Negative Ion Chemistry in the Terrestrial D Region and Signal Flow Graph Theory

J. Wisemberg and G. Kockarts
Institut d'Aeronomie Spatiale, B-1180 Brussels, Belgium

Aeronomic systems such as the negative ion chemistry in the D region are characterized by numerous reactions involving positive, negative, and neutral species. Classical solutions of such systems do not necessarily point out the role played by each parameter. When the chemical system is considered as a graph, it is possible to apply the signal flow graph technique, which allows a quantitative evaluation of the various paths and loops. A negative ion model is obtained for daytime conditions by using the signal flow graph technique, which is briefly described. This reference model is analyzed in terms of transmittances, path gains, and loop gains. An arbitrary variation of atomic oxygen and nitric oxide is introduced at a height of 65 km in order to show the induced effects on the negative ions and on the electron concentrations. Variations of the ratio \( \lambda \) between negative ions and electrons are also presented.

1. INTRODUCTION

Mass spectrometer observations [e.g., Narcisi and Bailey, 1965; Narcisi, 1967; Goldberg and Blumle, 1970; Narcisi et al., 1971, 1972; Arnold et al., 1971; Goldberg and Aikin, 1971; Joannisens and Krankowsky, 1972; Zbinden et al., 1974, 1975] have shown that the terrestrial D region is characterized by many positive and negative ions which result from external ionization processes leading initially to electrons, molecular oxygen, nitrogen, and nitric oxide positive ions. Heavy negative ions [Arnold and Henschen, 1978] as well as positive ions [Arijs et al., 1978; Arnold et al., 1978] have also been detected in the stratosphere with balloon-borne mass spectrometers.

Prior to any direct determination of negative ions in the D region, Reid [1964] showed that it is unlikely for \( \text{O}_3^- \) to be the dominant negative ion, although its formation is rather easy by electron attachment to atmospheric molecular oxygen. This ion is actually an initial step in a long chain of reactions which has been investigated in recent years for understanding of negative ion chemistry in the terrestrial atmosphere [e.g., Turco and Sechrist, 1972a, b; Thomas et al., 1973a, b; Thomas, 1974; Turco, 1974; Ferguson, 1974; Reid, 1976; Swider, 1977].

Approximately 60 chemical reactions are at the present time involved in the negative ion chemistry of the D region, and this number does not account for possible negative cluster formation. A similar situation occurs for the positive ions, leading to a total of the order of 120 chemical reactions. Comparisons between various theoretical models is not always easy, since they usually differ not only by the adopted reaction scheme and the corresponding reaction rates but also by the model of the neutral minor constituents involved in various production and loss processes. When the neutral model and some poorly known reaction rates are considered as variable parameters, it appears that there is no easy way to extract quantitative information regarding a specific parameter. In a system with a few reactions, a knowledge of the reaction rates and the neutral concentrations leads rather easily to a determination of the most important mechanisms. But in large systems, cycling processes and feedback mechanisms make such an analysis more difficult.

The purpose of the present paper is to introduce a new way to analyze D region ion chemistry by considering the large chemical system as a signal flow graph. Such a technique, summarized in Appendix A, gives direct access to the black box by assigning quantitative values to any path or loop in the system and by showing quantitatively how any input to the system is transmitted along the various paths. Comparisons with in situ measurements are left out for future work.

A daytime neutral model atmosphere as well as ion reaction rates and electron-ion pair production rates are presented in section 2. The signal flow graph technique is then applied to the negative ion chemistry in section 3, which also contains a discussion of some computational problems associated with the steady state solution. An oversimplified example is given in Appendix B in order to clarify the signal flow graph technique and to show the identity with a classical solution, which is, however, unable to give the same amount of physical information on the whole system. A reference model for the negative ions is presented in section 4 in terms of electron and ion concentrations, production, and loss rate. The importance of various reaction paths is discussed as a function of height. Using the reference model, a parametric analysis is made at 65-km altitude in section 5. Such an analysis indicates how variations of the neutral model can lead to different negative ion concentrations without any change of the adopted reaction rates. Finally, the potential contribution of signal flow graph technique is summarized in the last section.

2. RATE COEFFICIENTS, NEUTRAL MODEL, AND ELECTRON-ION PAIR PRODUCTION

When electrons are produced in the D region between the stratopause and the mesopause, a negative ion chemistry chain is initiated by attachment with major atmospheric neutral constituents and with ozone according to the following processes:

\[
e + \text{O}_3 \rightarrow \text{O}_2^- + \text{O}_2 \quad k_1 = 4 \times 10^{-30} \exp \left( -193/T \right) \quad (1)
\]

\[
e + \text{O}_3 + \text{N}_2 \rightarrow \text{O}_2^- + \text{N}_2 \quad k_2 = 1 \times 10^{-31} \quad (2)
\]

\[
e + \text{O}_3 \rightarrow \text{O}^+ + \text{O}_2 \quad k_3 = 9.1 \times 10^{-12} (T/300)^{1.46} \quad (3)
\]

where the reaction rate \( k_i \) in \( \text{cm}^3 \text{s}^{-1} \) is measured as a function of the temperature \( T \) by Truby [1972], \( k_2 \) in \( \text{cm}^3 \text{s}^{-1} \) is given by Phelps [1969], and \( k_3 \) in \( \text{cm}^3 \text{s}^{-1} \) is measured by Stelman et al. [1972]. A schematic diagram of negative ion reactions based on Ferguson's [1974] analysis is given in Figure 1. The dia-
Fig. 1. Schematic diagram of negative ion reactions in the daytime D region. Neutral constituents involved in the reactions are indicated in brackets. Dashed lines correspond to photodestruction processes. Arrows labeled $\alpha$ correspond to dissociative recombination for electrons and to neutral neutralization for negative ions. The external production leading to electrons $E$ and to positive ions is indicated by $\beta$ (cm$^{-3}$ s$^{-1}$).

