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Cross Sections and Electron Affinity for O^- Ions From O_2, CO, and CO_2 by Electron Impact*

G. J. SCHULZ
Westinghouse Research Laboratories, Pittsburgh, Pennsylvania

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Cross sections for the formation of O^- from O_2, CO, and CO_2 have been measured using an electron beam experiment in which an attempt is made to eliminate kinetic energy and angular discrimination by collecting most of the positive and negative ions produced in the tube. The cross sections are independent of electron current, pressure, and magnetic field. The values of these cross sections at their peak are 1.3×10^{-18} cm^2 at 6.7 eV in O_2, 1.6×10^{-19} cm^2 at 10.1 eV in CO, and 4.5×10^{-19} cm^2 at 8.2 eV in CO_2. O^- from CO_2 exhibits a second smaller peak at 4.2 eV with a cross section of 1.5×10^{-19} cm^2. Kinetic-energy measurements on the O^- ion from O_2 and CO_2 are not compatible with the value for the electron affinity (1.465 eV) obtained from photodetachment experiments but yield an electron affinity of 2.0 ± 0.1 eV and so suggest the existence of excited states of O^-. The experimental evidence from triatomic molecules N_2O, NO_2, and SO_2 is reviewed and is consistent with the higher value for the electron affinity for oxygen.

THE first five sections of this paper deal with cross section measurements for dissociative attachment of electrons in O_2, CO, and CO_2. The remainder of this paper is devoted to the electron affinity for atomic oxygen derived from electron beam experiments.

The cross-section measurements were undertaken in order to resolve the discrepancy in the cross section for O^- from O_2 obtained in two recent experiments: Buchelnikova[1] gives a cross section for O^- formation from O_2 equal to $(1.3\pm0.2)\times10^{-18}$cm^2, and Craggs, Thorburn, and Tozer[2] give a value of $(2.25\pm0.3)\times10^{-18}$ cm^2. Comparison of these values with electron swarms is difficult because the electron energy distribution of the electron swarm is not known accurately. A notable exception is a recent determination of the dissociative attachment cross section in water vapor by Hurst, O'Kelly, and Bortner[3] who used a small amount of water vapor in pure argon to interpret their data. They found their value of the cross section for H^- formation from H_2O only 20% higher than that determined by Buchelnikova. This gives added credibility to Buchelnikova's experiment. In view of this it seemed desirable to redetermine the cross section for O^- formation from O_2 in an independent electron beam experiment and also to confirm the cross sections in CO and CO_2.

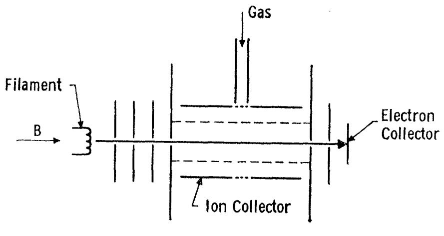

FIG. 1. Schematic diagram of tube.

I. EXPERIMENT

Figure 1 shows a schematic diagram of the tube employed for this study. It is similar to that described previously.[4] A thoria-coated iridium filament emits electrons which travel through the electron gun equipped for use with the retarding potential difference method. An electromagnet with a magnetic field variable up to 120 G or a permanent magnet (600 G) are used to align the electron beam. The collision chamber is formed by a cylindrical grid with a cylindrical ion collector mounted outside. All electrodes near the electron beam are gold plated, whereas the electron collector, and in some tubes also the ion collector, are plated with electrolytically deposited platinum black to reduce reflection of ions and electrons. The system is baked at 350°C and a background vacuum of 10^{-9} mm Hg is obtained.

In order to prevent gas contamination resulting from reactions of oxygen at the hot filament, a differential pumping system with a calculated speed of 130 liter/sec is used. The gas is introduced directly into the collision chamber through a 3-mm tube and pumped out after traversing the collision chamber. A baffled liquid air trap provides isolation of the vacuum system from the pumps. A 10-cm-diam valve is located between the liquid air trap and the diffusion pump. It was found that the oxygen gas did not remain pure for long periods of time when the valve was closed. It is believed that the filament converts oxygen to carbon monoxide with a high efficiency. This is essentially in agreement with recent experiments using a tungsten filament.[5] Most of the results reported here were obtained using a dynamic system. However, the absolute cross section for O_2^+ at 30 eV was obtained with a closed system, before the contamination was appreciable.

II. TUBE CHARACTERISTICS

The determination of the negative-ion cross section can be reduced to the problem of measuring the ratio

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* This research was supported in part by the Advanced Research Projetcs Agency and the Office of Naval Research.

[1] I. S. Buchelnikova, Zhur. Eksptl. i. Teoret. Fiz. **35**, 1119 (1953) [translation: Soviet Phys.—JETP **35**, 783 (1959)].

[2] J. D. Craggs, R. Thorburn, and B. A. Tozer, Proc. Roy Soc. (London) **A240**, 473 (1957).

[3] G. S. Hurst, L. B. O'Kelly, and T. E. Bortner, Phys. Rev. **123**, 1715 (1961).

[4] G. J. Schulz, J. Chem. Phys. **33**, 1661 (1960).

[5] J. A. Becker, E. J. Becker, and R. G. Brandes, J. Appl. Phys. **32**, 411 (1961).

of negative-ion current to positive-ion current, since positive-ion cross sections are known. The errors arising in such measurements have been discussed by Tozer.[6] Because negative ions produced by dissociative attachment possess kinetic energy and parent positive ions do not, one must ascertain that the instrument does not discriminate in favor of or against ions of kinetic energy. It has been recently pointed out by Dunn[7] that ions resulting from dissociative processes could have an angular distribution far from isotropic and this could strongly influence experiments in which ions are analyzed with a small acceptance angle in a fixed direction. In the present experiment, an attempt is made to collect all the positive and negative ions formed in the tube. This is facilitated by the fact that most of the ions are formed in the center of the tube where the gas stream crosses the electron beam. Assuming an isotropic distribution and no drawout field, only 4.5% of the ions would be lost to the ends of the tube.

