RADIO SCIENCE Journal of Research NBS/USNC–URSI
Vol. 68D, No. 2, February 1964

Comments on a Paper "Collisional Detachment and the Formation of an Ionospheric" by E. T. Pierce

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(Received August 12, 1963)

1. Number of Collisions

The collisional detachment coefficient D is directly proportional to the rate per ion I of collisions between the ion and a molecule M, in which the energy relative to the center of mass is greater than E_a, the electron affinity of the ion I. Pierce [1963] approximated this collision rate by calculating the number of collisions made by an ion per second and the fraction of ions of energy greater than E_a and taking the product of these two quantities as the required number. This gave

$$D=p\cdot(8\pi)^{1/2}\frac{L_M}{L_I}\cdot\frac{P}{5kT}\cdot\sigma^2\left(\frac{8kT}{\pi m}\right)^{1/2}\left(\frac{E_a}{kT}\right)^{1/2}\exp\left(-\frac{E_a}{kT}\right) \tag{1}$$

where p is a factor denoting the probability of detachment in any sufficiently energetic collision, L_M and L_I are the mean free paths for molecules and ions respectively, σ is the molecular diameter, T the temperature, P the pressure, m the molecular mass, and k is Boltzmann's constant. This assumes that the molecule and ion are the same radical, which is valid, as it is found that $O_2^-+O_2\rightarrow O_2+O_2+e^-$ is the only reaction contributing significantly to D. However kinetic theory gives a more exact expression for the number of collisions of center of mass energy greater than E_a, which gives

$$D=p\cdot\pi\sqrt{2}\frac{Lm}{L_I}\frac{P}{5kT}\sigma^2\left(\frac{8kT}{\pi m}\right)^{1/2}\left(\frac{E_a}{kT}+1\right)\exp\left(\frac{-E_a}{kT}\right) \tag{2}$$

where the symbols used are as in (1) and again it is assumed that the ion and molecule are both the same type.

This more exact form does not differ greatly from Pierce's form; one must multiply the values given by (1) by a factor $f=\frac{\sqrt{\pi}}{2}\left(\frac{E_a}{kT}+1\right)\left(\frac{E_a}{kT}\right)^{-1/2}$ to obtain the value given by (2). For possible values of E_a and T as discussed by Pierce, f is at most about 10.

2. The Probability Factor p

A method of obtaining the factor p introduced by Pierce is suggested by the paper of Phelps and Pack [1961] in which a value $E_a=0.46$ for the electron affinity of molecular oxygen is derived from the ratio of attachment to detachment for the process

$$O_2^-+O_2\rightleftarrows O_2+O_2+e.$$

Using this value and the experimental conditions, (2) gives a method of determining $\frac{D}{[O_2]}$ in terms of p, where $[O_2]\simeq\frac{P}{5kT}$=concentration of oxygen. This quantity is one of those measured by Phelps and Pack and a comparison of the calculated values with their experimental values over the range 400 to 600 °K gives $p=(2.2\pm0.6)\times10^{-2}$ and shows p increasing slightly with temperature. Hence it appears that, for temperatures such as found at heights from 40 to 100 km in the atmosphere, $p=0.02$ is a reasonable estimate.

3. Importance of Negative Ions Other Than O_2^-

Pierce states that "below 90 km the only important negative ion is O_2^-." While it is true that O_2^- is the only ion present at these heights for which collisional detachment is a significant process, it does not appear to be valid to assume that it is the only negative ion present. To obtain the parameter needed for the ionospheric balance equations it is necessary to multiply the value for D given by (2) by a factor $[O_2^-]/N^-$ where $[O_2^-]$ represents the concentration (cm^{-3}) of O_2^- ions and N^- is the total concentration of negative ions. An estimate of the ratio $[O_2^-]/N^-$ for nighttime conditions has been made and is shown on figure 1. This is based on a model of atmospheric composition obtained chiefly from the ARDC Handbook of Geophysics 1960, and from a paper by Barth [1961]. The balance equations for the various significant ion types and the values of the parameters appearing in these equations are discussed by Poppoff and Whitten [1963]. The