The dissociative recombination coefficients for $O_2^+$ and $NO^+$ are taken from Mul and McGowan [1979]:

$$e + O_2^+ \rightarrow \text{neutrals} \quad \alpha_2 = 1.9 \times 10^{-7} (300/T)^{0.5} \text{cm}^3 \text{s}^{-1} \quad (5)$$

and

$$e + NO^+ \rightarrow \text{neutrals} \quad \alpha_3 = 2.3 \times 10^{-7} (300/T)^{0.5} \text{cm}^3 \text{s}^{-1} \quad (6)$$

The recombination rate coefficient of electrons with other positive ions such as clusters is adopted as

$$e + Y^+ \rightarrow \text{neutrals} \quad \alpha_4 = 3 \times 10^{-6} \text{cm}^3 \text{s}^{-1} \quad (7)$$

in agreement with the values of Huang et al. [1978] for water cluster ions. Photodestruction cross sections have been measured and summarized by G. P. Smith et al. [1978] and by Lee and Smith [1979]. By using these cross sections and the solar fluxes of Smith and Gottlieb [1974] the following photodetachment rates are obtained: $J_{O_2^-} = 1.4 \text{ s}^{-1}$, $J_{O^-} = 0.38 \text{ s}^{-1}$, $J_{OH^-} = 1.1 \text{ s}^{-1}$, and $J_{NO_2^-} = 8 \times 10^{-4} \text{ s}^{-1}$. The photodissociation to $O^-$ and $CO_2$ with a rate $J_{CO_2^-} = 0.15 \text{ s}^{-1}$, whereas the photodissociation of $O_3^-$ leads to $O^-$ and $O_2$ with a rate $J_{O_3^-} = 0.47 \text{ s}^{-1}$. The photodissociation cross section of $O_3^-$ is, however, characterized by a fine structure which requires further studies [Lee and Smith, 1979]. Photodestruction of $CO_4^-$ and $O_4^-$ are assumed to give $O_2^-$ with rates of $J_{CO_4^-} = 6.2 \times 10^{-3} \text{ s}^{-1}$ and $J_{O_4^-} = 0.24 \text{ s}^{-1}$, although Cosby et al. [1976] are not excluding photodetachment. At the present time the branching ratio between photodetachment and photodissociation is, however, not known. According to Cosby et al. [1976], HCO$_3^-$ apparently neither photodetaches or photodissociates for wavelengths above 458 nm. Since the electron affinity of NO$_3^-$ is $3.9 \pm 0.2$ eV [Ferguson et al., 1972], no photodetachment mechanism for this ion is introduced in the present work. The negative ion system corresponds therefore to 44 ion neutral reactions given in Table 1, to three attachment processes given by equations (1) to (3), and to eight photodestruction processes. The coupling between the negative ions and the positive ions occurs through reactions (4) to (6), which imply a knowledge of the positive ion concentrations.

Instead of fulfilling the condition of electroneutrality with a fictitious positive ion $Y^+$, individual positive ions are computed with the measured reaction rates [Albritton, 1978; Ferguson, 1974] given in Table 2 without any temperature dependence. The sole significant photodissociation coefficient for positive clusters is computed for $O_2^+ \cdot H_2O$ with the cross sections of Smith and Lee [1978], and it leads to a value $J_{O_2^+ \cdot H_2O} = 0.42 \text{ s}^{-1}$. The introduction of a detailed positive ionic model is made to account for a possible simultaneous effect of certain parameters on the positive and negative ion chemistry. Such an effect could lead to a nonlinear coupling between positive and negative systems.

The neutral concentrations involved in Table 1 and in
rates are in cm$^3$ s$^{-1}$.

