$(NH_4)_2Cr_2O_7$(c) are consistent to within about one and one-half kcal./mole. The "best" value for the standard heat of formation of $CrO_4^{=}$(aq) is taken to be the average of the values based on CrO_3 and $(NH_4)_2Cr_2O_7$, namely, −208.6 kcal./mole.

From the "best" heat of formation of $CrO_4^{=}$(aq) and heats of reactions 1 and 3, the "best" heats of formation of $HCrO_4^-$(aq) and $Cr_2O_7^{=}$(aq) have been calculated to be −207.9 and −352.2 kcal./mole, respectively. These heats of formation have been combined with heats of solution and reaction from this and the earlier paper[2] to calculate "best" heats of formation of K_2CrO_4(c) and $K_2Cr_2O_7$(c) to be −332.8 and −488.3 kcal./mole, respectively. From heats of formation and entropies given in this paper and others tabulated by the Bureau of Standards,[7] free energies of formation of $CrO_4^{=}$(aq), $HCrO_4^-$(aq) and $Cr_2O_7^{=}$(aq) have been calculated to be −171.1, −180.0 and −305.9 kcal./mole, respectively.

Conclusions

Neuss and Rieman,[4] Tong and King[5] and Davies and Prue[6] are in fair agreement as to the value of K_3 at 25°. Their concordant results give us confidence in the reported values for K_3 that is substantiated by the satisfactory agreement between our calorimetric ΔH_3^0 and the ΔH_3^0 calculated from the temperature dependence of K_3. It also seems very likely that the reported values for K_2 and K_4 are at least approximately correct.

The equilibrium constant for reaction 1 has been less adequately investigated than has K_3. It is planned to reinvestigate in this Laboratory this equilibrium at 25° with the aim of checking the results of Neuss and Rieman.[4] It is also intended to investigate this equilibrium at several temperatures in order that an independent value of ΔH_1^0 may be obtained to be compared with the calorimetric ΔH_1^0 reported in this paper.

Charlottesville, Virginia

[Contribution from the Department of Chemistry, University of British Columbia]

The Ionization and Dissociation of Oxygen by Electron Impact[1]

By D. C. Frost and C. A. McDowell

Received June 30, 1958

The ionization and dissociation of molecular oxygen has been studied using the retarding potential difference (r.p.d.) method of obtaining essentially mono-energetic electrons. All the spectroscopically known excited states of molecular oxygen, *i.e.*, $^2\Pi_g$, $^4\Pi_u$, $^2\Pi_u$, $^4\Sigma_g^-$, and one additional state, have been observed. The vertical ionization potentials here determined are in very good agreement with those calculated from available spectroscopic data. Six different dissociation processes leading to the production of O^+ ions have been observed. These ions arise from either of these two types of processes: $O_2 + e = O^+ + O + 2e$ (a), $O_2 + e = O^+ + O^- + e$ (b). Each particular process has been identified by a careful study of the negative and positive ions formed. Ambiguities in earlier work, which arose largely from the difficulty of calibrating the negative ion energy scale, have been overcome by using sulfur hexafluoride as a calibrating gas.

Oxygen has been the object of many fairly detailed electron impact studies. The most detailed work is perhaps reported by Hagstrum.[2] Besides studying the various ionization and dissociation processes, Hagstrum measured the appearance potentials of the positive and negative oxygen ions. Hagstrum also determined the kinetic energies with which the various ions are formed in the different dissociation processes observed. Later work by Thorburn[3] has, however, shown that some of Hagstrum's observations are perhaps not quite as well founded as they formerly appeared. Examination of Thorburn's results indicates that these more recent observations are still not quite satisfactory.

