Nonthermal Rate Coefficients in the Ionosphere: The Reactions of \( \text{O}^+ \) With \( \text{N}_2, \text{O}_2, \) and NO

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The rate coefficient of a chemical reaction is given by the equation

\[
k = \sigma \bar{v}_\text{rel}
\]

where \( k \) is the reaction rate coefficient, \( \sigma \) is the cross section for reaction, and \( \bar{v}_\text{rel} \) is the mean relative speed between the reactants and is mathematically defined as

\[
\bar{v}_\text{rel} = \int_0^\infty v f(v) \, dv
\]

where \( f(v) \) is the relative speed distribution between the reactants.

The problem of the importance of the shape of \( f(v) \) for the determination of a rate coefficient arises when \( \sigma \) depends strongly on energy that using (1) leads to serious errors. In this case one has to consider the rigorous relation between \( k, \sigma \), and \( f \), which is [e.g., Hasted, 1964]

\[
k = \int_0^\infty \sigma v f(v) \, dv
\]

(3)

If (3) has to be used instead of (1), one should then in principle unfold \( \sigma \) from (3), using a proper expression for \( f(v) \) in the laboratory, and then convolute the resulting expression for \( \sigma \) with \( f(v) \) in the atmosphere in order to transpose the measurement of an energy dependent rate coefficient from the laboratory to the atmosphere.

Fortunately, the labor of carrying out the above procedure for energy dependent reactions can be avoided most of the time. In particular, when the reactants are in equilibrium with each other or, more generally, if they both have a Maxwellian velocity distribution, even if their temperatures differ, but if there is no mean relative drift present, the relative speed distribution, and therefore the rate coefficient, is uniquely a function of the mean energy in the center-of-mass system. The relative speed distribution is then given by the well-known expression [e.g., Banks, 1966; Tanenbaum, 1967; Light et al., 1969]

\[
f(v) = \frac{4}{\pi^{1/2}} \gamma \frac{\gamma v^3}{v^2} \exp(-\gamma v^2)
\]

(4)

where

\[\gamma^{-1} = \frac{2k_B T_e}{m_e} + \frac{2k_B T_x}{m_n}\]

(5)
The rate coefficient when \( f(v) \) is given to a good degree of approximation by (4) is defined here as the 'thermal' rate of a reaction. This rate is unique for a given value of the mean relative energy, which is proportional to \( \gamma^{-1} \).

In some instances the conditions under which an ion-neutral reaction takes place are such that (4) cannot be expected to be applicable. For example, in drift tube experiments in the laboratory a weakly ionized gas is accelerated by an electric field through a neutral 'buffer' gas in order to increase the mean relative energy between the reactants above the value that can be reached with afterglow techniques (in the latter experiments the reactants are in thermal equilibrium). Not only is there a mean relative drift present in that case, but the ion velocity distribution can also be highly distorted from the Maxwellian form [e.g., Wannier, 1953; Kihara, 1953; Skullerud, 1968; Wheaton and Woo, 1971; Lin and Bardsey, 1977]. In the atmosphere a similar situation exists, in particular at high latitudes when the ions are convected through the neutral atmosphere at speeds that often exceed the thermal speed of the neutrals. This situation in the atmosphere is precisely the one where the mean relative energy between the ion and neutral reactants exceeds the value that can be obtained with afterglow or other types of thermal equilibrium measurements. Therefore modelers often have to deal with a situation where not only does \( f(v) \) differ from (4) both in the laboratory and in the atmosphere, but \( f_{\text{elm}}(v) \) and \( f_{\text{lab}}(v) \) also differ from each other for the same value of the mean relative energy (see below).

One way to avoid the labor of inverting (3) for nonequilibrium situations has been to assume that the rate, and therefore \( f(v) \), is mainly a function of the mean relative energy in the center-of-mass system, \( KE_{\text{cm}} \). From basic arguments of physics it can be shown that \( KE_{\text{cm}} \) for an ion-neutral interaction is related to first order to the other parameters of interest through the relation [e.g., Kaneko et al., 1966; McFarland et al., 1973]

\[
KE_{\text{cm}} = \frac{m_n}{m_i + m_n} \left( \frac{m_i U^2}{2} + \frac{3kT_i}{2} - \frac{3kT_n}{2} \right) + \frac{3kT_n}{2} \tag{6}
\]

where \( m_i \) and \( m_n \) are the masses of the ion and neutral reactants, respectively, \( U \) is the magnitude of the relative drift between the two gases, \( k_B \) is the Boltzmann constant, and \( T_i \) and \( T_n \) are the ion and neutral temperatures, respectively.