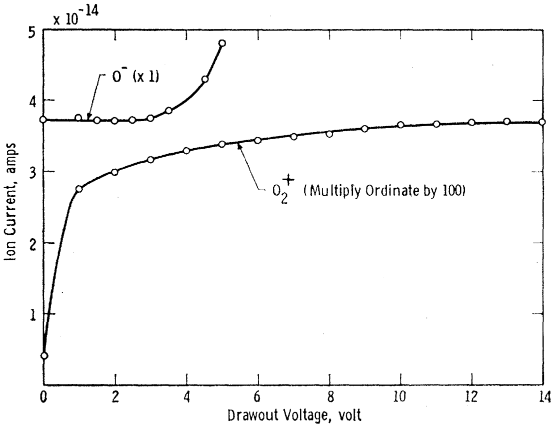

FIG. 2. Drawout characteristics for positive and negative ions in O_2 with a magnetic field of 120 G. The curve for O_2^+ is obtained at an electron energy of 30 eV and O^- at 6.7 eV. The data discussed in the paper are taken at drawout voltages of 12 V for positive ions and 0 V for negative ions. The rise of the negative-ion curve above 3 V is due to the collection of trapped inelastically scattered electrons at the ion collector.

Figure 2 shows that both the positive-ion current and the negative-ion current saturate as a function of drawout voltage. This is taken as an indication that all the ions are actually collected. In magnetic deflection mass spectrometers total collection of ions cannot be achieved and the ratios of negative to positive ion currents have been found to be erroneous, despite repeated efforts in this Laboratory, using two types of mass spectrometers (90° deflection[8] and cycloidal type[9]) to find operating conditions which would give the correct ratios. This difficulty seems to be associated solely with the drawout arrangement of the ion source. The same problem also afflicts a Lozier-type apparatus. Tozer[6] has analyzed the problem of the collection efficiency for positive and negative ions as it applies to the Lozier tube and corrected for the unequal collection efficiency by using drawout potentials in the ratio of the kinetic energies of formation of the respective ion. Lange[9] finds that the proper ratio of negative to positive ions in CO can be obtained using zero pusher voltage. However, there is a rapid variation of ion current with pusher voltage near zero pusher voltage so that this operating

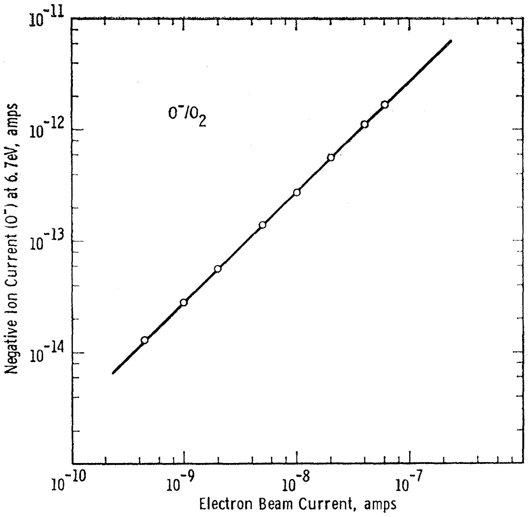

FIG. 3. Negative-ion current vs electron beam current. The linearity of the curve over two orders of magnitude shows that space charge effects are negligible. The data discussed in this paper are obtained at electron beam currents around 2×10^{-9} A.

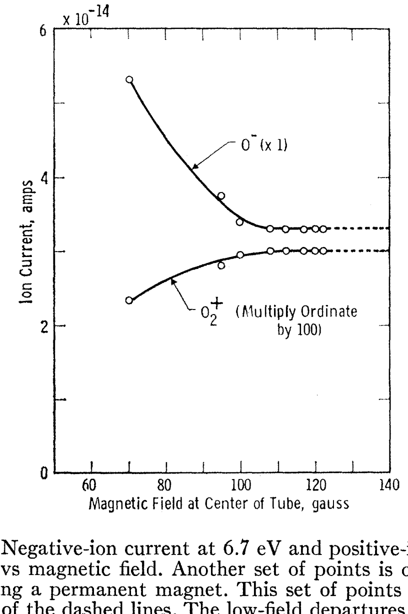

FIG. 4. Negative-ion current at 6.7 eV and positive-ion current at 30 eV vs magnetic field. Another set of points is obtained at 600 G using a permanent magnet. This set of points lies on the extension of the dashed lines. The low-field departures are caused by primary electrons reaching the collector.

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[6] B. A. Tozer, J. Electronics and Control 4, 149 (1958).

[7] G. H. Dunn, Phys. Rev. Letters 8, 62, 1962.

[8] R. K. Curran (private communication).

[9] W. J. Lange, Proceedings of the Mass Spectrometer Conference, Chicago, 1961 (unpublished).

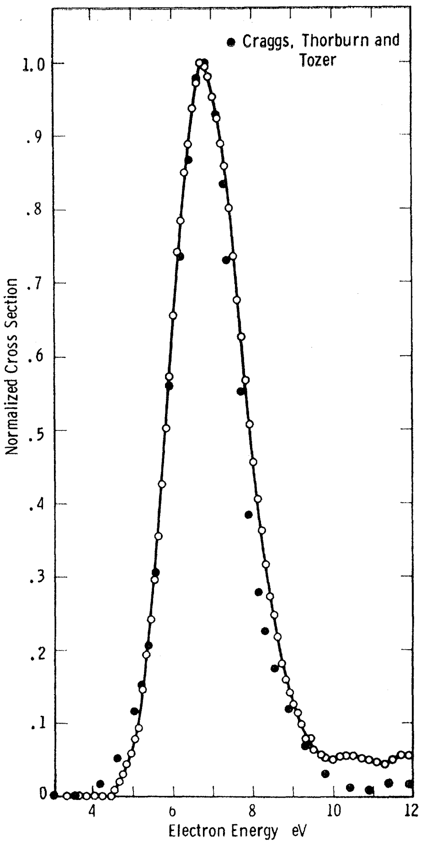

FIG. 5. Normalized cross section for formation of O^- vs electron energy and comparison with data of Craggs, Thorburn, and Tozer. The cross section at the peak is 1.3×10^{-18} cm^2.

condition is not useful, at the present time, for giving reliable ratios.

