

The former compound can exist in equilibrium with saturated solutions at 25° in which the ratio of acetic acid to water is between 2.3 and 7.7 by weight, and the latter can exist in equilibrium with saturated solutions in which the ratio is larger than 7.7.

Anhydrous lead acetate in contact with a saturated solution is metastable.

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[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

## THE ACTIVATION OF MOLECULAR OXYGEN BY ELECTRON IMPACT

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**Introduction.**—In the case of hydrogen<sup>2</sup> it was found that electrons of 11.4 e. volts or greater energy can transfer hydrogen molecules to an excited state ( $^1\Sigma_g^+ \longrightarrow ^3\Sigma_g^+$ ) and that such molecules can react with a copper oxide plate. Thus hydrogen molecules need not be ionized; excited states serve equally well as activated species. These studies were continued on oxygen and in the meantime Dalton<sup>3</sup> reported that oxygen molecules, activated by 8-volt electrons, react with a carbon surface. Wansbrough-Jones<sup>4</sup> studied the activation of oxygen, and detected no ozone below 25 e. volts nor below 0.8 mm. pressure. L. A. M. Henry<sup>5</sup> found however formation of ozone at much lower pressures than did Wansbrough-Jones, reporting critical voltages of 9.0 and 21.2 e. volts. In our own investigations on oxygen which were begun before any of the papers cited above appeared, it was decided to study the formation of ozone and the chemical reaction between a mercury surface and oxygen activated by electron impact and other materials. Since our results differ to some extent from those in the literature, they are reported in this paper. We have extended also the mode of interpretation of such experiments and interpret them in terms of efficiencies of energy transfer and of reaction.

### Experimental Procedure

Both static and flow methods were used. At first we followed the reaction by freezing out the product formed and determined its behavior with potassium iodide solution. Such experiments, however, were not very reproducible although we obtained

<sup>1</sup> This article is based upon a thesis presented to the Faculty of the Graduate School of the University of Minnesota by John L. Wilson in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

<sup>2</sup> Glockler, Baxter and Dalton, *THIS JOURNAL*, **49**, 58-65 (1927).

<sup>3</sup> Dalton, *ibid.*, **51**, 2366-2374 (1929).

<sup>4</sup> Wansbrough-Jones, *Proc. Roy. Soc. (London)*, **127A**, 530-539 (1930).

<sup>5</sup> Henry, *Bull. soc. chim. Belg.*, **40**, 339-360 (1931).

definite evidence of reaction in both methods with this chemical procedure. Since freezing out of the reaction product appeared difficult,<sup>6</sup> we considered other means of detection such as MoO<sub>3</sub>, PbO, Ag, etc., and finally we decided that a mercury surface offered the best possibilities. Although Wansbrough-Jones reports no reaction between oxygen and mercury in dry oxygen, we have found that a mercury surface can react readily with oxygen molecules when these are excited by electron impacts. Our further experiments were carried out in a static system, the reaction being followed by measuring the drop of pressure as a function of the time at given accelerating voltages of the electrons. The general plan of experimentation was the one already described in the former paper. The experimental tube is shown in Fig. 1. The applied voltages were read on large scale standard voltmeters and

we used an equipotential surface (oxide covered platinum) as a source of electrons. Both the reaction tube and the Pirani gage were immersed in liquid oxygen or nitrogen. The total volume of the closed system including reaction tube, gage and connecting tubing was 105 cc. The oxygen used was prepared from dry potassium permanganate mixed with barium peroxide, dried for months over potassium hydroxide and phosphorus pentoxide and admitted to the reaction system through a stop-cockless valve.<sup>7</sup> The reaction vessel was thoroughly baked out at 400° after each assemblage before being used and the mercury distilled in with the pumps running. The hot filament will remove oxygen gas even though no accelerating field is applied and it was necessary to determine the "zero" rate of pressure drop (no accelerating voltage applied) and subtract it from the total pressure drop at various voltages to obtain the net reaction rates. No pressure drop is observed when the filament is cold. The zero rates were large due to the fact that the volume of the system was small and the surface of the electron emitting system was large.