### TABLE 1. Negative Ion Reaction Rates*

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>$O_2^- + O \rightarrow e + O_3$</td>
<td>$1.5 \times 10^{-10}$</td>
</tr>
<tr>
<td>$O_2^- + O_2(A^\Delta) \rightarrow e + O_3 + O_2$</td>
<td>$2.0 \times 10^{-10}$</td>
</tr>
<tr>
<td>$O_2^- + CO + CO_2 + M \rightarrow CO_2^- + M$</td>
<td>$4.7 \times 10^{-9}$</td>
</tr>
<tr>
<td>$O_2^- + NO_2 \rightarrow O_3^- + O_2$</td>
<td>$6.0 \times 10^{-10}$</td>
</tr>
<tr>
<td>$O_2^- + O \rightarrow O^+ + O_2$</td>
<td>$7.0 \times 10^{-10}$</td>
</tr>
<tr>
<td>$O_2^- + NO_2 + M \rightarrow NO_2^- + M$</td>
<td>$1.5 \times 10^{-10}$</td>
</tr>
<tr>
<td>$O_2^- + M \rightarrow O_2 + M$</td>
<td>$3.4 \times 10^{-11}$</td>
</tr>
<tr>
<td>$O^+ + O_2(A^\Delta) \rightarrow e + O_3$</td>
<td>$3.0 \times 10^{-10}$</td>
</tr>
<tr>
<td>$O^+ + M \rightarrow e + NO_2$</td>
<td>$1.0 \times 10^{-12}$</td>
</tr>
<tr>
<td>$O^+ + NO \rightarrow e + NO_2$</td>
<td>$8.0 \times 10^{-10}$</td>
</tr>
<tr>
<td>$O^+ + H_2 \rightarrow e + H_2O$</td>
<td>$5.8 \times 10^{-10}$</td>
</tr>
<tr>
<td>$O^+ + NO \rightarrow e + H_2O + H$</td>
<td>$6.0 \times 10^{-11}$</td>
</tr>
<tr>
<td>$O^+ + NO_2 \rightarrow e + H_2O + M$</td>
<td>$1.9 \times 10^{-10}$</td>
</tr>
<tr>
<td>$O^+ + NO_2 \rightarrow e + 2H_2O + M$</td>
<td>$2.1 \times 10^{-10}$</td>
</tr>
<tr>
<td>$O^+ + CO_2 + M \rightarrow NO_2^- + M$</td>
<td>$2.0 \times 10^{-9}$</td>
</tr>
<tr>
<td>$O^+ + N_2 \rightarrow NO_2^- + N_2$</td>
<td>$2.6 \times 10^{-10}$</td>
</tr>
<tr>
<td>$O^+ + N_2 \rightarrow NO_2^- + N_2$</td>
<td>$5.5 \times 10^{-10}$</td>
</tr>
<tr>
<td>$O^+ + NO_2 \rightarrow NO_2^- + NO_3$</td>
<td>$2.8 \times 10^{-10}$</td>
</tr>
<tr>
<td>$O^+ + O_2 \rightarrow NO_2^- + O_2$</td>
<td>$8.4 \times 10^{-10}$</td>
</tr>
<tr>
<td>$CO_2^- + NO \rightarrow NO_2^- + CO_2$</td>
<td>$4.8 \times 10^{-11}$</td>
</tr>
<tr>
<td>$CO_2^- + O \rightarrow NO_2^- + CO_2$</td>
<td>$1.4 \times 10^{-10}$</td>
</tr>
<tr>
<td>$CO_2^- + O_2 \rightarrow NO_2^- + CO_2$</td>
<td>$1.3 \times 10^{-10}$</td>
</tr>
<tr>
<td>$CO_2^- + H \rightarrow CO_3^- + OH$</td>
<td>$2.2 \times 10^{-10}$</td>
</tr>
<tr>
<td>$NO_3^- + O_2 \rightarrow NO_2^- + O_2 + O_2$</td>
<td>$1.0 \times 10^{-13}$</td>
</tr>
<tr>
<td>$NO_3^- + NO \rightarrow NO_2^+ + NO_2$</td>
<td>$1.0 \times 12$</td>
</tr>
<tr>
<td>$NO_3^- + NO_2 + NO \rightarrow NO_2^- + NO_2 + NO$</td>
<td>$3.0 \times 10^{-10}$</td>
</tr>
<tr>
<td>$NO_3^- + NO_2 + NO \rightarrow NO_2^- + NO_2 + NO$</td>
<td>$1.2 \times 10^{-10}$</td>
</tr>
<tr>
<td>$NO_3^- + NO_2 + NO \rightarrow NO_2^- + NO_2 + NO$</td>
<td>$2.0 \times 13$</td>
</tr>
<tr>
<td>$OH^- + H \rightarrow e + H_2O$</td>
<td>$1.4 \times 9$</td>
</tr>
<tr>
<td>$OH^- + OH \rightarrow e + 2H_2O$</td>
<td>$9.0 \times 10^{-10}$</td>
</tr>
<tr>
<td>$OH^- + NO \rightarrow e + NO_2$</td>
<td>$2.0 \times 10^{-10}$</td>
</tr>
<tr>
<td>$OH^- + NO_2 \rightarrow e + NO_2 + NO$</td>
<td>$1.1 \times 9$</td>
</tr>
<tr>
<td>$OH^- + CO_2 + NO_2 \rightarrow HCO_3^- + O_2$</td>
<td>$7.6 \times 28$</td>
</tr>
<tr>
<td>$CO_2^- + O \rightarrow NO_2^- + CO_2$</td>
<td>$1.1 \times 10^{-10}$</td>
</tr>
<tr>
<td>$CO_2^- + NO \rightarrow NO_2^- + CO_2$</td>
<td>$2.0 \times 10^{-10}$</td>
</tr>
<tr>
<td>$CO_2^- + NO_2 \rightarrow NO_2^- + CO_2$</td>
<td>$1.1 \times 11$</td>
</tr>
<tr>
<td>$CO_2^- + O_2 \rightarrow NO_2^- + CO_2$</td>
<td>$6.0 \times 15$</td>
</tr>
<tr>
<td>$CO_2^- + H \rightarrow HCO_3^- + OH$</td>
<td>$1.7 \times 10^{-10}$</td>
</tr>
</tbody>
</table>

*From Albritton [1978]. Two-body rates are in cm$^3$ s$^{-1}$; three-body rates are in cm$^4$ s$^{-1}$.
†For $1.5 \times 10^{-10}$, read $1.5 \times 10^{-10}$.
‡Measured with $M = He$.

Table 2 are taken from the U.S. Standard Atmosphere (1976) for noon conditions at 45°N latitude. Such a model is similar to the recent mesospheric model developed by Kneshea et al. [1979]. Since NO and NO$_2$ concentrations are not given in this model, we adopt the high daytime values computed by Turco and Sechrist [1970, 1972b]. Vertical profiles of minor constituent used in our negative ionic reference model are summarized in Figure 2. Finally, the electron-ion pair productions used in the computations are shown in Figure 3. The quantities given in Figures 2 and 3 are variable, but they are adopted here as reference values. The effect of possible variations of atomic oxygen and nitric oxide will be described in section 5 as an application of the signal flow graph technique. This technique is presented in the following two sections for the negative ion model resulting from the reaction scheme, the electron-ion pair production, and the neutral model just described.

### 3. SIGNAL FLOW GRAPH TECHNIQUE AND ION CHEMISTRY

The ionic scheme given in Figure 1 has all the characteristics of the signal flow graph described in Appendix A. The various negative ionic species are nodes of the graph. Two consecutive nodes are joined by an edge indicating which neutral constituent is involved in the transformation, and successive edges form a path which can become a loop when the initial and final negative ions are identical. The input $g_i$ to the system represents the electron-ion pair production. Under equilibrium conditions between $k$ types of negative ions including electrons, equation (B3) of Appendix B reduces to

$$P_i = T_{(i-1)} \times g_i$$

where $P_i$ is the production rate (cm$^{-3}$ s$^{-1}$) of the $i$ type ion and $T_{(i-1)}$ is the transmittance given by

$$T_{(i-1)} = \sum_{\Delta = \Delta_i} g_{\Delta_i}$$

In (9), $n_i$ is the number of paths leading from the sole input to the $i$ type ion. The path gains $g_i$ and the amplification factors $\Delta_i$ are given by Mason's [1956] rules described in Ap-
Appendix A and applied to an oversimplified example in Appendix B. Computation of the production rates $P_i$ by (8) leads immediately to the concentrations $n_i$, since

$$n_i = P_i / L_i,$$  

where $L_i$ is the total loss rate in units per second of the $i$ type ion. It is shown in Appendix B that the total loss rates $L_i$ are simultaneously computed with the path gains $g_i$.

