to which the capillary was sealed. This loss would result in a larger apparent solubility.

The method as outlined has also been used to determine the solubility of these substances in salt solutions, in particular in 0.5 *M* potassium chloride and 0.5 *M* magnesium sulfate. The procedure is in all particulars the same as for water. A large volume of the salt solution of the desired concentration is made up and used throughout for dilutions, standard solutions, comparison solutions in the interferometer, etc., in the place of distilled water. In general, there appears to be no reason why the method should not be applicable to solubility measurements in practically any colorless aqueous solutions for any type of substance. Measurements of solubilities in non-aqueous solvents are also possible but these would in many cases involve difficulties inherent in the construction of the interferometer itself, which is primarily designed for aqueous solutions.[9]

In conclusion I take this opportunity to thank Professor Peter Debye for placing facilities at my disposal at the Physikalisches Institut, Leipzig, with which part of the work was done, and for valuable suggestions and advice.

Summary

1. A method for the determination of the solubility of difficultly soluble liquids in water and aqueous solutions is described.

2. The solubilities of 1,1-dichloro-ethane, 1,2-dichloro-ethane, 1,2-dichloropropane and 1,3-dichloropropane are given. A preliminary value for the solubility of carbon tetrachloride is also given.

DURHAM, NORTH CAROLINA

[CONTRIBUTION FROM GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 205]

THE ACTIVATION OF OXYGEN BY ELECTRON IMPACT

BY ROBERT H. DALTON

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Introduction

The purpose of this research was to study the chemical behavior of oxygen activated by electron impact and to measure the energy necessary for its activation. The general plan was to use an apparatus similar to that employed by Glockler, Baxter and Dalton[1] in the study of the reaction between copper oxide and active hydrogen.

The oxygen was introduced at pressures of 0.05–0.4 mm. of mercury into a four-electrode tube connected with a liquid-air trap and a Pirani pressure gage. A four-electrode tube was used in order that the energy loss of the

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[9] In this connection see Cohen and Bruins, *Proc. Acad. Sci. Amsterdam*, **24**, 114 (1921).

[1] Glockler, Baxter and Dalton, THIS JOURNAL, **49**, 58 (1927).

electrons might be studied by making current-potential curves as done by Franck[2] and others. With this arrangement it was possible to follow the course of any reaction which involved a change in the number of molecules or produced a substance condensable in liquid air. It was, of course, not possible to use gases which would undergo reaction when exposed to the hot filament. Several reactions were tried; the one finally studied was that of the activated oxygen with solid carbon to form carbon dioxide.

Materials and Apparatus.—The oxygen was obtained by heating mercuric oxide which was contained in a bulb attached to the apparatus. The mercuric oxide had been previously prepared in the apparatus by boiling mercury for some time with well-dried tank oxygen.

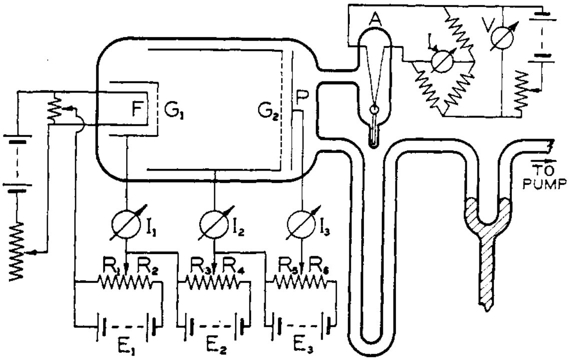

Fig. 1.

The carbon was present in the form of lampblack deposited on the end of grid G_2 with a smoky gas–oxygen flame, except in the case of a preliminary experiment in which graphite previously ignited *in vacuo* was used. The lampblack was deposited only on the end of the grid away from the filament, in order to avoid so far as possible any thermal reaction.

