

# Ion and Charge Exchange Reactions involving Atmospheric Gases

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In order to study reactions between ions and neutral particles, a series of experiments have been carried out which utilize time resolving mass-spectrometric monitoring of the afterglows in atmospheric gases produced by radio-frequency discharges. The following reactions have been investigated: (i) the charge exchange rates of the  $O^+$  ion with oxygen and nitrogen; (ii) the charge exchange rates of the  $He^+$  ion with oxygen and nitrogen. Rate coefficients and cross-sections are presented for some of these reactions, together with suggestions concerning the mechanisms of the reactions.

Since measurements of the rates of reaction between ionized and neutral atoms of atmospheric gases were required at thermal energies, the afterglow method was used. Microwave methods could not be used in the present studies since the charge transfer reactions investigated produce no obvious effect on the electron loss process.

The method is essentially that of Dickinson and Sayers<sup>1</sup> and consists of ionizing the gases under investigation with a high power radiofrequency discharge pulse and observing the ion density decay rate in the afterglow. The method assumes that the current flowing to the mass spectrometer collector is proportional to the instantaneous undisturbed ion density in the afterglow plasma. The discharge plasma is produced in a large glass envelope. In the afterglow, the ions and electrons rapidly reach thermal equilibrium with the gas. In this way, ions are produced having a Maxwellian energy distribution and their reaction with neutral species can be studied at thermal energies. Similar work has been carried out by Fite and his co-workers.<sup>2, 3</sup>

The great advantage of the mass-spectrometric method is that positive identification of the reactants and products in a given reaction can be obtained and also the mass spectrometer can be used as a monitor of any impurities present in the afterglow. These measurements are now possible due to the development of mass spectrometers with short ion path-lengths which reduce considerably the chance of reactions taking place between the ions and neutral species in the mass spectrometer itself.

In all the measurements carried out in the various gas mixtures, neutral helium was the dominant species present and  $He^+$  was the dominant ion formed in the ionizing pulse. In all cases, the helium was at a sufficiently high pressure so as to act as an effective buffer to the diffusion of ions and electrons to the walls of the discharge vessel. In one series of measurements described, the rate of decay of the  $He^+$  ion in the presence of neutral oxygen and then nitrogen was studied. The most important product of the reactions was in the first case the  $O^+$  ion and in the second case the  $N^+$  ion. The rate of decay of the  $O^+$  ion in the presence of molecular oxygen and then molecular nitrogen is also described.

## EXPERIMENTAL

The discharge vessel consisted of a Kodial glass cylinder of diameter 14.5 cm and overall length about 30 cm. The electrode system consisted of two parallel flat nickel discs of

11 cm diam. inside the vessel placed about 16 cm apart and two external sleeves of copper about 5 cm wide placed about 7 cm apart. The mass spectrometer was contained in a side-arm of the main discharge vessel, the ions formed in the discharge tube entering the mass spectrometer through a small circular orifice of 0.18 mm diam. at the centre of a Nilo-K disc of 2.5 cm diam. which was effectively sealed to the wall of the discharge vessel.

Particular attention was paid to obtaining good vacuum conditions. Kodial glass was used in preference to Pyrex glass: the latter is reputed to give off chloride ions when bombarded in a gas discharge. Bakable metal taps were used throughout the system to the exclusion of all grease joints and rubber gaskets. The discharge vessel was baked to 350°C using an oven and the rest of the tubulation, gas train, etc., was outgassed using heating tapes. Where possible, metal parts were outgassed by eddy current heating. This allowed the residual pressure in the system to be reduced to  $10^{-7}$  mm Hg. Cold traps were included above mercury diffusion pumps and in the gas circulating system. The mass spectrometer was differentially pumped, the gas being returned to the main discharge chamber. Hence, during operation, the system was isolated from the evacuating pumps. The gases used in the experiments were spectroscopically pure gases obtained from the British Oxygen Co. Ltd., and the glass containers were sealed to the system via metal taps. Pressure measurements were made with a McLeod gauge.