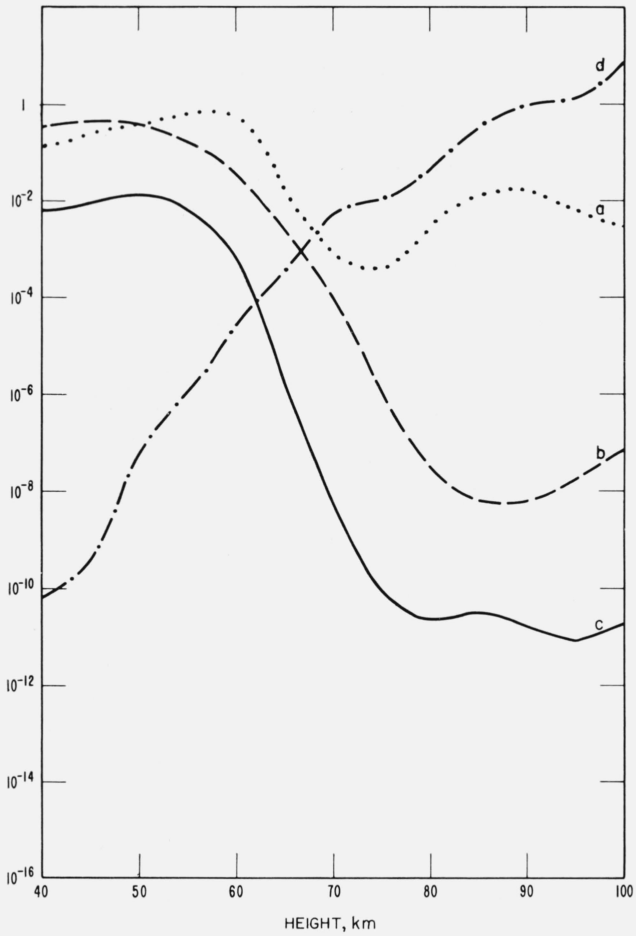

Figure 1. *Detachment coefficient—C and D at night.*

(a) Ratio $[O_2^-]$: N^- at night.
(b) D as given by Pierce for E_a=0.45 ev.
(c) Modified D for E_a=0.45 ev, night.
(d) C at night. Associative detachment.

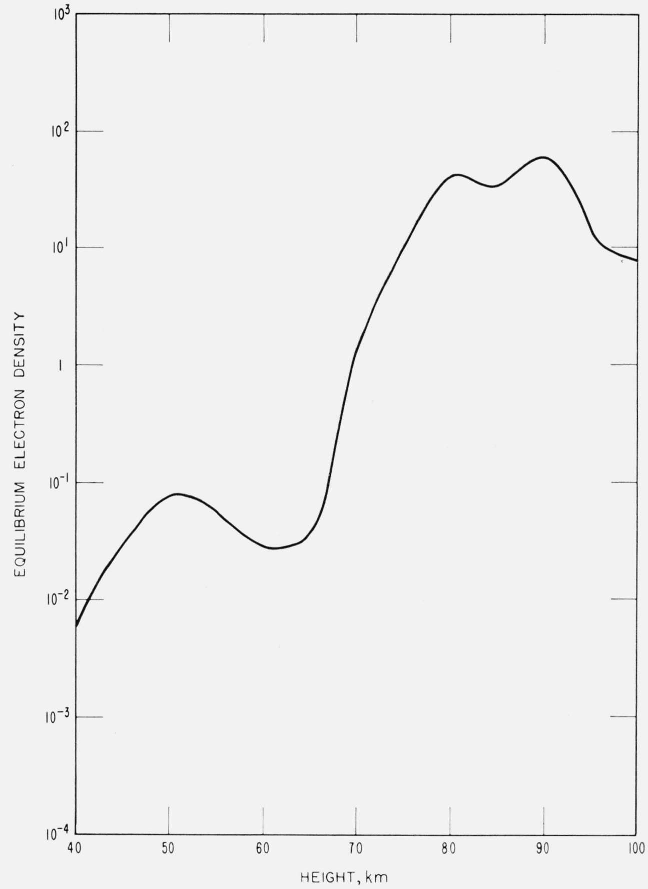

Figure 2. *Electron density profile including the effect of associative detachment* $E_a=0.45$ *ev* $\chi\theta=0°$ *(geomagnetic latitude).*

value of D for $E_a=0.45$ ev has been calculated using Pierce's model of atmospheric conditions and including the factors discussed in sections 1 through 3 and is plotted on figure 1, which also shows the values obtained by Pierce for this parameter.

4. The *C* Term at Night

Pierce includes both photodetachment and associative detachment [Whitten and Poppoff, 1962] in the term C and then assumes it to be zero at night, commenting that this probably invalidates his results above about 70 km. The calculations of ion concentrations mentioned in section 3 above may be used to obtain values for C at night and the result is shown on figure 1. It can be seen that, if $E_a=0.45$, this is the dominant term at heights above about 60 km.

5. Discussion

Figure 2 shows the electron density deduced using the parameters as shown on figure 1. The peak in electron density at 50 km at night discussed by Pierce is still evident although reduced in magnitude, chiefly because of the factor $p=0.02$. A second peak at about 90 km is due to the associative detachment process, and corresponds to the nighttime reflection height for VLF radio waves.

Comment by Dr. E. T. Pierce

I think that this note by Miss Arnold is a valuable correction and extension of my original paper; I quite agree with her conclusions, although our rapidly changing knowledge of the lower ionosphere may well invalidate these in turn before long. It is interesting to note that, even on the revised version, collisional detachment is the dominant detachment mechanism below about 60 km at night, thus leading to the electron density maximum of "C-region" at the stratopause. Although the peak electron density is only of the order of 10^{-1} cm^{-3} so that normally the C-region is merely of academic significance, it could become very important at times, such as polar cap events, when electron production in the lower ionosphere is greatly enhanced.

5. References

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(Paper 68D2–335)