Application of accelerating voltages from 3.5 to 20 e. volts (corrected for initial velocity) produces an increased pressure drop if the reaction tube is immersed in liquid oxygen or nitrogen. However, this increased action is considerably greater if a mercury mirror is present in the reaction vessel than when it is absent. If however the tube is kept at room temperature or at 300°, then the accelerating field has no influence on the rate of pressure drop. Therefore experiments were carried out with the tube immersed in liquid oxygen and with a mercury mirror deposited inside the reaction vessel.

<sup>6</sup> Ozone vapor pressure is 0.035 mm. at -190°, Spangenberg, *Z. physik. Chem.*, 118, 419 (1926).

<sup>7</sup> J. L. Wilson, *J. Phys. Chem.*, 35, 3353 (1931).

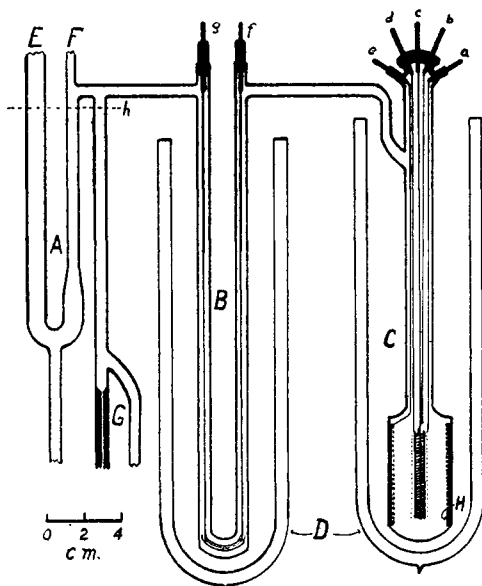


Fig. 1.—Reaction system: A, mercury cut-off; B, Pirani gage; C, reaction tube; D, Dewars; E, to pumps; F, to gas supply; G, McLeod gage; H, mercury surface; a-g, electrical connections; h, mercury level.

### Experimental Results

**Mercury Surface.**—Figure 2a shows the permanent drop in pressure as a function of the time with a mercury surface present in the tube. Many such experiments were carried out and the runs shown in Table I are only a sample of the results obtained. We can summarize these results by showing the number of molecules of oxygen which disappear per electron crossing the tube (Fig. 4). We find the following: (1) *electrons with velocities of 3–8 volts can cause oxygen molecules to disappear*; (2) *electrons above 8 volts velocity have a greater effect*. It becomes difficult to investigate the behavior of electrons of lower energy, because the emission from the filament is then very small.

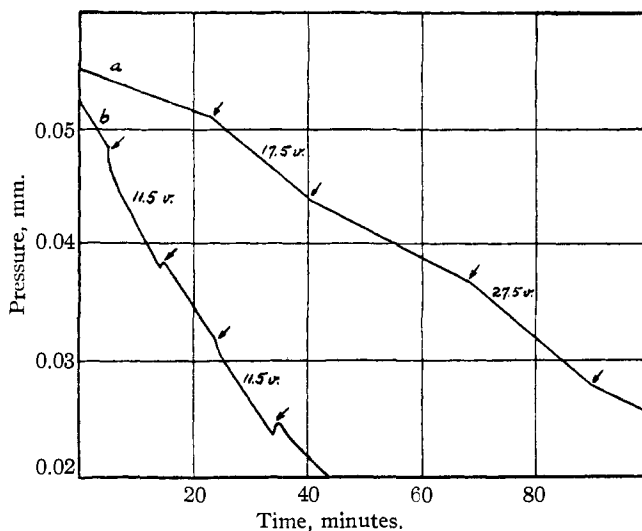


Fig. 2.—Pressure of oxygen as a function of time. Accelerating field on and off. (a) Mercury surface and low filament temperature. (b) Glass surface and high filament temperature.