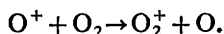
The ionizing pulses were of 10  $\mu$ sec duration at a frequency of 7 Mc/sec and a repetition frequency of 50 pulses/sec synchronized to the a.c. mains supply. The power in the pulse could be varied continuously from the minimum required to initiate the discharge to about 200 kVA. A constant discharge power of about 25 kVA was usually used in these experiments. Ion currents flowing to the mass spectrometer collector were usually  $\sim 10^{-9}$  A and in order to measure these currents as a function of time they were passed through the grid resistor of a wide-band amplifier, the resulting time-varying amplified voltage being displayed on an oscilloscope screen.

To obtain the gas mixture in the required proportions, the gas required at the lowest concentration, usually oxygen or nitrogen at a pressure of  $\sim 10^{-3}$  mm Hg, was first introduced and its pressure measured accurately with the McLeod gauge. Helium gas was then quickly introduced to raise the total pressure to approximately 0.5 mm Hg pressure. Measurements of decay rates of various ion species were obtained by photographing the oscilloscope display together with a calibration time trace. From the photographs, the concentration of the tuned ion species as a function of time in the afterglow was obtained. In some cases, it was found necessary to use a cine camera to record the oscilloscope traces, since a rapid movement of the oscilloscope trace resulted during the first few ionizing pulses.

## RESULTS

### OXYGEN

Preliminary measurements of the decay rate of the  $O^+$  ion density in oxygen were made by Dickinson and Sayers.<sup>1</sup> The discharge tube was not baked, the only attempt at cleaning it was by running a discharge in helium for several hours. From the semi-logarithmic plots of ion density as a function of time in the afterglow, a decay rate  $\lambda$  can be obtained for different partial pressures of oxygen. A plot of  $\lambda$  as a function of oxygen partial pressure should produce a straight line, the slope of which provides a value for the rate coefficient  $k$  of, in this case, the reaction



The value given by Dickinson and Sayers is

$$k = 2.5 \pm 0.4 \times 10^{-11} \text{ cm}^3 \text{ sec}^{-1} \text{ at } 293^\circ \text{K.}$$

The experiment was repeated in the present apparatus without baking and the value obtained for the rate coefficient was

$$k = 2.6 \pm 0.4 \times 10^{-11} \text{ cm}^3 \text{ sec}^{-1} \text{ at } 293^\circ \text{K.}$$

It was noticed, however, that under these conditions an ion of mass 12, probably carbon, was present in the afterglow as an impurity.

The experiment was repeated using the improved vacuum techniques described in the previous section. The decay of the  $O^+$  ion was much slower than before and the graph of decay constant against partial pressure of oxygen showed less scatter of the points about a straight line (see fig. 1). Also, ionized carbon was not

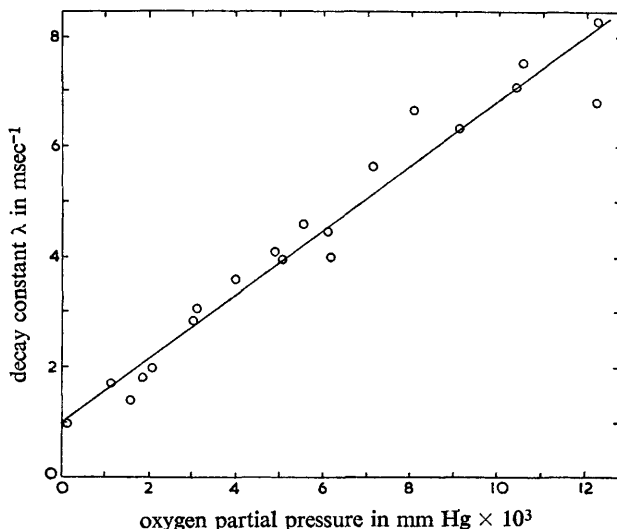


FIG. 1.—Decay constants for the  $O^+$  ion density in oxygen afterglows at 293°K.

observed in the afterglow. The reaction rate coefficient determined from these results is

$$k = (1.64 \pm 0.05) \times 10^{-11} \text{ cm}^3 \text{ sec}^{-1} \text{ at } 293^\circ\text{K}.$$

The corresponding cross-section is

$$\sigma = (2.15 \pm 0.06) \times 10^{-16} \text{ cm}^2.$$

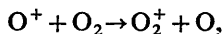
There seems little doubt that the lower value obtained is due to the more stringent vacuum techniques adopted in this work.

