

## The Mobility of $O_2^+$ and $O_4^+$ Ions in Oxygen and the Equilibrium Constant for the Reaction $O_2^+ + 2O_2 \rightleftharpoons O_4^+ + O_2$ at 273 and 294 K

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### Abstract

The zero-field mobilities of oxygen ions in oxygen have been measured by the Bradbury-Nielsen time-of-flight method at temperatures of 194, 273 and 294 K and at pressures in the range 0.1–3.5 kPa. The zero-field reduced mobilities of  $O_2^+$  and  $O_4^+$  have been determined to be  $2.248 \pm 0.015$  and  $2.077 \pm 0.014 \text{ cm}^2 \text{ s}^{-1} \text{ V}^{-1}$  at both 273 and 294 K. The thermal equilibrium constant for the reaction  $O_2^+ + O_2 + O_2 \rightleftharpoons O_4^+ + O_2$ , obtained by fitting to the variation of the mobility with gas pressure, was found to be  $(3.4 \pm 0.5) \times 10^{-17}$  and  $(1.2 \pm 0.2) \times 10^{-17} \text{ cm}^3$  at 273 and 294 K respectively.

### Introduction

Special interest attaches to the study of ion transport and reactions in oxygen because the gas is a major atmospheric constituent. For this reason there have been several investigations of the characteristics of both positive and negative oxygen ions in oxygen in recent years. The work of Snuggs *et al.* (1971) and Elford and Rees (1974) resolved almost all the anomalies which existed in earlier mobility and reaction data for negative oxygen ions. The reactions involving the most common positive oxygen ions,  $O_2^+$  and  $O_4^+$ , are also well understood. The equilibrium constant for the first association (or clustering) reaction



has been measured with mass-spectrometric techniques over a range of temperatures (Yang and Conway 1964; Durden *et al.* 1969; Conway and Janik 1970; Payzant *et al.* 1973) and it has been concluded that the energy required to dissociate  $O_4^+$  into  $O_2^+$  and  $O_2$  is 0.46 eV. Kebarle and his colleagues (Durden *et al.*; Payzant *et al.*) have also studied the approach to equilibrium and determined the forward and reverse rate constants over the temperature range 88–350 K. In contrast, the situation with regard to positive oxygen ion mobility data is still far from clear. No reliable measurements of the mobility of  $O_4^+$  ions exist and many of the mobility results for  $O_2^+$  were obtained at pressures sufficiently high that the ions spent a significant fraction of their flight time as  $O_4^+$  or some other ion. In addition there are no data for the mobility of oxygen ions at other than room temperature.

In this work experimental mobility data were taken over a large range of pressures at 194, 273 and 294 K. From the data at 294 and 273 K the mobility of  $O_2^+$  and  $O_4^+$  ions and the equilibrium constant for the reaction (1) were determined.

At 194 K the mobility was found to be independent of pressure, indicating that only one ion (probably  $\text{O}_4^+$ ) was present in significant quantities. Many of the experimental details will not be given here as they were identical with those described in a recent investigation of the mobility and reactions of positive hydrogen ions (Elford and Milloy 1974). In particular, the experimental methods and apparatus were common to both investigations.

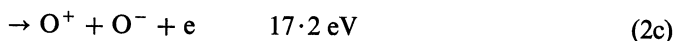
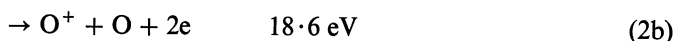
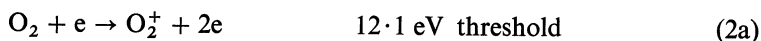
The mobility values quoted in this paper have been normalized to the standard gas number density and are referred to as reduced mobilities. The reduced mobility  $\kappa$  is obtained from the ionic drift velocity  $W$  by the relation

$$\kappa = W / \{ (E/N) N_s \},$$

where  $E$  is the electric field strength,  $N$  the gas number density and  $N_s$  the standard gas number density ( $2.687 \times 10^{19} \text{ cm}^{-3}$ ). Throughout the paper all values of  $\kappa$  are in units of  $\text{cm}^2 \text{ s}^{-1} \text{ V}^{-1}$ , all values of  $E/N$  are in townsend (1 Td  $\equiv 10^{-17} \text{ V cm}^2$ ) and all pressures quoted are in kilopascals (1 kPa = 7.501 torr).