The main difficulties in all the earlier work arise from the fact that the various workers used electron beams which had quite a large spread in their energy distribution. These experimental methods thus precluded the observation of fine details which are to be expected if the known spectroscopic data on oxygen are studied (see McDowell[4]). Furthermore, in studying negative ion efficiency curves, these workers were unable to observe the true shape of the electron resonance capture peaks, and also they were unable to calibrate accurately the negative ion energy scale. Both these major difficulties recently have been shown to be resolved if one uses essentially mono-energetic electrons.[5-7] It is now possible to calibrate the negative ion energy scale accurately by using the near-zero appearance potential of the SF_6^- ion from sulfur hexafluoride as a standard.[6] Our own previous work[5,8,9] has shown that the retarding potential difference method of obtaining essentially mono-energetic electrons developed by Fox, *et al.*,[7] yields accurate values for the excited states of molecular and atomic ions. It thus seems that the application of this method to oxygen would resolve many of the discrepancies noted in earlier electron impact studies of this molecule.

Experimental

The mass spectrometer used was that described in our earlier publications.[8,9] Krypton served as a calibrating gas for the measurements on the positive ions. Sulfur

---

[1] This work was supported in part by the Geophysical Research Directorate of the U. S. Air Force Cambridge Research Centre, Air Research and Development Command, under Contract No. AF19-(604)-2275, and by grants from the National Research Council of Canada.

[2] H. D. Hagstrum, *Rev. Mod. Phys.*, **23**, 185 (1951).

[3] R. Thorburn, "Report of Conference on Applied Mass Spectrometry," Institute of Petroleum, London, 1955, p. 185.

[4] C. A. McDowell, "Applied Mass Spectrometry," Institute of Petroleum, London, 1954, p. 129.

[5] D. C. Frost and C. A. McDowell, *Proc. Roy. Soc.* (*London*), **A232**, 227 (1955).

[6] W. M. Hickam and R. E. Fox, *J. Chem. Phys.*, **25**, 642 (1956).

[7] R. E. Fox, W. M. Hickam, T. Kjeldaas, Jr., and D. J. Grove, *Phys. Rev.*, **84**, 859 (1951).

[8] D. C. Frost and C. A. McDowell, *Proc. Roy. Soc.* (*London*), **A236**, 278 (1956).

[9] D. C. Frost and C. A. McDowell, *Can. J. Chem.*, **36**, 39 (1958).