Mason’s [1956] rules are strictly valid for linear systems of equations. Mutual neutralization between negative and positive ions as well as dissociative recombination between electron and positive ions can a priori introduce some nonlinearity, since the positive ions are not necessarily known. Such a nonlinearity can be removed with the help of the electroneutrality condition. Starting with two arbitrary relative distributions of $n$ positive ions with relative concentration $x_i^+$ and $m$ negative ions (including electrons) with relative concentration $x_j^-$ such that

$$\sum_{i=1}^n x_i^+ = \sum_{j=1}^m x_j^- = 1$$

it is possible to calculate an effective recombination coefficient

$$\alpha_{\text{eff}} = \sum_{i=1}^n \sum_{j=1}^m \alpha_{ij} x_i^+ x_j^-$$

where the recombination coefficients are given by (4) to (7). The corresponding total positive or negative concentration $n_i$ is then

$$n_i = (\gamma_i / \alpha_{\text{eff}})^{1/2}$$

where $\gamma_i$ is the input production rate. An initial set of positive and negative ions is obtained from the relations

$$n_i^+ = x_i^+ \times n_i$$

and

$$n_i^- = x_j^- \times n_i$$

The set of positive ions is used for a solution of the negative ion system, and the resulting negative ions are used to compute a new set of relative distributions $x_j^-$. The same procedure is used for the positive ions, and the iteration scheme (11) to (15) is repeated until convergence is reached. Convergence within 1% is obtained after three iterations.

Before solving the negative or positive ion system it is necessary to make a computer search of the various paths leading to a specific ion from the input $\gamma_i$. This can be done by associating a logical square matrix to the graph. The number of rows and columns of this matrix is equal to the number of nodes of the graph. An element $(i, j)$ of this matrix is set to 1 if the $i$th ion can lead to the $j$th ion. An element $(i, i)$ of this matrix is set to 1 if the $i$th ion can lead to the $j$th ion. In such a way any value 1 in the $i$th row indicates that the ion associated with the corresponding $j$th column can be produced by the $i$th ion. All unitary values in the $i$th row indicate the ‘descendants’ of the $i$th ion, and all unitary values in the $i$th column give the ‘ascendants’ of the $i$th ion. An analysis of each column leads then to the various paths which are memorized only if the last node is an input node and if a path does not go twice through the same node. Loops are obtained by considering each node as an input. Care must be taken to avoid multiple counting of loops resulting from input nodes which belong to the same loop. The total number of paths in Figure 1 is 729, and $O_3^-$ is produced by 12 paths, $O_2^-$ by 12 paths, $CO_3^-$ by 24 paths, $O^-$ by 28 paths, $CO_3^-$ by 32 paths, $O_3^-$ by 44 paths, $OH^-$ by 112 paths, $NO_3^-$ by 142 paths, $HCO_3^-$ by 156 paths, and $NO_3^-$ by 167 paths, respectively. The absolute abundance of a specific
ion is not correlated with the number of paths. Expression (8) shows that the ion concentration is actually proportional to the transmittance, which depends on the path gains and the amplification factors.

The efficiency of the signal flow graph technique is particularly high for large systems where the great number of paths and loops makes it very difficult to find the most important mechanisms leading to a specific ion. In the numerical results of the next section we have neglected the paths which contribute by less than 1% to the transmittance from the input to each \( i \) type ion.

### 4. Analysis of the Reference Model for Negative Ions

The signal flow graph technique can be applied at any height in the \( D \) region as long as transport processes are negligible. The neutral model combined with the reaction rates and the electron production given in section 2 leads to the vertical profiles shown in Figure 4. Only the most important negative ions and the electron concentration are indicated. The dimensionless ratio \( \lambda \) between the total negative ion concentration and the electron concentration is given to show the height range where negative ions are more abundant than electrons. The ratio \( \lambda \) becomes equal to 1 near 69-km altitude. In the height range where negative ions are important, \( NO_3^- \) is always the most abundant ion, although \( CO_3^- \) and \( HCO_3^- \) are not completely negligible. This result is in contradiction with the model of Thomas et al. [1973b], where photodetachment was introduced as an important process, but it is in better agreement with the calculations of Turco and Sechrist [1972a, b]. Furthermore, the presence of \( HCO_3^- \) in Figure 4 is a direct consequence of its small loss rate by mutual neutralization and photochemical reactions. The importance of this effect is shown in Figure 5, which shows the electron production resulting from several negative ions. Figure 5 indicates that the transmittances reach values much larger than 1 when electron production resulting from a negative ion \( XY^- \) is greater than the input value \( \gamma_e \). All curves or parts of curves to the right-hand side of the input \( \gamma_e \) correspond to amplification by chemical and photochemical processes such that the transmittance in (8) is greater than 1. At all heights below 82 km the electron production resulting from the negative ions is larger than the direct input production. Above 55-km altitude, \( O_2^- \) leads to the major electron production rate, although \( O_2^- \) is never a major negative ion in the region where negative ion concentrations are comparable to or greater than the electron concentration (see Figure 4).

Figure 5 should not be interpreted as a mysterious electric charge creation resulting from the input \( \gamma_e \) since the electron loss rates are always such that the electroneutrality condition is satisfied.

Negative ion production rates are shown in Figure 6 for the input \( \gamma_e \) of Figure 3. The production rates of negative ions are always equal to or greater than the electron production rates resulting from these ions, since mutual neutralization and photodissociation included in the transmittances leading to Figure 5 never lead to electron production. Furthermore, the losses of negative ions included in the transmittances leading to Figure 5 do not necessarily lead to electron production.

In our reference model, \( NO_3^- \) and \( CO_3^- \) and \( HCO_3^- \) are the major negative ions. The signal flow graph technique automatically allows a quantitative determination of the most important paths leading to these ions. Figure 7 shows the total production rates of \( NO_3^- \) and \( CO_3^- \) and the contribution of all paths leading to at least 1% of the total production. Each path is characterized by a number which is obtained by following the technique described in section 3, and the various paths are identified in Table 3. It appears that a path can be almost negligible in a certain height range and can become very important in another height range. The partial productions resulting from a specific path are not represented anymore in Figure 7 when they contribute less than 1% to the

![Figure 4](image-url)  
**Fig. 4.** Vertical profiles of negative ions and electrons. The ratio \( \lambda \) between the negative ion concentration and the electron concentration is given by the dotted-dashed lines, whereas the sum of the electron and negative ion concentration is given by the dashed line.