The apparatus used is shown diagrammatically in Fig. 1. Within the tube all metal parts are of platinum except for the short lengths of tungsten wire used to bring the leads through the glass. Attempts to protect the tungsten wires from the action of oxygen by plating them with gold were unsuccessful. The source of electrons is the calcium oxide coated filament F, operating on a potential drop of about 2 volts. Around this is a cylindrical electrode, G_1, with a circular grid of 50-mesh gauze 0.1 cm. from the filament. The next electrode is also cylindrical and has in the end a circular grid, G_2, of the same mesh as G_1. The distance from G_1 to G_2 is about 4 cm. One millimeter behind G_2 is the plate P.

The electrical connections are shown in the diagram; I_1, I_2, I_3 and I_4 are galvanometers. The potential P between filament F and grid G_1 is established by means of a storage battery and resistance in parallel. It is calculated by the expression

$$P = \frac{R_1}{R_1 + R_2}(E_1 - I_1R_2)$$

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[2] For a complete discussion of these methods see Franck and Jordan, "Anregung von Quantensprüngen durch Stösse," Springer, Leipzig, 1927.

Here R_1 and R_2 are the resistances indicated in the diagram, E_1 is the potential of the battery and I_1 is the current between the filament and the first electrode.

A connecting tube leads from the apparatus to the Pirani gage A, which consists of a fine platinum wire about 18 cm. long and 0.003 cm. in diameter. In the original experiments the wire was sealed in a straight glass tube 0.5 cm. in diameter. This form, while quite sensitive, was undesirable since when heated the wire became slack so that its position with respect to the walls, and hence the heat conductivity and apparent pressure, were variable. These difficulties were avoided by the arrangement shown in Fig. 1 in which the wire is stretched and centered by a small weight sliding in a glass tube. To maintain the walls at constant temperature the tube containing the wire was placed in a thermos bottle filled with water. The slight heating due to the Pirani wire did not raise the temperature of the water appreciably. The connections are shown in the figure and are those recommended by Campbell.[3] The Pirani wire is in one arm of a Wheatstone bridge the other three resistances of which are fixed. The voltage, V, necessary to balance the bridge is then a measure of the pressure. Over the pressure ranges for which the instrument was used (0.01 to 0.3 mm.) the pressure is a nearly linear function of $V^2 - V_0^2$, where V_0 is the voltage to balance the bridge when the pressure is negligible. If absolute pressure measurements are desired, the gage must be calibrated against a McLeod gage with each gas used.

Another connecting tube leads from the apparatus to a liquid-air trap, a mercury cut-off, devices for introducing various gases, a McLeod gage, another mercury cut-off and the pumps.

To prevent changes in pressure due to changes in temperature the electron tube was surrounded by a water jacket through which a stream of tap water was passed.

Procedure.—In general the current, potential and rate of reaction measurements were not taken simultaneously owing to the large number of instruments to be read. In making the rate of reaction runs the apparatus was pumped out to about 10^{-5} mm., the filament lighted and the trap at the tube immersed in liquid air. The gas was introduced, pressures being read both on the McLeod gage and the Pirani gage. The mercury cut-off at the tube was then closed and the rate of pressure change determined with various accelerating voltages between the filament and the first grid. These rates were followed by measuring the rate of deflection of the galvanometer I_4 when the bridge was balanced. Using a sensitive galvanometer changes of pressure of 10^{-5} mm. caused deflections of 1 cm.

In making the current-potential runs the method of Franck[2] was used. The oxygen was admitted as above and the plate current was measured with various accelerating potentials between the filament and the first grid, G_1. In most of the experiments a slight accelerating field of about 0.1 volt was maintained between G_1 and G_2 and a retarding field of 2.5 volts between G_2 and the plate, P.

A great deal of difficulty was encountered in obtaining sufficient electron emission to produce measurable chemical effects. In some cases the emission of a filament in oxygen gas was less than one-hundredth of its value in hydrogen.