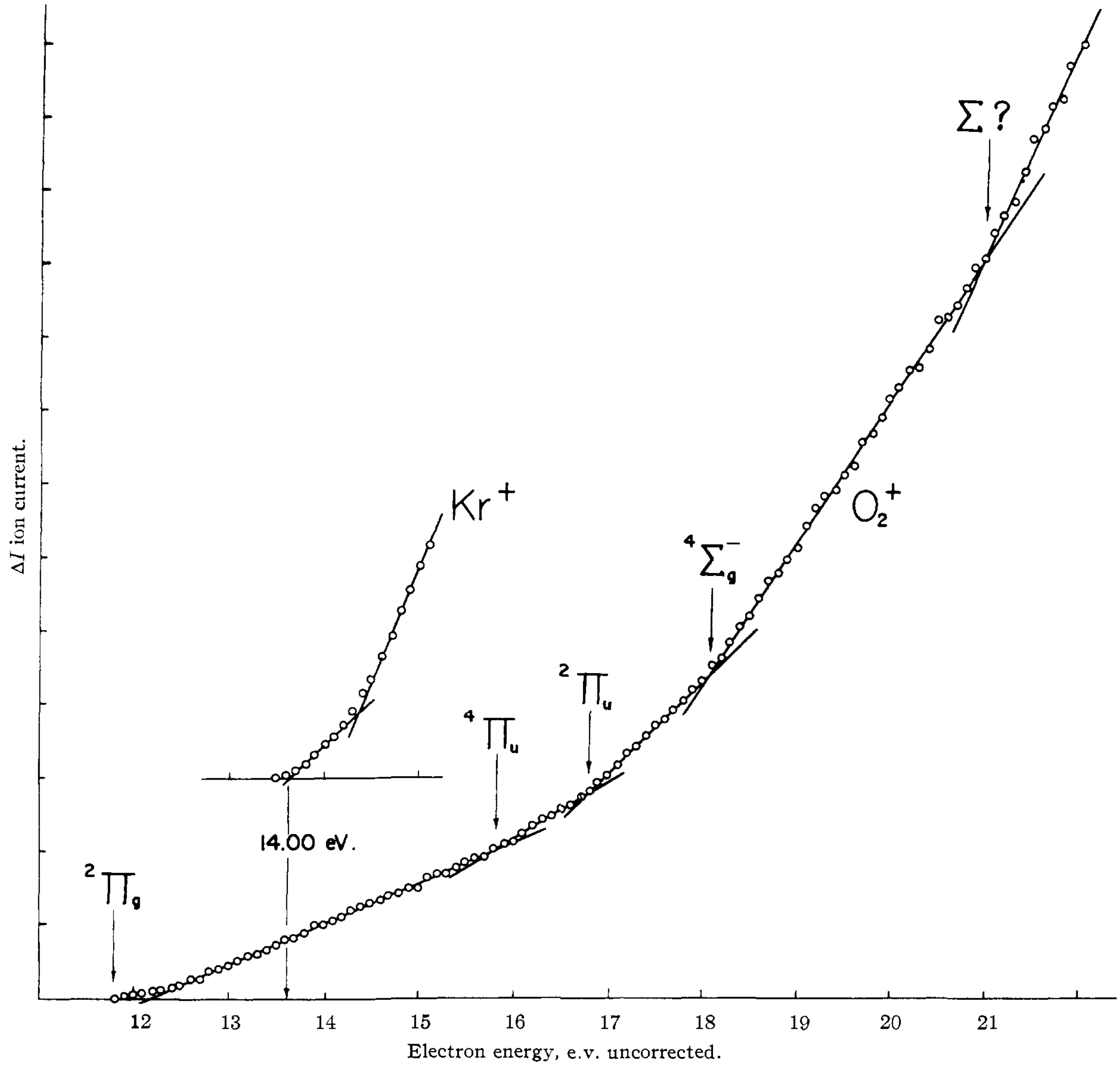

Fig. 1.—The ionization efficiency curve for the formation of the O_2^+ ion from oxygen by electron impact.

hexafluoride (Matheson Co. Inc.) was used to calibrate the negative ion energy scale. The ionization potential of krypton is 112914.5 cm.$^{-1}$ [10] or 13.997 e.v. if 8066.83 cm.$^{-1}$ equals 1 e.v.[11] The appearance potential of the SF_6^- ion from sulfur hexafluoride was taken as 0.03 e.v.[8]

Oxygen pressures of 5 × 10^{-6} mm. and 4 × 10^{-5} mm. were used for positive and negative ion studies, respectively, and 3 × 10^{-6} mm. pressure of each calibrating gas was found to give adequate Kr^+ and SF_6^- abundances.

The retarding potential difference (r.p.d.) method could not be used for O^- ions at high electron energies because of the small ion current. O^- appearance potentials under these conditions were obtained in the usual way from the initial portion of the O^- resonance capture process (of established onset energy). For the results quoted for the O_2^+ ion, the O^+ ion and the O^- ion at low energies (resonance capture process) the theoretical energy band width of the electrons was 0.1 e.v.

Experimental Results

The ionization efficiency curve for the O_2^+ ion is shown in Fig. 1. Here there are clearly five ionization processes observed. The energies at which these occur, with the standard deviations, are 12.21 ± 0.04, 16.30 ± 0.03, 17.18 ± 0.02, 18.42 ± 0.02, and 21.34 ± 0.02 e.v. These energies will later be shown to refer to the formation of the O_2^+ ion in its ground and first four excited states.

The O^+ ionization efficiency curve is shown in Fig. 2. This graph shows evidence for five distinct dissociation processes leading to O^+ ions. The energies at which these five dissociation processes occur are 17.30 ± 0.10, 18.99 ± 0.05, 20.42 ± 0.04, 21.30 ± 0.03 and 22.03 ± 0.03 e.v. Figure 3 shows the ionization efficiency curve for the formation of O^- ions at higher energies. These results were obtained using electrons with half the width of the normal energy distribution. Since the O^- ion here appears at 17.36 ± 0.04 and 21.22 ± 0.05 e.v., it is apparent that the first and fourth dissociation reactions leading to the formation of the O^+ positive ions in Fig. 2 must be ion-pair processes.