![Figure 5](image-url)  
**Fig. 5.** Vertical distribution of the electron production rates resulting from photodetachment and collisional detachment of various negative ions. The dashed curve represents the external input \( \gamma_e \) of Figure 3.
total transmittance leading to this ion. Understanding of the negative ion chemistry can be completed by showing the loss rates (in units per second) as in Figure 8. The extremely high loss rate of O⁻ explains why the ion is not even shown in Figure 4. The effect of the high production rate of O₂⁻ (see Figure 6) is easily attenuated by its high loss rate shown in Figure 8. Furthermore, the fact that NO₃⁻ is the major negative ion in the reference model can now be understood, since its loss rate in Figure 8 is extremely small. As a consequence, a weak production path can significantly contribute to the buildup of NO₃⁻ ions. As an example, path 77 (see Figure 7 and Table 3), which represents only 9% of the NO₃⁻ production at 50 km, is the second production path (25%) above 60-km altitude. Furthermore, the O₄⁻ production by the reaction between O₂⁻ and O₂ is so small that it represents less than 2% of the total O₂⁻ loss at 65 km. A similar situation is found for path 68, which accounts for approximately 6% of the NO₃⁻ production at 50 km. The transitions from O₂⁻ to CO₄⁻ and from CO₄⁻ to NO₃⁻ both represent less than 1% of the total losses of O₂⁻ and CO₄⁻, respectively. Such a situation could lead to the omission of path 77 or 68 if the signal flow graph technique had not been used, despite the fact that the cumulative production of the two paths represents approximately 30% of the NO₃⁻ production.

Finally, Figure 7 clearly indicates that above 60 km path 499 leads to practically all of the CO₃⁻ production and its extension (path 102) is responsible for the NO₃⁻ production, for which the loss rate is very small. As is pointed out in Appendix B, the relative losses along a specific path determine the path's absolute importance. Since atomic oxygen and nitric oxide influence the loss of CO₃⁻, one can expect variations of these neutral constituents to play a role in negative ion production. This aspect is discussed in section 5.

At lower heights, around 50 km, other paths besides path 499 become significant. The most important reaction chains at 50 km are shown in Figure 9, which also gives the major paths at 60 km. The appearance of these new paths at 50 km is essentially a consequence of the increase in the neutral concentration which favors the reaction O₂⁻ + O₂ + M → O₄⁻ + M with respect to the reaction O₂⁻ + O₁ → O₃⁻ + O₂. The situation for CO₄⁻ at 50 km is similar to that of CO₃⁻ at 60 km, since any increase in nitric oxide favors NO₃⁻ production. Furthermore, a decrease in ozone gives more importance to the paths going through CO₄⁻. Finally, the feedback reactions from O₂⁻ to e (see Figure 1) largely depend on the concentrations in atomic oxygen and excited molecular oxygen O₂(1Δg).

In summary, Figures 5 to 8, computed for an input γₑ, indicate the type of analysis which can be made with the signal...
4648 WISEMBERG AND KOCKARTS: D REGION NEGATIVE ION CHEMISTRY

TABLE 3. Paths Leading to NO₃⁻ and CO₃⁻ Ions

<table>
<thead>
<tr>
<th>Path No.</th>
<th>Path</th>
</tr>
</thead>
<tbody>
<tr>
<td>68</td>
<td>e → O₂⁻ → CO₂ → NO₃⁻</td>
</tr>
<tr>
<td>77</td>
<td>e → O₂⁻ → O⁻ → CO₃⁻ → NO₃⁻</td>
</tr>
<tr>
<td>82</td>
<td>e → O₂⁻ → O⁻ → CO₃⁻ → NO₃⁻</td>
</tr>
<tr>
<td>102</td>
<td>e → O₂⁻ → CO₂ → CO₃⁻ → NO₂ → NO₃⁻</td>
</tr>
<tr>
<td>104</td>
<td>e → O₂⁻ → CO₂ → CO₃⁻ → NO₂ → NO₃⁻</td>
</tr>
<tr>
<td>134</td>
<td>e → O₂⁻ → CO₂ → O₂ → CO₃⁻ → NO₂ → NO₃⁻</td>
</tr>
<tr>
<td>136</td>
<td>e → O₂⁻ → O₂ → CO₂ → CO₃⁻ → NO₂ → NO₃⁻</td>
</tr>
<tr>
<td>137</td>
<td>e → O₂⁻ → O₂ → CO₂ → O₂ → CO₃⁻ → NO₂ → NO₃⁻</td>
</tr>
<tr>
<td>162</td>
<td>e → O₂⁻ → O₂ → CO₂ → O₂ → CO₃⁻ → NO₂ → NO₃⁻</td>
</tr>
<tr>
<td>1000</td>
<td>e → O₂⁻ → CO₂ → CO₃⁻</td>
</tr>
<tr>
<td>501</td>
<td>e → O₂⁻ → CO₂ → CO₃⁻</td>
</tr>
<tr>
<td>503</td>
<td>e → O₂⁻ → O₂ → O₂ → CO₃⁻</td>
</tr>
<tr>
<td>504</td>
<td>e → O₂⁻ → CO₂ → O₂ → CO₃⁻</td>
</tr>
<tr>
<td>506</td>
<td>e → O₂⁻ → O₂ → CO₂ → O₂ → CO₃⁻</td>
</tr>
<tr>
<td>507</td>
<td>e → O₂⁻ → O₂ → CO₂ → O₂ → CO₃⁻</td>
</tr>
</tbody>
</table>

Flow graph technique. Similar studies can be undertaken by considering reaction rates, photodetachment rates, or neutral concentrations as variable parameters. Since we used only measured rate coefficients [Albritton, 1978; Ferguson, 1974; G. P. Smith et al., 1978; D. Smith et al., 1976; Truby, 1972; Phelps, 1969; Stelman et al., 1972; Mul and McGowan, 1979], we prefer to indicate in the following section the effect of variations in the neutral model which essentially results from theoretical computations [Keneshea et al., 1979; Turco and Sechrist, 1970, 1972b]. This does not imply that the neutral models are unreliable, but variations of neutral minor constituents are real geophysical phenomena which can induce significant ionospheric modifications.

5. EFFECT OF VARIATIONS OF THE MINOR NEUTRAL CONSTITUENTS

It has been shown in the preceding section how the height variation of the neutral atmosphere can affect the paths leading to NO₃⁻ and CO₃⁻ ions. Nitric oxide, atomic oxygen, ozone, and excited molecular oxygen are of major importance in the evaluation of the transmittances associated with the predominant paths. It is therefore interesting to evaluate their effects at 65-km altitude, where NO₃⁻ is the major negative ion in the reference model. At 65-km altitude the neutral model adopted in section 2 leads to the following concentrations: n(NO) = 2.9 × 10⁸ cm⁻³, n(O) = 3.5 × 10⁸ cm⁻³, n(O₃) = 1.3 × 10⁹ cm⁻³, and n(O₂) = 4.6 × 10⁹ cm⁻³.