Space charge effects could influence the measurements. Figure 3 shows that the negative-ion current is a linear function of electron-beam current and thus space charge effects are unimportant, as is expected at the low currents used in the present experiment.

The path length of the electrons could be influenced by the magnetic field.[6] Figure 4 shows a plot of ion current against magnetic field. Although the range over which the magnetic field could be varied is limited, there is a clear region of magnetic fields over which the ion current is independent of magnetic field. The data discussed below are taken at 120 G. Data taken with a 600-G permanent magnet are in agreement with the 120-G data.

The characteristics of the present tube differ from those of the Lozier tube used by Cragg's group with which the data presented in subsequent sections will be compared. Because of the nonlinearities with electron-beam current and pressure, they had to extrapolate their data to zero electron current and pressure and correct for kinetic energy discrimination. They could not correct for angular discrimination. In the present experiment, an attempt is made to collect all the ions produced in the tube and thus the present results should be free from errors resulting from kinetic energy and angular discrimination. The cross section is found to be independent of electron beam current, pressure, and magnetic field.

TABLE I. Energies at onsets and peaks for production of O^- from O_2, CO, and CO_2 in eV.

	O_2		CO		First process CO_2		Second process CO_2	
	Onset	Peak	Onset	Peak	Onset	Peak	Onset	Peak
Present work	4.4	6.7	9.4	10.1	3.85	4.4	6.6	8.2
Craggs *et al.*[a]	4.7	6.7	9.35	10.1	...	...	6.7	7.8
Randolph & Geballe[b]	3.75	6.2	...	...	...	...	...	...
Lagergren[c]	...	...	9.5	10	...	..	...	...
Lozier[d]	4.5	7.2	9.5	10	...	...	...	...
Buchelnikova[e]	4.63	6.2	...	...	...	...	...	...
Curran[f]	4.3	6.7	...	...	3.8	4.4	6.6	8.4
Kraus[g]					3.96	4.4	7.0	8.1

[a] See reference 2; and J. D. Craggs and B. A. Tozer, Proc. Roy. Soc. (London) **A247**, 337 (1958); **A254**, 229 (1960).
[b] P. L. Randolph and R. Geballe, thesis, University of Washington, 1958 (unpublished).
[c] C. R. Lagergren, thesis, University of Minnesota, 1955 (unpublished).
[d] W. W. Lozier, Phys. Rev. **46**, 268 (1934).
[e] See reference 1.
[f] See reference 8.
[g] K. Kraus, Z. Naturforsch. **16a**, 1378 (1961).

III. CROSS SECTIONS IN O_2

Figure 5 shows a plot of the normalized cross section for O^- formation vs electron energy using the retarding potential difference method. For comparison, the points obtained by Craggs, Thorburn, and Tozer[2] are indicated. The agreement is seen to be good. The onset of the present curve occurs at 4.4 ± 0.1 eV and the peak of the curve is at 6.7 eV, in excellent agreement with Craggs, Thorburn, and Tozer. The larger tailing at low energies of the curve by Craggs, Thorburn, and Tozer results from the larger electron energy spread in their experiment. There is also disagreement between the two curves above 10 eV. In this region, the cross section is found to be pressure dependent and the negative ion current has a subsidiary peak around 15 eV, which is not understood at the present time. The energy scale is calibrated using electron retarding curves.[4] Table I shows a comparison of energies at onset and peak obtained by others. Figure 6 shows the negative ion current at the peak of its cross section (6.7 eV) plotted against the positive ion current at 30 eV. The curve is obtained by varying the pressure in the collision chamber. There is a linear relationship between the O^- and O_2^+ currents; the ratio of O_2^+ at 30 eV to O^- at 6.7 eV can be fixed from the slope of the line as $R = 95$. Using Tate and Smith's value of 1.18×10^{-16} cm^2 for the positive ion cross section at 30 eV,[10] we obtain a cross section of 1.25×10^{-18} cm^2 for O^- formation at its peak. A confidence error of $\pm 15\%$ should be associated with this

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[10] J. T. Tate and P. T. Smith, Phys. Rev. **39**, 270 (1932).

TABLE II. Energy dependence of positive-ion cross section in O_2. The values given are in units of 10^{-16} cm^2 and are normalized to those of Tate and Smith[a] at 35 eV.

Electron energy (eV)	Present work	Tate and Smith[a]	Craggs, Thorburn, Tozer[b]
35	1.55	1.55	1.55
30	1.20	1.18	1.17
25	0.79	0.79	0.68
20	0.41	0.41	0.31
18	0.27	0.25	0.15
16	0.16	0.16	0.08
14	0.07	0.06	0.02

[a] See reference 10.
[b] See reference 2.

cross section. This cross section is in agreement with that given by Buchelnikova[1] (1.3×10^{-18}cm^2) but disagrees with that given by Craggs, Thorburn, and Tozer[2] (2.25×10^{-18}cm^2). The latter authors express doubts as to the correctness of Tate and Smith's cross section. For this reason, the absolute positive ion cross section at 30 eV as well as the energy dependence of the cross section was redetermined. Using a closed vacuum system and a calibrated high-pressure ionization gauge[11] the cross section for O_2^+ at 30 eV is found to be 1.04×10^{-16} cm^2, compared to Tate and Smith's value of 1.18×10^{-16} cm^2. This agreement is considered to be good and Tate and Smith's value can be accepted as being correct. Table II gives the energy dependence of the cross section, normalized to Tate and Smith's value at 35 eV. It is seen that the energy dependence obtained in the present experiment is in remarkably good agreement with the data of Tate and Smith, and the correction to Tate and Smith suggested by Craggs, Thorburn, and Tozer is not needed. Thus the present experiment gives a cross section of $(1.3\pm0.2)\times10^{-18}$ cm^2 for formation of O^- by dissociative attachment in O_2.