Figure 4 shows the resonance capture peak for the O^- ion at low electron energies. The SF_6^- ion resonance capture peak is also depicted as this is the

(10) R. E. Becker and S. Goudsmit, "Atomic Energy States," McGraw-Hill Book Co., New York, N. Y., 1952.

(11) J. W. M. DuMond and E. R. Cohen, *Phys. Rev.*, **82**, 555 (1951).

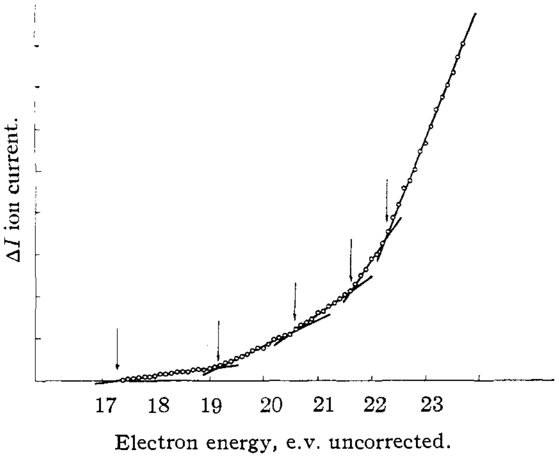

Fig. 2.—The ionization efficiency curve for the formation of the O^+ ion from oxygen by electron impact.

calibrating ion. The appearance potential for the O^- ion is 4.53 ± 0.03 e.v.

Discussion

The Molecular Oxygen Ion O_2^+.—The ground state of the oxygen molecule has the electronic structure

$$KK(\sigma_g2s)^2(\sigma_u2s)^2(\sigma_g2p)^2(\pi_u2p)^4(\pi_g2p)^2,{}^3\Sigma_g^- \quad (1)$$

The first ionization potential will therefore refer to the removal of an electron from the (π_g2p) orbital to form an O_2^+ ion in its ${}^2\Pi_g$ ground state. Earlier electron impact studies by Tate and Smith[12] and Hagstrum[2] yielded the values 12.5 ± 0.1 and 12.1 ± 0.2 v. Our value is 12.21 ± 0.04 v. Recent photo-ionization studies by Watanabe[13] give the value 12.075 ± 0.01 v. for the first ionization potential.

Careful study of the initial portion of the ionization efficiency curve for this O_2^+ ion by our method shows that the curve is non-linear over the first 0.5 e.v. Since about 80% of the electron energy distribution we use lies within 0.15 e.v., the non-linearity of the true ionization efficiency curve is not likely to extend over more than 0.3 e.v. This curvature may be attributed to vertical transitions from the ground ${}^3\Sigma_g$ state of the oxygen molecule to the first two vibration levels of the ${}^2\Pi_g$ ground state of the O_2^+ ion, since these levels are separated by only 0.25 e.v. The O_2^+ ${}^2\Pi_g$ ions have an equilibrium internuclear distance 0.085 A. less than that of the ground state of the oxygen molecule, so it is quite likely that the O_2^+ ion will be formed by transitions to other than the $v' = 0$ vibrational level of the ground state.

Equation 1 indicates that the second ionization potential will involve the removal of an electron from the (π_u2p) orbital with the formation of an O_2^+ ion with the configuration $(\pi_u)^3(\pi_g)^2$. This configuration can give rise to the electron states ${}^4\Pi_u$, ${}^2\Phi_u$ and ${}^2\Pi_2$, but Mulliken[14] has shown that only the ${}^4\Pi_u$ and ${}^2\Pi_u$ states of the O_2^+ ion need here be considered. Two Rydberg series have been observed for oxygen.