Results of the Current-Potential Experiments.—The results of the current-potential measurements will be presented first. Fig. 2 shows a curve obtained with oxygen at 0.4-mm. pressure and is the graph of Expt. 1. The accelerating voltages (uncorrected, even for I_1) between the filament and the grid G are plotted as abscissas and the plate currents in arbitrary units as ordinates. Two breaks in the curve are apparent, a small one at about 9 volts (uncorrected) and a very pronounced one at about 12.5 volts

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[3] Campbell, *Proc. Phys. Soc. London*, **33**, 287 (1921).

(uncorrected). All of the curves in which the oxygen pressure was greater than 0.1 mm. show these two breaks but their relative magnitude varies. At high pressure the second predominates markedly, but as the pressure becomes lower it diminishes in magnitude and finally at the lowest pressures investigated has disappeared entirely, as may be seen in Fig. 3, which is the graph of Expt. 8 made at 0.05 mm.

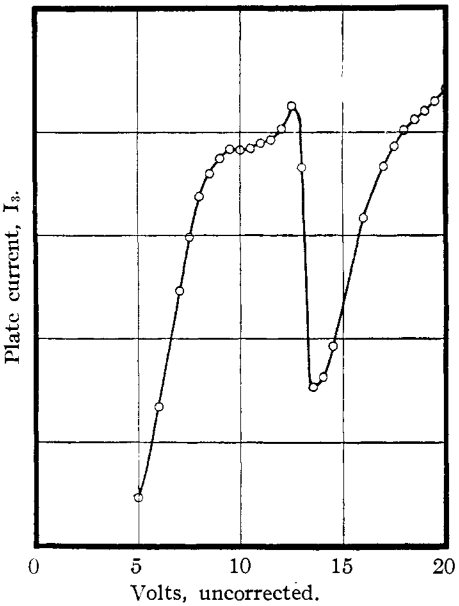

Fig. 2.

The results of all the current potential runs are summarized in Table I. The first line gives the experiment number; the second, the pressure of oxygen in millimeters of mercury; and the third and fourth give the values of the potential in volts (corrected) at which the first and second breaks occur.

The corrected voltages were obtained as follows. The true potential of the grid was determined by the equation given earlier. This is, however, not a true measure of the energy of the electrons since some energy is required to remove the electrons from the filament. This initial velocity correction was determined by taking the voltage at the foot of the curve obtained by plotting the values of the total emission against the voltage, in the region from 0 to 3 volts. The average of three determinations gave 0.9 volt for this correction. Subtracting this value from the applied potential gives for practical purposes the maximum voltage of the electrons and is spoken of as the corrected voltage. The maximum value is of interest rather than the average, which is about a volt lower, since the critical voltage is taken as the point where the cur-

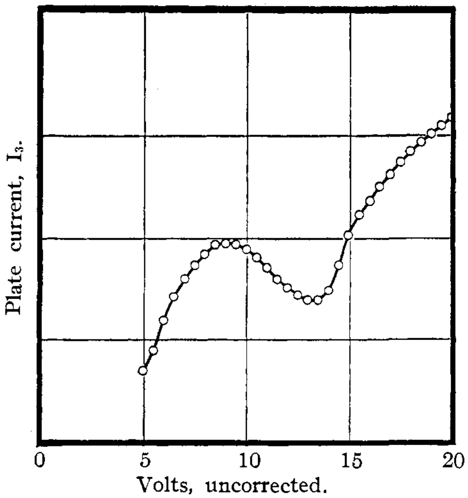

Fig. 3.

rent first starts to change, which is the point at which the fastest electrons just attain the critical voltage.