In (6), \( T_i \) is defined by the expression

\[
3k_B T_i = \int f_i(v_i) m_i (v_i - \bar{v}_i)^2 d^3v_i \tag{7}
\]

where \( f_i \) is the ion velocity distribution, \( v_i \) is an ion velocity, and \( \bar{v}_i \) is the value of the mean ion drift. This definition of \( T_i \) is used throughout the present work.

There are problems with using \( KE_{\text{cm}} \) as a unique parameter for the description of a reaction rate. This is illustrated in the series of papers by Albritton et al. [1977], Viehland and Mason [1977], and Lin and Bardsey [1977]. It is clearly shown in these papers that both \( f_{\text{lab}}(v) \) and \( k_{\text{lab}} \) are not functions of \( KE_{\text{cm}} \) only but also depend strongly on the ion to buffer mass ratio and on the potential of interaction between the ions and the neutral buffer gas. Hence the difference between the rate coefficients measured in a drift tube for a helium buffer as opposed to an argon buffer gas can amount to more than a factor of 2 for the \( O^+ \) reaction with \( N_2 \). We can argue further that in nonequilibrium situations in the atmosphere the rate coefficient will differ from the laboratory rate at the same value of \( KE_{\text{cm}} \) even if the 'buffer' is the same in both cases. The reason is that the ion velocity distribution in nonequilibrium situations in the atmosphere differs in shape from that in the laboratory, even for the same \( KE_{\text{cm}} \) value and the same buffer gas [cf. Schunk and Walker, 1972; St.-Maurice and Schunk, 1973, 1974, 1977; St.-Maurice et al., 1976].

One way to relate various nonequilibrium situations to one another is to find a connection between a measured rate coefficient and the equivalent thermal rate, i.e., the thermal value of the rate coefficient for which \( KE_{\text{cm}} \) is the same as in the measurement. The value of the thermal rate is easily found if \( \gamma^{-1} \) in (4) is replaced by \( 4KE_{\text{cm}}/3m_i \) and the resulting \( f(v) \) is inserted in (3). In the latter expression, \( \mu_i \) is the reduced mass of the reactants. The thermal rate presents the advantage that it is uniquely a function of \( KE_{\text{cm}} \). Furthermore, it allows one to judge the importance of the departures from equilibrium under the various conditions encountered in the laboratory and atmosphere.

There now exist some methods by which the thermal rate can be inferred from drift tube measurements. Lin and Bardsey [1977] have perfected a Monte Carlo calculation by which \( f_{\text{lab}}(v) \) can be calculated. The cross section \( \sigma \) is then inverted from (3), and the calculation of the thermal rate becomes straightforward. Alternatively, Viehland and Mason [1977] have devised an analytical method by which the value of the thermal rate can be inferred from a drift tube measurement without having to invert first for the cross section.

In this paper we relate the value of ion-neutral rate coefficients for several atmospheric conditions to the value of the thermal rate with the same mean relative energy \( KE_{\text{cm}} \). The present work, coupled with the techniques presented by Viehland and Mason [1977] or Lin and Bardsey [1977], will allow modelers to use properly the drift tube measurements of energy dependent rates in the atmosphere or vice versa.

Although we do not present a general method of inversion of the type derived by Viehland and Mason [1977], we are able to show from relative speed distribution calculations in the atmosphere that the rate coefficient remains close to thermal in most atmospheric situations of interest, including high latitudes. This part of the work is presented in the next three sections. In section 5 we study in more detail the reactions of \( O^+ \) with \( N_2, O_n, \) and \( NO \) in the atmosphere, since the cross sections for these reactions have already been published by Albritton et al. [1977].

2. Energy Dependent Reactions in Slowly Convecting Regions of the Ionosphere

At mid-latitudes the ion velocity distribution is Maxwellian with a temperature which is greater than or equal to the neutral temperature, the exact difference depending on the altitude and the time of day. Although some relative ion-neutral drifts are present, we assume that their value at mid-latitudes is not substantial in general (less than 300 m/s) and can be neglected (see below).

Since the relative speed distribution is given by (4) in the case of two Maxwellians with different temperatures but no relative drift, the reaction rate for any ion-neutral reaction is then the same as the thermal rate value. This result applies to ordinary conditions at middle latitudes or in the absence of substantial convection at high latitudes.
3. ENERGY DEPENDENT RATES IN THE CONVECTING TOPSIDE IONOSPHERE

The 'topside' ionosphere as defined here is the region where the ionospheric plasma becomes fully ionized, i.e., where the ion-ion collision frequency is greater than the ion-neutral collision frequency.

