Collisional Detachment and the Formation of an Ionospheric C Region

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A simple expression is derived for the collisional detachment coefficient in terms of pressure, temperature, and the electron affinity, $E_a$, of the $O_2$ ion. By using this expression, it is calculated that at night the profile of electron density against height has a maximum near the stratosphere at 50 km. The magnitude of the electron density at the maximum depends critically upon $E_a$. If the probability of detachment approaches unity for molecular energies exceeding $E_a$, it may be deduced that $E_a$ must be at least greater than 0.45 ev. Some comments are made on the conflict, in considering stratospheric ionization, between the concepts of ionospheric physics and those of atmospheric electricity.

1. Introduction

Many calculations of electron densities in the lower ionosphere have been made by solving the balance equations governing the production and loss of ionization. These equations, in the convenient form essentially given by Crain [1961], are

$$\frac{dN}{dt} = Q - AN - BNN^+ + (C+D)N^- \quad (1a)$$

$$\frac{dN^-}{dt} = AN - (C+D)N^- - EN^-N^+ \quad (1b)$$

$$\frac{dN^+}{dt} = Q - BNN^+ - EN^-N^+ = \frac{dN}{dt} + \frac{dN^-}{dt} \quad (1c)$$

In the equations, $N$, $N^-$, and $N^+$, represent the respective concentrations of electrons, negative ions, and positive ions, while $Q$ is the rate of electron (and consequently positive ion) production. The rate coefficients are $A$ for electron attachment to neutral molecules, $B$ for electron-ion recombination, and $E$ for ion-ion recombination; and the electron detachment terms are represented by $(C+D)$. It is convenient to consider $D$ as being the collisional detachment coefficient, while $C$ combines the photodetachment and associative detachment [Whitten and Poppoff, 1962] processes.

There has been a tendency in the past to ignore the collisional detachment process in favor of photodetachment. Certainly photodetachment is the only important detachment mechanism in the formation of the daytime $D$ region at heights above some 60 km. However, even by day it appears that collisional detachment may be significant at levels below 60 km, while at night it is probably dominant at these altitudes. This dominance has interesting consequences upon ionospheric structure, and it is the purpose of the present paper to examine these effects.

2. Collisional Detachment Coefficient

An approximate expression for the coefficient $D$ can be obtained without much difficulty. Below 90 km the only important negative ion is $O_2^-$, formed by the attachment of an electron to an oxygen molecule. If collisional detachment is to occur, the molecule impinging on the $O_2^-$ ion must possess energy greater than the electron affinity, $E_a$, of the ion. (It is assumed that on the average the relative motion of the ion and molecule is represented by considering the ion to be at rest.) There is no general agreement regarding the magnitude of $E_a$. The accepted value some 20 years ago was about 1.0 ev [Bates and Massey, 1943], but more recent work has indicated lower values. Among these are the 0.25 ev of Bailey and Branscomb [1960], the estimate from 0.15 ev to 0.50 ev of Mulliken [1961], the 0.46 ev of Phelps and Pack [1961], and the 0.74 ev of Jortner and Sokolov [1961].

All the values for $E_a$, however, much greater than the average kinetic energy of a molecule which, under thermal equilibrium, is only a few hundredths of an electron volt for heights below 100 km. It follows that if a molecule is to exceed the minimum energy, $E_a$, for detachment, its speed must be perhaps three or four times the most probable molecular velocity. Under these circumstances, simple kinetic theory shows that the fraction of molecules possessing energies exceeding $E_a$ is represented approximately by

$$\left(\frac{4}{\pi}\right)^{1/2} \left(\frac{E_a}{kT}\right)^{1/2} \exp\left(-\frac{E_a}{kT}\right) \quad (2)$$

where $k$ is Boltzmann's constant and $T$ the temperature. The number of collisions made by an ion in a second is given by

$$\left(2\frac{1}{\pi}\right)^{1/2} \pi \sigma \sqrt{c} \left(\frac{L_M}{L_T}\right) \quad (3)$$