The temperature dependence of the rate coefficient for the  $O^+$  ion reaction with oxygen has also been investigated. Prolonged baking was required in order to obtain measurements at the higher temperatures in order to reduce the impurity level. Measurements were also made below room temperature by surrounding the discharge vessel with solid carbon dioxide. Rate coefficients and corresponding cross-sections for the various temperatures are given in table 1. Over this restricted range of temperature, the rate coefficient appears to be approximately proportional to the inverse square root of the temperature.

TABLE 1

temp. °K	rate coefficient, $\text{cm}^3 \text{ sec}^{-1} \times 10^{11}$	cross-section, $\text{cm}^2 \times 10^{16}$
452	$1.35 \pm 0.05$	$1.32 \pm 0.05$
388	$1.72 \pm 0.06$	$1.95 \pm 0.07$
293	$1.64 \pm 0.05$	$2.15 \pm 0.06$
210	$2.40 \pm 0.10$	$3.70 \pm 0.20$

The charge exchange reaction occurring here is



and it has been suggested <sup>4</sup> that the dominant mechanism is ion-atom interchange. The observed increasing cross-section as the temperature decreases is in qualitative agreement with the theory of this process. However, on the basis of the Gioumousis and Stevenson equation <sup>5</sup> the theoretical rate coefficient for the reaction is  $9 \times 10^{-9} \text{ cm}^3 \text{ sec}^{-1}$  which is an order of magnitude greater than the present results.

By studying the emission of the oxygen red line (6300 Å) from the night-time *F* layer, which he assumed was emitted from decaying excited oxygen atoms formed in the above charge exchange reaction, Nakamura <sup>6</sup> has calculated a value for the rate coefficient as

$$k = 1.3 \times 10^{-11} \text{ cm}^3 \text{ sec}^{-1}$$

at the temperature in the *F* layer ( $\sim 1400^\circ\text{K}$ ). This value is in close agreement—perhaps fortuitously—with the present work. The phenomena of clean-up of oxygen was always noticeable in the afterglow to some extent. Hence the photograph of the oscilloscope trace had to be taken as soon as possible after the initiation of the discharge.

#### OXYGEN+NITROGEN MIXTURES

The reaction between the ionized oxygen atom and the nitrogen molecule is of especial interest in the upper atmosphere for it is known that the concentration of molecular nitrogen is considerable. The method of examining the reaction is to add nitrogen to a mixture of oxygen and helium, such as that used in the previous experiment. Any change in the decay rate of the  $\text{O}^+$  ion must be due to the added component. An effective total rate coefficient  $k_T$  may be given by the relation

$$k_T = k_O + \alpha k_N$$

where  $k_O$  is the rate coefficient for ion loss due to the oxygen molecule,  $k_N$  is the rate coefficient for ion loss by the nitrogen molecule, and  $\alpha$  is the ratio of the nitrogen partial pressure to the oxygen partial pressure.

The measurements were made in two series, in one of which the nitrogen-oxygen ratio was approximately 1:1 and in the other series the ratio was approximately 2:1. It was not consistently possible to obtain nitrogen and oxygen pressures that had exact 1:1 or 2:1 ratios, but these ratios were maintained to within 10 %.

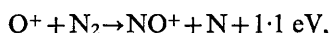
The results observed for the decay rate  $\lambda$  as a function of oxygen or nitrogen partial pressure were somewhat scattered, and to obtain reasonable accuracy in the final value of the rate coefficient  $k_T$ , many more measurements were taken than with pure oxygen. The values of the effective total rate coefficient  $k_T$ , obtained for the two different mixtures at  $293^\circ\text{K}$ , together with the value for the rate coefficient of the  $\text{O}^+$  ion in pure oxygen, are shown in fig. 2. From this graph the rate coefficient for the loss of oxygen by reaction with molecular nitrogen at  $293^\circ\text{K}$  is