### Production of Ions

At pressures less than about 1 kPa the primary ions  $\text{O}^+$  and  $\text{O}_2^+$  were produced mainly by electron impact. The following processes are known to occur:



The  $\text{O}^+$  ions are converted to  $\text{O}_2^+$  ions in the charge-exchange reaction



The rate constant for this reaction, about  $2 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$  at near thermal energies (McFarland *et al.* 1973, and references therein) is so large that the  $\text{O}^+$  ions only survive a few collisions. Thus the only primary ion species produced in the source which can exist in significant quantities outside it is  $\text{O}_2^+$ .

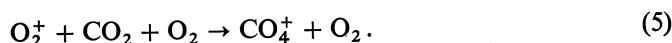
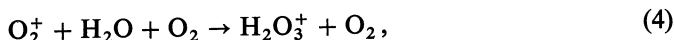
At pressures greater than about 1 kPa the ions were formed mainly by  $\alpha$ -particle impact (Elford and Milloy 1974). The ionization cross sections under these conditions do not appear to be known but there was no evidence that any ion species other than  $\text{O}_2^+$  was emitted from the source. There was also no evidence that the results reported below were affected by the presence of ions in different excitation states.

### Identification of Ion Species

#### 273 and 294 K

Two impurity ion species were detected in the drift tube used for the mobility measurements. The identities of these ions were first investigated by observing the effects of repeated flushing of the experimental tube with oxygen, by observing changes in the ion-current versus shutter-frequency spectrum with time and by placing a

liquid nitrogen trap in the gas inlet line. The identities deduced in this way were confirmed by using the drift-tube-mass-spectrometer system at 294 K to analyse the ions present under conditions of pressure and  $E/N$  identical with some of those used in the experimental tube. It was concluded from these tests that, apart from O<sub>2</sub><sup>+</sup>, O<sub>4</sub><sup>+</sup> and trace quantities of O<sub>6</sub><sup>+</sup> ions, there were small but significant quantities of H<sub>2</sub>O<sub>3</sub><sup>+</sup> and CO<sub>4</sub><sup>+</sup> ions present in the drift tube used for the mobility measurements. These impurity ions were probably formed in the reactions



Reaction (4) has been studied in detail (see e.g. Good *et al.* 1970; Fehsenfeld *et al.* 1971; Young and Falconer 1972). The water vapour was a slow outgassing product and the CO<sub>2</sub> was introduced with the gas (Matheson research grade). The relative abundance of the impurity ions increased with increasing pressure and the upper pressure limit for mobility measurements of the O<sub>2</sub><sup>+</sup>–O<sub>4</sub><sup>+</sup> system was set when the CO<sub>4</sub><sup>+</sup> ion peaks significantly distorted the oxygen ion peaks in the current-frequency spectrum. The exact level of CO<sub>2</sub> present in the incoming gas is not known but was stated by the supplier to be less than 10 p.p.m. The zero-field reduced mobilities of H<sub>2</sub>O<sub>3</sub><sup>+</sup> and CO<sub>4</sub><sup>+</sup> ions were measured at 294 K and 2 kPa and found to be  $2.29 \pm 0.01$  and  $1.99 \pm 0.01$  respectively.

#### 194 K

At 194 K an impurity ion species was detected at pressures greater than 1.0 kPa. This ion species was not positively identified when the drift-tube-mass-spectrometer system was used, probably because relatively low pressures were used (the upper pressure limit of this system is 0.4 kPa) and because of mass discrimination effects at the sampling aperture (Milloy and Elford 1975). The most abundant ion at this temperature was found with the mass-spectrometer system to be O<sub>4</sub><sup>+</sup>, but small quantities of O<sub>2</sub><sup>+</sup> and O<sub>6</sub><sup>+</sup> ions were also observed.