In an analysis of minor constituents in the middle atmosphere, Ackerman [1979] indicates that nitric oxide measurements at 65 km range between 10⁷ cm⁻³ and 2 × 10⁸ cm⁻³. We adopt here an arbitrary variation from 10⁷ cm⁻³ to 10⁹ cm⁻³. When all other parameters of the reference model are kept constant, such a variation leads to the results shown in the left part of Figure 10. It appears that an increase of NO at 65-km altitude leads to an increase of NO₃⁻ accompanied by a decrease of CO₃⁻, of HCO₃⁻, and of the electron concentration. The dimensionless ratio λ is also shown, and the vertical arrow corresponds to the nitric oxide concentration in the reference model. It is important to note that a variation of NO can lead to a significant change of the rate λ between negative ions and electrons. It should be noted that variations of NO at 65 km do not significantly modify the input ηe of Figure 3, since at this altitude the electron-ion pair production essentially results from cosmic rays without Lyman α production of NO⁺.

A detailed analysis of the nitric oxide effect is presented in Table 4. This table gives the total transmittance T; and the total loss L of NO₃⁻ as a function of the nitric oxide concentration. Path gains gᵢ, amplification factors Δᵢ/Δ, and partial transmittances Tᵢ are given for several paths labeled i and shown in Table 3. The transmittances Tᵢ are related by (8) to the production in Figure 7. The lines labeled % give the importance of path i in percents. It appears that the importance of a path changes as a function of the nitric oxide concentration but not in the same way as the corresponding path gain. As an example, path 82 has a path gain g₈₂ unaffected by nit-
ric oxide variations. But its amplification factor $\Delta_{22}/\Delta$ decreases slowly with an increase of nitric oxide, and the partial transmittance $T_{22}$ decreases in the same way as $\Delta_{22}/\Delta$. The two other paths 77 and 102 have path gains which increase with nitric oxide. In this case the decrease of the amplification factors $\Delta_{27}/\Delta$ and $\Delta_{102}/\Delta$ is not sufficient to prevent an increase of the partial transmittances $T_{77}$ and $T_{102}$. As a result, the importance of path 82 strongly decreases when nitric oxide increases, and this path represents less than 1% of the total transmittance when the nitric oxide concentration reaches a value of $10^8$ cm$^{-3}$.

A similar analysis made for CO$_3^-$ indicates a decrease of the transmittance resulting from a decrease in the amplification factor of path 499 which always remains the most important path.

The right-hand part of Figure 10 shows the effect of a variation in atomic oxygen. Since O, O$_3$, and O$_2$(As) are not independent quantities in the neutral chemistry, variations of atomic oxygen are assumed to be accompanied by ozone and excited molecular oxygen such that the ratios $n(O_3)/n(O)$ and $n(O_2(As))/n(O_2)$ are identical to the values of the reference model as well as the nitric oxide concentration. Figure 10 shows that any increase in atomic oxygen produces an increase of the electron concentration and a subsequent decrease of the ratio $\lambda$. The concentrations of NO$_3^-$ and HCO$_3^-$ decrease when atomic oxygen increases. The maximum in CO$_3^-$ concentration results from a competition between CO$_3^-$ partial production and loss rates as a function of atomic oxygen. For atomic oxygen concentrations greater than $8 \times 10^9$ cm$^{-3}$ the increase of CO$_3^-$ production is smaller than the increase of CO$_3^-$ loss by atomic oxygen.

6. CONCLUSION

In a study of $D$ region ion chemistry the quantitative effect of any parameter can be analyzed in detail by applying Mason’s [1956] rules to the corresponding signal flow graph. With these rules it is possible to evaluate quantitatively each production path and to know how each parameter influences the path gain or the amplification factor which is a measure of the chemical loops present in the system.

Negative ion clusters have been omitted in this paper, but any new reaction or new rate coefficient can be introduced in a straightforward manner. The major objective here is to present a tool appropriate to the analysis of large chemical systems under steady state conditions without transport effects. Nevertheless, the example at 65-km altitude clearly indicates significant variations of the negative ion concentrations as a function of adopted nitric oxide and atomic oxygen concentrations.

**APPENDIX A: SIGNAL FLOW GRAPH AND MASON’S RULES**

A graph is a set of nodes and edges which join two distinct nodes. The nodes in Figure 1 are the various negative ions and the edges are the oriented lines joining the ions. A path is composed by successive edges which never pass through the same node. A loop is a path for which the first node is identical to the last node. When numerical values are given to each edge, the value for a certain path or loop is simply the product of the values of the edges composing the path or the loop. These values are sometimes called path gains or loop gains.

Let us consider a system of $k$ linear equations given by

$$x_i = \sum_{j=1}^{m} c_{ij} x_j + d_i \tag{A1}$$

The flow graph associated with this system has the following characteristics: each unknown quantity $x_i$ is associated with a node of the graph, each coefficient $c_{ij}$ is the value of the edge oriented from $j$ toward $i$, and the term $d_i$ represents various external inputs to the system. The edge joining an input IN to a node always has a value equal to 1.

