0. The best over-all fit is afforded by the 0.94 curve. The extension towards higher temperatures is presented in Figure 2 (solid lines). The 0.94 curve has a minimum at about 650°K. For temperatures above 750°K, it can be approximately described by

$$k_1 (T) = 0.58 \, k_1 (300) \left(1 + \frac{T}{1660}\right) \tag{24}$$

The computation of the solid curves in Figure 2 was based on Equation (23) for the steric factor P which means that all degrees of freedom of the activated

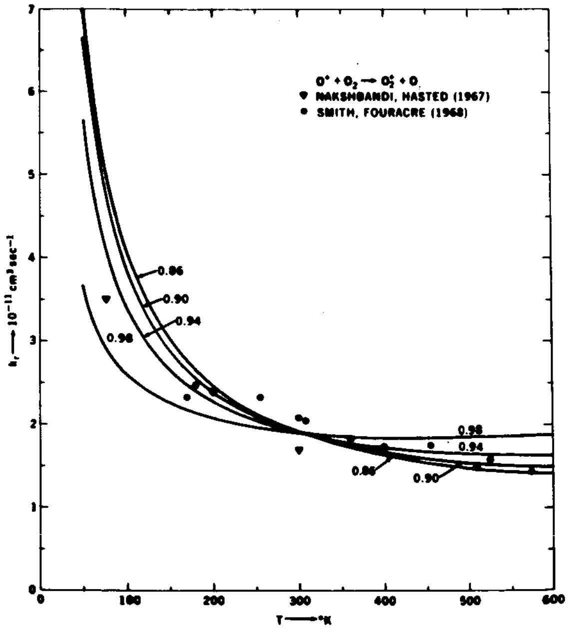

Figure 1

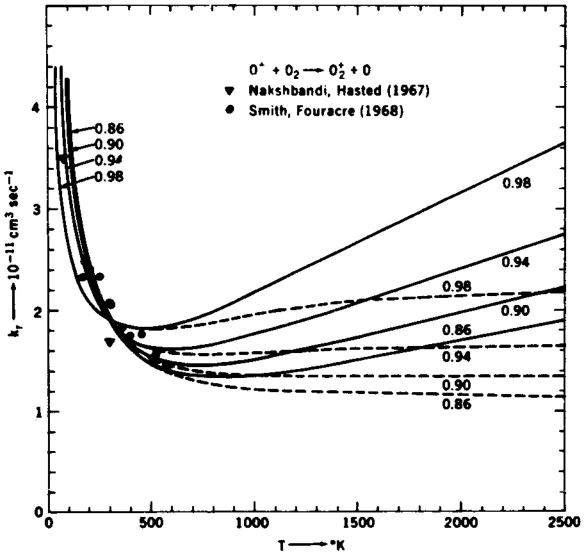

Figure 2

complex are assumed to be excited up to their full thermal equilibrium extent. While this is surely the case for laboratory conditions, it must be doubted that in the ionosphere the complex experiences a sufficient number of collisions during its relatively short lifetime to guarantee the full excitation of all degrees of freedom, in particular the vibrational degrees. A complete quantitative study of this question appears extremely difficult, and it shall therefore not be undertaken here. We can, however, roughly estimate the importance of this effect by assuming that only one of the two vibrational degrees of freedom is excited. This leads to the dashed curves in Figure 2.

The assumption that underlies the calculation of the dashed curves in Figure 2 is merely based upon the fact that one of the two vibrational degrees of freedom, stemming from the molecular reactant, is already fully excited before the complex is formed, while the other has to be excited during the lifetime of the complex. It is not intended to claim that the situation in the ionosphere can be quantitatively described in this way. The only aim of these considerations is to exhibit the possibility of a discrepancy between laboratory and ionospheric reaction rates and to estimate its order of magnitude.

So far all computations were carried out for $v_s = 0$. k_1 as a function of v_s, related to k_1 for $v_s = 0$, is shown in Figure 3 (left half) for different gas temperatures T. We see that k_1 increases with v_s, preferentially for low temperatures, but that the effect is so small that it should not contribute to any ionospheric phenomenon. The same holds true for all activation energies below A_0.

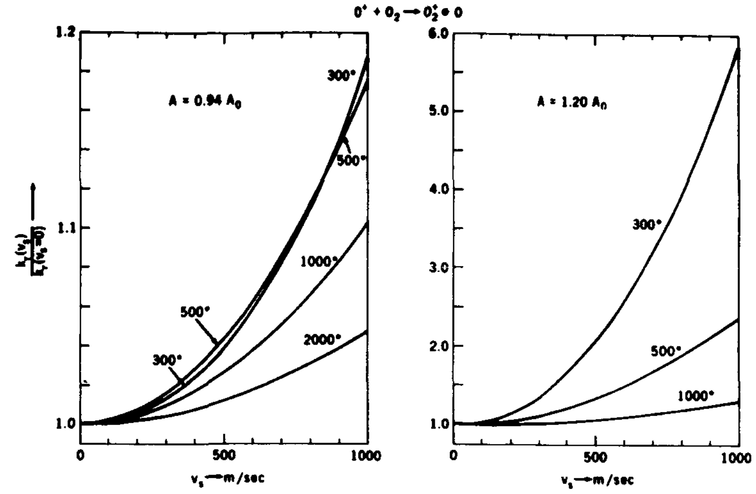

Figure 3

However, for activation energies above A_0, the effect becomes increasingly stronger. This is illustrated in the right half of Figure 3 for a hypothetical activation energy $A = 1.20 A_0$.