### Experimental Results

The zero-field reduced mobility  $\kappa_0$  could be accurately determined from the data, since at all pressures  $\kappa$  was found to be independent ( $<0.1\%$  dependence) of  $E/N$  in the range 0–10 Td. The variation of  $\kappa_0$  with pressure at 194, 273 and 294 K is shown in Fig. 1. At pressures less than about 0.5 kPa a larger  $E/N$  range could be used, and  $\kappa$  was found to be independent of  $E/N$  up to 20 Td. At higher  $E/N$  values  $\kappa$  was a decreasing function of  $E/N$  at 273 and 294 K and an increasing function of  $E/N$  at 194 K.

From the variation of  $\kappa_0$  with pressure at 273 and 294 K, the values of  $\kappa_0$  for O<sub>2</sub><sup>+</sup> and O<sub>4</sub><sup>+</sup> ions and the equilibrium constant for reaction (1) were determined in the following way. First it was established that the ion-current-frequency peaks were symmetrical and that  $\kappa$  was independent of the  $E/N$  value in the region between the source and the first electrical shutter. From these facts it was deduced that reaction (1) was in equilibrium by the time the ions reached the first shutter. It was then assumed that the identity of any single ion changed a number of times in its drift between the shutters. Under these conditions the variation of  $\kappa_0$  with gas

number density can be written

$$\kappa_0 = (\kappa_1 + \kappa_2 K_E N)/(1 + K_E N), \quad (6)$$

where  $\kappa_1$  and  $\kappa_2$  are the zero-field reduced mobilities of  $O_2^+$  and  $O_4^+$  respectively and  $K_E$  is the equilibrium constant defined to be the ratio of the forward to the reverse rate coefficients for reaction (1). Using equation (6), curves of best fit were obtained to the data at 273 and 294 K; these curves are shown by continuous lines in Fig. 1. The values of  $\kappa_1$ ,  $\kappa_2$  and  $K_E$  obtained from these fits were:

Parameter	$T = 273 \text{ K}$	$T = 294 \text{ K}$
$\kappa_1 (O_2^+)$	$2.248 \pm 0.007$	$2.248 \pm 0.007$
$\kappa_2 (O_4^+)$	$2.077 \pm 0.006$	$2.077 \pm 0.006$
$K_E (\text{cm}^3)$	$(3.4 \pm 0.5) \times 10^{-17}$	$(1.2 \pm 0.2) \times 10^{-17}$

The quoted errors are the fitting uncertainties. The maximum errors in the mobility data are the fitting errors plus a possible systematic error of  $\pm 0.4\%$  due to uncertainties in the experimental parameters. In the temperature range 273–294 K the values of  $\kappa_0$  for both  $O_2^+$  and  $O_4^+$  ions are independent of temperature while the equilibrium constant varies by about a factor of three.

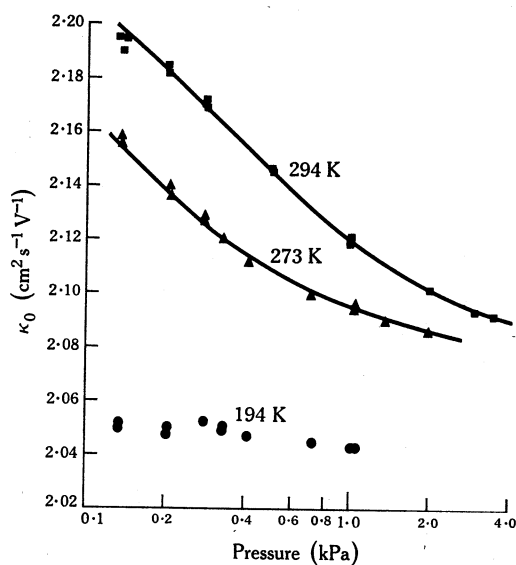


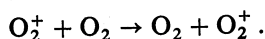
Fig. 1. Variation with pressure of the reduced zero-field mobility  $\kappa_0$  of oxygen ions in oxygen at the three indicated gas temperatures.