**Glass Surface.**—We have also studied the removal of oxygen molecules upon a glass surface as well as upon mercury and we find that the zero rates are the same in the two cases, which means that they are not caused by the adsorption of oxygen but are due to the hot filament. The rates of pressure drop obtained are smaller than with mercury surfaces (Fig. 4). Figure 2b shows that with glass surfaces the rate of pressure drop is not constant while the accelerating field is applied, but increases as expected when the field was first put on, gradually decreasing to the zero rate, showing a steady state. This observation was not made with fresh mercury surfaces and we believe that the difference lies in the fact that excited oxygen molecules can react with mercury surfaces in a permanent fashion (acti-

vated adsorption)<sup>8</sup> while glass surfaces can only adsorb them into a more loosely bound state. The condition of the glass surface has a considerable effect. A freshly baked glass surface can remove more oxygen than a surface already partially covered (Fig. 4). With glass surfaces a further observation was made. When the accelerating field was removed, the pressure would rise to a point which would have been reached with the rate at no field, and when this situation has been attained the drop in pressure follows the zero rate as expected. Fresh mercury surfaces did not show this phenomenon. Furthermore, there was left a permanent brown deposit on the tube wall after the mercury had been removed (Fig. 3). No deposit was formed in the runs with glass surfaces. After a mercury surface had been used for many runs this behavior of pressure changes was also noted to a slight extent. A newly baked glass surface can adsorb activated oxygen molecules according to Henry, who baked out his apparatus before every run. We also found that a very fresh glass surface adsorbs better than a used one. We preferred to use a mercury surface because it is a more certain way of removing oxygen from the reaction tube.

#### Efficiency of Mercury Surfaces.—

We used the same mercury surface for several experiments at different voltages and convinced ourselves that the removal of oxygen had not decreased for any of the experiments. We repeated runs at the same voltage with a virgin and a used surface and found no difference in the capacity for adsorption. Calculations showed that we never exceeded a monomolecular layer.

**Initial Velocity Correction.**—This correction was determined by a series of ionization runs (Lenard curves) in oxygen and helium and in mixtures of the two gases. Furthermore, the minimum velocity which electrons must have to reach the plate was measured. Retarding voltages were applied

<sup>8</sup> M. Polanyi, *Z. Elektrochem.*, **35**, 561 (1929); H. S. Taylor, *THIS JOURNAL*, **53**, 578 (1931).

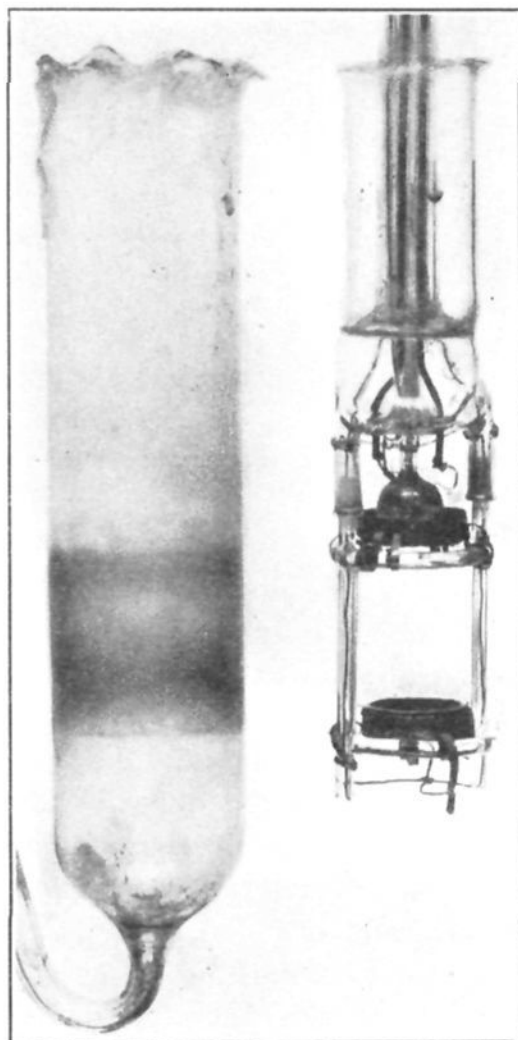


Fig. 3.—Permanent deposit of mercury oxide.

to the electron stream from which the initial velocity could be obtained. Five different ways of obtaining this correction gave consistent results and the correction amounts to 2.5 volts.