$$k_N = (2.7 \pm 0.2) \times 10^{-11} \text{ cm}^3 \text{ sec}^{-1},$$

corresponding to a cross-section of

$$\sigma = (3.6 \pm 0.3) \times 10^{-16} \text{ cm}^2.$$

The addition of a third gas to the discharge increases considerably the possible ion-exchange reactions. However, most reactions can be excluded in favour of the reaction,



and it is assumed that this is the most important reaction mechanism. The result obtained for this reaction can be compared with the value of the charge exchange cross-section measured by Hasted <sup>7</sup> using beam techniques. The value he obtained was

$$\sigma = 2.8 \times 10^{-16} \text{ cm}^2$$

at an energy corresponding to 32,000°K, and this value tended to zero as the energy was reduced. The value obtained for the cross-section in the present work, although carried out at a lower energy, is larger than the above value.

The results described in this and the previous section have been described in more detail by Batey.<sup>8</sup>

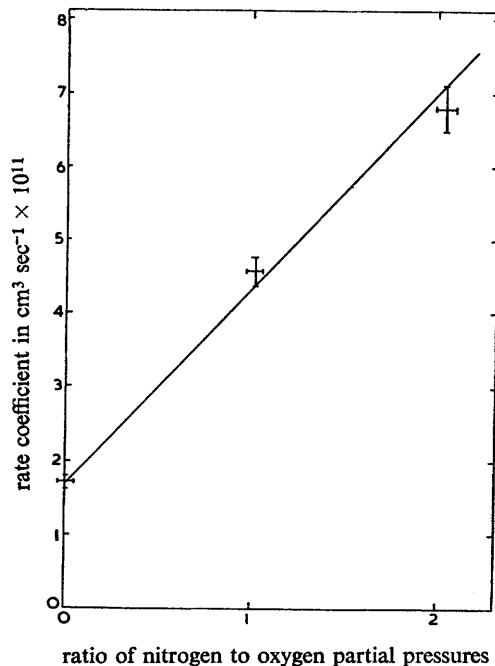


FIG. 2.—Variation of the effective rate coefficient for the reactions of the  $\text{O}^+$  ion in  $\text{N}_2 + \text{O}_2$  mixtures with the composition of the mixture at 293°K.

#### HELIUM + NITROGEN MIXTURES

The partial pressures of nitrogen were in the range  $10^{-4}$  to  $10^{-3}$  mm Hg and helium was added to make the pressure up to about 0.6 mm Hg. In fig. 3 the decay constant  $\lambda$  for the  $\text{He}^+$  ion density is shown as a function of the nitrogen partial pressure for two different discharge powers. The curve is expected to be a straight line with a small intercept on the decay constant axis corresponding to decay of the  $\text{He}^+$  ion by diffusion and conversion to the molecular ion only. However, the curves in fig. 3 show intercepts on the nitrogen partial pressure axis.

In order to explain this it has been suggested that a significant amount of dissociation of molecular nitrogen, which is assumed to be the neutral reacting species, occurs in the ionizing pulse. It must be further assumed that the number of dissociations is independent of the nitrogen partial pressure so that the partial pressure of molecular nitrogen is decreased by a constant difference from the measured value. The value of this constant difference would decrease with a decrease in the

discharge power, and so the forms of the curves in fig. 3 are explained. This assumption is not very satisfactory and the effect could be due to the phenomena of clean-up of nitrogen in the discharge.