At high latitudes the ionospheric plasma may acquire a substantial mean drift due to the $E \times B$ drift motion of the plasma in convection regions. In the topside ionosphere, the ion velocity distribution in this case is a drifting Maxwellian with an elevated temperature. The ion temperature is raised mainly through the few ion-neutral collisions and through heat conduction [e.g., Roble and Hastings, 1977].

The derivation of an explicit expression for $f(v)$ for the case of two Maxwellian velocity distributions with unequal temperatures and with a mean relative drift $U$ between the reactants can be found in work by Burgers [1969] or Woo and Wong [1971]. They obtain an expression equivalent to

$$f(v) = \frac{4}{\pi^{1/2} \gamma^{3/2} v^2 \exp \left[ -\gamma (v^2 + U^2) \right]} \sinh \left( \frac{2 v U}{\gamma v U} \right)$$

We note that in the limit $\gamma U^2 < 1$ we recover the result (4) to leading order. This means that if the value of the relative ion-neutral drift does not exceed the 'thermal speed' of the system defined here as $(1/\gamma)^{1/2}$, the relative speed distribution (4) will give a fair description of $f(v)$ provided that other nonthermal effects (i.e., departures from the displaced Maxwellian form) are not too significant. More exact comparisons between these various situations are provided in the examples below.

The main difference between (4) and (8) is that distribution (8) is more sharply peaked than (4) at a given value of the mean relative energy $KE_{cm}$. In fact, the larger the value of the relative drift $U$ is, the more sharply peaked the relative speed distribution becomes. This is illustrated in Figure 1. Curve C (solid line) describes the relative speed distribution for $O^+$ ions reacting with $N_2$ with no relative drift between the two species.

Fig. 2. Same as Figure 1 except that $T_{eff} = 2344^\circ K$ and the buffer gas is argon. For the drift tube distribution, curves B, $E/N = 135$ Td.
The values selected for the various parameters are $T_n = 298^\circ K$, $T_t = 2617^\circ K$, and $U = 0$, which corresponds to a value $KE_{cm} = 0.230$ eV or $T_{eff} = 2 KE_{cm}/3k_B = 1783^\circ K$. For curve A (solid line) we have selected the same value of $KE_{cm}$. However, this time we have chosen $T_t$ to be equal to 765$^\circ K$ and $U = |v_1| = 1.7$ km/s. This yields a value $\gamma U^3 = 3.0$. Physically, this situation is such that the ion 'directed' energy $m_u U^2/2$ is greater than the ion 'random' energy $3k_B T_t/2$. Thus the larger the value of $\gamma U^3$, the less random energy there is, and the more sharply peaked the relative speed distribution becomes. In the limit of an ion beam with no random energy the relative speed distribution (8) would resemble a delta function peaked at a relative energy equal to $KE_{cm}$.

Figure 2 illustrates what happens when $\gamma U^3$ is small (0.50) again for the $O^+$ reaction with $N_2$. A comparison between curves A and C shows that in that case the drifting and the nondrifting Maxwellian yield a very similar relative speed distribution. For curve C we have $T_t = 3495^\circ K$, $T_n = 298^\circ K$, and $U = 0$. For curve A, $T_t = 2594^\circ K$, $T_n = 298^\circ K$, and $U = 1.2$ km/s. In both cases, $T_{eff} = 3344^\circ K$, or $KE_{cm} = 0.303$ eV.

For comparison purposes we also show in Figures 1 and 2 the relative speed distributions calculated by Lin [1976] for $O^+$ ions in a drift tube in the laboratory. The buffer gases are helium for Figure 1 and argon for Figure 2. In both figures the ion temperature and the mean ion drift are the same as for the drifting Maxwellians, curves A. It is therefore apparent that compared to the Maxwellian descriptions, curves A and C, there is a substantial enhancement of particles in both the low-energy and the high-energy tail of the speed distribution of a drift tube. The rate coefficient of energy dependent reactions is accordingly affected by the non-Maxwellian shapes [e.g., Albritton et al., 1977].

In Figures 1 and 2 we have plotted the function $\sigma v f(v)$ (dashed lines). We selected the strongly energy dependent reaction

$$O^+ + N_2 \rightarrow NO^+ + N \quad (9)$$

to illustrate our point. For the two figures we used the cross section published by Albritton et al. [1977]. The integral of $\sigma v f(v)$ gives the reaction rate through (3).

