The Mobility of
Negative Ions in Oxygen (293 K)

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Abstract

The Bradbury–Nielsen time-of-flight method has been used to measure the mobilities of six species of negative ions in oxygen at 293 K for gas pressures within the range 1·3–22 torr and E/N values within the range 3–130 Td. The species were identified as O^-, O_2^-, O_3^-, O_4^-, CO_3^- and CO_4^- by the addition of known quantities of selected contaminants and by the removal of condensible impurities via a liquid nitrogen trap. The present mobility data for O^-, O_2^-, O_3^-, CO_3^- and CO_4^- agree with those of Snuggs *et al.* (1971) to within the combined limits of experimental error over the common range of E/N values. However, the present data for O_4^- are in significant disagreement with those of Snuggs *et al.* for this ion. The zero field reduced mobilities ($cm^2 s^{-1} V^{-1}$) were estimated to be $2·55 \pm 0·03$ for O_3^-, $2·30 \pm 0·02$ for O_4^-, $2·51 \pm 0·03$ for CO_3^-, $2·38 \pm 0·02$ for CO_4^- and $3·01 \pm 0·04$ for a species of unknown identity. Previous measurements of the mobility of negative ions in oxygen, made without direct mass identification, have been examined and the identifications of the ions are discussed.

1. Introduction

Although there have been a very large number of studies of the mobility of negative ions in oxygen (Nielsen and Bradbury 1937; Doehring 1952; Burch and Geballe 1957; McDaniel and Crane 1957; Chanin *et al.* 1962; Eiber 1963; Beaty *et al.* 1964; Rees 1965; Voshall *et al.* 1965; Dutton and Howells 1968; Shafer and Beaty 1969; McKnight 1970; Varney 1970; McKnight and Sawina 1971; Snuggs *et al.* 1971; Harrison and Moruzzi 1972) much of the data is confusing and in many cases the experimental scatter is large. Only recently, since the advent of direct identification of ion species by means of quadrupole mass spectrometers, has the situation become clearer. However, even in the most extensive investigation of this type (Snuggs *et al.*) the zero field mobilities were quoted with an error of $\pm 3\%$ and the data were scattered by $\pm 1\%$ about the curves of best fit. Moreover the data concerning cluster ions are limited, and this information is important when assessing the data in the literature.

The aim of the present work was to obtain data of high precision over a large range of values of pressure p and E/N (where E is the electric field strength and N is the gas number density) with particular emphasis on studying the mobility of cluster ions formed by reactions with impurities. Since a drift tube with no facilities for direct mass identification of ion species was used in this work, it was necessary to identify the ions by the introduction of known contaminants to pure gas samples.

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The present work is intended to supplement that of Snuggs et al. (1971) and to make use of the particular advantages, in terms of measurement signal, low noise, high stability and accuracy of pressure measurement, that are the features of drift tubes operated under static gas conditions at relatively high gas pressures. Measurements with this type of drift tube are also not subject to the formation and dissociation of ion species which may occur in the ion extraction system of a combined drift-tube–mass-spectrometer apparatus.

In an attempt to resolve some of the anomalies in previous sets of data, we have made a detailed investigation of the experimental parameters and the purity of the oxygen used in these previous measurements. Although the suggested reassignment of the identities of ions measured by some other workers and the assessment of their error limits has had to be somewhat arbitrary, the evidence leading to each reassignment is given and discussed. As a result of this examination it has been found that the data for the zero field reduced mobilities of oxygen negative ions in oxygen now fall into reasonable agreement, with one notable exception which is discussed in Section 4a.

2. Experimental Apparatus

The method used to measure ion mobilities was that of Bradbury and Nielsen (1936). The experimental tube, measuring equipment and technique have been described in detail by Crompton et al. (1970) and Elford (1972) and is not discussed here. The negative ions were formed by attachment of electrons produced by α-particle ionization, and this limited the measurements to pressures greater than $\sim 1 \cdot 5$ torr. The frequencies at which the peaks of the ion current spectrum had their maximum value were determined graphically. Because of the number of ion species each producing its own spectrum of ion current maxima, care had to be taken to ensure that any interference between the maxima of different species did not give rise to a significant error in the measurement of the ionic drift velocity.

A typical ion-current–shutter-frequency spectrum is shown in Fig. 1a. It illustrates the low scatter in the ion current measurements (none of the 300 datum points are shown since 95 % of them fall within the thickness of the line), the degree of resolution, and the complexity that can occur. Five ion species denoted by A, B, C, D and E are present in Fig. 1a, each contributing a spectrum of ion current maxima. A separation of this spectrum into the individual ion current spectra for each species was performed graphically and is shown in Fig. 1b. Note that the ion species D has a distorted ion current spectrum as a result of ions undergoing reactions during transit. Although reaction rates may be derived by fitting theoretical expressions to such ion current curves (see e.g. Snuggs et al. 1971), this has not been attempted in the present work as there is too great a possibility of a significant interference from other species for such a procedure to yield accurate reaction rates.

The oxygen used in the present work was obtained from two sources:

(1) Airco reagent grade gas in a 1 litre pyrex glass flask. This was stated by the supplier to contain an impurity level of < 400 p.p.m., comprising nitrogen 192 p.p.m., argon 192 p.p.m. and carbon dioxide 9 p.p.m. These are general values for gas of this grade and not for the particular flask. An assay by the supplier of a similar flask to that used gave a carbon dioxide level of 65 p.p.m. and hence it must be concluded that the amount of carbon dioxide in the gas employed in the present

measurements could easily have been much greater than the 9 p.p.m. general value. The Airco gas was of the same type as that used by Chanin *et al.* (1962) and Rees (1965).

(2) Research grade gas supplied by the Matheson Company in a high pressure stainless steel cylinder. The analysis provided by the supplier showed: nitrogen, <4 p.p.m.; argon, <5 p.p.m.; carbon dioxide, <2·5 p.p.m.

The significance of the impurity levels of carbon dioxide is discussed in Sections 3*b* and 4. The experimental tube was operated in a water bath to prevent significant fluctuations in gas temperature and all data were taken at 293 K.
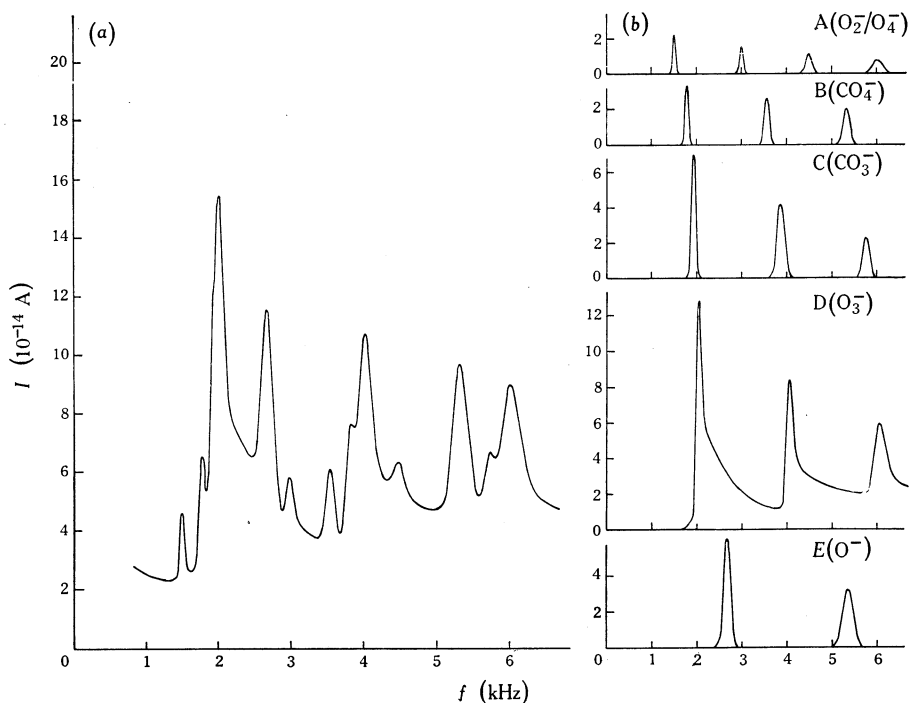

Fig. 1. Typical ion current spectrum (*a*) for Matheson research grade oxygen without further purification ($p_{273} = 2\cdot74$ torr and $E/N = 51\cdot8$ Td) and its decomposition (*b*) into the contributions of five separate ion species A–E. The background electron current has been removed in (*b*). Note that the distortion in the spectrum for species D is caused by ions undergoing reaction during transit.