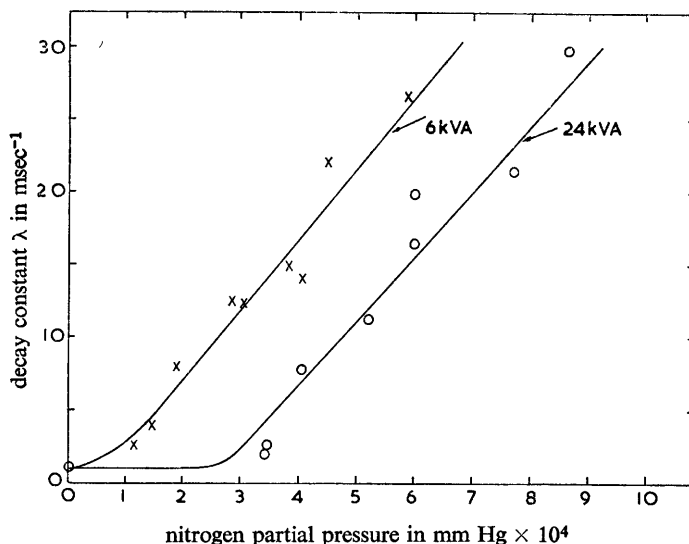


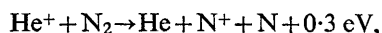
FIG. 3.—Decay constant for the  $\text{He}^+$  ion density in helium+nitrogen afterglows as a function of the nitrogen partial pressure for two discharge powers at 293°K.

On the assumption that the neutral reacting species was  $\text{N}_2$ , the rate coefficient at various temperatures—determined from straight lines drawn to the results as indicated in fig. 3—and the corresponding cross-sections are given in table 2.

TABLE 2

temp. °K	rate coefficient, $\text{cm}^3 \text{ sec}^{-1} \times 10^9$	cross-section, $\text{cm}^2 \times 10^{14}$
503	1.03	0.59
408	1.40	0.89
293	1.45	1.09
195	1.75	1.60

Similar measurements have been made by Fite and his co-workers<sup>2</sup> who find cross-sections of  $\sim 10^{-15} \text{ cm}^2$ . The present results are not sufficiently accurate to define the form of the dependence of the rate coefficient on temperature. However, since the cross-section decreases with increasing temperature, it may be deduced that if the mechanism of the charge exchange process is charge transfer the energy defect for the transfer is very small and the process may be accidentally resonant. Bates and Patterson<sup>9</sup> have suggested that the complex ion  $\text{HeN}^+$  is unlikely to be formed, and so the mechanism of the process is unlikely to be an ion-atom interchange reaction. In the present experiments the dominant nitrogen ion in the afterglow was found to be the atomic ion  $\text{N}^+$ , contrary to the observations of Fite who found the  $\text{N}_2^+$  ion to be dominant. The mechanism of the exchange reaction in the present experiments therefore appear to be dissociative charge transfer :



although the energy defect is rather larger than would be expected on the basis of

the experimentally determined variation of the cross-section with temperature. Some evidence was found of the presence in the afterglow of a very small density of a positive ion of mass 18 a.m.u., but it is possible that this was the ion  $\text{H}_2\text{O}^+$  released from the walls of the discharge vessel rather than the ion  $\text{HeN}^+$ .

#### HELIUM + OXYGEN MIXTURES

The first measurements in helium+oxygen mixtures were made by a similar method to that used for the experiments in helium+nitrogen mixtures. Oxygen partial pressures between  $10^{-4}$  to  $10^{-3}$  mm Hg were used, and helium was added to make the total pressure 0.6 mm Hg. However, it was noticed that the spectrometer signals representing the decay of the  $\text{He}^+$  ion density changed with time quite rapidly after initiation of the discharge, and that the value obtained for  $\lambda$  was dependent on the time between the initiation of the discharge and the exposure of the recording film. At a given measured pressure the values obtained for  $\lambda$  varied by up to a factor of three depending on this time. In order to investigate this effect further, the signals were photographed with a cine camera. The decay constants determined from various frames of a typical cine film are shown in fig. 4 as a function