TABLE I

Expt.	$v$	$i$	$P$	$(\Delta P/\Delta t)$	$E$	$-M_{O_2}$	$M/E$	$\lambda$	$Z$	$ZE$	$M/ZE$
1	3.7	115	25.2	33.4	7.25	23.2	0.032	1.08	1.29	9.40	0.025
2	5.5	52	33.0	10.4	3.26	7.2	.022	0.82	2.24	7.30	.010
3	5.5	110	22.1	37.8	6.93	26.3	.038	1.23	1.00	6.93	.038
4	7.5	45	32.0	10.7	2.84	7.4	.026	0.85	2.08	5.91	.013
5	9.5	43	33.0	47.2	2.73	32.8	.120	.82	2.24	6.12	.054
6	11.5	58	35.0	77.4	3.65	53.7	.147	.78	2.47	9.02	.060
7	11.6	46	28.0	56.6	2.92	39.3	.134	.97	1.00	4.07	.084
8	11.5	126	26.0	89.4	7.95	62.0	.078	1.04	1.30	11.00	.056
9	11.5	120	26.2	100.0	7.56	69.5	.092	1.03	1.42	10.70	.065
10	14.7	42	30.0	41.7	2.62	28.9	.110	0.90	1.85	4.85	.060
11	17.5	50	33.0	43.5	3.15	30.2	.096	.82	2.22	7.00	.043
12	18.5	124	23.2	94.5	7.82	65.6	.084	1.17	1.10	8.60	.076

$v$  = volts (corr.);  $i$  = current to plate (microamps.);  $P$  = press. (mm. Hg)  $\times 10^3$ ;  $(\Delta P/\Delta t)$  = (mm. Hg per sec.)  $\times 10^7$ ;  $E$  = electrons per sec.  $\times 10^{-14}$ ;  $-M_{O_2}$  = molecules per sec.  $\times 10^{-12}$ ;  $\lambda$  = M. F. P. of elec. (cm.);  $Z$  = impacts per electron with molecules;  $ZE$  = total impacts  $\times 10^{-14}$ .

**Average Temperature in the Reaction Region.**—A large temperature gradient exists in the reaction space because the hot filament is at about  $900^\circ$  while the walls of the vessel are at liquid oxygen temperature ( $-190^\circ$ ). We determined the average temperature of the gas experimentally as follows. The volume of the system was 105 cc. With the reaction system immersed in liquid oxygen the pressure was read with the filament off. The filament was then turned on and the pressure was read again. Assuming ideal gas laws it was possible to calculate the average temperature of the gas contained in the tube ( $147^\circ\text{K}$ ). A calculation based on geometrical considerations and assuming the temperature of the filament to be  $900$ – $1200^\circ\text{K}$ . checked the experimentally determined temperature satisfactorily.

**Discussion of Results.**—The results of electron-activated reactions can be stated by noting the pressure drop as a function of the time for a given electron current, by giving the number of molecules reacting per electron crossing the reaction tube or by calculating the number of molecules changed ( $M$ ) per ion ( $N$ ) produced by electrons,  $M/N$ .<sup>9</sup> The latter ratio has meaning only if the activating electrons have speeds greater than the ionization potential of the molecules of the gas and if in addition *the ions are the only agents causing reaction*. The meaning of  $N$  should include all possible active species such as vibrationally excited molecules, electronically excited molecules, ions and atoms. If in a given voltage range several of these activated species can be produced then  $N$  should represent their

<sup>9</sup> S. C. Lind, "The Chemical Effects of Alpha Particles and Electrons," The Chemical Catalog Co., Inc., New York, 1928.

sum. We consider the mechanism of these activation reactions. The number of gas molecules ( $M$ ) removed per second will depend upon the number of electrons ( $E$ ) entering the reaction region per second, upon the number of impacts ( $Z$ ) these electrons make with gas molecules, upon the efficiency ( $e$ ) for inelastic collisions between electrons and gas molecules, upon the number of impacts ( $y$ ) which the activated molecules make with normal gas molecules during their life in the reaction tube, and upon the efficiency of reaction ( $e'$ ) between excited and normal molecules. The number of efficient encounters ( $ye'$ ) between activated molecules ( $Z E e$ ) and normal ones is limited by the energy available for activation. Thus we have

$$M = Z E e y e'$$

The number of molecules reacting is produced by activations of various types depending on the velocity of the activating electrons

$$M = M_1 + M_2 + \dots$$

Each group  $M_1, M_2, \dots$  should be considered separately as above and for each group the various factors,  $e, y, e'$  may be different. However, because electron streams available at present have a rather wide velocity distribution and molecules of the type studied here ( $O_2$ ) have many closely-spaced energy states it is not possible to study the problem in much detail. We therefore consider the situation in an average way over certain voltage ranges.