One remarkable thing about the behavior of $\sigma v f(v)$ shown in the figures is how far in the tail of the relative speed distribution the function $\sigma v f(v)$ reaches a maximum. This is because the cross section is so energy dependent [see Albritton et al., 1977, Figure 9]. Thus the value of a reaction rate will be significantly different from thermal only if the actual relative speed distribution differs from the relative speed distribution (4) in the high-energy tail of the distribution. For drifting Maxwellian distributions this will be the case only if $\gamma U^3 > 1$. Then as can be seen from Figure 1, where $\gamma U^3 = 3$, the reaction rate can be smaller than thermal by as much as a factor of 2. On the other hand, if $\gamma U^3 = 1$ (Figure 2), the rate is only of the order of 10% smaller than thermal for reaction (9) in the topside ionosphere because the high-energy tails of the thermal (curve C) and nonthermal (curve A) distributions are very similar. In the atmosphere we may use the Wannier relation between $T_t$, $T_n$ and the mean relative drift $U$ to find the approximate value of $T_t$,

$$3k_B T_t = 3k_B T_n + m_u U^2 \quad (10)$$

where $m_u$ is the mean mass of the neutral atmospheric constituent. Heat exchange with the electron gas probably raises the value of $T_t$ further [e.g., Robie and Hastings, 1977] in the present case. The most abundant ions generally have a mass that is smaller than or of the same order of magnitude as the mean atmospheric mass. Thus in general the ion 'directed' energy is smaller than the ion 'random' energy if we use (10) as a lower limit on $T_t$. Therefore $\gamma U^3$ tends to be smaller than 1 for the more common ions in the convecting topside. As a result the energy dependent rates tend to be only a few percent smaller than thermal.

As a concrete example we have compared the thermal rate coefficient to the coefficient obtained with a drifting Maxwellian for $O^+$ ions reacting with $O_2$ and $N_2$. We used an atomic oxygen atmosphere and related $T_t$ to $U$ through (10) for a neutral temperature varying between 800$^\circ K$ and 1200$^\circ K$. We used the cross sections of Albritton et al. [1977] for both reactions. The results were as follows: for the reaction of $O^+$ with $N_2$ the rate is equal to thermal to within 5% for $T_{eff} \leq 1500^\circ K$. Above $T_{eff} \geq 2000^\circ K$ the reaction rate becomes 12-15% smaller than thermal up until $T_{eff} \approx 6000^\circ K$, where we stopped our calculations. For the $O^+ + O_2$ reaction the difference with the thermal rate is even smaller, less than 5% in all cases.

4. NON-MAXWELLIAN ION VELOCITY DISTRIBUTIONS IN THE HIGH-LATITUDE REGIONS OF THE ATMOSPHERE

The Relative Speed Distributions

The presence of a convection electric field at high latitudes not only creates a relative ion-neutral drift but also can distort the velocity distribution of the ions in regions where the plasma is weakly ionized. In particular, when the ion mean drift approaches or exceeds the thermal speed of the neutral gas, distortions from the Maxwellian form become important [cf. St.-Maurice and Schunk [1974] for a qualitative description]. The magnetic field, on the other hand, has the effect of maintaining a shape for the ion velocity distribution that is much closer to a displaced Maxwellian than in the laboratory, for a given value of the electric field and the ion-neutral collision frequency. This is true if the ratio of the ion-neutral collision frequency to the ion cyclotron frequency is much smaller than 1, i.e., above about 140 km. The ion velocity distribution then has to be symmetric about an axis that goes through the $E \times B$ drift point in velocity space.

St.-Maurice and Schunk [1977] have shown that to the lowest order of approximation the ion velocity distribution of a drifting ion gas in the $F$ region can be expressed as a bi-Maxwellian drifting at the $E \times B$ drift, with two temperatures, $T_{hi}$ and $T_{li}$, the parallel direction being defined as the direction parallel to the magnetic field. We have calculated $f(v)$ numerically for several drifting bi-Maxwellian ion velocity distributions in the ionosphere. For these distributions we have adopted the temperature ratios $T_{hi}/T_{li}$ calculated by St.-Maurice and Schunk [1977] to characterize the distributions.