3. Identification of Ion Species

The identities of the ion species observed in the present work were investigated in the following ways. Firstly, liquid nitrogen trapping was introduced. Those ion species with current maxima which decreased were taken to be ion cluster species, the neutral of the cluster being that of a condensible impurity. Secondly, specific impurities were introduced and the increase or decrease in certain species was observed. In order to confirm the identities, a comparison was made with the zero field mobility values of Snuggs *et al.* (1971) as these data are considered to be the most reliable at present available for direct mass identified ion species. The tests for ion identity are now considered in detail.
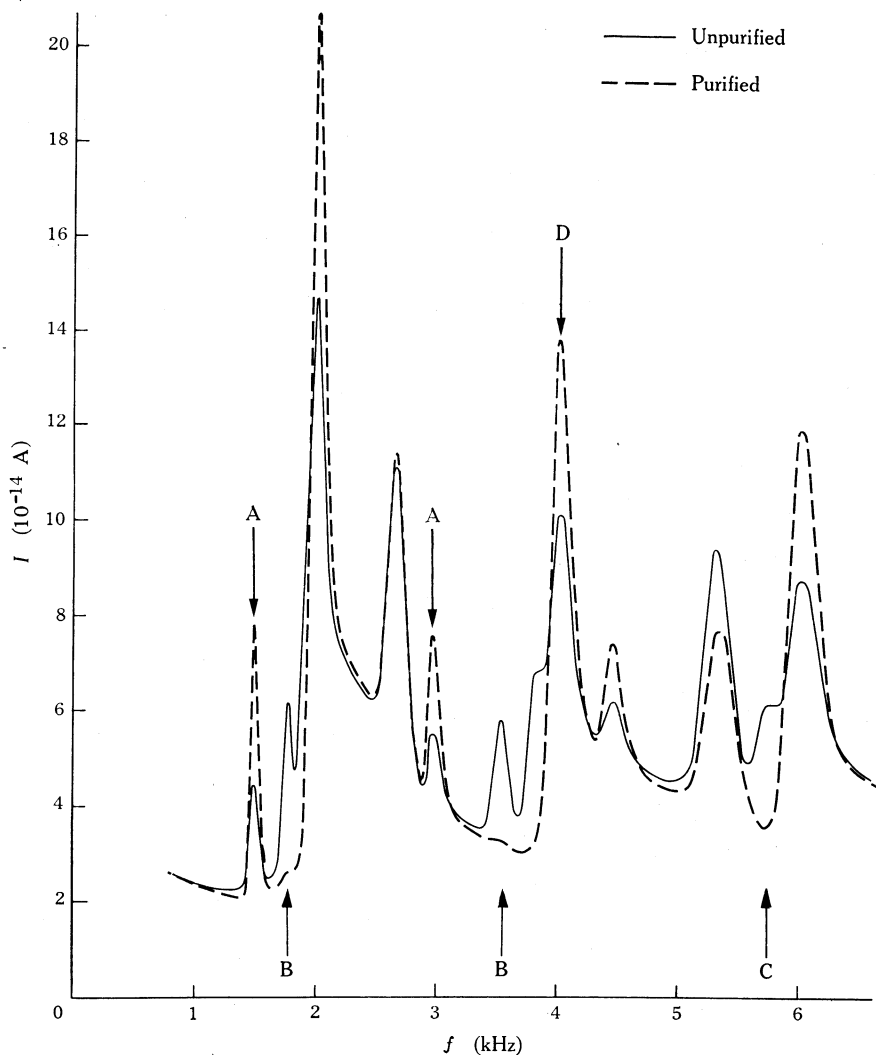
Fig. 2. Comparison of the ion current spectra for Matheson research grade oxygen before and after purification by liquid nitrogen trapping. The reduction of the maxima for B and C shows that these species are associated with condensible impurity molecules.

(a) Effect of Trapping Out Impurities

The effect of reducing the level of condensible impurities in the gas can be seen from Fig. 2. The ion current spectrum (solid curve) was taken with Matheson research grade oxygen without purification and shows five ion species to be present. The measurement was repeated under the same experimental conditions but with research grade gas which had previously been maintained in a volume separate from the experimental tube but in contact with a liquid nitrogen trap for approximately 24 hr. The ion current spectrum was measured immediately on letting the gas into the experimental tube. During the measurement a liquid nitrogen trap situated in the pumping line close to the tube envelope was kept cold. The ion current

spectrum taken under these conditions (dashed curve of Fig. 2) shows several significant differences from that taken with the unpurified gas. Both the maxima corresponding to species B and C have been reduced to a negligible level, while the decrease in the maxima of species B is equal to the increase in the corresponding maxima of species A, and the decrease in the maxima of species C is equal to the increase in the corresponding maxima of species D. From these observations it can be concluded that B and C are cluster ions formed by the reaction of the oxygen ion species A and D respectively with molecules of condensible impurities. Further evidence for the identities of the species B and C was obtained by selective addition of contaminants.
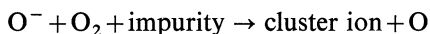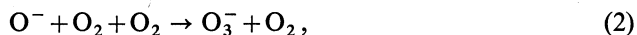
(b) Effect of Adding Contaminants

No information was obtained concerning the identity of species F since this species was found to be unobservable when the Matheson research grade gas was used (without liquid nitrogen trapping), the Airco oxygen having been expended. In an effort to produce species F, the contaminants H_2, N_2 and CO_2 were added both singly and in various combinations and over a range of impurity levels to the Matheson gas. No species F peak was observable in the ion current spectra taken throughout these tests and the identity of species F is therefore unknown. The measurements of species F could be disregarded were it not for the fact that both Chanin et al. (1962) and Rees (1965) used oxygen from an Airco flask similar to the one used in the present work and observed an ion species which had a zero field reduced mobility in close agreement with the present value for species F. The identification of the ion species observed by Chanin et al. and Rees is discussed in detail in Sections 5e and 5g respectively.

Addition of hydrogen. One of the most useful tests for establishing the identity of an ion species is the addition of hydrogen to the oxygen sample. The presence of hydrogen makes possible the associative detachment reaction

$$O^- + H_2 \rightarrow H_2O + e^-, \tag{1}$$

which was first demonstrated by Moruzzi and Phelps (1966). The rate coefficient was estimated to be about 11×10^{-10} cm^3 s^{-1}. This reaction greatly reduces the number density of the O^- ions and so virtually prevents the formation of any product ions by competing reactions such as

$$O^- + O_2 + O_2 \rightarrow O_3^- + O_2, \tag{2}$$

$$O^- + O_2 + \text{impurity} \rightarrow \text{cluster ion} + O$$

or

$$O^- + O_2 \rightarrow O_2^- + O. \tag{3}$$

Fig. 3a (solid curve) shows an ion current spectrum taken at 2·74 torr and $E/N = 56·6$ Td* with Matheson gas which had not been further purified. When 500 p.p.m. of H_2 was added, the ion current spectrum shown by the dashed line was obtained. This particular spectrum has been displaced vertically downwards to fit the first-order peak of species A. The displacement compensates for the increase in background current due to electrons produced by associative detachment in the

* 1 townsend (Td) = 10^{-17} V cm^2.

reaction (1). The peaks corresponding to species C and D were greatly reduced while that corresponding to species E was eliminated, thus indicating that the impurity species C has O^- as its parent ion. On the basis of this test, the oxygen ion species D and E may be tentatively identified as O_3^- and O^-. Species A and B are unaffected by the addition of hydrogen and hence have O_2^- as their parent ions. Species A may be identified as O_2^-, O_4^-, or related to these ions in some way (Section 4a). It should be noted that an additional ion species (X of Fig. 3a, dashed curve) was observed when hydrogen was added to the oxygen sample. Species X is not related to a condensible impurity since the magnitude of the ion current peak due to this species was unaffected by liquid nitrogen trapping. However, in the absence of other information it is not possible to identify species X. (See note added in proof p. 355.)
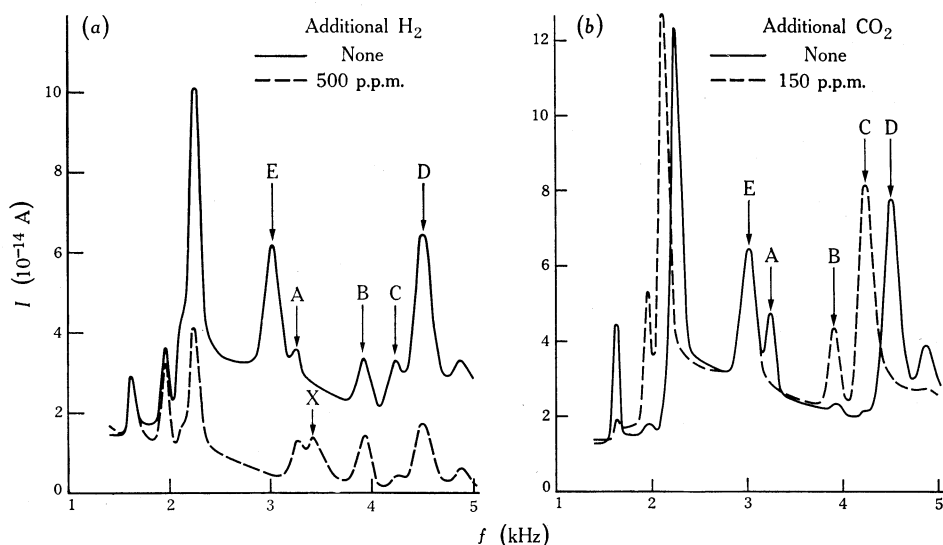

Fig. 3. Effect of the addition to Matheson research grade oxygen ($p_{273} \approx 2 \cdot 75$ torr, $E/N = 56 \cdot 6$ Td) of the impurities (a) hydrogen and (b) carbon dioxide in the concentrations indicated. Before addition of the impurities, the oxygen in (a) had not been further purified while that in (b) had been held in contact with a liquid nitrogen trap for 3 hours. The impurity spectrum in (a) has been displaced vertically and normalized to the species A peak of the original spectrum so as to take account of the increased electron current background due to the associative detachment reaction of H_2 with O^- ions. Note the reduction of the maxima for species C, D and E, and the appearance of an additional species X, upon the addition of hydrogen, and the increase in the maxima for species B and C upon the addition of carbon dioxide.