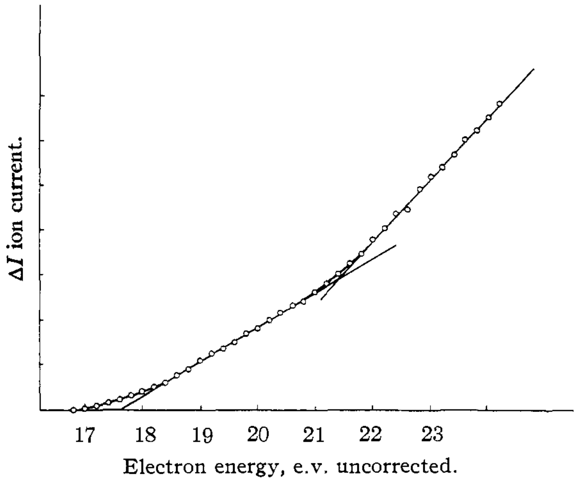

Fig. 3.—The ionization efficiency curve for the formation of the O^- ion from oxygen by ion pair processes as the result of electron impact.

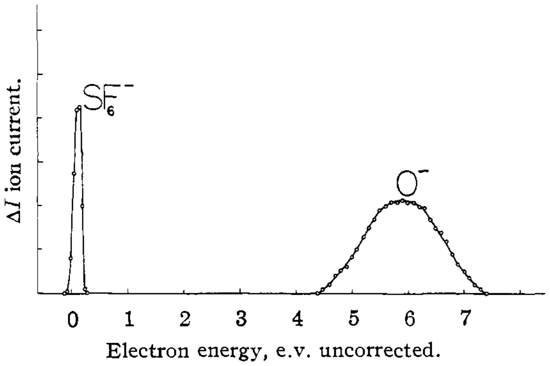

Fig. 4.—The resonance capture peak for the formation of O^- ions from oxygen by electron impact.

These go to limits at 18.16 e.v.,[15] 18.2[16] and 16.11 e.v.[16] These limits refer to the upper ${}^4\Sigma_g^-$ and lower ${}^4\Pi_u$ components of the first negative band system of molecular oxygen, the ${}^4\Sigma_g^-$–${}^4\Pi_u$ separation being 2.05 e.v.[17] The second ionization potential we observed to be 16.30 e.v. This obviously refers to the formation of the O_2^+ ion in its ${}^4\Pi_u$ state.

The third ionization potential we observed for the O_2^+ ion occurs at 17.18 e.v. As it is known that the second negative bands of oxygen involve transitions between the ${}^2\Pi_g$ ground state of O_2^+ and an upper ${}^2\Pi_u$ state, 4.81 e.v. above the ground ${}^2\Pi_g$ state, it is apparent that this third ionization potential which we observed must refer to the formation of the O_2^+ ion in its ${}^2\Pi_u$ excited state.

We observed the fourth ionization potential of the O_2^+ ion to occur at 18.42 e.v. Since the ${}^4\Sigma_g^-$ state of O_2^+ is known to lie at the limit of the Rydberg series observed by Price and Collins at 18.16 e.v., it is evident that this fourth ionization potential which we found must be due to the formation of the O_2^+ ion in its ${}^4\Sigma_g^-$ state. This is most easily envisaged to be formed by the removal of an electron from the (σ_g2p) orbital of equation 1 leading to an

---

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

[13] K. Watanabe, *J. Chem. Phys.*, **26**, 542 (1957).

[14] R. S. Mulliken, *Rev. Mod. Phys.*, **4**, 3 (1932).

[15] Y. Tanaka and T. Takamine, *Phys. Rev.*, **59**, 771 (1941).

[16] W. C. Price and G. Collins, *ibid.*, **48**, 714 (1935).

[17] T. E. Nevin, *Phil. Trans.*, **A237**, 481 (1938); *Proc. Roy. Soc. (London)*, **A174**, 371 (1940);. T. E. Nevin and T. Murphy, *Proc. Roy. Irish Acad.*, **46**, 169 (1941).

ion with the electronic configuration (σ_g) $(\pi_u)^4$ $(\pi_g)^2$ and so in a $^4\Sigma_g{}^-$ state.

Between 18.5 and 25 e.v. our work shows evidence for only one further ionization potential, *i.e.*, that found at 21.34 ± 0.02 e.v. This could be the ion formed by the removal of an electron from a $(\sigma_u 2s)$ or a $(\sigma_g 2p)$ orbital with or without simultaneous excitation of another electron in one of the other orbitals. It is not possible at the present time to say what the particular electronic structure of this ion may be, as it has not been detected spectroscopically.