When the ion drift is so large that the bi-Maxwellian description itself does not hold, we have used the empirical approach of St.-Maurice et al. [1967] to describe the non-Maxwellian ion velocity distribution with the use of the non-dimensional parameter $D'$ in the equation

$$g(v) dv = \frac{n_i}{\pi} \exp \left[ -u^2 - (c's' - D'y')B_d(2D'c's' - D'y') dc'd' \right] du'd' \quad (11)$$

where

$$B_d(X) = I_d(X) e^{-X} \quad (12)$$

$$X' = X/V_{AC} \quad (13)$$
and where \( g(v) \) is the ion velocity distribution, \( I_0 \) is the modified Bessel function of order zero which is bounded for small arguments, \( n_i \) is the ion density, \( v = (u, c_i, \theta) \) is the ion velocity vector written in a cylindrical coordinate system centered on the \( E \times B \) drift with its axis parallel to the magnetic field direction. We have used the values of \( D' \) measured by St.-Maurice et al. [1976] for \( O^+ \) ions to estimate the effect of the highly non-Maxwellian ion velocity distributions on the reaction rates. At very high temperatures \((T_i > 4000^\circ K)\) we have arbitrarily used \( D' = 2 \) as an upper limit to the non-Maxwellian character of the ion velocity distribution. The largest value of \( D' \) measured by St.-Maurice et al. [1976] was about 1.2 when \( O^+ \) was the dominant ion, for temperatures less than \( 3000^\circ K \). However, there were indications that \( D' \) could be larger when \( O^+ \) was a minor ion and the ion temperature was greater than \( 3000^\circ K \). As was mentioned above, the description given by (11) is applicable above about 150 km in the ionosphere, where \( \nu_{th}/G_i \ll 1 \). Below that altitude the ion velocity distribution becomes similar to the distributions seen in the laboratory, but the ratio \( E/N \), where \( E \) is the electric field strength and \( N \) is the neutral gas density, rapidly goes to zero because of the large increase in neutral gas density with decreasing altitude.

A comparison between the various relative speed distributions of \( O^+ - N_2 \) at high energy with \( O \) as a buffer in the atmosphere is shown in Figure 3. The solid curve A is for an assumed displaced Maxwellian \( O^+ \) velocity distribution with the temperature and the mean drift velocity of the ion gas related by (10) when \( KE_{cm} = 0.62 \) eV. Curve C (shown by the open circles) is the result of using a drifting bi-Maxwellian for the ion velocity distribution. Solid curve B results from using (11) with \( D' = 2 \), a probable upper limit to the non-Maxwellian character to the \( O^+ \) velocity distribution for the temperatures considered in the present work. We also calculated the relative speed distribution of a nondrifting thermal Maxwellian with the same \( KE_{cm} \) as the other three curves. The resulting speed distribution is so close to the bi-Maxwellian result that it could not be shown on the figure.

A comparison between the three curves A, B, and C and the nondrifting Maxwellian results therefore reveals the following:

1. The speed distributions in the atmosphere are much closer to a thermal description than in the laboratory, even with the limiting case considered here \((D' = 2 \text{ in (11)})\). This conclusion can be drawn by comparing the curves in Figure 3 with curves B of Figures 1 and 2, which show the behavior of the relative speed distribution calculated by Lin and Bardsley [1977] for a drift tube in the laboratory for a helium and an argon buffer, respectively. (2) The drifting bi-Maxwellian description increases the number of high- and low-energy particles relative to the drifting Maxwellian description in such a way that the resulting speed distribution is almost identical to a nondrifting Maxwellian. In other words, the use of a bi-Maxwellian description for the ion velocity distribution in the atmosphere tends to cancel the effects on the relative speed distribution due to drifting character of the velocity distribution. Therefore \( KE_{cm} \) tends to describe \( f(v) \) accurately for a larger range of situations than could have been expected. (3) If there are situations for which the parameter \( D' \) reaches a large enough value \((\geq 2)\), the non-Maxwellian character of the velocity distribution may modify the shape of the relative speed distribution much more noticeably than a bi-Maxwellian description.

The reason the relative speed distribution is not more distorted from the nondrifting Maxwellian (thermal) shape in the atmosphere is twofold. First, the non-Maxwellian character of the distribution is less pronounced than in the laboratory under similar drift conditions because of the stabilizing effect due to the magnetic field in the atmosphere. Second, the neutral buffer \((O \text{ or } N_2) \) has a mass which is the same as, or even greater than, the ion mass. Thus the 'directed' energy \( mU^2/2 \) cannot exceed the 'random' kinetic energy \( 3k_B T_i/2 \). As a result, \( \gamma^2 \) remains smaller than 1 even for very large electric field strengths, and (4) tends to describe the relative speed distribution well.

The Rate Coefficients

The general effects of non-Maxwellian ion velocity distributions on energy dependent rates in the ionosphere can be inferred from the above. First, if the electric field in the atmosphere is small enough that the most important non-Maxwellian character of the drifting ion velocity distribution is the appearance of two temperatures, the chemical rate coefficient will be very close to thermal. For \( O^+ \) ions this means an agreement between the two rates to within 5% even for the highly energy dependent reaction of \( O^+ \) on \( N_2 \).