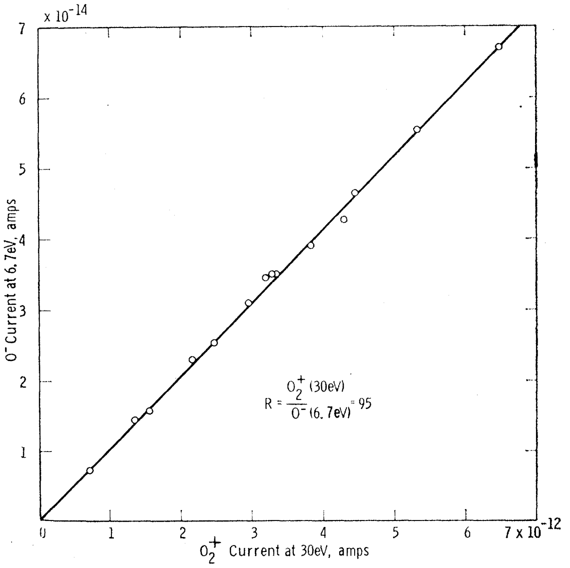

FIG. 6. Negative-ion current at the peak vs positive-ion current at 30 eV. The ratio of positive-ion current at 30 eV to negative-ion current at peak is 95 for O_2; 615 for CO (background not subtracted, see discussion), and 640 for the second O^- peak in CO_2.

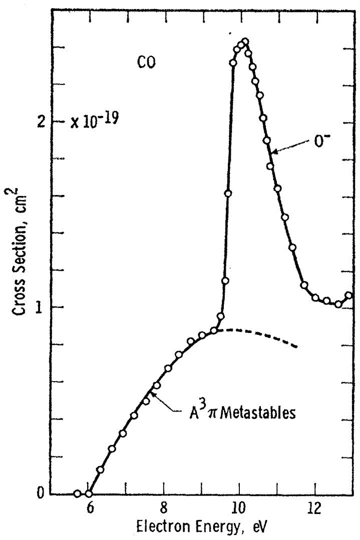

FIG. 7. Current arriving at collector vs electron energy in CO.

IV. CROSS SECTIONS IN CO

Figure 7 shows the current arriving at the collector as a function of electron energy in CO. The curve with an onset around 6 eV is probably due to metastable CO molecules in the $a^3\pi$ state hitting the grid and releasing secondary electrons which are collected on the ion collector.[12] The onset at 9.4 eV is interpreted as the arrival of negative ions, O^-, at the collector. The cross-section scale is determined as discussed in Sec. III. In order to obtain the cross section for O^- formation at the peak, the curve for the "background" has to be subtracted. This leads to a cross section for O^- formation from CO equal to $(1.6\pm0.3)\times10^{-19}$ cm^2.

This value should be compared to the value quoted by Craggs and Tozer,[13] namely, 2.7×10^{-19} cm^2. Their cross-section measurement is done in two ways. Their first measurement compares the negative-ion current to the positive-ion current and the negative-ion cross section is determined from this ratio and the known cross section for positive ions. However, they find, as in the case of oxygen, a shape of the positive-ion cross section vs electron energy different from that found by Tate

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[11] G. J. Schulz and A. V. Phelps, Rev. Sci. Instr. 28, 1051 (1957).

[12] This mechanism can be verified as follows. The potential of the ion collector is biased 10 V negative with respect to the grid so that negative ions cannot reach the ion collector. The current arriving at the ion collector is now of the opposite sign and has the same shape and onset (6 eV) as the "background current" of Fig. 7. The discontinuity at 9.4 eV with a peak of 10.1 eV is not present. This current results from CO metastables hitting the ion collector and releasing secondary electrons which are collected on the grid.

[13] J. D. Craggs and B. A. Tozer, Proc. Roy. Soc. (London) **A247**, 337 (1958).

TABLE III. Energy dependence of positive-ion cross section in CO. The values given are in units of 10^{-16} cm^2 and are normalized to those of Tate and Smith[a] at 100 eV.

Electron energy (eV)	Present work	Tate and Smith[a]	Craggs and Tozer[b]
16	0.12	0.11	0.13
18	0.27	0.26	0.37
20	0.47	0.41	0.60
25	0.91	0.97	1.21
30	1.39	1.46	1.77
35	1.66	1.78	2.22
40	2.00	2.11	2.51
50	2.42	2.54	2.82
60	2.73	2.77	2.96
70	2.94	2.93	3.02
80	3.13	3.03	3.03
100	3.07	3.07	3.07

[a] See reference 10.
[b] See reference 13.

and Smith. In order to resolve this discrepancy, the present tube was used to measure the energy dependence of the positive ion cross section. Essentially, good agreement is found with the results of Tate and Smith, as shown in Table III. If the results of Craggs and Tozer are normalized to the positive-ion curve of Tate and Smith, the value of the cross section for O^- becomes 1.8×10^{-19} cm^2, in good agreement with the present value quoted above.

The second approach used by Craggs and Tozer was a comparison between the negative-ion yield in CO and O_2. Normalizing to their value of the negative-ion cross section in O_2, they find a cross section in CO of 2.8×10^{-19} cm^2. However, if one normalizes to the negative-ion cross section for O_2 found in this work, the cross section in CO becomes 1.7×10^{-19} cm^2, again in agreement with our value.

V. CROSS SECTIONS IN CO_2

Figure 8 shows the cross section vs electron energy for negative-ion formation in CO_2. Two peaks are evident with onsets at 3.85±0.1 and 6.6±0.1 eV. The cross section for the second peak has been previously determined by Craggs and Tozer,[14] but they did not observe the first peak. The negative ion involved in both these peaks has been identified by Curran in a mass spectrometer as O^-.[15]

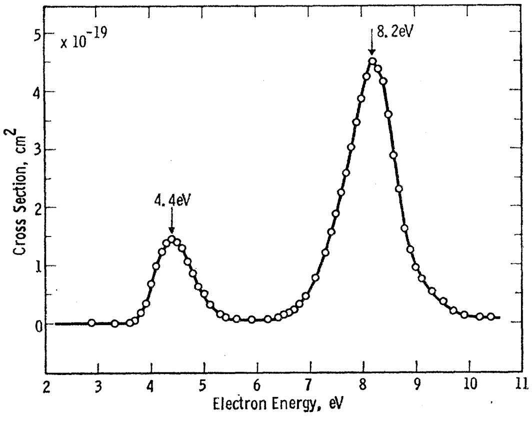

FIG. 8. Negative-ion formation in CO_2. Both peaks are due to O^- ions.