**Molecules Reacting ( $M$ ).**—The number of molecules reacting per second is

$$M = \frac{\Delta P}{\Delta t} \frac{V \times 273 \times 6.06 \times 10^{23}}{22,400 \times 147 \times 760} = 6.95 \times 10^{18} \times \frac{\Delta P}{\Delta t}$$

These quantities are given in Table I. ( $\Delta P/\Delta t$ ) is the net pressure drop in mm. per second,  $V$  = volume of reaction vessel (105 cc.).

**Electron Collisions ( $Z$ ).**—The number of collisions which an electron makes in crossing the tube is obtained by considering the process one of diffusion.<sup>10</sup> If " $a$ " is the distance between the grid and plate (1 cm.),  $\lambda$  is the M. F. P. of the electron at pressure  $P$  (mm.), and for oxygen molecules the M. F. P. is  $6.3 \times 10^{-6}$  cm. at 760 mm. pressure, then

$$Z = \frac{3}{2} \frac{a^2}{\lambda^2} \quad \lambda = \frac{0.0271}{P}$$

The distance between the emitting surface and the first grid was small (about 1 mm.) compared to the M. F. P. of the electrons (8 mm. in the pressure range used) so that about 90% of the electrons passed through the first grid and received their full energy before making a collision.

**The Number of Electrons ( $E$ ).**—The number of electrons crossing the reaction vessel per second is given by  $E = (6.06 \times 10^{23} \times i)/(96,540 \times 10^9) = 6.3 \times 10^{15} \times i$ , where the current ( $i$ ) is the electron current reaching the plate expressed in microamperes.

<sup>10</sup> G. Glockler, *Proc. Nat. Acad. Sci.*, **12**, 178 (1926).

**The Ratio  $M/E$ .**—The number of molecules removed per second depends upon the number of electrons crossing the tube per second and the ratio of these two quantities will depend upon the pressure and the efficiency of the mercury surface. This ratio (Fig. 4) is of no particular significance as far as reaction mechanism is concerned and we only discuss it here to point out that our work checks the results of Henry. He worked at about the same pressures and the distances between grid and plate were also nearly the same. His  $M/E$  ratios are of the same order of magnitude and his curve (Fig. 12 of his paper) shows the same trend for this ratio after resonances (8 volts) as our curve (Fig. 4). He also finds that at 12.5 volts (the ionization potential of oxygen molecules), no increase in the ratio is to be observed. Our results differ from Henry's in that we find some reaction occurring at lower voltages (3.5 to 8).

**The Efficiency of Electron Collision ( $e$ ).**—We consider this question in relation to the energy of the impacting electrons and the possible excitation states of the oxygen molecules. Figure 5<sup>11</sup> shows that the oxygen molecule has many excited states. Although electrons cannot transfer energy to the hydrogen molecule below an electronically excited state (11.5 e. volts) (the dissociation energy is 4.32 e. volts), they can in the case of nitrogen and carbon monoxide excite vibrations of the atoms of these molecules with 5 volts energy.<sup>12</sup> It is therefore not improbable that low velocity electrons (3–8 e. volts) can transfer energy to the vibrational states of the oxygen molecules,<sup>13</sup> especially since they are said to have an electron affinity which would mean that the electrons can attach themselves to such molecules and their whole kinetic energy may then appear in the vibrational states of the resulting ion. Furthermore, the molecules of oxygen have metastable states ( $^1\Sigma_g^+$ ) 1.62 e. volts above the normal state ( $^3\Sigma_g^-$ ). Electrons may excite molecules to this metastable state in one of its vibrational configurations, although this state cannot be reached by light absorption. These excitations will take place with a certain efficiency of energy transfer, providing the possibility of activating oxygen molecules by low velocity electrons (3–8 e. volts). These efficiencies of inelastic electron collisions are not known but are probably small (0.1–0.001).