On the other hand, if the non-Maxwellian character of the ion velocity distribution grows to the point that the ion velocity distribution becomes doubly humped \((D' > 1.3 \text{ in (11)})\), the rate coefficient could become noticeably larger than thermal, as much as 20% near \( T_{e,f} = 6000^\circ K \) when \( D' = 2 \). The reason for this difference can be seen by comparing the two broken curves in Figure 3. These curves show the behavior of the product \( \sigma(v) f(v) \) as a function of the relative speed between the reactants. However, in view of the substantial difference at high energy between the two relative speed distributions that are compared in Figure 3 the difference between the two rate coefficients could have been expected to be larger. The reason this is not the case is that even though the non-Maxwellian speed distributions reveal an enhancement of high-energy ions between 1 and 2 thermal speeds, at very high energy the non-Maxwellians have a smaller population than a comparable displaced Maxwellian.

For ions other than \( O^+ \) the bi-Maxwellian description is expected to be valid over a larger energy range [cf. St.-Maurice and Schunk, 1977; St.-Maurice et al., 1976]. We therefore expect the energy dependent rates to have a value close to
thermal for most applications. The exception would be with heavy ions for the reason discussed in the preceding section.

5. **APPLICATION TO THE ENERGY DEPENDENT RATES O⁺ WITH O₂, N₂, AND NO**

We summarize our results for reaction (9) and the reactions

\[
\begin{align*}
O^+ + O_2 &\rightarrow O_2^+ + O \\ O^+ + NO &\rightarrow NO^+ + O
\end{align*}
\]

in Figures 4, 5, and 6. We show the behavior of the rate coefficients as functions of \( T_{\text{eff}} = 2KE_{\text{cm}}/3k_B \) under various sets of conditions, using the cross sections presented by Albritton et al. [1977].

Our results are summarized in Figure 4 for the \( O^+ + N_2 \) reaction. Curve A represents ionospheric conditions for both Maxwellian \( (U = 0) \) and bi-Maxwellian distributions for \( U \neq 0 \). The calculations cover a range of neutral atmospheres varying from pure molecular nitrogen to pure atomic oxygen. The spread in the data points used to plot curve A is less than 5% of mean. The results demonstrate that \( T_{\text{eff}} \) (or \( KE_{\text{cm}} \)) is a good
unique variable to parameterize a rate coefficient in many atmospheric applications. This also means that unless \( T_{\text{eff}} > 4000^\circ \text{K} \), the reaction rate coefficient in mid-latitudes, or at high latitudes in the \( F \) region, is the same as the thermal rate coefficient, i.e., essentially that given by curve A (see section 4).

In the convecting regions of the 'topside' ionosphere the reaction rate is slightly smaller than thermal for the \( \text{O}^+ + \text{N}_2 \) reaction. This is shown by curve F in Figure 4. The neutral temperatures used in the computations varied from \( T_n = 700^\circ \text{K} \) in the nonconvecting regions to \( T_n = 1200^\circ \text{K} \) for \( T_i \geq 2000^\circ \text{K} \). We used (10) to relate \( T_i, T_n, \) and \( U \).

To illustrate the importance of the ion to neutral mass ratio in atmospheric applications, we have calculated the reaction rate coefficient for reaction (9) under the assumption that the ion velocity distribution in the atmosphere is a drifting Maxwellian, but with a helium 'buffer,' and the relation between \( T_i \) and \( U \) still given by (10) (curve B). Although this case is unrealistic, since the main atmospheric constituent is seldom helium, it illustrates our point well. The rate in this case is smaller than thermal by as much as a factor of 2 for \( T_{\text{eff}} \geq 1500^\circ \text{K} \). Equivalently, we would have obtained the result, curve B, if we had used the oversimplified assumption of a displaced Maxwellian for the ion velocity distribution in a drift tube in the laboratory, therefore neglecting the important non-Maxwellian corrections for that case.

Curve C in Figure 4 shows the result of using an oversimplified approach such as (1) for the rate coefficient. For that curve we show how \( \delta_{\text{rel}} \delta_{\text{rel}} \) varies as a function of \( T_{\text{eff}} \). The resulting rate coefficient is considerably lower than even the preceding case because the use of (1) is equivalent to the assumption that \( f(v) \) is a delta function peaked at \( v = \delta_{\text{rel}} \).

With such a relative speed distribution the important effect of the high-energy tail particles on the rate is completely neglected (Figures 1-3).