The ratio of the positive-ion cross section at 30 eV to the peak negative-ion cross section at 8.2 eV is found to be 640. Taking Craggs and Tozer's cross section for positive ions at 30 eV (3.3×10^{-16} cm^2), the negative-ion cross section becomes equal to 5.15×10^{-19} cm^2. The author's own value for CO_2^+ at 30 eV (2.87×10^{-16} cm^2) would yield a negative-ion cross section of $4.5 \pm 0.7 \times 10^{-19}$ cm^2. These two values should be compared with Craggs and Tozer's value of $(5.07 \pm 0.5) \times 10^{-19}$ cm^2. The agreement between the present value and that given by Craggs and Tozer is considered to be satisfactory.

VI. ELECTRON AFFINITY MEASUREMENTS BY ELECTRON BEAM TECHNIQUES

In principle, the electron affinity of atoms such as oxygen can be measured by measuring the energy of the incident electrons and the kinetic energy of the negative

TABLE IV. Some recent values of electron affinity for atomic oxygen obtained by electron beam experiments.

Parent gas	Dissociation energy of broken bond, eV	Apparent electron affinity, eV	Method
O_2	5.11	2.0[a]	Kinetic energy
		1.5[b]	Pair formation
		2.1[c]	Pair formation
		2.0[d]	Kinetic energy and pair formation
CO	11.11	1.6[e]	Onset
		1.7[e]	Pair formation
		1.9[c]	Pair formation
CO_2	5.6	>2.0[a]	Kinetic energy
N_2O	1.7	>1.9[f]	Kinetic energy
NO_2	3.12	>1.8[g]	Onset
		2.2[h]	$NO_2 + e \rightarrow O^- + NO^+$
SO_2	5.68	>1.9[i]	Onset, see Table V

[a] Present work.
[b] See reference 33.
[c] See reference 32.
[d] R. Thorburn, *Applied Mass Spectrometry* (The Institute of Petroleum, London, 1954).
[e] C. R. Lagergren, thesis, University of Minnesota, 1955 (unpublished).
[f] See reference 21.
[g] See reference 23.
[h] See reference 24.
[i] Average value, see Table V.

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[14] J. D. Craggs and B. A. Tozer, Proc. Roy. Soc. (London) **A254**, 229 (1960).

[15] R. K. Curran (private communication). Both peaks are found in the mass spectrometer. However, the ratio of the peak height is altered because of discrimination against ions of kinetic energy. The relative height of the second peak is underestimated using a mass spectrometer. The onsets found by Curran are 3.8±0.1 and 6.6±0.1 eV, in excellent agreement with the values found in the present experiment.

ion. Branscomb, Burch, Smith, and Geltman[16] have measured the photodetachment threshold for O^- and have obtained a value of 1.465±0.005 eV for the electron affinity of atomic oxygen. Thus, all electron-beam experiments have to be evaluated in terms of their agreement with this value. This has been done most recently by Craggs and Tozer. The values found by various experimenters for the electron affinity of O by electron impact on O_2 as listed by Craggs and Tozer[14] are 2.5, 2.2, 2.0, 1.5 eV; CO yields 1.6, 1.5, 1.7, 1.7, 1.6 eV. There seems to be a definite trend for the electron affinity determined by electron impact on O_2 to be higher than that determined from CO. This can also be seen from Table IV, where recent values of the electron affinity obtained from beam experiments are summarized.

Craggs and Tozer analyzed the possibility that the electron-energy scale would be nonlinear but discarded this possibility because it did not conform to experimental evidence. The author agrees with this conclusion. They then proceeded to show that the discrepancy between the electron affinity values could possibly be explained in terms of an instrumental effect common to all electron impact systems which do not employ an effective electron energy filter and that the discrepancy depends on the kinetic energy of the negative ions. The present experiment shows that even using an effective electron-energy filter, the discrepancy cannot be eliminated and that there is no inherent dependence on the kinetic energy.[17]

VII. ELECTRON AFFINITY OF O FROM CO_2, O_2

Figure 9 shows a plot of the kinetic energy of the O^- ion vs electron energy in CO_2. Values for the kinetic energy are obtained (a) from ion retarding curves at a fixed electron energy and (b) from the shift in onset with a fixed retarding voltage between the grid and the ion collector. The electron-energy scale is calibrated using electron retarding curves and the ion kinetic energy using retarding curves on the parent positive ions. This procedure has been described previously and has been applied to measurements of the kinetic energy of H^- from H_2O,[18] and of H^- from H_2.[19] The proper electron affinity for H has been obtained in these two experiments.

An unusual behavior is observed for ion retarding curves in the energy range of the second peak in CO_2. These curves exhibit an unusually long "tail" indicating that the number of high energy ions is scarce. This may be due to the possibility that some of the O^- produced is accompanied by the production of CO in a vibrationally excited state; or that the negative ions are scattered primarily in the forward direction. Since a retarding curve taken with high enough sensitivity measures the maximum kinetic energy of the ions produced, this does not interfere with proper kinetic energy measurements. A line marked "theory" is drawn with the proper slope (28/44) to intercept the axis at the accepted value of $D-A$, the difference between the dissociation energy, $D(CO-O)=5.6$ eV, and the electron affinity, $A=1.5$ eV. The experimental points lie on a single line of proper slope which intercepts the axis at an apparent $(D-A)=3.65$ eV. Assuming the value of D to be correct, this leads to an apparent electron affinity of 1.95 eV. This apparent value of the electron affinity does not depend on the kinetic energy of the ion produced. The region of the first peak in CO_2 involves negative ions with kinetic energies around 0.5 eV (similar to the kinetic energies obtained in O^- from CO) and the second peak involves ions of kinetic energy above 2 eV (similar to the kinetic energies involved in O_2).