Table I

Results of Current Potential Runs

Experiment	1	2	3	4	5	6	7	8	9		
Pressure	0.40	0.32	0.28	0.22	0.18	0.11	0.08	0.05	0.05		
First break	8.1	7.8	7.5	7.9	7.9	7.6	8.2	7.9	8.2	Mean	7.9
Second break	10.7	10.7	10.2	10.5	10.5	10.8	Not measurable			Mean	10.6

Results of the Rate Experiments.—The experiments on the rate of reaction proved definitely that bombardment with electrons having energies in the neighborhood of the previously-determined critical potentials produced an active form of oxygen capable of reacting with carbon to form carbon dioxide. However, it is not possible to fix accurately the potential at which reaction begins. This is due mainly to the poor emission of the filament in oxygen, which means that the rate of reaction is so low that it cannot be determined accurately. In order to obtain sufficient emission to work with, the filament must be large and must run at as high a temperature as possible. As a result of this the electron distribution is poor and the curves instead of breaking sharply when the critical potential is reached, bend gradually over a considerable voltage range. The fact that the oxygen molecule shows an affinity toward electrons also spoils the electron distribution. Another difficulty arose from the fact that when the filament was lighted a pressure decrease began although no accelerating potential was applied. Attempts to remove this zero rate by running for some time with high oxygen pressure and by cooling the tube failed, but since this zero

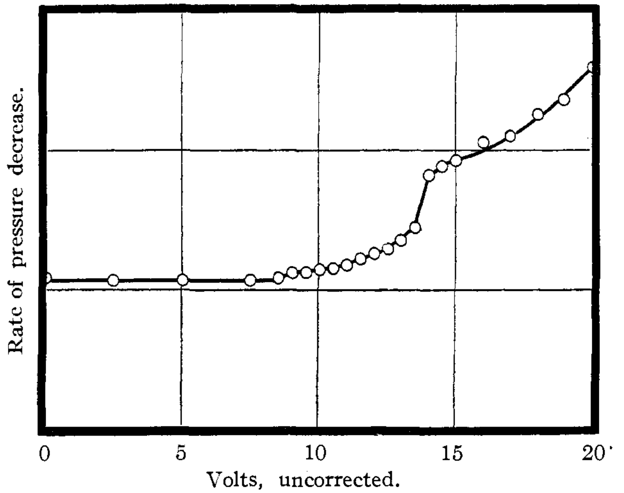

Fig. 4.

rate proved to be fairly constant it was possible to study the superimposed electronic effect.

Figure 4 shows a graph of Run 10 made at a pressure of 0.3 mm. The accelerating voltages (uncorrected) between the filament and G_1 are plotted as abscissas and the rate of pressure decrease in arbitrary units as ordinates. In this case two breaks are clearly present, one at 8.5 volts (uncorrected) and the second at 13 volts (uncorrected). This is in fair agreement with the current-potential data, as will be seen by referring to Fig. 2. In fact, Expt. 10 was made immediately following Expt. 1, keeping everything as nearly the same as possible.

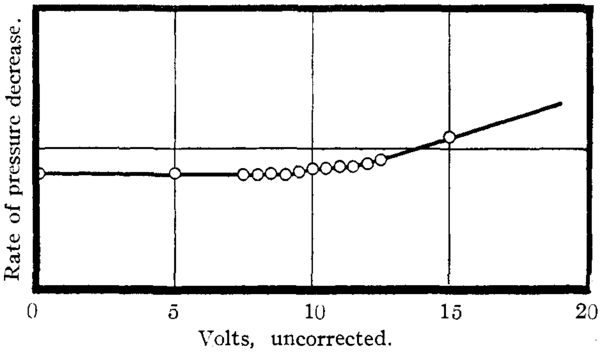

Fig. 5.

Here just as in the current-potential work if we go to low pressures the second break disappears. This is shown in Fig. 5, which is a graph of Run 15 made at 0.11-mm. pressure.

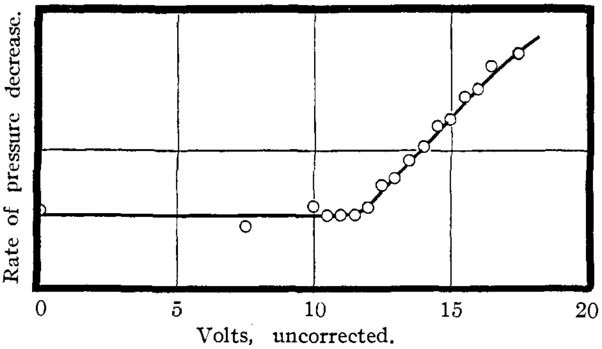

Fig. 6.