Addition of nitrogen. The addition of 1400 p.p.m. of N_2 had no significant effect on the ion current spectra and it may therefore be concluded that none of the impurity ion species are related to nitrogen.

Addition of carbon dioxide. The effects of carbon dioxide on negative-ion–molecule reactions in oxygen were first investigated by Moruzzi and Phelps (1966) who showed that, in the presence of CO_2, the ions O_2^- and O^- are converted to CO_4^- and CO_3^- respectively. The reaction which they postulated for the formation of CO_4^- is

$$O_2^- + O_2 + CO_2 \rightarrow CO_4^- + O_2. \tag{4}$$
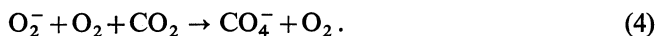
The CO_3^- is formed in a similar reaction:

$$O^- + O_2 + CO_2 \rightarrow CO_3^- + O_2. \tag{5}$$
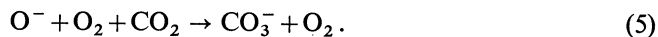
Both CO_3^- and CO_4^- may also be formed in two body reactions:

$$O_3^- + CO_2 \rightarrow CO_3^- + O_2 \tag{6}$$

and

$$O_4^- + CO_2 \rightarrow CO_4^- + O_2. \tag{7}$$

By examination of the rates for the above reactions, it is possible to determine which are the dominant reactions under the present experimental conditions. The reaction rates used in this examination were: reaction (4), 2×10^{-29} cm^6 s^{-1} (Moruzzi and Phelps 1966); reaction (5), 3×10^{-29} cm^6 s^{-1} (Moruzzi and Phelps 1966); reaction (6), 4×10^{-10} cm^3 s^{-1} (Fehsenfeld *et al.* 1967); reaction (7), $4 \cdot 3 \times 10^{-10}$ cm^3 s^{-1} (Fehsenfeld *et al.* 1969). It was found that the dominant reactions were (6) and (7) under the present experimental conditions. It should be noted, however, that the above-quoted are thermal reaction rates and apply with any certainty only at relatively low values of E/N.

One or both of the cluster ions CO_3^- and CO_4^- has been observed in ion mobility measurements in which mass identification was employed. Shafer and Beaty (1969) reported the observation of CO_3^- but not CO_4^-, while McKnight (1970) reported the observation of both CO_3^- and CO_4^- and found that, at high pressures (> 4 torr) and at very low values of E/N ($\ll 2$ Td), these cluster ions were the principal ions present. Both CO_3^- and CO_4^- were also observed by Snuggs *et al.* (1971). In view of this evidence it would seem very probable that the impurity ion species B and C are CO_4^- and CO_3^- respectively. Additional evidence tends to confirm this identification: the addition of hydrogen as a contaminant indicates that species B and C have O_2^- and O^- as their parent ions respectively and, when measurements are made over a long period of time with a given gas sample, both the peaks due to B and C increase in magnitude, as would be expected as a result of outgassing.

In order to confirm that species B and C are specifically connected to CO_2 and not to other contaminants (e.g. water vapour), tests were made by adding CO_2 in known amounts to a previously purified sample of oxygen. Fig. 3*b* shows the effect of adding 150 p.p.m. of CO_2 to a sample of oxygen at $p_{273} = 2 \cdot 75$ torr and $E/N = 56 \cdot 6$ Td. In the pure sample, the peak in the ion current spectrum (solid curve) due to species C is only just observable, even in the second-order of the ion current spectrum. When CO_2 is added (dashed curve) the peaks due to species B and C are greatly enhanced at the expense of those due to species A and D. We therefore conclude that species B and C are cluster ions and assume that an oxygen ion is attached to one CO_2 molecule in each case.

As a result of the above-described tests, these tentative identifications may be made:

Species	Probable identity	Species	Probable identity
A	O_2^-, O_4^-, or related to them	D	O_3^-
B	CO_4^-	E	O^-
C	CO_3^-	F	impurity (unknown identity)

4. Discussion and Comparison of Mobility Data

The present mobility data for each of the ion species A–F are now examined and compared with the corresponding data obtained by Snuggs *et al.* (1971; hereinafter designated SN). The tentative identifications advanced in Section 3 are given in parentheses after the species letter. The present reduced mobility of species $A(O_2^-/O_4^-)$, $B(CO_4^-)$, $C(CO_3^-)$, $D(O_3^-)$, $E(O^-)$ and F(impurity) are listed in Tables 1*a*–1*f* as a function of $E/p_{273.2}$, E/N and $p_{273.2}$. The reduced mobility κ is defined by

$$\kappa = \frac{W}{760\,E/p_{273\cdot2}} = \frac{273\cdot2\,Wp_T}{760\,ET} \quad cm^2\,s^{-1}\,V^{-1},$$

where W (cm s^{-1}) is the drift velocity, T (K) is the gas temperature, and the conversion from E/p to E/N is $E/N = 2\cdot828\,E/p_{273\cdot2}$ Td. The units of κ are $cm^2\,s^{-1}\,V^{-1}$ throughout this paper.
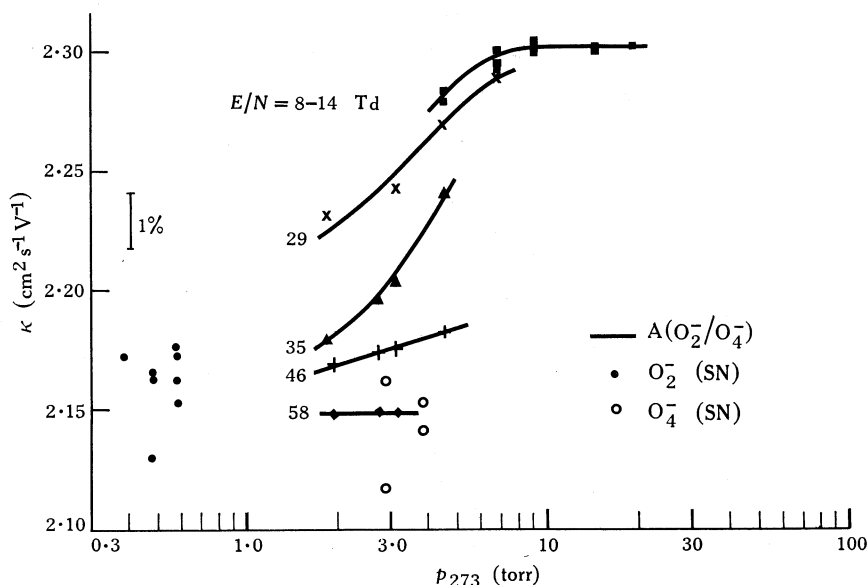
Fig. 4. Reduced mobility κ of the ion species $A(O_2^-/O_4^-)$ as a function of p_{273} at the indicated values of E/N. The data of SN for O_2^- at $E/N < 10$ Td are shown by full circles and for O_4^- at $E/N < 5$ Td by open circles. For $E/N < 10$ Td the reduced mobility is expected to be independent of E/N.