Curve D reflects the uncertainty introduced by possible large departures of the ion velocity distribution from a displaced Maxwellian in the atmosphere. For that curve we have used the values for \( D' \) discussed earlier. At high temperatures \( (3000^\circ \text{K} < T_i < 6000^\circ \text{K}) \) we believe that curve D gives an upper limit on the non-Maxwellian rate. Thus in the \( F \) region of the ionosphere the increase in the reaction rate due to the non-Maxwellian effects derived by St.-Maurice and Schunk should lie somewhere between curves A and D. From the measurements reported by St.-Maurice et al. [1976] and from plasma instability considerations [Ott and Farley, 1975] we would estimate the rate coefficient to be closer to curve A than to curve D.

Finally, for comparison purposes only we show the \( T_{\text{eff}} \) dependence of the \( \text{O}^+ + \text{N}_2 \) rate coefficient calculated from the expression given by McFarland et al. [1973]. McFarland's expression (curve E) represents a fit to the data of Johnsen and Biondi [1973] at intermediate energies and probably reflects experimental problems encountered in the early work [see Albrighton et al., 1977]. Curve A, which is based on the most recent measurements of Albrighton et al. [1977], is in excellent agreement with an in situ determination of the rate coefficient made by Torr et al. [1977], using Atmosphere Explorer satellite data.

In Figures 5 and 6 we repeated the calculations made in Figure 4 but for reactions (15) and (16), respectively. The conclusions are similar to those drawn for Figure 4. However, the minimum in \( \sigma \) is less pronounced for (15) than it is for (9) and less pronounced for (16) than it is for (15). The difference between the rates calculated in curves A through F is accordingly smaller.

We have derived new expressions for the energy dependent rate coefficients of reactions (9), (15), and (16) in the atmosphere, using the results presented in curves A of Figures 4, 5, and 6. We recall that these expressions are representative of mid-latitude conditions or of high-latitude conditions below the \( F \) peak and for \( T_{\text{eff}} < 4000^\circ \text{K} \). For \( T_{\text{eff}} \) values between \( 4000^\circ \text{K} \) and \( 6000^\circ \text{K} \) the rates may be up to 20% larger below the \( F \) peak. In the topside convecting regions the rate is about 13% smaller than that given below for reaction (9), but the difference is smaller for the other two reactions. The actual rate could also be larger for reaction (9) in particular, since we neglected vibrational effects in the atmosphere.

A polynomial fit to the rate coefficients curves A as functions of \( T_{\text{eff}} \) gives, in units of cubic centimeters per second,
O$^+$ + N$_2$ $\rightarrow$ NO$^+$ + N

$$k_1 = 1.53 \times 10^{-12} - 5.92 \times 10^{-13} \left( \frac{T_{e}}{300} \right)$$

$$+ 8.60 \times 10^{-11} \left( \frac{T_{e}}{300} \right)^3 \quad 300 \leq T_{e} \leq 1700^\circ K$$

$$k_2 = 2.73 \times 10^{-18} - 1.55 \times 10^{-18} \left( \frac{T_{e}}{300} \right)$$

$$+ 1.483 \times 10^{-12} \left( \frac{T_{e}}{300} \right)^3 \quad 1700 < T_{e} \leq 6000^\circ K$$

O$^+$ + O$_2$ $\rightarrow$ O$_3^+$ + O

$$k_3 = 2.82 \times 10^{-11} - 7.74 \times 10^{-12} \left( \frac{T_{e}}{300} \right)$$

$$+ 1.073 \times 10^{-14} \left( \frac{T_{e}}{300} \right)^3 - 5.17 \times 10^{-14} \left( \frac{T_{e}}{300} \right)^3 \quad 300 < T_{e} \leq 1500^\circ K$$

O$^+$ + NO $\rightarrow$ NO$^+$ + O

$$k_4 = 8.36 \times 10^{-11} - 2.02 \times 10^{-12} \left( \frac{T_{e}}{300} \right)$$

$$+ 6.95 \times 10^{-14} \left( \frac{T_{e}}{300} \right)^3 \quad 320 < T_{e} \leq 1500^\circ K$$

$$k_5 = 5.33 \times 10^{-11} - 1.64 \times 10^{-14} \left( \frac{T_{e}}{300} \right)$$

$$+ 4.72 \times 10^{-14} \left( \frac{T_{e}}{300} \right)^3 - 7.05 \times 10^{-14} \left( \frac{T_{e}}{300} \right)^3 \quad 1500 < T_{e} \leq 6000^\circ K$$

These expressions fit the rates presented in Figures 4, 5, and 6 to within 5% and are essentially coincidental with the 'thermal distribution' values of Albritton et al. [1977].