The various electron impact and spectroscopic ionization potentials found for oxygen are collected in Table I.

TABLE I

ADIABATIC AND VERTICAL IONIZATION POTENTIALS AND INTERATOMIC DISTANCES FOR O_2 AND $O_2{}^+$

Electronic state of the $O_2{}^+$ ion	Spectroscopic ionization potential of O_2 (e.v.)	Electron impact ionization potential of O_2 (e.v.)	Interatomic distance (A.)
$^2\Pi_g$	12.16[a]	12.21 ± 0.04	1.1227
$^4\Pi_u$	16.11[16]	16.30 ± .03	1.3813
$^2\Pi_u$	16.97[b]	17.18 ± .02	1.4089
$^4\Sigma_g{}^-$	18.16[15,16]	18.42 ± .02	1.2795
?	......	21.34 ± .02	....
			1.207 (O_2)

[a] The value given for the first spectroscopic ionization potential depends on the value chosen for $D(O_2{}^+)$ in its $^2\Pi_g$ state. A short extrapolation of the $^2\Pi_g$ state gives $D(O_2{}^+)^2\Pi_g$ as 6.57 e.v.[18,19] Hence from the cycle

$$D(O_2) + I(O) = D(O_2{}^+) + I(O_2)$$

we get $I(O_2) = 12.16$ e.v. The true value for $I(O_2)$ is likely to be nearer the value of 12.075 e.v. obtained by Watanabe.[13] This gives $D(O_2{}^+)^2\Pi_g$ as 6.65 e.v. [b] Assuming Watanabe's value for $I(O_2)$ to be correct, then the ionization potential of oxygen referring to the formation of the $O_2{}^+$ ion in its $^2\Pi_u$ state is 16.89 e.v.

The interatomic distance of the $^3\Sigma_g{}^-$ ground state of oxygen is 1.2074 Å., so if the "width" of the lowest vibrational eigen-function in this state is assumed to be 0.1 Å., then electronic transitions obeying the Franck–Condon principle will reach the lowest vibrational energy levels of those states of the $O_2{}^+$ ion having interatomic distances between 1.16 and 1.26 Å. The interatomic distances for the various known states[20] of the $O_2{}^+$ ion are given in Table I where that for the $^3\Sigma_g{}^-$ ground state of O_2 is included for comparison. The interatomic distances of the $^4\Pi_u$, $^2\Pi_u$ and $^4\Sigma_g{}^-$ states of the $O_2{}^+$ ion lie outside the limits of 1.16 and 1.26 Å., so on these grounds the electron impact ionization potentials leading the formation of the $O_2{}^+$ ion in these states, would be expected to be greater than the corresponding spectroscopic or adiabatic ionization potentials. The data in Table I show that this expectation is fulfilled.

The Formation of Atomic Oxygen Ions. (i) **O^- Ions at Low Energies.**—The appearance potential of the O^- ion formed by the resonance capture process

$$O_2 + e^- = O + O^- \qquad (2)$$

was found to be 4.53 ± 0.03 e.v. (see Fig. 4). This is fairly close to the value found by Thorburn,[3] namely, 4.7 e.v., and less than the value of 6.3 e.v. observed by Hagstrum.[2] The formation of the O^- ion from O_2 by process 2 can be represented energetically by the equation

$$V(O^-) = D(O_2) - E(O) + K + E \qquad (3)$$

where $V(O^-)$ is the appearance potential of the O^- ion, $D(O_2)$ is the dissociation energy of the oxygen molecule, $E(O)$ is the electron affinity of the oxygen atom, K is the kinetic energy with which the fragment may be endowed, and E is the excitation energy of either the O atom, or the O^- negative ion, or both. If $D(O_2) = 5.115$ e.v.,[21] and $E(O) = 1.45 \pm 0.15$,[22] then

$$V(O^-) = 3.67 \text{ e.v.} + K + E \qquad (4)$$

If the fragments are formed in their ground states, the kinetic energy K is 0.86 e.v. Earlier workers have used retarding potential techniques to determine $V(O^-)$ for ions at zero kinetic energy. Values which have been reported are 2.9,[23] 2.9[2] and 3.2.[24] The discrepancies between these values and ours probably are due to uncertainty in the calibration of the electron energy scale in earlier work. Here it is to be noted that the unambiguous SF_6 method we have used was only recently introduced.[6] The O^- ion resonance capture peak which we observed using electrons with about 0.2 e.v. energy band width extended over about 3 e.v. and was nearly symmetrical, about a maximum of 5.98 e.v.