Tabulating the data as a function of gas pressure has two advantages: it enables the degree of experimental scatter to be assessed and permits a dependence of the ion mobility on gas pressure to be observed. Such a dependence indicates the presence of an ion–molecule reaction and, in such cases, the mobility cannot be taken as that of an ion species which has retained its identity throughout its transit of the drift tube. In the present work only the data for species A show a systematic dependence of mobility on pressure, thus indicating the presence of an ion–molecule reaction. In order to illustrate this dependence, the mobility data for species A have been plotted in Fig. 4 as a function of $p_{273\cdot2}$ for five values of E/N, the range of pressures being 1·3–20 torr. The lower limit to the gas pressure was set by insufficient ion
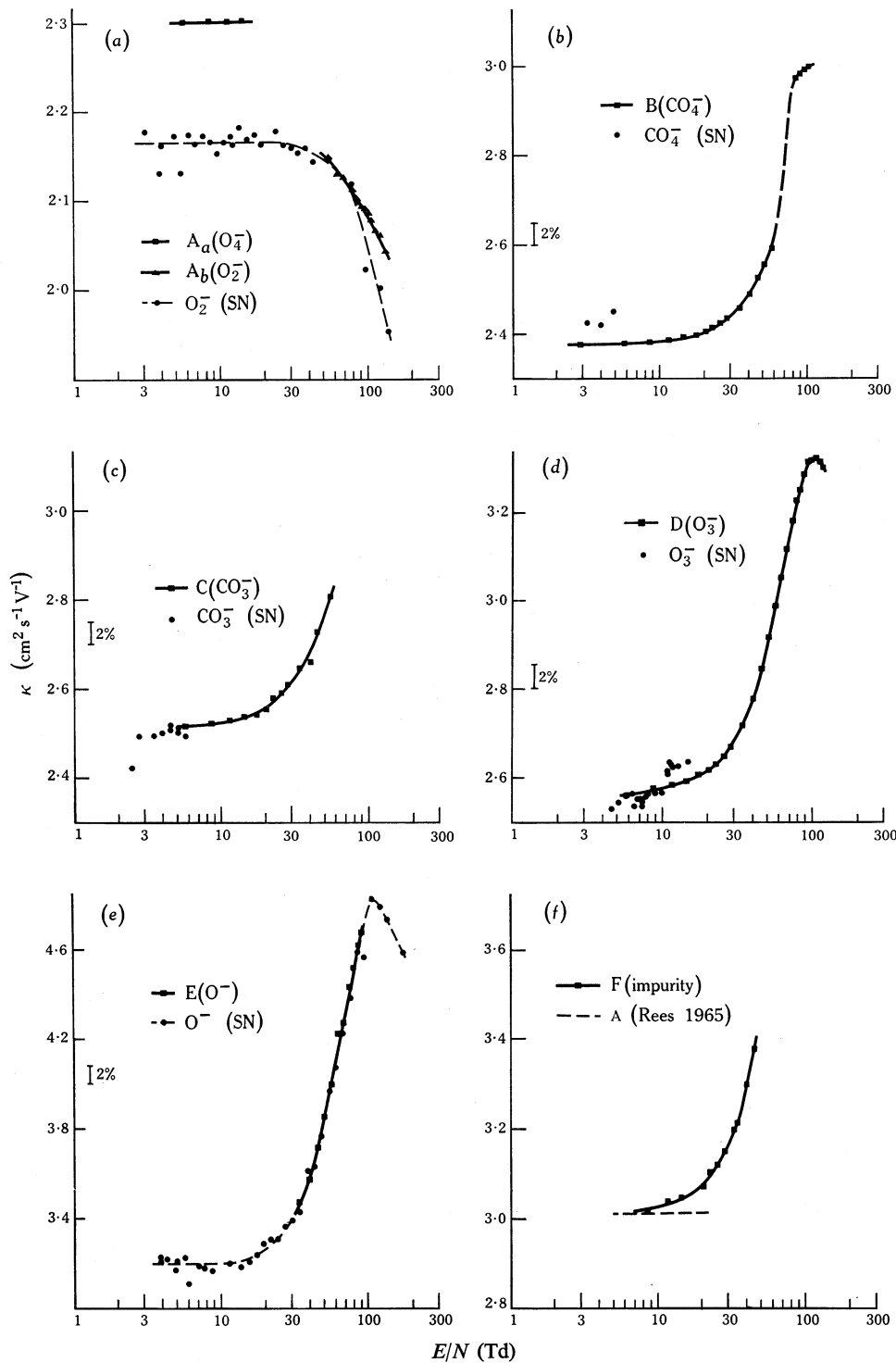
Fig. 5. Comparison of the present results with those of SN for the reduced mobility κ as a function of E/N for the indicated ion species. The data of SN for species $Ab(O_4^-)$ are not shown here for clarity but may be seen in Fig. 4.

current for accurate measurement and the upper limit was set by the dominance of clustering reactions with impurities. The cause of the pressure dependence of the reduced mobility of species A at a fixed value of E/N is discussed in subsection (a) below.

The 'best estimate' values of the reduced mobility given in Tables 1a–1f are plotted as a function of E/N in Figs 5a–5f. The data of SN, where available, are included for comparison.

(a) Species $A(O_2^-/O_4^-)$

The largest variation observed in the reduced mobility of species A with change of pressure was at $E/N = 28 \cdot 7$ Td, where the reduced mobility increases by $2 \cdot 6 \%$ as the gas pressure increases from $1 \cdot 85$ to $6 \cdot 86$ torr. The variation with gas pressure decreases as the value of E/N increases, and becomes negligible for $E/N \gtrsim 60$ Td.

Table 1. **Reduced mobility of negative ions in oxygen (293 K)**

E/p_{273} (V cm^{-1} torr^{-1})	E/N (Td)	κ (cm^2 s^{-1} V^{-1}) at p_{273} (torr) of:								
		1·31	1·85	2·74	3·17	4·58	6·86	9·22	14·8	19·8
			(a) Species $A(O_2^-/O_4^-)$							
2·022	5·72								2·299	2·300
3·035	8·58							2·303	2·299	2·301
4·052	11·46					2·280	2·299	2·298	2·301	
5·067	14·33					2·283	2·291	2·302		
6·081	17·20					2·278	2·294	2·300		
7·094	20·06					2·283	2·295	2·304		
8·108	22·93					2·280	2·293	2·304		
9·125	25·81					2·274	2·292			
10·157	28·73		2·231		2·242	2·269	2·288			
12·204	34·52		2·179	2·196	2·203	2·240				
14·238	40·27		2·170	2·183	2·191	2·208				
16·272	46·02		2·168	2·173	2·174	2·182				
18·321	51·82		2·150	2·151	2·156					
20·356	57·57		2·148	2·149	2·149					
22·389	63·32		2·129	2·129						
24·424	69·08		2·130	2·120						
26·461	74·84		2·124	2·117						
28·467	80·51		2·113							
30·500	86·26		2·103							
32·534	92·02		2·084							
34·567	97·77	2·093	2·088							
36·600	103·52	2·085	2·086							
38·634	109·27		2·077							
40·667	115·02		2·065							
42·67	120·68	2·060								
46·67	131·99	2·041								

E/p_{273}	E/N	Best estimate	E/p_{273}	E/N	Best estimate
		Species $Aa(O_4^-)$			
2·022	5·72	2·300	4·052	11·46	2·300
3·035	8·58	2·301	5·067	14·33	2·302

E/p_{273}	E/N	Best estimate	E/p_{273}	E/N	Best estimate
		Species $Ab(O_2^-)$			
20·36	57·57	2·149	34·57	97·77	2·090
22·39	63·32	2·129	36·60	103·5	2·085
24·42	69·08	2·125	38·63	109·3	2·077
26·46	74·84	2·120	40·67	115·0	2·065
28·47	80·51	2·113	42·67	120·7	2·060
30·50	86·26	2·103	46·67	132·0	2·041
32·53	92·02	2·084			

Table 1 (*Continued*)

E/p_{273}	E/N	$p_{273} = 1\cdot84$	$2\cdot75$	$3\cdot17$	$4\cdot58$	$6\cdot86$	$9\cdot22$	$14\cdot8$	$19\cdot8$	$21\cdot8$	Best estimate
				(*b*) *Species* $B(CO_4^-)$							
1·012	2·862						2·396			2·376	2·376
2·023	5·722						2·386	2·371	2·375		2·377
3·036	8·587					2·381	2·384	2·377	2·377		2·380
4·050	11·45					2·387	2·386	2·382			2·385
5·064	14·32					2·390	2·391				2·391
6·078	17·19					2·397	2·398				2·397
7·090	20·05					2·405	2·406				2·405
8·103	22·92					2·416	2·412				2·414
9·125	25·81				2·418	2·427					2·423
10·139	28·68				2·429	2·437					2·433
12·175	34·43				2·459						2·459
14·230	40·25			2·493	2·485						2·489
16·274	46·03		2·523	2·528	2·517						2·523
18·321	51·82		2·541	2·564							2·553
20·368	57·61		2·590	2·591							2·590
30·50	86·26	2·968									2·968
32·53	92·02	2·977									2·977
34·57	97·77	2·992									2·992
36·60	103·5	2·991									2·991

E/p_{273}	E/N	$p_{273} = 2\cdot74$	$4\cdot58$	$6\cdot86$	$9\cdot22$	Best estimate
			(*c*) *Species* $C(CO_3^-)$			
2·025	5·728				2·514	2·514
3·038	8·592				2·521	2·521
4·051	11·46				2·527	2·527
5·063	14·32				2·536	2·536
6·076	17·18				2·540	2·540
7·089	20·05				2·554	2·554
8·103	22·92			2·575	2·579	2·577
9·119	25·79			2·589		2·589
10·139	28·68		2·599	2·619		2·609
12·175	34·44		2·645			2·645
14·205	40·17		2·658			2·658
16·234	45·91		2·723			2·723
20·373	77·62	2·803				2·803