6. SUMMARY AND DISCUSSION

We have studied the problem of the transposition of the laboratory measurement for energy dependent ion-neutral reaction rates to the ionosphere. We neglected vibrational and rotational effects and assumed that only elastic collisions are present in the gases. From our present understanding of kinetic processes in the earth's atmosphere we concluded that the chemical reaction rate coefficient is essentially 'thermal' in the ionosphere, i.e., the same as in the laboratory for the same value of KE$_{cm}$ (equation (6)) for afterglow experiments or any other measurement where the ions are in thermal equilibrium with the buffer gas. We also found that the rate is nearly 'thermal' in most of the convected regions at high latitudes.

The fact that the chemical reaction rate is 'thermal' in the ionosphere means that a drift tube measurement cannot always be transposed directly from the laboratory to the atmosphere by simply using the mean energy parameter KE$_{cm}$, as has been done in the past. The error involved with this procedure varies from one situation to another. For O$^+$ ions and reactions (9), (15), and (16) it is easy to show from the work of Albritton et al. [1977] or Viehland and Mason [1977] that this error can be of the order of 25% or less, depending on the rates considered, if the buffer gas is helium, and a factor of 2 if the buffer gas is argon. Two procedures that can be used to obtain the 'thermal' rate value from a drift tube measurement are the 'direct' approach of Lin and Bardsley [1977] and the 'analytical' approach of Viehland and Mason [1977]. With the first method the relative speed distribution is calculated with a Monte Carlo computation, whereas this procedure is avoided in the second case. Both methods appear to work well.

We find that the close agreement between the rate coefficient in the ionosphere and its 'thermal' value is somewhat fortuitous in fast convecting regions. It is due in large part to the fact that the mean mass of the neutral atmosphere is of the same order of magnitude as the ion mass in the situations that we have considered in this paper.

On the basis of the cross sections presented by Albritton et al. [1977] we have calculated the reaction rate coefficients of O$^+$ reacting with O$_2$, N$_2$, and NO in the ionosphere. The expressions that we obtained as functions of the parameter T$_{e}$ used in previous ionospheric work are given in (17)–(19). The rates for reactions (9) and (15) are smaller than was previously assumed. In the case of the O$^+$ + N$_2$ reaction, because the minimum value in the rate coefficient for the new measurement is reached at a higher value of the relative energy than was previously assumed, the rate coefficient differs significantly from that used conventionally, i.e., the expression derived by McFarland et al. [1973]. At 1500 K effective temperature, for example, the difference amounts to nearly a factor of 3.

Finally, some caution should be exercised, especially with regard to the rate at which O$^+$ reacts with N$_2$. At energies of interest for ionospheric studies, reaction (9) is controlled essentially by particles in the high-energy tail of the velocity distributions. Unfortunately, the calculations of ion velocity distributions both for the laboratory and for the atmosphere are geared to describe the bulk of the ion velocity distribution rather than the high-energy tail population. This adds some uncertainty to the computation of the chemical reaction rate. Moreover, in view of the near equivalence between vibrational and kinetic energy in raising the value of the chemical rate (9) [Schmeltekopf et al., 1968] it is possible that only a small amount of vibrationally excited N$_2$ could lead to a significant increase in the reaction rate both in the laboratory and in the atmosphere.

Acknowledgments. We are grateful to S. L. Lin, who gave us permission to present some of his unpublished calculations of O$^+$–N$_2$ relative speed distributions in drift tubes. We also thank D. L. Albritton for some pertinent comments and suggestions. This research was supported under NSF grants ATM 74-21090 A02 to the University of Michigan and ATM 76-82323 to Utah State University and under Air Force grant FF4628-77-C-0007 to the University of Michigan.

The Editor thanks D. L. Albritton and E. C. Whipple for their assistance in evaluating this paper.

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(Received April 25, 1977; accepted October 20, 1977.)
Correction

In the paper 'Nonthermal Rate Coefficients in the Ionosphere: The Reactions of O+ With N₂, O₂, and NO' by J.-P. St.-Maurice and D. G. Torr (Journal of Geophysical Research, 83(A3), 969-977, 1978), Figures 5 and 6 are switched. The figures and their captions are printed correctly below.

Fig. 5. Same as Figure 4 but for the reaction O+ + O₂ → O₂⁺ + O.

Fig. 6. Same as Figure 4 but for the reaction O+ + NO → NO⁺ + O.