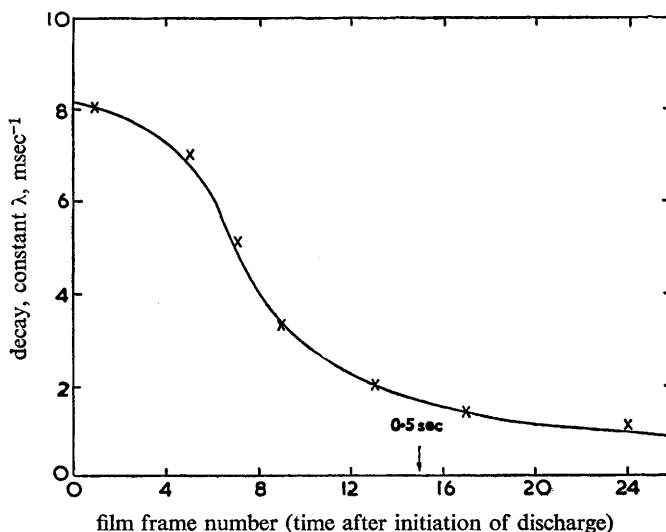


FIG. 4.—Typical variation of  $\lambda$  for the  $\text{He}^+$  ion density in helium+oxygen afterglows with time after initiation of the discharge. Initial partial pressure of oxygen is  $3 \times 10^{-4}$  mm Hg.

of the frame number. The frames were numbered starting from "1" at the first afterglow to be recorded. The time after initiation of the discharge is also indicated in fig. 4.

The shape of the curve in fig. 4 is largely explained by the phenomenon of clean-up. During an ionizing pulse, and in the afterglow following it, a proportion of the oxygen ions diffusing to the walls of the discharge vessel becomes permanently attached there. This process occurs during every ionizing pulse, but the number of available sites for oxygen on the walls becomes smaller as the number of occupied sites increases, and so the clean-up rate may be expected to decrease with time. The decay constant for the  $\text{He}^+$  ion density by charge exchange with oxygen may, therefore, be expected to decrease rapidly at first, and then more slowly as the rate of clean-up of oxygen decreases. The diffusion of oxygen from other parts of the



apparatus into the discharge vessel would tend to reduce the rate of decrease of the oxygen partial pressure in the discharge vessel. The initial slow rate of decrease of the decay constant is difficult to explain. It seems that before the oxygen may be adsorbed on to the walls, the walls must first be prepared by bombardment with oxygen ions. A possible reason for this is that the sites for oxygen must first be made available by the removal of other less active atoms, such as helium, which may initially occupy the sites.

If the curve of the decay constant against frame number is extrapolated to zero frame number, the decay constant indicated should be that which would be observed if the clean-up were not important. In fig. 5 the values of the extrapolated

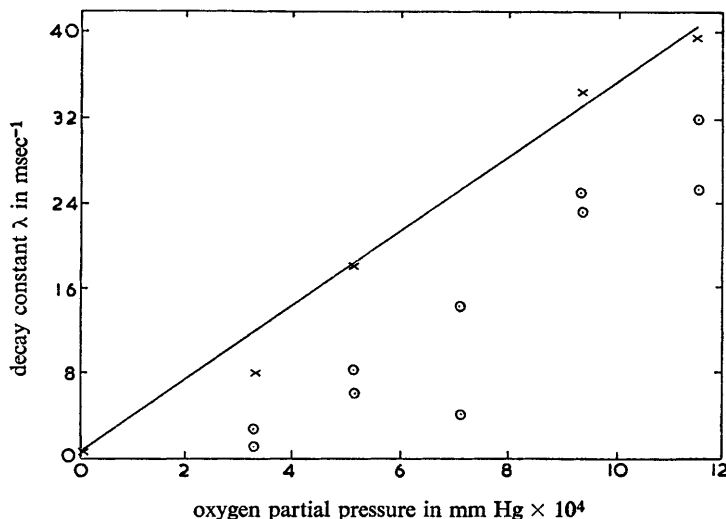


FIG. 5.—Variation of the extrapolated  $\lambda$  for the  $\text{He}^+$  ion density in helium+oxygen afterglows with the partial pressure of oxygen at 308°K.