E/p_{273}	E/N	$p_{273} = 1\cdot31$	$1\cdot85$	$2\cdot74$	$3\cdot17$	$4\cdot58$	$6\cdot86$	$9\cdot16$	Best estimate
				(*d*) *Species* $D(O_3^-)$					
2·025	5·728							2·559	2·559
3·039	8·595						2·576	2·572	2·574
4·052	11·460					2·577	2·584	2·580	2·580
5·067	14·331					2·586	2·588	2·590	2·588
6·081	17·20					2·598	2·604	2·600	2·601
7·094	20·06					2·610	2·612	2·615	2·612
8·108	22·93					2·627	2·629	2·631	2·629
9·125	25·81					2·644	2·651		2·648
10·162	28·74		2·680	2·666	2·671	2·666	2·670		2·668
12·204	34·52		2·729	2·717	2·720	2·711			2·716
14·238	40·27		2·787	2·777	2·778	2·769			2·775
16·272	46·02		2·848	2·842	2·845	2·836			2·843
18·321	51·82		2·926	2·903	2·915				2·915
20·356	57·57		2·989	2·982	2·987				2·986
22·383	63·31		3·053	3·048					3·050
24·45	69·14			3·112					3·112
26·45	74·81		3·181	3·178					3·180
28·47	80·51		3·222						3·222
30·50	86·26		3·251						3·251
32·53	92·01	3·284	3·280						3·282
34·57	97·77	3·304	3·304						3·304
36·60	103·52	3·315	3·311						3·313
38·63	109·27		3·321						3·321
40·67	115·02		3·313						3·313
42·67	120·68		3·300						3·300

Table 1 (*Continued*)

E/p_{273}	E/N	$p_{273} = 1.85$	2.74	3.17	Best estimate
		(*e*) *Species* E(O$^-$)			
12·20	34·51	3·473			3·473
14·26	40·33		3·570		3·570
16·30	46·10		3·714	3·719	3·717
18·33	51·84		3·844	3·853	3·849
20·37	57·61		4·004	3·991	3·998
22·39	63·33	4·210	4·229		4·220
24·42	69·07	4·292	4·248		4·270
26·48	74·91	4·412	4·422		4·417
28·47	80·51	4·514			4·514
30·50	86·26	4·607			4·607
32·53	92·02	4·667			4·667
34·57	97·77	4·674			4·674

E/p_{273}	E/N	$p_{273} = 4.58$	6.86	9.16	Best estimate
		(*f*) *Species* F(impurity)			
3·038	8·592			3·019	3·019
4·051	11·46			3·028	3·028
5·063	14·32			3·036	3·036
7·089	20·05			3·070	3·070
8·103	22·92		3·097	3·102	3·100
9·119	25·79		3·117		3·117
10·14	28·68	3·151	3·143		3·147
11·65	32·95		3·195		3·195
12·18	34·44	3·210			3·210
14·20	40·17	3·298			3·298
16·23	45·91	3·372			3·372

Such a pressure dependence suggests that the ions are undergoing a large number of collisions in which they change identity with another species which subsequently changes back to the original species. The most probable such reaction is

$$O_2^- + O_2 + O_2 \rightleftarrows O_4^- + O_2. \tag{8}$$
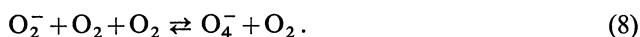
It was established that the reaction was in equilibrium by performing the following test. A value of p and E/p was selected such that a significant deviation of κ had occurred from the value $\kappa_{p\to\infty}$, and tests were made to see if the measured mobility was a function of the residence time of the ions in a region before they entered the drift chamber. The chosen values were $E/N = 29$ Td and $p_{273.2} = 3.17$ torr, and the value of E/N in the region before the drift chamber was varied from 4·2 to 34 Td. No significant change in the mobility was observed ($<0.2\%$), the only alteration in the ion current spectrum being the appearance of species B(CO_4^-) when there was a long initial residence time. In addition to this test it was observed that the peak corresponding to species A(O_2^-/O_4^-) did not appear to be distorted. It was therefore concluded that equilibrium had been attained in such a case. Assuming reaction (8) to be correct, the measured mobility κ_m is related to the mobilities κ_1 and κ_2 of O_2^- and O_4^- ions respectively by the relation

$$\kappa_m = \frac{\kappa_1(1/K_e N) + \kappa_2}{1/K_e N + 1}, \tag{9}$$

where K_e is the equilibrium constant. At very high gas number densities $\kappa_m \to \kappa_2$.

The data of Table 1a show that, for $p_{273} > 9$ torr and $5 \cdot 7 < E/N < 23$ Td, the reduced mobility is in fact independent of pressure. If reaction (8) has been correctly assumed, the value of the reduced mobility in this range of parameters will be that for O_4^- ions. To obtain the variation of the reduced mobility of O_4^- ions as a function of E/N, the data of Table 1a were examined at each value of E/N for those values of κ which showed no change with increase in pressure. These were averaged to provide the 'best estimate' values of the mobility of species $Aa(O_4^-)$ that are listed in Table 1a and also plotted in Fig. 5a (full squares). It is found on extrapolation to $E/N = 0$ that $\kappa_0 = 2 \cdot 30 \pm 0 \cdot 02$ for species $Aa(O_4^-)$.

The reduced mobility of O_2^- ions was found in a similar manner except that in this case the selection was for values of κ which did not change significantly with further decrease in pressure. These were averaged to provide the 'best estimate' values of the mobility of species $Ab(O_2^-)$ that are listed in Table 1a and also plotted in Fig. 5a (full triangles). Although it is clearly desirable for data at low E/N values to be obtained at low gas pressures, no measurements could be taken at pressures of less than $1 \cdot 3$ torr due to insufficient electron, and hence negative ion, current. This is a consequence of using the α-particle ionization source.

A comparison of the present 'best estimate' values for species Aa with the data of SN supports the identification of species Aa as being O_2^-. There is excellent agreement (to within $\pm 1 \%$) over the E/N range 57–85 Td, although at higher E/N values the data diverge, the present values being 3 to 4% higher than those of SN at $E/N \approx 130$ Td. This difference is within the combined experimental error of the two sets of data.

Difficulties arise as soon as the present data for O_4^- are compared with those of SN (Figs 4 and 5a). SN state that the zero field mobilities of O_2^- and O_4^- are virtually identical (to within 1%) and this similarity has also been remarked by Shafer and Beaty (1969) and by McKnight and Sawina (1971). If this is so then it is not possible to obtain a variation of the reduced mobility with pressure, contrary to the findings of the present work. From Fig. 4 it would appear that as the pressure decreases the present data tend toward the value $\kappa_0 = 2 \cdot 16$ given by SN for O_2^-. It would therefore be of interest to use the relation (9) to see whether the present κ_0 values for O_4^- and those of SN for O_2^- are consistent with the measured value of the equilibrium constant obtained by Conway and Nesbitt (1968) for reaction (8). Unfortunately the present data do not extend over a sufficiently large range of pressures at low values of E/N to make such a test conclusive. There is some indication, however, that the pressure dependence of the present data for values of $E/N < 24$ Td is different from that predicted by the relation (9). The measurements of SN on O_4^- were made at pressures of $3 \cdot 1$ and $4 \cdot 2$ torr and over the E/N range $3 \cdot 1$–$4 \cdot 6$ Td. On the basis of the present results, the reduced mobility would be expected to be $2 \cdot 30$ at these values of E/N and p, which is in serious disagreement with SN's value of $2 \cdot 14$. It should be noted that the pressure range used by SN is too small and the measurement error too large to ensure that the mobility is independent of pressure and hence that the ion which they observed as O_4^- had remained unchanged during its passage through the drift chamber. McKnight and Sawina used a larger range of pressures ($0 \cdot 5$–4 torr) but the large error of their data ($\sim \pm 5 \%$) and the fact that their data were taken at a significantly different gas temperature (310 K) precludes making a meaningful comparison with the present data. No experimental details of the measurements of Shafer and Beaty (1969) have been published.

In order to explain the disagreement with the results of SN it might be suggested that the present value for O_4^- is not correctly ascribed and that the reaction scheme applicable is not given by (8). There are immediate difficulties in postulating the identity of species A at high pressure if reaction (8) is ruled out, since it has already been shown that species A is not a cluster with a condensible impurity (such as CO_2 and H_2O) but is related to O_2^-. The noncondensible impurity H_2 has been shown to cause no change in species A while CO has been shown by Moruzzi and Phelps (1966) to have the same effects as H_2. It seems very difficult therefore to find an alternative identity for species A at high pressures other than O_4^-. The cause of the disagreement between the present data for O_4^- and those of SN and others is unknown.