It was concluded from the small dependence of  $\kappa_0$  on pressure at 194 K that only one ion species was present in significant quantities at a pressure  $< 1$  kPa. From the work with the drift-tube and mass-spectrometer system and from the results of Conway and Janik (1970) and Payzant *et al.* (1973) it was concluded that the ion in question was  $O_4^+$ .

## Discussion

It has been shown that  $K_E$  decreases by almost a factor of three when  $T$  is increased from 273 to 294 K. In view of this large variation, it is at first sight

surprising that  $\kappa$  should be independent of  $E/N$  up to 20 Td at pressures where there are comparable quantities of O<sub>2</sub><sup>+</sup> and O<sub>4</sub><sup>+</sup> ions. One might expect that by  $E/N = 20$  Td the ion energy in the centre of mass frame would have increased sufficiently to alter the equilibrium constant, the relative abundance of the ions and hence the mobility. If charge-exchange effects were absent and if it is assumed that the mean free time of the O<sub>2</sub><sup>+</sup> ion is essentially constant, the change in total ion energy when  $E/N$  is increased from zero to 20 Td would be about 12% (Wannier 1953). This corresponds to a 6% change in energy for O<sub>2</sub><sup>+</sup> ions in the centre of mass frame, and on this basis one would expect  $K_E$  to change by a factor of 2.4. The reason no dependence on  $E/N$  is observed in this range is in fact due to the thermalizing effect of the charge-exchange process



A charge transfer collision between a fast ion and a gas molecule at rest results in the formation of a fast neutral particle and an ion with nearly zero velocity. This has a dramatic effect on the velocity averages (Skullerud 1969) and hence on the mean energy.

Table 1. Values of  $\kappa_0$  for oxygen ions in oxygen at  $\sim 294$  K

Values in parentheses are previous results corrected to take account of the time spent by O<sub>2</sub><sup>+</sup> ions in transit as O<sub>4</sub><sup>+</sup> (see text)

Authors	Mass identification	Reduced mobility $\kappa_0$	
		O <sub>2</sub> <sup>+</sup>	O <sub>4</sub> <sup>+</sup>
Dutton and Howells (1968)	No	$\sim 2 \cdot 14^A$	$(2 \cdot 20)$
Fleming and Rees (1969)	No	$2 \cdot 15 \pm 0 \cdot 03$	$(2 \cdot 19)$
Varney (1970)	Yes	$2 \cdot 4 \pm 0 \cdot 1$	$(2 \cdot 42)$
Snuggs <i>et al.</i> (1971)	Yes	$2 \cdot 24 \pm 0 \cdot 07$	$(2 \cdot 26)$
Present work	Indirect	$2 \cdot 248 \pm 0 \cdot 015$	$2 \cdot 077 \pm 0 \cdot 014$

<sup>A</sup> Error limit not quoted.

<sup>B</sup> O<sub>4</sub><sup>+</sup> ions not observed in a mass spectrometer at pressures  $\sim 0 \cdot 13$  kPa.

In Table 1 the values of  $\kappa_0$  obtained in the present work for O<sub>2</sub><sup>+</sup> and O<sub>4</sub><sup>+</sup> at  $\sim 294$  K are compared with the four most recent determinations of the mobilities of positive oxygen ions in oxygen. Earlier investigations of the mobility of O<sub>2</sub><sup>+</sup> ions have been summarized by Snuggs *et al.* (1971) and are now only of historical interest. The values of  $\kappa_0$  for O<sub>4</sub><sup>+</sup> ions quoted in Table 1 are the only ones available. At first sight there are large differences between many of the O<sub>2</sub><sup>+</sup> ion results. These differences are somewhat reduced when the results are corrected to take account of the fact that in each investigation the pressures used were sufficiently high that the ions spent a significant part of their transit times as O<sub>4</sub><sup>+</sup> ions. The corrected results are shown in parentheses in Table 1. The O<sub>4</sub><sup>+</sup> ion results are more confusing. Whereas both Dutton and Howells (1968) and Fleming and Rees (1969) reported that  $\kappa_0$  for O<sub>4</sub><sup>+</sup> was larger than  $\kappa_0$  for O<sub>2</sub><sup>+</sup>, it is concluded from the work of Snuggs *et al.* (1971) and from the present work that the opposite is the case. It seems likely that the more mobile of the ions present in the work of Dutton and Howells and of Fleming and Rees was an impurity ion, probably H<sub>2</sub>O<sub>3</sub><sup>+</sup>. This