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where \( \sigma \) is the molecular diameter, \( n \) the number of molecules per unit volume, \( \bar{c} \) the average molecular speed, and \( L_M \) and \( L_I \) the mean free paths, respectively, for molecules and ions. Expression (3) may be rewritten as

\[
(2)^{1/2} \pi \sigma^2 \left( \frac{L_M}{L_I} \right) \frac{P}{kT} \left( \frac{8kT}{\pi m} \right)^{1/2} D \tag{4}
\]

with \( m \) denoting the molecular mass and \( P \) the pressure. The product of (2) and (4) is apparently the collisional detachment coefficient, \( D \), but one qualification and one modification are still necessary. The modification is that according to Phelps and Pack [1961] only molecular oxygen is effective in producing detachment; thus for application to the atmosphere, the product of (2) and (4) should be divided by a factor of five. The qualification is that if the product of (2) and (4) is taken as representing \( D \), this means that all impinging molecules with energies greater than \( E_a \) produce detachment. This is not true, and a factor \( p \) representing the probability of detachment per collision must be introduced.

The complete expression for \( D \) is, therefore,

\[
\frac{1}{5} \left( \frac{4}{\pi} \right)^{1/2} \frac{(E_a)^{1/2}}{(kT)^{1/2}} \exp \left( -\frac{E_a}{kT} \right) \left( \frac{L_M}{L_I} \right) \frac{P}{kT} \left( \frac{8kT}{\pi m} \right)^{1/2} D \tag{5}
\]

This may be simplified using the plausible values of \( \sigma = 4 \times 10^{-8} \text{ cm} \);

\[
m = 5 \times 10^{-23} \text{ g}; \quad k = 1.4 \times 10^{-16} \text{ erg/deg};\]

and \( \left( \frac{L_M}{L_I} \right) \approx \frac{75}{(T)^{1/2}} \)

The result is

\[
D \approx \frac{P}{T} \left( \frac{E_a}{kT} \right)^{1/2} \exp \left( -\frac{E_a}{kT} \right) \times 2 \times 10^6 \tag{6}
\]

with \( P \) in microbars and \( T \) in \( ^{0} \text{K} \). In any calculations, \( E_a \) and \( kT \) must, of course, be in the same units; this implies that with \( k \) in erg/deg \( E_a \) must be in ergs (1 ev = 1.6 \times 10^{-12} \text{ erg}).

Pressure and temperature data as a function of height are given in table 1, the information being obtained from the Handbook of Geophysics [1960]. Figure 1 has been constructed using (6) with \( p = 1 \) and the values for \( P \) and \( T \) listed in table 1. Obviously, because of the exponential term in (6), the result for \( D \) is extremely dependent upon the value of \( E_a \); this has already been emphasized by Crain [1961]. Temperature is also a critical influence in determining \( D \), and it is interesting to note the maximum and minimum in \( D \) corresponding to the temperature maximum and minimum at the stratopause and mesopause, respectively. Crain [1961] gave the simple expression 100 \( P \) for \( D \), with \( P \) now being in atmospheres; this result is also shown on figure 1. Since Crain's expression does not include the effect of temperature, it is not easy to compare with the other curves of figure 1, but it seems to approximate most closely to the curve for \( E_a = 0.40 \text{ ev} \). At a temperature and number density corresponding to a height of 65 km, the experimental results of Phelps and Pack [1961] indicate that log \( D = -3.8 \). Figure 1 shows that this would imply \( E_a \) being between 0.45 and 0.50 ev, a conclusion in agreement with the value of 0.46 ev deduced by Phelps and Pack from their work.

### Table 1. Atmospheric parameters as a function of height

<table>
<thead>
<tr>
<th>Height</th>
<th>Temperature</th>
<th>Pressure</th>
<th>Attachment coefficient A</th>
</tr>
</thead>
<tbody>
<tr>
<td>km</td>
<td>°K</td>
<td>Microbar</td>
<td>sec⁻¹</td>
</tr>
<tr>
<td>40</td>
<td>201</td>
<td>3000</td>
<td>9.2 \times 10⁻²</td>
</tr>
<tr>
<td>45</td>
<td>276</td>
<td>1600</td>
<td>2.4 \times 10⁻²</td>
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<td>283</td>
<td>879</td>
<td>7.2 \times 10⁻²</td>
</tr>
<tr>
<td>55</td>
<td>276</td>
<td>484</td>
<td>3.4 \times 10⁻²</td>
</tr>
<tr>
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<td>254</td>
<td>257</td>
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<td>139</td>
<td>1.9</td>
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<tr>
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<td>166</td>
<td>3.69</td>
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<tr>
<td>90</td>
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<tr>
<td>100</td>
<td>199</td>
<td>0.214</td>
<td>8.5 \times 10⁻⁴</td>
</tr>
</tbody>
</table>