The system (A1) can be solved by classical methods. Such a procedure, however, gives no information on the relative importance of the various paths or loops in the associated graph. Mason [1956] developed a technique which expresses each unknown $x_i$ of the system (A1) as a function of the various inputs and a quantity called transmittance, which depends on the values associated with the edges composing the graph. For $m$ inputs IN corresponding to the values $d_i$ in (A1), each unknown $x_i$ is given [Henley and Williams, 1973] by

$$x_i = \sum_{j=1}^{m} T_{(i,j)} \times (IN) \tag{A2}$$

where the transmittance $T_{(i,j)}$ is

$$T_{(i,j)} = \sum_{i=1}^{\Delta} g_{\Delta} \Delta_{\Delta}/\Delta \tag{A3}$$

**TABLE 4. Signal Flow Graph Characteristics for NO$_3^-$ as a Function of Nitric Oxide Concentration at 65-km Altitude**

<table>
<thead>
<tr>
<th>n(NO) cm$^{-3}$</th>
<th>1 $\times$ 10$^7$</th>
<th>5 $\times$ 10$^7$</th>
<th>1 $\times$ 10$^8$</th>
<th>5 $\times$ 10$^8$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_{77}$</td>
<td>1.29 $\times$ 10$^{-3}$</td>
<td>1.34 $\times$ 10$^{-3}$</td>
<td>1.39 $\times$ 10$^{-3}$</td>
<td>1.80 $\times$ 10$^{-3}$</td>
</tr>
<tr>
<td>$L_{77}$</td>
<td>17.4</td>
<td>21.2</td>
<td>21.6</td>
<td>22.3</td>
</tr>
<tr>
<td>$%_{77}$</td>
<td>2.09 $\times$ 10$^{-6}$</td>
<td>1.04 $\times$ 10$^{-5}$</td>
<td>2.10 $\times$ 10$^{-5}$</td>
<td>1.04 $\times$ 10$^{-4}$</td>
</tr>
<tr>
<td>$T_{77}$</td>
<td>1.78 $\times$ 10$^9$</td>
<td>9.87 $\times$ 10$^6$</td>
<td>7.05 $\times$ 10$^6$</td>
<td>3.24 $\times$ 10$^6$</td>
</tr>
<tr>
<td>$T_{77}$</td>
<td>0.372</td>
<td>1.03</td>
<td>1.48</td>
<td>3.38</td>
</tr>
<tr>
<td>$g_{77}$</td>
<td>7.7</td>
<td>1.8</td>
<td>&lt;1.0</td>
<td>&lt;1.0</td>
</tr>
<tr>
<td>$g_{82}$</td>
<td>4.44 $\times$ 10$^{-7}$</td>
<td>4.42 $\times$ 10$^{-7}$</td>
<td>...</td>
<td>...</td>
</tr>
<tr>
<td>$\Delta_{77}/\Delta$</td>
<td>3.74 $\times$ 10$^{10}$</td>
<td>2.08 $\times$ 10$^{10}$</td>
<td>...</td>
<td>...</td>
</tr>
<tr>
<td>$%_{102}$</td>
<td>0.166</td>
<td>0.092</td>
<td>...</td>
<td>...</td>
</tr>
<tr>
<td>$%_{102}$</td>
<td>4.85</td>
<td>59.3</td>
<td>60.9</td>
<td>62.4</td>
</tr>
<tr>
<td>$%_{102}$</td>
<td>2.78 $\times$ 10$^{-6}$</td>
<td>1.38 $\times$ 10$^{-5}$</td>
<td>2.78 $\times$ 10$^{-5}$</td>
<td>1.38 $\times$ 10$^{-4}$</td>
</tr>
<tr>
<td>$\Delta_{102}/\Delta$</td>
<td>3.74 $\times$ 10$^{10}$</td>
<td>2.08 $\times$ 10$^{10}$</td>
<td>1.48 $\times$ 10$^{10}$</td>
<td>6.82 $\times$ 10$^{10}$</td>
</tr>
<tr>
<td>$T_{102}$</td>
<td>1.04</td>
<td>2.88</td>
<td>4.11</td>
<td>9.43</td>
</tr>
</tbody>
</table>
n being the number of paths joining the input (IN)j to the node i. In expression (A3), \( g_t \) is the numerical value (path gain) associated with each path joining the input j to the node i. The path gain \( g_t \) is always a product of edge values \( c_{ij} \). The quantities \( \Delta \) and \( \Delta_i \) depend on the structure of the various loops in the graph; \( \Delta \) is given by [Mason, 1956; Henley and Williams, 1973]

\[
\Delta = 1 - \sum_i \Delta_i - \sum_i \Delta_2 + \cdots \quad (A4)
\]

where \( \Sigma_i \) is the sum of all loop gains in the graph, \( \Sigma_2 \) is the sum of products of all loop gains taken two at a time but excluding touching loops, and \( \Sigma_3 \) is the sum of products of all loop gains taken three at a time but excluding touching loops; \( \Delta_2 \) is obtained from \( \Delta \) by deleting the loop gain terms touched by the \( h \)th path.

For a given input the transmittance is the product of \( g_t \) by \( \Delta/\Delta \) where \( g_t \) is the path gain and \( \Delta/\Delta \) is a factor resulting from all recycling loops existing in the graph. If there is no loop in the graph, \( \Delta/\Delta \) is equal to 1.

**APPENDIX B: SIGNAL FLOW GRAPH AND ION CHEMISTRY IN THE D REGION**

When transport processes are neglected, the steady state concentrations of positive (or negative) ions in the D region are obtained by equating production and loss terms for each ion. Furthermore, the electroneutrality condition can be used in a way such that the system of equations is linear. Mason’s rules, described in Appendix A, are therefore directly applicable. Instead of writing a system of equations like (A1) in terms of concentrations it is more efficient to work with productions from 02- to e and from e to 02-. The line from 02- to e represents the three 02- loss processes of Table B1 giving rise to electrons. The input to the system is characterized by a production rate \( \gamma_e \) cm\(^{-3}\) s\(^{-1}\), and the path values are indicated on the line. Note that the value of the input line is 1.

\[
P_i = \sum_{j \neq i} \left( \frac{r_{ij}}{L_j} \right) P_j + \gamma_i \quad (B3)
\]

where \( P_i \) and \( L_i \) are the production rate (in cubic centimeters per second) and the total loss rate in units per second of the \( j \) type ion, respectively. The system of equations (B3) is formally identical to the system (A1), and Mason’s rules (A2), (A3), and (A4) can be used to obtain the productions \( P_i \) in terms of inputs and transmittances. Knowing each production \( P_i \) as unknown leads to a simple interpretation of the physical process is important and how an input to the system is transferred to an ion through a specific path. Such an advantage is particularly rewarding when a large number of reactions are involved. Finally, the adoption of the production rate \( P_i \) as unknown leads to a simple interpretation of the terms \( r_{ij}/L_j \) which can be considered as relative loss rates. The coefficient \( r_{ij} \) is the loss rate of the \( j \) type ion toward \( i \) type ions, and \( L_i \) is the total loss rate of the \( j \) type ion.