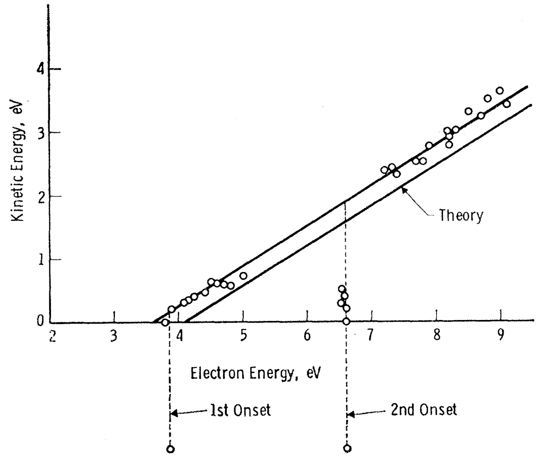

FIG. 9. Kinetic energy vs electron energy for O^- from CO_2 using the retarding potential difference method. The line marked "Theory" is drawn with the theoretical slope of 28/44 through the accepted value for the intercept on the horizontal axis. The values used are $D(CO-O)=5.6$ eV and $A(O)=1.5$ eV and the intercept on the horizontal axis is 5.6—1.5=4.1 eV. The line drawn through the experimental points intercepts the axis 3.65 eV which would lead to an apparent electron affinity of 1.95 eV. The points are obtained from both ion retarding curves and from the shift in onset.

It should be noted that the onset of negative ions of zero energy in CO_2 should occur, using $A=1.5$ eV, above 4.1 eV. Actually, the onset occurs at 3.83 eV. This value is a result of six determinations in a mass spectrometer (Curran) and about ten determinations in the present tube. The confidence error is less than ±0.1 eV.

Figure 10 shows a typical set of measurements of ion kinetic energy vs electron energy obtained over a period of two years, with many different types of tubes for O^-

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[16] L. M. Branscomb, D. S. Burch, S. J. Smith, and S. Geltman, Phys. Rev. **111**, 504 (1958).

[17] If the ion measuring system has a low sensitivity or if the negative ions are scattered preferentially in the direction of the electron beam, one could underestimate the kinetic energy at a fixed electron energy. The ion retarding curve would merge into noise at a lower retarding voltage. One has to be careful about this possibility for ions whose cross section is low or for systems which collect only a small fraction of the ions produced. In such instances the electron affinity would be underestimated.

[18] G. J. Schulz, J. Chem. Phys. **33**, 1661 (1960).

[19] G. J. Schulz, Phys. Rev. **113**, 816 (1959).

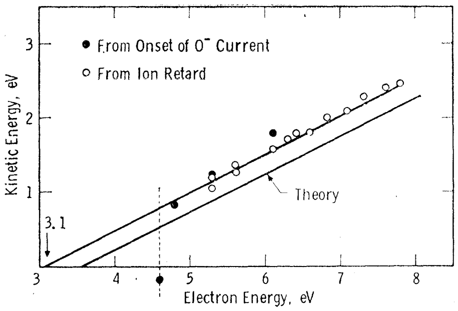

FIG. 10. Kinetic energy vs electron energy for O^- from O_2. The line, drawn with the proper slope of 0.5 through the experimental points intercepts the abscissa at a value $(D-A)=3.1$, giving an apparent electron affinity $A(O)=2.0$ eV.

from O_2. All experiments use the retarding potential difference method and the points obtained from the ion retarding curves[20] are shown with different symbols than the curves obtained from the shift in onset. The value for the electron affinity from this plot is 2.0 eV. Figure 11 shows a plot of kinetic energy of the H^- ion obtained by electron impact in H_2O, using identical techniques as those employed in O_2. There is complete agreement between theory and experiment. Figure 11 can be taken as an indication that the method employed in these measurements is a valid one.

VIII. ELECTRON AFFINITY OF O FROM N_2O, NO_2, SO_2

Beside the experiments discussed, there are the experiments in N_2O, NO_2, and SO_2, which must be considered. The dissociation energies of the N_2—O and NO—O and SO—O bonds are, however, less certain than the dissociation energies of the diatomic molecules discussed in this paper. If one assumes that the thermochemical value for these bonds is the correct one, then we can deduce electron affinities for atomic oxygen. The thermochemical value, $D(N_2—O)$, is 1.67 eV, the value for $D(N_2—O)-A(O)$ found in electron beam experiments[21] is -0.25 eV so that $A(O)$ becomes 1.9 eV. Although Curran and Fox[22] recently found from positive-ion data a value of $D(N_2—O)$ which is lower by 0.3±0.2 eV, the thermochemical value should be preferred at this time.

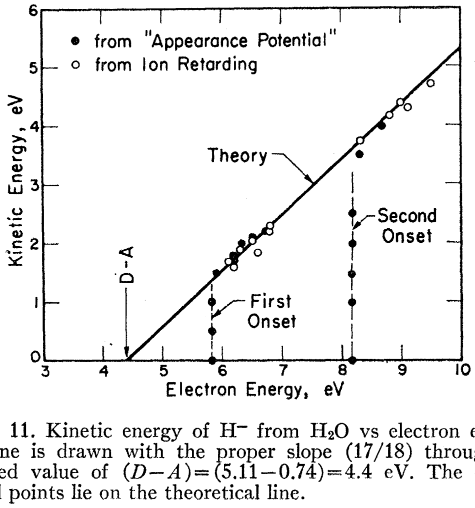

FIG. 11. Kinetic energy of H^- from H_2O vs electron energy. The line is drawn with the proper slope (17/18) through the accepted value of $(D-A)=(5.11-0.74)=4.4$ eV. The experimental points lie on the theoretical line.

In NO_2, the thermochemical value is $D(NO—O)=3.12$ eV, the onset for O^- is at 1.35 eV,[23] from which we find $A(O)>1.8$ eV. The electron affinity could be larger than the value given above by an amount equal to the internal energy of the NO fragment. Collin and Lossing find the onset of the process $NO_2+e\rightarrow O^-+NO^+$ at 10.1 eV.[24] This value has been recently confirmed by Curran.[25] Combined with the ionization potential of NO (9.25 eV) and the thermochemical dissociation energy, this leads to $A(O)=2.2$ eV.