(b) Species B(CO_4^-)

The present data for species B(CO_4^-) are listed in Table 1b and cover the E/N ranges 2·9–58 and 86–104 Td. The most reliable data at a given value of E/N are those taken at the highest electric field strengths, i.e. at the highest gas pressures. A plot of these 'best estimate' values (Fig. 5b) shows excellent agreement with the data of SN over the small range of E/N in common. The reduced zero field mobility for species B is estimated to be $2·38 \pm 0·02$, which is in good agreement with SN's value of $2·45 \pm 0·07$ for CO_4^-. This agreement suggests that the previous tentative identification of species B as CO_4^- is correct.

As E/N increases up to a value of 58 Td, the size of the CO_4^- peak in the ion current spectrum steadily decreases due to the reduction in the number density of O_2^- ions produced by associative electron attachment. At values of E/N immediately greater than 58 Td, the CO_4^- peak is too small for accurate measurement. However, at much higher values of E/N the number density of O_2^- ions rapidly increases due to the charge exchange reaction

$$O^- + O_2 \rightarrow O_2^- + O, \tag{10}$$

and this results in a CO_4^- peak in the ion current spectrum which is again sufficiently large for measurement. These higher E/N measurements of the mobility of CO_4^- ions cover the range 86–104 Td.

(c) Species C(CO_3^-)

Data for species C(CO_3^-) are listed in Table 1c. These results are more limited than for the other investigated species owing to the small abundance of this ion. When the present data are plotted (Fig. 5c) it is found that they can be reasonably extrapolated to give a zero field reduced mobility of $2·51 \pm 0·03$. The good agreement with SN's value for CO_3^- of $2·50 \pm 0·07$ confirms the previous tentative identification of species C as CO_3^-.

(d) Species D(O_3^-)

The data for species D(O_3^-) are listed in Table 1d. They cover the E/N range 5·7–121 Td and exhibit a maximum at $E/N \approx 110$ Td (Fig. 5d). The maximum difference between the present data and those of SN is less than 2%, thus confirming the suggested identity of this ion. The zero field mobility is estimated as $2·55 \pm 0·03$, which is in excellent agreement with SN's value of $2·55 \pm 0·08$.

(e) Species E(O$^-$)

The present data for species E(O$^-$) are listed in Table 1*e*. Although the data are limited they are sufficient for comparison with those of SN (Fig. 5*e*). The agreement holds to within 2%, which is well within the combined experimental errors over the common E/N range of 35–98 Td. Species E may therefore be confirmed as being O$^-$. The present data do not extend below $E/N = 35$ Td, where the variation of κ with E/N is still quite rapid. It was therefore not possible to obtain a zero field reduced mobility for O$^-$ from the present data, and to do so it would be necessary to use an alternative type of ion source to obtain values at low E/N. At higher pressures the frequency of reactions to form O$_3^-$ or CO$_3^-$ results in O$^-$ being seriously attenuated.

(f) Species F(*identity unknown*)

The data for species F(identity unknown) are listed in Table 1*f*. There are no data of SN with which this ion species may be compared and, for reasons given earlier, we conclude that this species is an impurity ion of unknown identity. The data for this species have been shown graphically (Fig. 5*f*) to enable a comparison to be made with the data of Rees (1965) for one of the ion species he observed. The zero field reduced mobility of species F is $3 \cdot 01 \pm 0 \cdot 04$.

(g) Summary

The tentative identifications advanced in Section 3 for the present ion species are consistent with the data of SN with one exception, that of species A, where there is a serious disagreement. The most that can be said about the present species A is that it is related to O$_2^-$ and is not connected with an impurity molecule.

5. Former Measurements without Mass Spectrometry

In the light of the present data and those of SN, it is of interest to examine some of the previous investigations of negative ion mobilities in oxygen, in which no direct mass identification was employed, in order to see if a number of existing anomalies can be resolved. In examining these older sets of data, we pay particular attention to the gases used and the care taken to remove impurities, since the serious effect which even trace levels of certain impurities can have on mobility measurements has only recently been established.

(a) Nielsen and Bradbury (1937)

Nielsen and Bradbury (1937) obtained the oxygen from a commercial cylinder and purified it by passage through liquid nitrogen traps. No impurity levels were quoted. The gas pressures used were in the range 2–10 torr. Two ion species were found with zero field reduced mobilities of $3 \cdot 1$ (their species A) and $2 \cdot 66$ (their species B) (note that these values have been reduced to a temperature of 273 K, while the authors quoted values reduced to a temperature of 293 K). The lower mobility ion was only observed at long ion ages, i.e. at low initial values of E/p, and hence may be considered to be a clustered ion. Nielsen and Bradbury suggested that their species A was O$_2^-$ but it would seem more probable from its mobility that it was O$^-$. However, the mobility of $3 \cdot 1$ is close to that found by Rees (1965) and

Chanin *et al.* (1962) for one of their ions and to that of the present species F. It is unprofitable to speculate further owing to the limited information available.

(b) Doehring (1952)

Doehring (1952) measured the mobility of one species of negative ion in oxygen over the E/N range of 2–30 Td and at pressures ranging from 15 to 50 torr. The oxygen was obtained by electrolysis of a barium hydroxide solution and was passed through traps containing P_2O_5 and NaOH. The oxygen was finally liquefied before the boil off was allowed to enter the drift tube. These precautions and the care taken in the preparation of the drift tube would have ensured a low level of CO_2 but, at the relatively high pressures used, extremely low levels of CO_2 would be required to prevent the formation of either CO_3^- or CO_4^- (see subsection *c* below). The value of the zero field mobility obtained by Doehring was $2·48 \pm 0·1$ (normalized to standard gas molecular density $2·69 \times 10^{19}$ cm^{-3}). By comparison with the present data, the ion observed by Doehring would appear to have been either O_3^- or CO_3^- and, in view of the high pressures used, CO_3^- is the more probable.

(c) McDaniel and Crane (1957)

The experimental tube used by McDaniel and Crane (1957) incorporated neoprene O-rings and was constructed primarily of brass. Three different sources of oxygen were used: (1) 'the best grade commercially available in steel tanks', (2) 'a tank of commercial welding grade oxygen', and (3) 'a break-seal glass bulb of spectro-scopically pure oxygen (Linde)'. No levels of impurities were quoted for any of these three lots of oxygen and the measured mobilities were identical for gas samples taken from each. The gas pressures ranged from 100 to 250 torr and the E/p range was $1·1$–$7·9$ V cm^{-1} torr^{-1}. No attempt was made to purify the gas samples.

One ion species only was observed by McDaniel and Crane and it is highly probable that the species was a clustered ion. In the present work, despite efforts to employ oxygen of much higher purity than that used by McDaniel and Crane, it was found to be impossible to obtain a significant abundance of unclustered ions at pressures greater than ~ 20 torr. At the much higher pressures used by McDaniel and Crane, the presence of trace amounts of CO_2 would cause the primary oxygen ions to cluster. The most dominant primary oxygen ion formed in McDaniel and Crane's experiment was O_2^- and hence the cluster ion which we postulate that they observed would have been CO_4^-. Their value of the zero field reduced mobility was $2·46 \pm 0·05$, and this is in good agreement with SN's value of $2·45 \pm 0·07$ for CO_4^- and with the present value of $2·38 \pm 0·02$ for the ion species B which has been identified as CO_4^-.

(d) Burch and Geballe (1957)

The oxygen used by Burch and Geballe (1957) was either from Airco Pyrex glass flasks or 'generated from $KMnO_4$ with precautions to ensure purity'. Mass spectro-metric analysis of the generated gas indicated that the impurity level was less than 40 p.p.m. The apparatus was outgassed and evacuated to 10^{-7} torr before filling with oxygen. The gas pressures used ranged from $8·6$ to $25·2$ torr and the E/p values from 8 to 50 V cm^{-1} torr^{-1}. Three ion species were observed by Burch and Geballe, the relative abundances of which depended on the values of p, E/p and the drift length d. Their species were designated A, B and C.

Species A.   The electrons in this experiment were produced in a discharge, and it is apparent from the values of E/p used that the dominant initial negative ion species formed was O^-. At low values of pd the abundance of this ion species should not be seriously attenuated by ion–molecule reactions and, on these grounds, Burch and Geballe identified species A as O^- with a zero field reduced mobility estimated to be $\sim 3 \cdot 4$. They also cite the close agreement with the value of $3 \cdot 38$, which they calculated from Langevin's theory, as additional evidence in favour of this identification. However, Langevin's theory cannot be applied validly to such a case and any agreement must be regarded as fortuitous. The close agreement with SN's κ_0 value for O^- of $3 \cdot 20 \pm 0 \cdot 09$ suggests that the identification of Burch and Geballe's ion species A as O^- is correct.