The shape of the resonance capture peak should be a reflection of the O_2 molecular ground state eigenfunction in the potential energy curve for the $O_2{}^-$ molecular ion. This is illustrated in Fig. 5 where the O^- ion peak is drawn to scale and the upper curve is constructed so that it crosses the approximate boundaries of the Franck–Condon region at points corresponding to the upper and lower threshold energies at which the O^- ion peak is observed. The upper $O_2{}^-$ state dissociation limit must lie below the O^- ion appearance potential at 4.53 e v., and must involve an O atom in the ground or first excited state. No excited states of the O^- ion are known so the dissociation limit has been put at an energy of $D(O_2) - E(O) = 3.67$ e.v. Recently Dibeler, Reese and Mann[25] have observed the $O_2{}^-$ ion in the mass spectrum of perchloryl fluoride. This proved that the $O_2{}^-$ must be stable enough to have a life-time greater than 10^{-6} sec. This $O_2{}^-$ ion must have a shallow minimum in its potential energy curve at a distance greater than the internuclear distance of oxygen; otherwise $O_2{}^-$ could be observed in the mass spectrum of O_2.

(ii) **O^+ and O^- Ions Formed at Higher Energies.**—There are several processes by which atomic positive and negative ions may arise through the electronic bombardment of oxygen molecules. Table II gives the minimum energies which such processes may be expected between zero and 23 e.v.

Above the O^- resonance capture peak, the O^+ and O^- ions were first formed at 17.30 and 17.36

---

(18) R. S. Mulliken and D. S. Stevens, *Phys. Rev.*, **44**, 720 (1933).

(19) A. G. Gaydon, "Dissociation Energies of Diatomic Molecules," Chapman and Hall, London, 1953.

(20) G. Herzberg, "Spectra of Diatomic Molecules," D. van Nostrand Co., New York, N. Y., 1950.

(21) P. Brix and G. Herzberg, *J. Chem. Phys.*, **21**, 2240 (1953).

(22) L. M. Branscombe and S. J. Smith, *Phys. Rev.*, **98**, 1127 (1955).

(23) W. W. Lozier, *ibid.*, **46**, 268 (1934).

(24) Private communication from J. Marriott.

(25) V. H. Dibeler, R. M. Reese and D. E. Mann, *J. Chem. Phys.*, **27**, 176 (1957).

e.v., respectively. Since there is no known state of the O_2^+ ion in this vicinity which could give rise to O^+ ions, it is probable that the fragments are produced as an ion-pair. Thorburn[3] also observed an ion-pair near to these energies. Table II shows that 17.28 e.v. is the minimum energy required to produce the ion-pair $O^+(^4S_u) + O^-(^2P_u)$ from the $O_2(^3\Sigma_g^-)$ ground state. This is obviously the process which we observed.

O^+ ions are next observed at 18.99 e.v. and clearly arise from vertical transitions to near the 18.73 e.v. dissociation limit of the $O^+\ ^2\Pi_u$ state. This state has an internuclear distance appreciably greater than the $O_2\ ^3\Sigma_g^-$ state, and vertical transitions might well be expected to give rise not only to O_2^+ ions, but also to O^+ ions. Hagstrum[2] and Thorburn[3] attribute their O^+ ion current increase at near 19 e.v. to the same process, namely

$$O_2(^3\Sigma_g^-) + e = O^+(^4S_u) + O(^3P_g) + 2e + K$$

It would thus seem that the fragments are formed with about 0.26 e.v. of excess kinetic energy.