4. THE REACTION $O^+ + N_2 \rightarrow NO^+ + N$

As mentioned before, the existing laboratory results for k_2 as a function of T are incompatible with each other. We must, therefore, refrain from trying to determine A of this reaction and from extrapolating the experimental values for k_2 to higher temperatures. What we can do, however, is to give a representation of k_2 as a function of both T and A (Figure 4). The results shown in Figure 4 were obtained for the parameters $\sigma = 2.55 \quad 10^{-8}$ cm, $\eta = 1.76 \quad 10^{-24}$ cm^3, and $A_0 = 4.80 \quad 10^{-13}$ erg or 6.91 kcal/mole.

The data points of Nakshbandi and Hasted (1967) can approximately be reproduced by a curve lying between curves 5 and 6 of Figure 4. This means that k_2 increases monotonically with T and reaches a value at 2000°K 1.65 times that at 300°K.

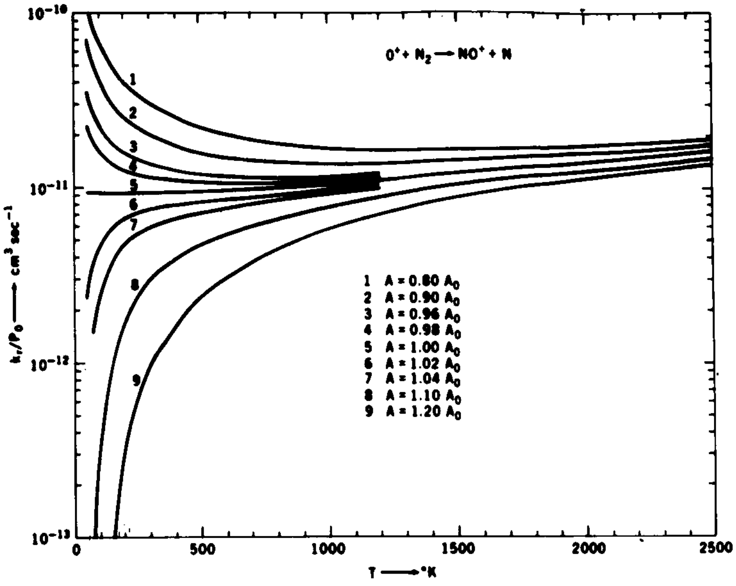

Figure 4

The results of Dunkin et al. (1968), on the other hand, can be approximated by a curve in the vicinity of curve 1 in Figure 4. Correspondingly, k_2 has a weak minimum around 1100°K and retains a nearly constant value of about half that at 300°K up to 2000°K. Thus, a reaction rate of $k_2 \approx 1.0\ \ 10^{-12}\ cm^3\ sec^{-1}$ for $T = 300°K$ (Dunkin et al., 1968) should result in a value of k_2 between 0.5 and 0.7 $10^{-12}\ cm^3\ sec^{-1}$ for F-region temperatures.

5. THE EFFECT OF ENHANCED VIBRATIONAL EXCITATION OF N_2 ON THE REACTION $O^+ + N_2 \rightarrow NO^+ + N$

The theory presented in section 2 is bound to the restrictions $T_i = T_v$ (T_v = vibrational temperature of N_2). Therefore, modifications are necessary in order to use it for a description of the experimental results of Schmeltekopf et al. (1967) who find that for a gas temperature $T = T_i = T_n = 300°K$ the reaction rate k_2 experiences an increase by a factor of 30 when T_v is changed from 300°K to 6000°K.

Equation (20) can easily be generalized to

$$k_r = \left(1 - e^{-h\nu/kT_v}\right) \sum_{j=0}^{\infty} e^{-j(h\nu/kT_v)} k_{rj}\left(A_j, T\right) \tag{25}$$

with A_j and k_{rj} given by Equations (21) and (17a), (17b) or (18a), (18b), respectively. The difficulty lies in the steric factor, i.e. in the temperature T_c of the activated complex. After (22), P is given by

$$P = P_0 \frac{T_c^{7/2}}{T^4} \frac{\left(1 - e^{-h\nu/kT_v}\right)}{\left(1 - e^{-h\nu/kT_c}\right)^2} \tag{26}$$

A straightforward purely theoretical determination of T_c appears extremely intricate. However, T_c can be readily estimated in the following semi-empirical way: For $T = T_v$, the average internal energy of the activated complex is

$$U_c = \frac{7}{2} kT + 2h\nu \left(1 - e^{-h\nu/kT}\right) \sum_{j=1}^{\infty} j\, e^{-j(h\nu/kT)} \tag{27}$$