Experiments at intermediate pressures show in general only one break, which occurs at about the average of the two critical potentials determined in the current potential experiments. An illustration of this case is given in Fig. 6, which is a graph of Expt. 12 in which the oxygen pressure is 0.22

mm. The data from the most reliable reaction rate experiments are summarized in Table II. The first line gives the experiment number, the second the pressure of oxygen in millimeters of mercury, and the third and fourth give the voltages (corrected) at which breaks in the rate of reaction curves occur.

TABLE II

REACTION RATE DATA

Experiment	10	11	12	13	14	15
Pressure	0.30	0.24	0.22	0.22	0.12	0.11
First break	7	9.3	9.1	9.2	<8.30	7.5
Second break	10.8	..	..	..	..	..

The earlier experiments are not included in the table since the readings were not taken near enough together to determine the point where a break occurs and since a more crude form of apparatus was then in use. They are not, however, in disagreement with the above results.

Considering the results of all the experiments it appears that at both the critical potentials observed an active form of oxygen is produced which reacts with the carbon.

The Reaction Product.—It is natural to suppose that the product of the reaction is carbon dioxide, since carbon monoxide will not be frozen out by liquid air at these pressures. The following experiments substantiated this supposition. The product from a number of runs was allowed to accumulate in the liquid-air trap, the residual oxygen was pumped out, the mercury cut-off at the pumps closed and the liquid air removed. A series of pressure readings was then made on the McLeod gage with the mercury at different heights. The product behaved as a perfect gas up to pressures of 18 cm. and so cannot have been water vapor. There was no permanent change in pressure on lighting the filament, which eliminates ozone as a possibility. Finally, some of the product was collected in a small side tube, cooled in liquid air, sealed off, and opened under barium hydroxide solution. A small quantity of a white precipitate of barium carbonate was obtained. Thus the product must consist at least in a large part of carbon dioxide.

Discussion

It is interesting to compare the values of the critical potentials found with the known energy levels of oxygen. The band spectra of oxygen have been only partially worked out. There are electronic levels at about 1.7 volts and at 6 volts.[4] It is thought that the convergence limit of the oscillational states of the 6-volt electronic level corresponds to the energy for dissociation into two normal atoms. This gives about 7 volts for the work of dissociation of the normal molecule. Above 6 volts there are no levels given till ionization into O_2^+ between 14 and 15 volts. Thus spectroscopi-

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[4] Birge, *Bull. Nat. Res. Council*, **57**, 244 (1926).

cally there are no energy levels yet given in the neighborhood of 7.9 or 10.6, though it is probable that such exist.

The work of various investigators on the determination of the critical potentials of oxygen by electron impact methods is not in good agreement. For the first critical potential, values varying from 7.9 to 9.2 volts have been reported.[5] However, the later work, which is probably more reliable, gives values close to 8 volts. A second critical potential is found by most observers at about 15.5 volts and is accepted as the ionization potential.[6]

Thus the first potential found in the present work is in good agreement with previous values and is apparently a resonance potential of the oxygen molecule. The second potential and its peculiar dependence on the pressure cannot be interpreted with any certainty, but some possibilities may be considered. Perhaps the simplest explanation is that we are dealing with a previously unrecorded critical potential of the molecule, but this would give no reason for such a marked dependence on the pressure. Or it might be that the second potential represented dissociation of the molecule into a normal and an excited atom. Since dissociation to normal atoms requires 7 volts, that leaves 3.6 volts for the atomic excitation. It seems probable from the study of the auroral lines that there is an atomic level in this region. Another explanation might be that the second break is due to carbon dioxide, which is reported as having a resonance potential at 10.0 volts.[7] This would account for the variation with the pressure since at low oxygen pressures the carbon dioxide would diffuse rapidly to the liquid-air trap while at higher pressures its removal would be retarded. This hypothesis would also account for the fact that previous potential work in oxygen has not in general revealed a critical point at 10.6 volts. It would require, on the other hand, that inelastic collisions of electrons with carbon dioxide be much more efficient than those with oxygen.