Species B.   The abundance of ion species B was found to increase as the value of pd increased and was the dominant ion at high values of pd and low values of E/p. These facts suggested to Burch and Geballe that species B was the product of an ion–molecule reaction and they considered this ion to be O_3^- with a zero field reduced mobility of $2 \cdot 6$. Assuming that no liquid nitrogen trap was used to remove the CO_2 impurity from the Airco oxygen, at the gas pressures used it is far more likely that CO_3^- rather than O_3^- was formed. Species B is therefore tentatively suggested as being CO_3^-. The κ_0 value of $2 \cdot 6$ is in good agreement with SN's value of $2 \cdot 50 \pm 0 \cdot 07$ for CO_3^- and the present value of $2 \cdot 51 \pm 0 \cdot 03$ for species C which has been identified as CO_3^-. However, the experimental scatter in Burch and Geballe's measured mobilities includes most of the present data for both CO_3^- and O_3^-, and some of their data may indeed refer to O_3^-.

Species C.   This species was identified by Burch and Geballe as O_2^-. Species C was the dominant ion at very high values of E/p ($> 35 \, \mathrm{V \, cm^{-1} \, torr^{-1}}$) and was presumably formed by charge exchange from O^- by reaction (10). This identification is therefore almost certainly correct, the zero field reduced mobility of $1 \cdot 95$ being in fair agreement with that of SN for O_2^-. However, to obtain their value of κ_0 for species C, Burch and Geballe had to extrapolate their data to $E/p = 0$ from $E/p = 22 \, \mathrm{V \, cm^{-1} \, torr^{-1}}$. Such an extrapolation would appear to be inaccurate and some doubt must therefore be placed on the κ_0 value listed by Burch and Geballe for species C.

(e) *Chanin* et al. (1962)

The experimental tube used by Chanin *et al.* (1962; hereinafter designated CPB) was built to u.h.v. specifications and was outgassed. It is therefore unlikely to have introduced significant impurities to the gas samples. The oxygen used was of reagent grade and supplied by the Air Reduction Sales Company. No attempt was made to purify this gas and no impurity levels were quoted. It is probable that the gas samples contained significant CO_2 impurity levels. The gas pressures were in the range $0 \cdot 1$ to 500 torr but no pressures were quoted for the negative ion mobility measurements.

Two ion species were observed (hereinafter designated species A and B) at 300 K. The data for species A and B covered the E/p ranges $0 \cdot 15$–$1 \cdot 5$ and 3–$10 \, \mathrm{V \, cm^{-1} \, torr^{-1}}$ respectively. In both cases the measured mobilities were independent of E/p and hence it was possible to extrapolate to $E/p = 0$ to obtain κ_0. The values found were $2 \cdot 7$ and $3 \cdot 0$ for species A and B respectively. The authors suggested that species A was O_2^- and speculated that species B was O^- or O_3^-.

Species A.   Beaty *et al.* (1964) carried out some negative ion mobility measurements in O_2 and, although they do not quote any numerical values, they make the statement that 'the mobility of O_2^- reported by CPB is not in agreement with the present data, using Eiber's [1963] identification'. The doubt concerning the mobility of species A was resolved by Voshall *et al.* (1965) who state that the CPB value of 2·7 was in error 'probably due to a failure to correct for the effects of diffusion'. The mobility quoted by CPB for species A should therefore be disregarded in favour of the value quoted by Voshall *et al.* There is no case for including the data of CPB for species A on a graph of available data for O_3^- as has been done by SN.

Species B.   It is worth noting that the CPB value of κ_0 for their species B is in close agreement with the value of κ_0 for species F of the present measurements. The gas used by CPB was obtained from the same commercial source as the gas used in the early part of the present work and it was in this gas that the present species F was observed. It would therefore seem possible that species B of CPB is an impurity ion of unknown identity and not O^- or O_3^- as CPB suggest.

(*f*) *Voshall* et al. (*1965*)

The experimental tube used by Voshall *et al.* (1965; hereinafter designated VPP) was that employed by Pack and Phelps (1961) to measure electron drift velocities. This tube was baked to 400°C, with a pressure of $\leqslant 10^{-7}$ torr being obtained after the bakeout. A rate of rise of pressure of less than 10^{-8} torr min^{-1} was obtained. It is therefore reasonable to assume that the tube used by VPP had such a low outgassing rate that the contamination of the gas samples due to this effect can be ignored. The gas used was research grade oxygen from the Matheson Company. The maximum impurity was given as 400 p.p.m. N_2, but no value was given for the CO_2 level. With such a large N_2 level it is not unreasonable to assume that the CO_2 level was $\geqslant 2$ p.p.m. As already stated, such a CO_2 level can result in large abundances of cluster ions if data are taken at high gas pressures. Although the inlet line and valves were baked, no liquid nitrogen traps were used and hence it seems probable that the oxygen used by VPP was significantly contaminated by CO_2.

Only one ion species was observed by VPP and they assumed that this species was O_2^-. At 300 K the range of number densities used was $7 \times 10^{17} - 2 \cdot 5 \times 10^{19}$ cm^{-3}, corresponding to a p_{273} range of 22–780 torr. The E/N range was 0·1–3 Td, over which κ was presumably constant to within the experimental scatter, since VPP stated that an average κ_0 of 2·42 was calculated from the data. No dependence on gas number density was observed. If the identity of this ion is correct then its κ_0 value is anomolously high, being approximately 10% higher than that of SN. On the other hand if the ion is CO_4^- then its κ_0 value is in excellent agreement with both that of SN and the present work. In view of gas purity considerations it would seem probable that the ion observed by VPP was CO_4^-. In order to check this suggestion we have studied the ion current spectrum obtained under the conditions used by VPP. These conditions were the least favourable for clustering, i.e. the lowest pressure (22 torr) and the highest E/N (3 Td). The single peak observable in the first order of the ion current spectrum was symmetrical but, at higher orders where the resolution is improved, the presence of a second ion could be observed. The peak in the first-order spectrum corresponded to a mobility of 2·41 which agrees with that of the present species B(CO_2^-). This tends to confirm the suggestion that the ion observed by VPP was not O_4^- but CO_4^-.

The suggestion that the ion observed by VPP at 300 K was not O_2^- appears to have been made first by Conway and Nesbitt (1968) although they did not offer an alternative identity. Conway and Nesbitt also suggested that the ions observed by VPP at 195, 88 and 77 K were not O_2^- but possibly complex ion clusters of O_2^- with a number of O_2 molecules. Conway and Nesbitt attributed the pressure dependence observed by VPP at low temperatures to the formation of these clusters.

(g) Rees (1965)

The gas used by Rees (1965) was Airco 'assayed reagent grade' and was stated by the supplier to contain 190 p.p.m. of N_2, 190 p.p.m. of Ar and 9 p.p.m. of CO_2. The gas pressures covered the range 2·5 to 70 torr. Rees employed a liquid nitrogen trap situated in the pumping line near the experimental tube, but it is possible that when high gas pressures were used the trapping was ineffective. Since these higher pressures would have been used at low E/N, it seems probable that clustering to form CO_4^- and CO_3^- would have been significant under these conditions.

Species A. The data of Rees (1965) for his species A are constant with increasing E/N up to 22 Td. Although his data agree to within the combined error limits with SN's values for O^- there are strong grounds for believing that his species A is not O^-. As SN point out, at the pressures used by Rees (~ 5 torr for his species A measurements), O^- ions would have been converted virtually entirely to O_3^-. In the present measurements, no O^- (species E) ion peak was observable at pressures greater than 3·2 torr and $E/N < 40$ Td. At higher pressure and lower E/N, the O^- abundance would be even more attenuated. It therefore seems certain that Rees's species A is not O^-. When we used oxygen from an Airco flask similar to that used by Rees and carried out measurements over a similar E/N range, we observed an ion with a zero field reduced mobility of 3·01, which is in excellent agreement with the κ_0 of Rees's species A. Over their common E/N range the two sets of data agree to within 2% (Fig. 5f). This ion is an impurity ion. When purer gas from another commercial source was used and further purified by the use of a liquid nitrogen trap, no trace of this ion was found. The suggestion by SN that the ion labelled O^- by Rees is probably an impurity ion is therefore almost certainly correct. We do not speculate as to its identity.

Species B. If high pressures were used ($p > 10$ torr) at low values of E/N (< 10 Td) CO_3^- should have been observed. It would seem likely therefore that at these low E/N values Rees's species B was CO_3^- and if this is so the values of κ_0 are in excellent agreement:

| Reference	CO_3^- identification	κ_0
SN	Mass identified	2·50 ± 0·07
Rees	Ion species B, low E/N, assumed CO_3^-	2·52 ± 0·05
Present work	Ion species C, assumed CO_3^-	2·51 ± 0·03

What then is the identity of Rees's ion species B at higher values of E/N? We speculate that species B goes over to O_3^- for $E/N > 15$ Td, the transition being smooth as E/N increases. This would give agreement to within 3% with the present work (species D) at these higher values of E/N.