Further evidence regarding $A(O)$ can be obtained from electron impact experiments on SO_2. The onsets of S^- and O^- can be determined and a lower limit of the electron affinities of the two atoms can be obtained by using thermochemical values. The most recent thermochemical values are given by Marsden[26] as $D(S—O—O)=11.04$ eV and $D(SO)=5.36$ eV. From this it follows [using $D(O)_2=5.11$ eV]that $D(SO—O)$ is 5.68 eV and $D(S—O_2)$ is 5.93 eV. It would seem that one should be able to obtain a consistent set of appearance potentials for S^- and O^- because contact potentials are the same for both determinations. Table V summarizes the experimental evidence. There is no clear-cut criterion which would enable us to reject any of the experiments listed in Table V.[27] The average values are 2.3eV for the electron affinity of S (compared to Branscomb's[28] value of 2.07 eV) and 1.9 eV for the electron affinity of O.

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[20] Ion retarding curves are evaluated in two different ways: (1) Linear extrapolation of the ion retarding curve is combined with the electron energy as determined from the peak of the electron distribution and (2) the tail of the ion retarding curve is combined with the high-energy tail of the electron distribution. Both these methods give points which lie on the experimental curve shown in Fig. 10.

[21] G. J. Schulz, J. Chem. Phys. **34**, 1778 (1961).

[22] R. K. Curran and R. E. Fox, J. Chem. Phys. **34**, 1590 (1961).

[23] R. E. Fox, J. Chem. Phys. **32**, 285 (1960). The kinetic energy of the O^- has been measured in a subsequent experiment by Curran and found to be less than 0.05 eV.

[24] J. Collin and F. P. Lossing, J. Chem. Phys. **28**, 900 (1957).

[25] R. K. Curran, to be published. His value for the onset of the process $NO_2+e\rightarrow O^-+NO^+$ is 10.05±0.1 eV, and a break is observed at 11.85±0.1 eV, resulting probably from the process $NO_2+e\rightarrow O+NO^+$. Assuming ions of zero kinetic energy to be produced, the separation of these two breaks gives $A(O)=1.8$ eV.

[26] D. G. H. Marsden, J. Chem. Phys. **31**, 1144, 1959.

[27] K. Kraus, Z. Naturforsch. **16a**, 1378 (1961), used both the retarding potential difference method and the conventional method for the determination of the onset of O^- and obtained values differing by 0.7 eV. Such a large discrepancy cannot be generally attributed to the different methods of measurements. The possibility arises that the high onset obtained by the retarding potential difference method is due to insufficient sensitivity. Kraus' paper does not state which method was used for the onset of S^-.

[28] L. M. Branscomb, *Advances in Electronics and Electron Physics* (Academic Press Inc., New York, 1957), Vol. 9, p. 43.

TABLE V. Energies at onset for S^- and O^- from SO_2 and resulting electron affinities, in eV.

Author	Onset of O^-	Onset of S^-	Lower limit for A(O)	Lower limit for A(S)	Method
Rosenbaum, Neuert[a]	3.5	3.6	2.2	2.3	Conventional
Curran[b]	3.8	3.5	1.9	2.4	Retarding potential difference method
Kraus[c]	3.5		2.2	2.2	Conventional
Kraus	4.21	3.75	1.47	2.2	Retarding potential difference method
Average			1.9	2.3	

[a] O. Rosenbaum and H. Neuert, Z. Naturforsch. **9a**, 990 (1954).
[b] R. K. Curran (private communication).
[c] See reference 27.

IX. ION PAIR FORMATION

Another method for the determination of the electron affinity uses the study of the ion pair formation. O^+ ions can be formed by (a) $e+O_2 \rightarrow O^+ + O^- + e$ or (b) $e+O_2 \rightarrow O^+ + O + 2e$. It is believed that the O^+ ion does not have kinetic energy near the threshold and thus the difference in appearance potentials is the electron affinity of O. Since one measures the voltage difference between two onsets, the absolute calibration of the energy scale is immaterial. Possibility for error arises from the uncertainty that the kinetic energy of the ions is truly zero at their onset[29]; from the possibility that the sensitivity is insufficient to determine the onset of the first break accurately,[30] from the possibility of background O^+ currents from atomic oxygen dissociated at the filament, and from the rather unlikely possibility that process (b) proceeds through an intermediate state or that the potential curve has a "hump".[31] Some of the values of electron affinity from pair formation are listed in Table IV. The values seem, again, to bunch around 2.0 and 1.5 eV. A more thorough analysis of ion pair formation, with particular attention to the cause for the discrepancy between the results of Hagstrum[32] (2.1 eV) and Randolph and Geballe[33] (1.5 eV) may prove to be fruitful.

X. CONCLUSIONS REGARDING THE ELECTRON AFFINITY OF OXYGEN

The present work on the determination of the electron affinity of oxygen was originally undertaken in order to demonstrate that the accepted value of the electron affinity (1.465 eV) could be obtained by electron beams using monoenergetic beam techniques (retarding potential difference method) in conjunction with good control of the electron beam (elimination of contact potentials, reduction of electron reflection). This attempt was frustrated from the beginning by the fact that the measurements of the electron affinity for O using oxygen gas resulted in a value about 2.0 eV. Various corrections suggested in the literature were analyzed but no justification for using any of them was found. Thus, one is forced to the conclusion that the electron affinity of oxygen is 2.0 eV and that an excited state exists about 0.5 eV above the ground state. On this model, Branscomb *et al.* would have measured photodetachment from this excited state.

In order to substantiate this result, an experiment on H^- production from H_2O and H_2 done with identical methods as those used for O_2 yielded the well-known electron affinity of H. An experiment on O^- from CO_2 yielded an electron affinity for oxygen around 2.0 eV, in agreement with the results in O_2, Further evidence comes from experiments on N_2O, NO_2, and SO_2; although the dissociation energies in these molecules are less well established than those in O_2 and CO, the evidence strongly favors an electron affinity for oxygen to be 2.0 eV.