If T_v is greater than T, the activated complex is supplied with a fraction α of the excessive vibration energy of N_2,

$$\Delta U_{N_2} = h\nu \left(1 - e^{-h\nu/kT_v}\right) \sum_{j=1}^{\infty} j\, e^{-j(h\nu/kT_v)} - h\nu \left(1 - e^{-h\nu/kT}\right) \sum_{j=1}^{\infty} j\, e^{-j(h\nu/kT)} \tag{28}$$

Thus, T_c can be obtained from the determining equation

$$U_c + \alpha \Delta U_{N_2} = \frac{7}{2} kT_c + 2h\nu\left(1 - e^{-h\nu/kT_c}\right) \sum_{j=1}^{\infty} j\, e^{-j(h\nu/kT_c)} \qquad (29)$$

α has to be determined empirically by selecting it so that the theoretical result gives the best fit to the experimental result.

Figure 5 shows k_2 as a function of T_v. The thicklined curve represents the smoothed data of Schmeltekopf et al. (1967). The thinlined curves are the theoretical results for four gas temperatures between 300°K and 2000°K, computed for $\alpha = 0.40$ and $A = A_0$. It is clearly recognizable that the increase of k_2 with T_v is much more pronounced for low temperatures than it is for higher temperatures. This means that the effect of an enhanced vibrational excitation of N_2 on ionospheric F-region phenomena should be much stronger for nighttime and solar minimum conditions than for daytime and solar maximum conditions, respectively.

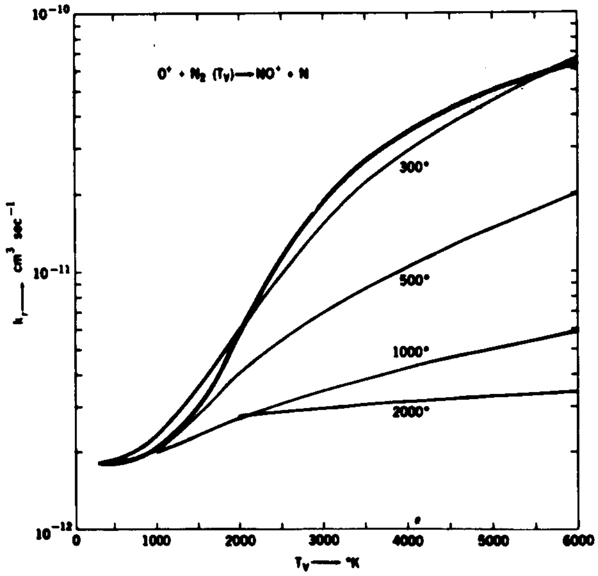

Figure 5

The choice of the activation energy $A = A_0$ is to some extent arbitrary. Computations for different activation energies were carried out. They showed that a slight dependency on A exists but that in no case the qualitative characteristics, as described above, were changed. Thus, we can and will put emphasis only on these qualitative features.

6. CONCLUSIONS

In the present paper an attempt is made to theoretically describe the reaction rate k_r of an ion-molecule interchange reaction as a function of the temperature T, the relative flow velocity v_s of the gases, and the parameters A (activation energy) and P_0 (constant part of the steric factor P). The resulting formulae are applied to the reactions $O^+ + O_2 \rightarrow O_2^+ + O$ and $O^+ + N_2 \rightarrow NO^+ + N$.

For the first reaction, the rate constant k_1 is found to have a minimum at about 650°K and a nearly linear increase for the range of ionospheric temperatures. The possibility of a discrepancy between laboratory and ionospheric reaction rates is discussed. It is shown that k_1 depends on v_s only weakly but that the dependency can become important for higher activation energies.

For the second reaction, the experimental situation is contradictory. Therefore, a determination of A becomes impossible, and k_2 is presented as a function of both T and A. For further experiments it may be suggested to emphasize low temperature measurements since they contain more information about this reaction than high temperature data (see Figure 4).

By introducing an additional parameter, the theory is extended in order to make it applicable for a study of the effect of enhanced vibrational excitation of N_2 on the reaction rate k_2. It is found that the effect strongly decreases with increasing gas temperature T. Therefore, it should be more important for the ionosphere under nighttime and solar minimum conditions than under daytime and solar maximum conditions.

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FIGURE CAPTIONS

Figure 1. k_1 as a function of T for the activation energies $A/A_0 = 0.86, 0.90, 0.94, 0.98$. Triangles: Experimental results of Nakshbandi and Hasted (1967). Circles: Experimental results of Smith and Fouracre (1968)

Figure 2. Ibid. for Figure 1. Solid curves: Both vibrational degrees of freedom of the activated complex excited. Dashed curves: Only one vibrational degree of freedom of the activated complex excited

Figure 3. k_1 as a function of v_s. Left half for $A = 0.94A_0$, right half for $A = 1.20A_0$

Figure 4. k_2 as a function of T for nine different activation energies between $0.80A_0$ and $1.20A_0$

Figure 5. k_2 as a function of the vibrational temperature of N_2, T_v. Thick-lined curve: Experimental results after Schmeltekopf et al. (1967) for a gas temperature T = 300°K. Thinlined curves: Theoretical results for the gas temperatures 300, 500, 1000, 2000°K