In the next voltage range (8–12 e. volts) it becomes possible to excite oxygen molecules to new electronic states with their accompanying vibrational and rotational energy levels. The efficiencies of such inelastic collisions have not been determined for many substances. For helium<sup>14</sup> it is known that the transition  $1S \rightarrow 2s$  (19.77 e. volts) can be brought about by electron impact with efficiencies of the order of 0.001. In

<sup>11</sup> Mulliken, *Review of Modern Physics*, **4**, 51 (1932).

<sup>12</sup> W. Harries, *Z. Physik*, **42**, 26–42 (1927).

<sup>13</sup> G. Hertz, *Verhandl. d. phys. Ges.*, **19**, 268 (1917).

<sup>14</sup> G. Glockler, *Phys. Rev.*, **33**, 175 (1929).

mercury vapor such efficiencies are of the order of a few per cent.<sup>15</sup> Transition probabilities for molecules are not known but are presumed to be of small magnitude. However, we can use our experimental data in an attempt to obtain some information concerning these efficiencies in the voltage range considered (8–12 e. volts).

Above 12 e. volts it becomes possible to ionize an oxygen molecule by electron impact. The probabilities of ionization impact between electron and oxygen molecules have been studied.<sup>16</sup> We use these probability factors to calculate the number of oxygen ions produced by one electron.

The quantities discussed so far give us the number of activated, excited or ionized molecules of oxygen produced by the electrons traversing the reaction region between grid and plate. In order to lead to reaction these energy rich species must either decompose into oxygen atoms which can be removed by the mercury surface or they will make further impacts with the normal molecules of the gas. We wish to know then what the possibilities for further collision may be between the activated species and the normal molecules.

**Impacts between Activated and Normal Molecules ( $\gamma$ ).**—The number of impacts which an excited molecule or ion will make with the normal molecules of the gas depends upon the diameters of the excited and the normal molecules and upon the average life ( $\tau$ ) of the excited state. The excited atoms have larger diameters<sup>17</sup> than the normal ones. For oxygen no experiments are known which would give the diameter of the excited states or ions. There are so many activated states possible that it is necessary to consider an average diameter. We shall assume that excited molecules have an average diameter  $\sigma_1 = 10^{-7}$  cm. while the normal molecule has a diameter  $\sigma_2 = 1.81 \times 10^{-8}$  cm. The diameter of the oxygen ion is taken equal to the diameter of the excited state. In order to calculate the number of impacts made between one of the activated molecules and the normal ones we obtain their mean free path  $\lambda^*$  from kinetic theory. We next consider that the average excited molecule or ion is created by electron impact anywhere in the reaction space between grid and plate and we desire to know the average distance ( $d^*$ ) which it will have to travel to reach the wall. This distance  $d^*$  (=1.5 cm.) is obtained from a geometrical consideration.<sup>18</sup> Again, considering the process of one diffusion, we have

$$Z^* = \frac{3}{2} \times \frac{d^{*2}}{\lambda^{*2}} = \frac{3.38}{\lambda^{*2}}$$

<sup>15</sup> H. Sponer, *Z. Physik*, **7**, 185 (1921); G. Hertz, *ibid.*, **32**, 298 (1925).

<sup>16</sup> Tate and Smith, *Phys. Rev.*, **39**, 270 (1932).

<sup>17</sup> Ruark and Urey, "Atoms, Molecules and Quanta," McGraw-Hill Book Co., New York, 1930, p. 497.