suggested identity is consistent with the present conclusion that the mobility of  $\text{H}_2\text{O}_3^+$  ions is 2% larger than the mobility of  $\text{O}_2^+$  ions, and with the observation that significant quantities of  $\text{H}_2\text{O}_3^+$  ions were observed in this work although the ultimate pressure in both the systems used ( $\sim 10^{-9}$  kPa) was two orders of magnitude lower than in the apparatus used by Fleming and Rees.

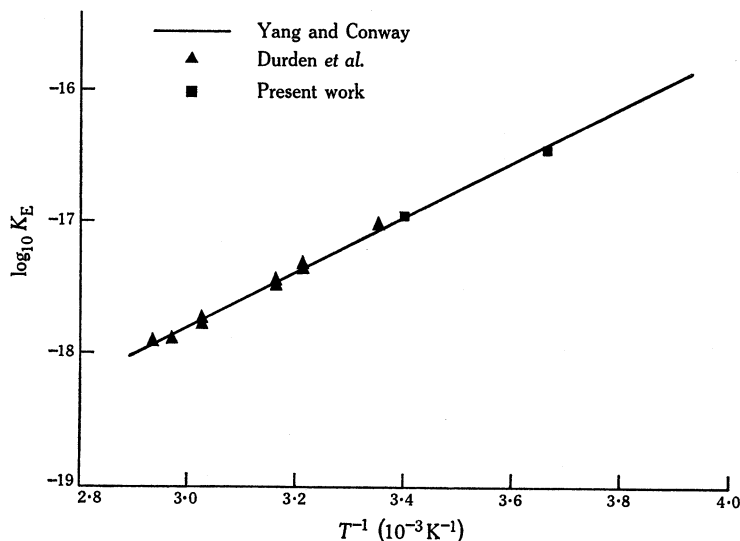


Fig. 2. Plot of  $\log_{10} K_E$  as a function of  $T^{-1}$ . (Values of  $K_E$  are in units of  $\text{cm}^3$ .) The results from the present work are compared with the data of Yang and Conway (1964) and Durden *et al.* (1969).

There is excellent consistency between the values of the equilibrium constant determined in this work and the results of the most recent mass-spectrometric determinations. The results are compared on a Van't Hoff plot in Fig. 2: the continuous line in the figure is the curve of best fit to the data of Yang and Conway (1964), while the triangles represent the data of Durden *et al.* (1969) and the results of the present work are shown by squares. The accuracy of the method used here to determine the equilibrium constants is critically dependent on the scatter in the mobility measurements. In this work it was necessary for the random errors to be less than about  $\pm 0.15\%$  in order to determine the equilibrium constant to  $\pm 15\%$ , although this restriction would have been relaxed if the difference between the mobilities of  $\text{O}_2^+$  and  $\text{O}_4^+$  ions had been larger. The error limits quoted compare favourably with the previous investigations.

## Conclusions

All previous investigations of the zero-field mobility of positive oxygen ions in oxygen have been restricted to the pressure range where the ions spend significant fractions of their transit time as both  $\text{O}_2^+$  and  $\text{O}_4^+$  ions. Partly for this reason there had been no previous unambiguous determinations of the zero-field mobility of either ion. The present study has concentrated on the pressure dependence of the mobility over a large pressure range so that, by fitting the data to the relationship describing the rapid change of ion identity, the mobilities of both ions have been

derived. The equilibrium constant for the reaction  $\text{O}_2^+ + 2\text{O}_2 \rightleftharpoons \text{O}_4^+ + \text{O}_2$  has also been determined, but unfortunately it is not possible to use this information about the reaction to discuss the structure of the O<sub>4</sub><sup>+</sup> ion since no theoretical estimates of the structure have yet been reported.

### Acknowledgments

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