Species C. In view of the previous comments on gas purity, we propose that Rees's ion species C at low E/N values was in fact not O_2^- but CO_4^-. The agreement

with SN and the present data over the common E/N range is then excellent, as is the agreement of the κ_0 values:

Reference	CO_4^- identification	κ_0
SN	Mass identified	$2 \cdot 45 \pm 0 \cdot 07$
Rees	Ion species c, low E/N, assumed CO_4^-	$2 \cdot 39 \pm 0 \cdot 05$
Present work	Ion species B, assumed CO_4^-	$2 \cdot 38 \pm 0 \cdot 02$

SN have commented that Rees's species c is probably not O_2^- and have suggested that the ions were either O_4^- or CO_4^-. In the light of the present work CO_4^- is the more likely. Whether the CO_4^- were formed via

$$O_2^- + 2O_2 \rightarrow O_4^- + O_2 \quad \text{and} \quad O_4^- + CO_2 \rightarrow CO_4^- + O_2$$
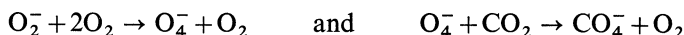
as suggested by SN or via reaction (4) (see Moruzzi and Phelps 1966) is more open to question.

Table 2. Reclassification of ion species identifications of Rees (1965)

Ion species		Rees's identification*	New identification*
O^-	(E)	A	—
O_2^-	(Ab)	c	—
O_3^-	(D)	B	B ($E/N \gtrsim 15$)
O_4^-	(Aa)	—	D
CO_3^-	(C)	—	B ($E/N \lesssim 15$)
CO_4^-	(B)	—	c (low E/N)
Impurity 1 (F)		—	A
Impurity 2		D	D
Uncertain†		—	c (high E/N)

* Letters denoting Rees's species are printed in small capitals.
† Both Rees's species c (high E/N) and the present species A are considered to be the same ion and are related to O_2^-. The species is not considered to be related to an impurity molecule.

At higher values of E/N, lower pressures were used and the trapping of the CO_2 would have been more efficient. Moreover the production of CO_4^- (assumed to be by the three-body process (4)) would have been much reduced as the pressure was lowered. It therefore seems probable that at higher values of E/N the ion observed was not a cluster ion. The values of the mobility at high E/N for Rees's species c lie within 2% of those of the present work for our species A, the identity of which has been discussed in Section 4a.

Species D. Rees suggested that his species D was an impurity ion. However, the close agreement (2%) with the value of κ_0 given by SN for O_4^- led SN to suggest that species D may in fact have been O_4^-. If this identification is correct then it is puzzling why the ion was not observed in the present work. The zero field mobility would suggest that Rees's species D was possibly O_2^- but Rees stated that no significant dependence of mobility on pressure was observed. In view of this evidence it is concluded that Rees' original contention that his species D was an impurity ion emitted from the coated filament is probably correct. The suggested reassignments

of the identities of the ions observed by Rees together with the ion species observed in the present work are summarized in Table 2.

(h) Dutton and Howells (1968)

Dutton and Howells (1968) used a four-gauze electrical shutter method in a drift tube built and operated to u.h.v. standards. The gas was obtained from the British Oxygen Company and was stated to be spectroscopically pure. The impurity levels were listed at 5 p.p.m. CO_2, 1 p.p.m. H_2 and 495 p.p.m. N_2. The pressures covered the range $1 \cdot 17$–$7 \cdot 71$ torr, and two species were observed for all values of $E/N > 50$ Td. The zero field reduced mobilities of the two species were $2 \cdot 5$ and $2 \cdot 4$. The identity of the faster ion was considered to be O_3^- but the presence of such a high CO_2 level as 5 p.p.m. makes it probable that this species was CO_3^-. If this is so, the value obtained by Dutton and Howells of $2 \cdot 5$ is in good agreement with the value of κ_0 obtained by SN and the present value for CO_3^- ions. The slower ion was suggested as being O_2^- and was measured over the E/N range 51–141 Td. The extrapolation of the data from $E/N = 51$ to 0 Td in order to obtain the estimated zero field reduced mobility of $2 \cdot 4$ is likely to introduce an uncertainty of the order of 1% (see Fig. 5a).

6. κ_0 of Negative Ions in Oxygen (~ 293 K)

In the previous section the identity of the ions observed by a number of workers has been discussed and in many cases alternative identities have been proposed. Although this is a somewhat presumptuous procedure, it would seem reasonable to attempt to reassess the early data in the light of the more accurate measurements and better established identities that are now available. The data from 1937 until the present for the zero field reduced mobilities have been collated in Table 3. Where the identity of the ion species has been changed from that postulated by the authors this is indicated by an appropriate note. The grounds for making such changes are given in Section 5. The data for each ion species are in general within the error bars indicated. The only major discrepancies are between the present results and those of SN and others for O_4^-. This discrepancy has already been discussed in Sections 4a and 5.

7. Conclusions

Although the use of drift tubes combined with mass spectrometers has led to rapid advances in the acquisition of reliable mobility data for those ion–molecule systems in which a number of reactions may occur, such experiments have two defects, apart from complexity and cost, when compared with the use of a drift tube alone: the absolute error is significantly larger than that obtainable with a drift tube alone, and the data are subject to effects introduced by the sampling procedure. The ideal situation is to have available data which are in agreement from both types of mobility measurements. This situation has now been achieved in the case of negative ions in oxygen with one exception, that of the mobility of O_4^- ions. Apart from this case the present data are in excellent agreement with those of SN, the estimated error in the present data being a factor of 2 to 3 times less than that estimated by SN. It appears unlikely that much additional mobility data for O_4^- can be obtained by a drift tube alone and further investigations of the mobility of this ion by combined drift-tube–mass-spectrometer systems are desirable.

Table 3. Zero field reduced mobilities of negative ions in oxygen (~ 293 K)

Author	κ_0 for indicated ion species*								Mass analysis
	O^-	O_2^-	O_3^-	O_4^-	CO_3^-	CO_4^-	Impurity 1	Impurity 2	
Present results			2·55±0·03	2·30±0·02	2·51±0·03	2·38±0·02	3·01±0·04		No
Harrison and Moruzzi (1972)	3·4±0·3[1]	2·1±0·2[1]	2·5±0·25[1]						Yes
McKnight and Sawina (1971)		2·2±0·1		2·2±0·1					Yes
Snuggs et al. (1971)	3·20±0·09	2·16±0·07	2·55±0·08	2·14±0·08	2·50±0·07	2·45±0·07			Yes
Varney (1970)		2·4±0·1							Yes
Dutton and Howells (1968)		2·4			2·5[2]				No
Voshall et al. (1965)		2·34[3]				2·42[4]			No
Rees (1965)	3·2±0·3	2·25±0·15	2·50±0·1		2·52±0·05[5]	2·39±0·05[6]	3·01±0·06[7]	2·18±0·04	No
Eiber (1963)						2·7[8]	3·0[9]		Yes
Chanin et al. (1962)									No
McDaniel and Crane (1957)						2·46±0·05[10]			No
Burch and Geballe (1957)	3·4±0·1[1]	1·95±0·1[1]			2·6±0·1[11]				No
Doehring (1952)					2·48±0·1[12]				No
Nielsen and Bradbury (1937)			2·66[13]				3·1[14]		No

* Notes on particular measurements:

[1] Error bar not stated by authors; error assessed by an examination of the experimental scatter only.

[2] Ascribed by Dutton and Howells to O_3^-; more probably CO_3^-.

[3] Quoted as E. C. Beaty (personal communication); no experimental details are available and therefore the identity of this ion cannot be discussed.

[4] Ascribed by Voshall et al. to O_2^-; more probably CO_4^-.

[5] Ascribed by Rees to O_3^-; more probably CO_3^-.

[6] Ascribed by Rees to O_2^-; more probably CO_4^-.

[7] Ascribed by Rees to O^-; more probably species F of the present work (the identity of this ion species is unknown).

[8] Quoted value is stated to be $\sim 15\%$ too high by Voshall et al. and should be considered as being superseded by their value.

[9] Ascribed by Chanin et al. to either O^- or O_3^-; more probably an impurity ion (species F of the present work).

[10] Ascribed by McDaniel and Crane to O_3^- or O_2^-; more probably CO_4^-.

[11] Ascribed by Burch and Geballe to O_3^-; more probably CO_3^-; see also note 1.

[12] Identity of ion not stated by Doehring; probably CO_3^-; see also note 1.

[13] Ascribed by Nielsen and Bradbury to either $O_2^-.H_2O$ or O_4^-; more probably O_3^-; quoted value has been corrected to standard gas number density.

[14] Ascribed by Nielsen and Bradbury to O_2^-; more probably an impurity ion (species F); quoted value has been corrected to standard gas number density.

Note added in proof

Measurements of the ion species present in oxygen contaminated with hydrogen using a drift-tube–mass-spectrometer system and conditions of pressure and E/N similar to those used here have indicated that species X is OH^- (H. B. Milloy, personal communication).

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