Because one measures the maximum kinetic energy of negative ions in electron beam experiments, the existence of the excited state of O^- should be evidenced by a break in the retarding curve,[34] if both species are present. In one series of retarding experiments, a break was actually found and plotting the position of this break against electron energy (similar to Fig. 10), an electron affinity of 1.5 eV was found. Because of the difficulty of locating breaks in retarding curves, this experiment is not considered conclusive at this time. It suggests that both species of O^- negative ions (in the ground and excited state) are present in electron beam experiments in O_2.

The arguments advanced against the existence of an excited state of O^- are theoretical and experimental. These have been summarized by Branscomb.[28] However, it should be noted that the experimental aspects

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[29] Since the potential energy curves for $O^+ + O^-$ and $O^+ + O$ have attractive branches, it is reasonable to assume that the kinetic energy near threshold is zero. This is consistent with experimental measurements of the kinetic energy.

[30] The cross section for process (a) above is usually smaller than that for process (b). Thus, one could overestimate the energy for the onset of process (a) and thus underestimate the electron affinity.

[31] The possibility has been raised by Lagergren [C. R. Lagergren, thesis, University of Minnesota, 1955 (unpublished).] that the process $CO+e \rightarrow C^+ + O + 2e$, proceeds via an intermediate state, namely, $C^* + O + e$, where the carbon is in an excited state and subsequently autoionizes. Such a process would invalidate the simple interpretation advanced above, but no conclusive proof for such a process has been offered to date.

[32] H. D. Hagstrum, Revs. Modern Phys. **23**, 185 (1951).

[33] P. L. Randolph and R. Geballe, thesis, University of Washington, 1958 (unpublished).

[34] Photodetachment experiments have an onset at the minimum energy necessary to detach an electron and thus the onset corresponds to the detachment energy of an excited state, if it exists. The existence of the ground state would be evidenced by a break in the photodetachment cross section about 0.5 eV above onset which has not been observed. The problem arises whether the photodetachment cross section for the ground state is comparable to that for the excited state. A. Dalgarno (private communication) suggested that the photodetachment cross section from the ground state could be smaller than that for the excited state, if the latter actually exists.

of this argument may not be as convincing as has been believed. Hasted[35] measured the detachment cross section for O$^-$ with rare gas atoms and found this cross section to be independent of the manner in which the negative ions were produced. The two methods of production of O$^-$ were by electron bombardment of O$_2$ and by presumed thermal dissociation of N$_2$O to N$_2$ and O followed by radiative attachment to O. Recently, it was found,[21,22] however, that O$^-$ can be produced from N$_2$O by very low-energy electrons (peak at 0.7 eV) and that these ions may well be in the ground state of O$^-$. Thus, Hasted may have used identical O$^-$ ions for his two experiments.

Recently, Dunn[7] showed that the angular distribution of the particles in dissociative attachment may be far from isotropic. In fact, depending on the intermediate state excited, the distribution could be sharply peaked in either the forward or perpendicular direction. Thus, an instrument with a limited angular acceptance angle could discriminate against certain ionic species. This phenomenon may be the cause for much of the discrepancy between various experiments.

The possibility that kinetic-energy measurements in oxygen containing gases are affected by some, as yet unknown, difficulty cannot be dismissed. Further verification of the electron affinity of oxygen in different types of experiments is needed before one can state with certainty that an excited state of O$^-$ exists.

ACKNOWLEDGMENTS

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[35] J. B. Hasted, Proc. Roy. Soc. (London) **A222**, 74 (1954).

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Nuclear Magnetic Resonance in Gaseous He^3[†]

K. Luszczynski, R. E. Norberg, and J. E. Opfer[*]
Washington Univeristy, Saint Louis, Missouri

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Relative nuclear magnetic susceptibility, self-diffusion coefficient D, and spin lattice relaxation time T_1 (characteristic of wall relaxation) were measured in He^3 gas between 1.7 and 4.2°K in the range of pressure between 0.08 and 56 atm. These results were derived from measurements of free induction decays and spin echoes at 20.00 Mc/sec. Values for the density of the gas were deduced on the assumption that the gas obeys Curie's law. At moderate densities D was found to be inversely proportional to the density, while T_1 was found to increase with the density of the gas. Experimental results obtained for the self-diffusion coefficient are compared with theoretical values. Details of experimental procedure are described.

INTRODUCTION

THE investigation of the transport processes of He^3 gas and its equation of state at low temperatures has many interesting aspects, since we expect to find the properties of He^3 gas to be affected appreciably by quantum mechanical effects.[1] Out of the four transport coefficients of viscosity, thermal conduction, thermal diffusion, and self-diffusion we can measure the coefficient of self-diffusion D, using nuclear magnetic resonance techniques.

The spin-echo technique[2–4] of nuclear magnetic resonance is particularly well suited to measurements of self-diffusion in media containing magnetic nuclei in sufficient concentration. Also the amplitude of the nuclear magnetic signal, under certain well specified conditions, is proportional to the nuclear magnetic susceptibility of the sample. If the relationship between the susceptibility and density of the sample is known, it is then possible to derive relative values for the density, which, in turn, can be converted into absolute values by comparison with an absolute determination of the density at any suitable point. It is thus possible, in principle, to construct an equation of state of the sample, in this case He^3 gas, and evaluate its virial coefficients. Results obtained from measurements of this type are reported here.

EXPERIMENTAL DETAILS

Nuclear magnetic resonance signals were observed at 20.00 Mc/sec, that is, in a field of $H_0=6180$ G produced by a 12-in. electromagnet with a 3-in. gap.

The sample container was in the form of a nylon

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[*] National Science Foundation Cooperative Graduate Fellow.

[1] J. de Boer, *Progress in Low-Temperature Physics*, edited by C. J. Gorter (North Holland Publishing Company, Amsterdam, 1957), Vol. 1, p. 381 and references contained therein.

[2] E. L. Hahn, Phys. Rev. **80**, 580 (1950).

[3] H. Y. Carr and E. M. Purcell, Phys. Rev. **94**, 630 (1954).

[4] R. L. Garwin and H. A. Reich, Phys. Rev. **115**, 1478 (1959).