decay constant at 308°K have been plotted against the partial pressure of oxygen. As the point at zero oxygen partial pressure, which corresponds to the decay of the  $\text{He}^+$  ion density in pure helium, is more accurately known than all the other points the best fit line to the experimental points has been drawn to pass exactly through this point. The points lying below the line, and marked with dots, represent decay constants that have been determined from a particular frame number of the cine films. They show how clean-up may affect the value obtained for the decay constant if the measurements are not made immediately after initiating the discharge. It would be possible to fit lines to the results modified by clean-up in the same way that lines were fitted to the results of the helium+nitrogen experiments, i.e., with an intercept on the partial pressure axis (see fig. 3). However, the intercept in these results is smaller than that in the helium+nitrogen results. As oxygen is a more reactive gas than nitrogen, the clean-up of oxygen was expected to be faster than that of nitrogen, and so a larger intercept was expected in the helium+oxygen results on the basis of the suggested clean-up mechanism. A reliable prediction of the variation of the intercept with the gas concerned cannot be made on the basis of the dissociation mechanism suggested in order to explain the intercept, because the cross-sections for the dissociating reactions are not known. The use of the cine camera technique in further helium+nitrogen experiments is, therefore,



required before the cause of the intercept may be satisfactorily explained. The rate coefficient determined from the line drawn in fig. 5 on the assumption that the neutral reacting species is the  $O_2$  molecule is

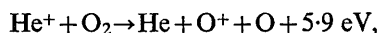
$$k = (1.05 \pm 0.08) \times 10^{-9} \text{ cm}^3 \text{ sec}^{-1},$$

and the corresponding cross-section is

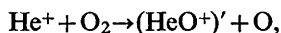
$$\sigma = (7.7 \pm 0.6) \times 10^{-15} \text{ cm}^2.$$

The errors in these measurements are probably due largely to inaccuracies in the measurement of pressure. Fite and his co-workers<sup>2</sup> have recently made similar measurements and found a rate coefficient of  $5 \times 10^{-10} \text{ cm}^3 \text{ sec}^{-1}$ , and a corresponding cross-section of about  $5 \times 10^{-15} \text{ cm}^2$ .

In the present experiments, as in those of Fite and his co-workers, the dominant oxygen ion in the early afterglow was the atomic ion  $O^+$ . This suggests that the process occurring is either dissociative charge transfer,



where some of the energy released is taken into excited states of the products, or the ion-atom interchange reaction suggested by Bates and Patterson,<sup>9</sup>



followed by a radiative dissociation,



Evidence was found to suggest the presence of a very small density of a positive ion at mass 20 a.m.u. in the very early afterglow. This signal appeared only when oxygen was admitted to the discharge vessel, and so was possibly the ion  $\text{HeO}^+$ . In fact, the rate coefficient for the  $\text{He}^+ + O_2$  reaction determined by the present experiments is in agreement with the value indicated by Bates and Patterson for the ion-molecule reaction (on the basis of the Gioumouis and Stevenson equation). If the ion-molecule reaction is the dominant charge exchange process, the  $\text{HeO}^+$  ion must dissociate very rapidly after formation because the mass 20 a.m.u. ion was present only in very small quantities in the very early afterglow. Fite and his co-workers found no trace of the  $\text{HeO}^+$  ion in helium+oxygen afterglows, and they suggest that dissociative charge transfer is the dominant process.

Design and construction of the apparatus used in the initial stages of the work, together with the results concerning the  $O^+$  ion, are due to Dr. G. R. Court and P. H. Batey.

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<sup>1</sup> Dickinson and Sayers, *Proc. Phys. Soc.*, 1960, **76**, 137.

<sup>2</sup> Fite, Smith, Stebbings and Rutherford, *J. Geophys. Res.*, 1963, **68**, 3225.

<sup>3</sup> Fite, Rutherford, Snow and Van Lint, *Disc. Faraday Soc.*, 1962, **33**, 264.

<sup>4</sup> Bates, *Proc. Phys. Soc. A*, 1955, **68**, 344.

<sup>5</sup> Gioumouis and Stevenson, *J. Chem. Physics*, 1958, **29**, 294.

<sup>6</sup> Nakamura, *J. Geomag. Geo-elec.*, 1961, **12**, 114.

<sup>7</sup> Hasted, *Proc. Roy. Soc. A*, 1951, **205**, 421.

<sup>8</sup> Batey, *Ph.D. Thesis* (University of Birmingham, England, 1962).

<sup>9</sup> Bates and Patterson, *Planet. Space. Sci.*, 1962, **9**, 599.