<sup>18</sup> *Loc. cit.*, Ref. 9, p. 94.



for the number of collisions with normal molecules made by an excited molecule in traveling the distance  $d^*$ . The actual zig-zag distance ( $D^*$ ) traveled by excited molecules or ions while in the tube is

$$D^* = Z^* \lambda^*$$

and since their speed may be taken equal to the thermal velocity of the molecules (461 meters per second) we find how many seconds ( $t$ ) they will be in the reaction tube if they do not return to normal or recombine in the case of ions

$$46,000 \text{ cm.} : 1 \text{ sec.} :: D : t$$

The excited molecules will not live long enough to reach the wall unless they are in metastable states. Their existence is terminated after the period ( $\tau$ ) when they return to normal. The average duration in an upper quantum state has been calculated<sup>19</sup> to be of the order of  $10^{-7}$  sec. However, the return to normal means emission of radiation and we must consider the possibility of "light-imprisonment" which will increase " $\tau$ ." If we take  $\tau = 10^{-6}$  seconds<sup>20</sup> we can calculate the number of collisions ( $y$ ) which an excited molecule will make during its average life in the reaction tube (Table II)

$$Z : t :: y : \tau$$

**Recombination of Ions.**—If the excited states are ions it becomes of importance to know whether or not they recombine in the gas phase. The recombination coefficient ( $\alpha$ ) is usually<sup>21</sup> given as  $1.32 \times 10^{-6}$  for oxygen at atmospheric pressure and room temperature. It is both a function of pressure and temperature and we estimate for oxygen at low pressure<sup>22</sup> and at the average temperature of our reaction tube:  $\alpha = 148 \times 10^{-10} \times (273/147)^3 = 10^{-7}$  so that ions will recombine at a rate given by

$$\frac{d\nu_1}{dt} = -10^{-7} \times \nu_1 \times \nu_3$$

where  $\nu_1$  = concentration of ions and  $\nu_3$  = concentration of electrons. From the number of electrons ( $E$ ) crossing the reaction region per second, we find the number of ions produced per second ( $N^*$ ) and we suppose that these ions have to reach the wall by a process of diffusion. They travel the distance  $d^*$  in the time  $t$ , so that their drift-speed is  $d^*/t$ . We have then

$$\frac{N^* d^*}{V} = \nu_1 \times \frac{d^*}{t} \text{ or } \nu_1 = \frac{N^* t}{V}$$

The concentration of slow electrons  $\nu_3$  is twice the concentration of the positive ions, for at every inelastic impact two electrons are created per ion.

<sup>19</sup> R. C. Tolman, *Phys. Rev.*, **23**, 693 (1924).

<sup>20</sup> Foote and Mohler, "Origin of Spectra," Chapt. IV; Koenig and Ellett, *Phys. Rev.*, **39**, 576-584 (1932).

<sup>21</sup> K. K. Darrow, "Electrical Phenomena in Gases," Williams and Wilkins Co., Baltimore, Md., 1932, p. 263.

<sup>22</sup> J. J. and G. P. Thomson, "Conduction of Electricity through Gases," Cambridge University Press, 1928, p. 37.

The initial electron traveling with full velocity across the reaction tube has little chance to recombine with the positive ions. Recombinations  $R(t)$  occurring in the time  $t$  in the whole reaction volume are

$$R(t) = 2 \times 10^{-7} \times N^* \times t^2$$

From the values of  $Z^*$  and  $R(t)$  it is seen that the ions have a fair chance to recombine and thereby react and that they have opportunity to make impacts with other molecules while in the state of ions.

TABLE II

Expt.	$\text{O}_2$ molecules in V. $\times 10^{13}$	$\lambda^*$ M. F. P. of activated mol. cm.	$Z^*$ No. of coll. between $\text{O}_2$ and $\text{O}_2^+$	$D^*$ (cm.)	$\times 10^{-3}$ (sec.)	$y = Z^*/t$	$R(t)$	$N^* \times 10^{18}$	$M/N$
1	17.5	0.038	2340	89.1	1.94	1.21			
2	22.9	.029	4020	116.4	2.53	1.59			
3	15.4	.043	1830	78.7	1.71	1.07			
4	22.2	.030	3750	112.5	2.45	1.53			
5	23.0	.029	4020	116.4	2.53	1.59			
6	24.3	.027	4630	125.0	2.66	1.74			
7	19.4	.034	2920	99.0	2.15	1.36			
8	18.0	.037	2470	91.4	1.99	1.24			
9	18.2	.036	2600	93.6	2.04	1.27			
10	20.8	.032	3300	105.3	2.29	..	4.03	3.93	7
11	22.9	.029	4020	116.4	2.53	..	19.6	15.30	2
12	16.1	.041	2010	82.5	1.79	..	22.1	34.45	2