### 3. Structure of the Lower Ionosphere at Night

The maximum of \( D \) at the stratopause has an interesting consequence upon the electron density profile in the lower ionosphere. The effect is best illustrated by considering conditions at night. Cosmic rays are the only important ionizing agency; and the factor \( Q \) of (1) may be written, in ion pairs cm⁻³ sec⁻¹, as

\[
Q = 15 \left( \frac{P}{kT} \right) \cos^{-1} \theta \times 10^{-19} \tag{7}
\]

where \( \theta \) is a geomagnetic latitude equated with the angle of dip. Equation (7) is a representation valid at low and mid latitudes of the results given by Curtis [1956], and is in good agreement with the later information of Webber [1962].

In order to determine electron densities at any height, it is necessary to estimate the coefficients in (1). There is no major disagreement between various authorities, for example Webber [1962]; Latter and Lelevier [1963], regarding the attachment coefficient \( A \); the values given in table 1 represent a composite of theoretical and other information. The electron-ion recombination is a dissociative process involving the positive ions which may be \( O_2^+, N_2^+, \) and \( NO^+ \). Most experimental results suggest that \( NO^+ \) is the dominant positive ion in the lower ionosphere. The dissociative recombination coefficients for both \( O_2^+ \) and \( N_2^+ \) as measured experimentally exceed \( 10^{-7} \text{ cm}^3 \text{ sec}^{-1} \), but until recently no comparable measurements were available for \( NO^+ \). Nicolet and Aikin [1960] suggested that the value of \( B \) was an order of magnitude less for \( NO^+ \) than for \( O_2^+ \). This would give \( B \approx 3 \times 10^{-8} \).
Figure 1. Collisional detachment coefficient versus height.
Figure 2. Electron density versus height.
Latitude 0°; $B = E = 4 \times 10^{-8}$
Figure 3. Electron density versus height.
Latitude $0^\circ$; $B = E = 2 \times 10^{-7}$

$cm^3$ sec$^{-1}$ for NO$^+$, and an effective $B \approx 4 \times 10^{-8}$
$cm^3$ sec$^{-1}$ for the lower ionosphere as a whole, the
increase being in order to take account of positive
ions other than NO$^+$. However, Syverson et al.
[1962] have recently measured $B$ for NO$^+$ and found
it to be $1.3 \times 10^{-7}$ cm$^3$ sec$^{-1}$. Thus a plausible
value for $B$ in the lower ionosphere would be $2 \times 10^{-7}$
$cm^3$ sec$^{-1}$, and the variation with height is likely
to be slight. Since night conditions are being
considered, $C$ can be equated to zero if associative
detachment is ignored. The calculations for $D$
have already been given. As regards the ion-ion
recombination coefficient $E$, there is a present
tendency to believe that it is of the order of $10^{-7}$
Webber [1962] gives a value of approximately $2 \times 10^{-7}$ cm$^3$ sec$^{-1}$ for heights of from 40 to 100 km. This suggests that the very considerable simplification of the ionospheric balance equations involved in taking $B = E$ is entirely justifiable, given the present uncertain knowledge of these coefficients.

Equation (1) yields a very simple solution for $N$, when equilibrium conditions are assumed so that the derivatives are zero, and with $B = E$. At night the solution is

$$N = \left( \frac{Q}{B} \right)^{1/2} \left( \frac{D + (QB)^{1/2}}{A + D + (QB)^{1/2}} \right)$$

(8)
Profiles of electron densities against height, as derived from (8), are plotted in figures 2, 3, and 4. In each figure, the profiles obtained using values of D involving electron affinities of from 0.25 to 0.65 ev are shown; p in (6) is taken as being unity. The figures also include the profile derived when Crain's expression for D is employed. Figure 2 is drawn for $B = E = 4 \times 10^{-8}$ cm$^3$ sec$^{-1}$ and with a latitude of 0° inserted in (7) for Q. Figure 3 is at the same latitude but with $B = E = 2 \times 10^{-7}$ cm$^3$ sec$^{-1}$, and there is a reduction in electron density by a factor of approximately two as compared with figure 2. Figure 4 is for a latitude of 50° with $B = E = 2 \times 10^{-7}$ cm$^3$ sec$^{-1}$.