The author wishes to express his thanks to Professor Tolman, to Dr. Baxter, and especially to Dr. Glockler, for their assistance in this research; also to the Carnegie Institution of Washington for financial aid received through a grant made to Professor A. A. Noyes.

Summary

The critical potentials of oxygen gas have been determined at various pressures. In addition to the value of 7.9 volts which has been found by previous experimenters, a second critical value was found at 10.6 volts. The latter appears distinctly only at pressures above 0.1 mm., but becomes very pronounced at pressures of 0.2 to 0.4 mm.

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[5] Foote and Mohler, Bureau of Standards Publication No. 400, **1920**; Boucher, *Phys. Rev.*, **19**, 202 (1922); Franck and Hertz, *Verh. deut. physik. Ges.*, **15**, 34 (1913); Hughes and Dixon, *Phys. Rev.*, **10**, 502 (1917).

[6] H. D. Smyth, *Proc. Roy. Soc. London*, **105A**, 116 (1924).

[7] Mackay, *Phys. Rev.*, **24**, 319 (1924).

The reactivity toward carbon of oxygen gas excited by electron impact was studied. There was no reaction below 7.9 volts, but between 7.9 and 10.6 volts a reaction commenced and increased in rapidity up to the highest potentials investigated. The product of the reaction is carbon dioxide, at least in large part.

PASADENA, CALIFORNIA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

THE HEATS OF DISSOCIATION OF THE MOLECULES, CH, NH, OH AND HF

BY DONALD STATLER VILLARS

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In an investigation on the dissociation energetics of the molecule of hydrogen cyanide, it was necessary to make an estimate of the heats of dissociation of its different possible decomposition products. Although it sounds strange to the chemist to speak of the molecules, CH, NH and OH, still their existence is definitely proved by the observation of band spectra[1] which are ascribed to them. The molecules, unsaturated chemically, are most probably extremely reactive, but we should not consider them unstable, in the sense that they have a tendency to decompose. The knowledge of the heats of dissociation of these molecules has great theoretical importance in studying the dissociation of other compounds, as well as hydrogen cyanide.

In order to calculate these heats, I have made use of two empirical principles discovered by band spectroscopists. First, Kuhn[2] has shown that the restoring force constant, C, in the equation for the vibration of a harmonic oscillator is approximately proportional to the heat of dissociation of the molecule.

$$C \equiv \mu\omega_0^2 = kD \qquad (1)$$

ω_0 is the frequency of vibration for infinitely small displacement and is determined experimentally by the difference between the first and second vibrational energy levels of the molecule as measured from its band spectrum; μ is the resultant mass and equals $m_1m_2/(m_1 + m_2)$ for a diatomic molecule. Second, Mecke[3] has shown that molecular constants vary with the atomic number in much the same manner as other physical and chemical constants. The method of estimation, then, is to determine

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[1] CH: Heurlinger and Hulthén, *Z. wiss. Phot.*, **18**, 241 (1919); *Compt. rend.*, **173**, 524 (1921); *Z. Physik*, **11**, 284 (1922). NH: Hulthén and Nakamura, *Nature*, **119**, 235 (1927). OH: Grebe and Holtz, *Ann. Physik*, **39**, 1243 (1912); Heurlinger, "Dissertation," Lund, 1918; Fortrat, *J. phys.*, **5**, 20 (1924); Jack, *Proc. Roy. Soc. London*, **115A**, 373 (1927); **118A**, 647 (1928).

[2] Kuhn, *Z. Physik*, **39**, 77 (1926).

[3] Mecke, *Physik. Z.*, **28**, 483 (1927).