Although a detailed proof is not simple, it has been shown [Henley and Williams, 1973] that Mason’s rules lead to solutions of the system (A1) identical to results obtained from other methods. For comprehension of the signal flow graph technique we consider an oversimplified scheme of reactions involving only electrons and 02- ions as given in Table B1. When Mason’s rules are applied to the corresponding system (B3), it is useful to check two points: (1) the solution obtained with Mason’s rules is identical to the classical algebraic solution of system (B3); (2) the solution obtained with Mason’s rules is identical to the solution obtained by equating electron or 02- production rates to their corresponding loss rates.

The signal flow graph is shown in Figure B1, where transitions from 02- to e and from e to 02- are represented by the top and bottom perimeters of the graph, respectively. This procedure is not mandatory, but it decreases significantly the total number of paths which have to be memorized in the graph analysis. The system (B3) reduces to

\[
P_e = \frac{\gamma_e}{1 - \left( \frac{\gamma_e}{L_0} \right) L_e} \quad (B4)
\]

and

\[
P_{O_2^-} = \frac{\gamma_{O_2^-}}{1 - \left( \frac{\gamma_{O_2^-}}{L_{O_2^-}} \right) L_{O_2^-}} \quad (B5)
\]

The algebraic solutions of this system are

\[
P_e = \frac{\gamma_e}{1 - \left( \frac{\gamma_e}{L_0} \right) L_e} \quad (B6)
\]

and

\[
P_{O_2^-} = \frac{\gamma_{O_2^-}}{1 - \left( \frac{\gamma_{O_2^-}}{L_{O_2^-}} \right) L_{O_2^-}} \quad (B7)
\]
According to Mason's rule (A2) and noting only one input IN = y, in Figure B1, one obtains with m = 1

\[ P_e = T_{(e^{-1})} \times y_e \]  

(B8)

and

\[ P_{O^2^-} = T_{(O_{2}^{-1})} \times y_r \]  

(B9)

Since there is only one path joining the input y, to the node e or O₂⁻, the transmittances \( T_{(e^{-1})} \) and \( T_{(O_{2}^{-1})} \) are given from (A3) as

\[ T_{(e^{-1})} = g_{e} A_{c} / A \]  

(B10)

\[ T_{(O_{2}^{-1})} = g_{r}' A_{r}' / A \]  

(B11)

For the electrons the path gain is \( g_{e} = 1 \) along the path IN \( \rightarrow e \) and for O₂⁻, the path gain is \( g_{r}' = 1 \times (r_{O_{2}^{-} / L_{e}}) \) along the path IN \( \rightarrow e \) \( \rightarrow O_{2}^{-} \). Since the graph in Figure B1 contains only one loop, (A4) leads to

\[ \Delta = 1 - \sum_{i=1}^{n} = 1 - (r_{e,O_{2}^{-} / L_{O_{2}^{-}}})(r_{O_{2}^{-}/L_{e}}) \]  

(B12)

Since this sole loop touches the path IN \( \rightarrow e \) and the path IN \( \rightarrow e \rightarrow O_{2}^{-} \), one has \( \Delta = \Delta' = 1 \). The transmittances (B10) and (B11) can finally be written as

\[ T_{(e^{-1})} = 1/[1 - (r_{e,O_{2}^{-} / L_{O_{2}^{-}}})(r_{O_{2}^{-}/L_{e}})] \]  

(B13)

and

\[ T_{(O_{2}^{-1})} = (r_{O_{2}^{-}/L_{e}})/[1 - (r_{e,O_{2}^{-} / L_{O_{2}^{-}}})(r_{O_{2}^{-}/L_{e}})] \]  

(B14)

which lead with (B8) and (B9) to production rates identical to (B6) and (B7). Denoting a concentration by the corresponding chemical symbol in brackets, it can be seen from Table B1 that

\[ L_{e} = k_{1}[O_{2}][M] + k_{2}[O_{2}] + \alpha_{1}[M^{*}] \]  

(B15)

\[ r_{O_{2}^{-} / e} = k_{1}[O_{2}][M] + k_{2}[O_{2}] \]  

(B16)

\[ L_{O_{2}^{-}} = k_{3}[O] + k_{4}[O_{2}]/\Delta_{e} + J_{1} + \alpha_{2}[M^{*}] \]  

(B17)

and

\[ r_{e,O_{2}^{-}} = k_{5}[O] + k_{4}[O_{2}]/\Delta_{e} + J_{1} \]  

(B18)

where \( L_{e} \) and \( L_{O_{2}^{-}} \) are the total loss rates in units per second for electrons and \( O_{2}^{-} \) ions, respectively; \( r_{O_{2}^{-} / e} \) is the partial loss rate of electrons which are converted in \( O_{2}^{-} \); and \( r_{e,O_{2}^{-}} \) is the partial loss rate of \( O_{2}^{-} \) ions which lead to electrons. The relative loss rates \( r_{e}/L_{e} \) play the fundamental role in the transmittances. Substitution of (B15) to (B18) in the transmittances leads to production rates \( P_{e} \) and \( P_{O_{2}^{-}} \), which, if divided by \( L_{e} \) and \( L_{O_{2}^{-}} \), respectively, give electron and \( O_{2}^{-} \) concentrations identical to the classical result obtained without graph analysis.

The fundamental advantage of the application of Mason's rule is the access to the various transmittances which give a physical insight into the way in which a complicated system depends on some specific reactions. The term \( g_{i} \) in the transmittance gives the path gain toward a specific constituent when a path I is followed from the input. In other words, \( g_{i} \) measures the capacity of a specific path to transmit an external production. The term \( A_{i} / A \) is an amplification factor resulting from recycling processes. This factor measures the feedback mechanisms in the chemical system.

Acknowledgments. We are grateful to S. P. Zimmerman, T. J. Keneshea, and C. R. Philbrick for sending us numerical values for the neutral atmosphere model. The constructive comments of the anonymous referees are also appreciated. The Editor thanks G. C. Reid for his assistance in evaluating this paper.

REFERENCES


Mul, P. M., and J. W. McGowan, Merged electron-ion beam experiments, III. Temperature dependence of dissociative recombination for atmospheric ions \( NO^{+}, O_{2}^{+}, \) and \( N_{2}^{+}, \) J. Geophys. Res., 78, 1591-1601, 1973.


(Received January 22, 1980; revised March 19, 1980; accepted April 9, 1980.)