4. Discussion

The salient feature of figures 2, 3, and 4 is the maximum of ionization reached by most of the curves at a height of about 50 km. The ionization of the lower ionosphere by cosmic rays [Moler, 1960; Goldberg, 1963] is sometimes considered to represent an ionospheric C layer. Certainly the electron density profile between 40 and 60 km has claims to this term, since there is a definite maximum and the formative agencies are cosmic rays and collisional detachment. Associative detachment has been neglected, but it is probably likely to be significant in comparison with the collisional process only at heights above 70 km.

It would appear from figures 2 through 4 that at the peak of the profile the electron density is approaching or above 10 cm$^{-3}$ for $E_a < 0.45$ ev. It would also seem unlikely that an electron density greater than 10 cm$^{-3}$ could exist by night at 50 km without frequent detection by radio means; there is little evidence of this. The obvious deduction is that the electron affinity of the O$^+$ ion is larger than 0.45 ev. However, it should be remembered that the calculations have been performed with p set equal to unity in (6). Massey [1950] suggests that p may become appreciable only when the energy of relative motion of the ion and molecule is considerably larger than the detachment energy, $E_a$. If this is true, the collisional detachment coefficient will be extremely small; it will have no practical significance in the lower ionosphere; and the maximum of ionization at the stratopause, although still present, will be at such a low electron density as to be of only academic interest.

One further complication is perhaps worthy of mention. The ionization has so far been considered entirely in terms of electrons and ions of molecular size. However, workers in atmospheric electricity believe the only important ions in the atmosphere at stratospheric heights to be the "small" or "cluster" ions of atmospheric electricity. These are commonly regarded—on the basis of very little concrete information—as consisting of a molecular ion surrounded by a cluster of several molecules; this concept is in opposition to work in gaseous electronics [Loeb, 1955] which indicates that the formation of stable clusters is a very unlikely process. If, however, clusters exist, figure 5 represents the dual approach. The ionospheric physicist considers only the effects occurring to the left of the central dividing line; the researcher in atmospheric electricity believes that the processes to the left occur so rapidly that he need examine only those to the right of the division. Obviously a true analysis should envisage the possibility of reactions that bridge the separation, for example, the recombination of electrons and positive cluster ions.

![Diagram of Processes of Ionospheric Physics and Atmospheric Electricity](image-url)
As an illustration of the difference in approach, the state of ionization at 40 km may be calculated. With $\theta = 0$, the rate of production of ionization $Q$ is $12.5 \times 10^{-2}$ ion pairs cm$^{-3}$ sec$^{-1}$. The attachment coefficient, $A$, has the value of $9.2 \times 10^2$ sec$^{-1}$; $B = 2 \times 10^{-7}$ cm$^3$ sec$^{-1}$; and $D$ for $E_0 = 0.40$ ev and $p = 1$, is $3.2$ sec$^{-1}$. Hence, by using (8) and its allied solutions of (1), the concentrations per cm$^3$ are $N^+ \approx 790$, $N^- \approx 787$, and $N \approx 3$; this would be the electrical state of the atmosphere as estimated by the ionospheric physicist. The same value of $Q$ applies to the atmospheric electrical approach, but the balance equation now has the simple form

$$Q = \alpha n^2$$  \hspace{1cm} (9)

where $n$ is the cluster ion concentration, and $\alpha$ the recombination coefficient between cluster ions. The value of $\alpha$ at 40 km may be estimated from the work of Sagalyn and Faucher [1954] as $1.5 \times 10^{-8}$ cm$^3$ sec$^{-1}$. Hence $n \approx 3000$ cm$^{-3}$. Thus the worker in atmospheric electricity would predict the electrical state at a height of 40 km as comprising ions consisting of molecular clusters, the concentrations of positive and negative ions being equal and about 3000 cm$^{-3}$ in value. On the other hand, the ionospheric physicist would estimate the electrical constituents of the atmosphere at 40 km as being 3 free electrons per cm$^3$; a concentration of molecular sized negative ions of about 800 cm$^{-3}$; and a density of positive ions, again of molecular size, equal to the sum of the electron and negative ion concentrations. The discord between the two approaches is evident.

I am indebted to Dr. Cullen Crain for several occasional conversations, short but instructive, on the topics of this paper. Miss Helen Arnold and Miss Anne Best assisted in the calculations.

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5. References


Loeb, L. B. (1955), Basic processes of gaseous electronics, University of California Press (Berkeley and Los Angeles).