TABLE II

MINIMUM ENERGIES FOR IONIC DISSOCIATION PROCESSES IN O_2

	Process		Products	Minimum energy (e.v.)
1	$O_2(^3\Sigma_g^-)$	→	$O(^3P_g) + O^-(^2P_u)$	3.67
2	$O_2(^3\Sigma_g^-)$	→	$O^+(^4S_u) + O^-(^2P_u)$	17.28
3	$O_2(^3\Sigma_g^-)$	→	$O^+(^4S_u) + O(^3P_g)$	18.73
4	$O_2(^3\Sigma_g^-)$	→	$O^+(^2D_u) + O^-(^2P_u)$	20.60
5	$O_2(^3\Sigma_g^-)$	→	$O^+(^4S_u) + O(^1D_g)$	20.70
6	$O_2(^3\Sigma_g^-)$	→	$O^+(^2D_u) + O(^3P_g)$	22.05
7	$O_2(^3\Sigma_g^-)$	→	$O^+(^2P_u) + O^-(^2P_u)$	22.30
8	$O_2(^3\Sigma_g^-)$	→	$O^+(^4S_u) + O(^1S_g)$	22.90

At 20.42 e.v. there is evidence for an additional process giving rise to O^+ ions, and these must be formed through transitions to the dissociation limit of the $O_2^{+4}\Sigma_g^-$ state. Here again the internuclear distance is greater than that of the O_2 ground state. The dissociation limit of the $^4\Sigma_g^-$ state of O_2^- is 20.70 e.v. (see Table II). It is likely that our appearance potential for this process is a little too low. Thorburn[3] observed both O^+ and O^- ions at this potential. In our work, however, the second process giving rise to O^- ions does not occur until 21.22 ± 0.05 e.v. O^+ ions are also observed at 21.30 ± 0.05 e.v. It must again be pointed out that Thorburn's method for calibrating the negative ion electron energy scale is not unambiguous, and it is highly likely that his negative ion appearance potentials may be in error. The ion-pair process which we observe to occur at 21.3 e.v. most probably is that associated with the formation of $O^+(^2D_u) + O^-(^2P_u)$ at a minimum energy of 20.60 (see Table II).

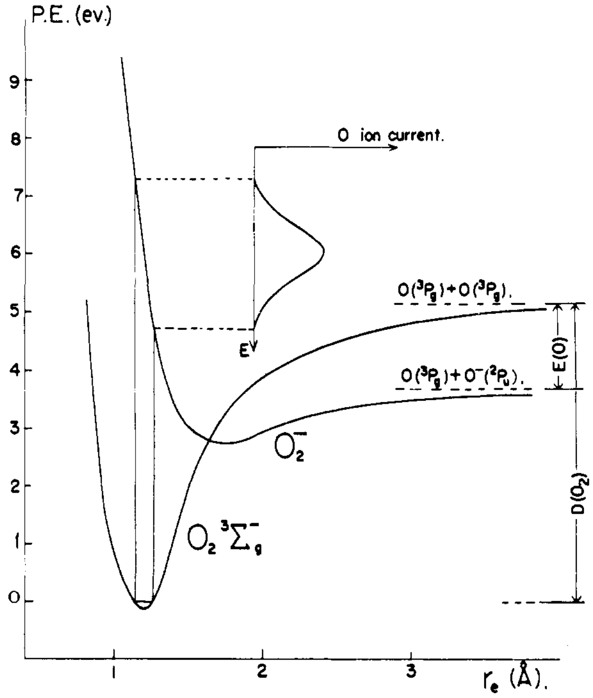

Fig. 5.—Potential energy diagram to illustrate the formation of the O^- ion from oxygen by a resonance capture process.

At an energy of 22.03 e.v. there is evidence for a further process resulting in O^+ formation. It is probable that transitions are taking place to a repulsive O_2^+ state of minimum energy 18.73 or 20.70 e.v. The latter involves about 2 e.v. less kinetic energy and is to be preferred since Hagstrum[2] has indicated that there is little kinetic energy associated with this group of O^+ ions.

VANCOUVER, CANADA