**Reaction Caused by Slow Electrons (3–8 E. Volts).**—We see from Fig. 4 that there is some pressure drop observed when electrons of velocity 3–5 e. volts impact on oxygen molecules. Oxygen molecules can thus be activated by such slow electrons so that they may react with a mercury

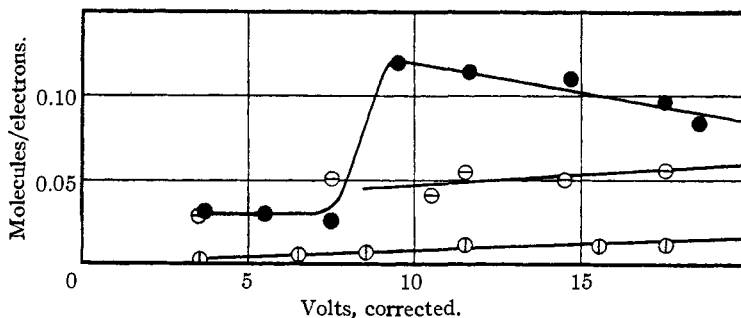
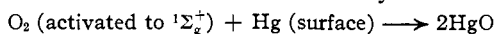


Fig. 4.—Molecules reacting per electron: ●, on fresh mercury surface; ○, on freshly baked glass surface; ⊙, on used glass surface.

surface. The only state to which oxygen molecules can be raised in this voltage range is the metastable state  ${}^1\Sigma_g^+$  in its various vibrational configurations. These excited molecules cannot decompose in the gas phase into atoms until the activating electrons have reached 5.2 e. volts of energy which corresponds to the heat of dissociation. Since the activated mole-

cules are in metastable states we may suppose that they can withstand impacts ( $\gamma$ ) in the gas phase and that they arrive at the wall in the metastable condition and there react with the mercury-surface



whereas ordinary oxygen molecules do not react rapidly with mercury. If the impacting electrons have energies greater than 5.2 e. volts and if they can transfer this energy to the oxygen molecules we may expect dissociation into two normal atoms. In this voltage range 5–8 e. volts not more than one molecule can be dissociated. The mechanism of activation considered in the voltage range 3–5 e. volts can still be operative and we must content ourselves with an "average" picture of the reaction mechanism over the range 5–8 e. volts. We have discussed above the efficiencies of electron impact (energy transfer by the electrons) and we shall calculate the "average" chance that a molecule shall suffer an inelastic impact *and* react at the mercury surface. This averaging process is also made necessary since our electron stream has a fairly wide velocity distribution. In the range 3–8 e. volts we have then

$$M = Z E e e'$$

Since only enough energy is available to dissociate one molecule, impacts ( $\gamma$ ) are of no importance unless they become large in numbers and cause molecules (5–8 e. volts) to return to normal before reaching the mercury surface. From Fig. (6) we find  $M = 0.02 \times Z \times E$  and we obtain  $e \times e' = 0.02$ . The main interest in this combined probability is its small magnitude as is expected from general considerations. The efficiencies " $e$ " are known to be small and the probabilities of reaction " $e'$ " are of small value as expected. These reaction efficiencies are of fundamental importance, as they are analogous to specific reaction rates. Their knowledge enables us to predict reactions and they are quantities independent of impacts and of all external situations. They concern only the activated state and its reaction partner. They are quantities which can be deduced from a complete theory of molecular structure.

We have considered the possibility of successive impacts between initial electrons and oxygen molecules but they are negligible in our experiments. It is not possible to extend these studies below 3 e. volts for the emission from the filament becomes too small. We can then summarize our finding: *"In the velocity range 3–8 e. volts, electrons can transfer energy to oxygen molecules, activating them so that they can react with a mercury surface. The average probability of reaction is small as expected."* Further research will enable us to obtain the quantities " $e$ " and " $e'$ " with greater accuracy and it will also be possible to decide the minimum heat of activation if the experiments can be extended to the lower voltages.

**Reaction in the Range 8–12 E. Volts.**—Such electrons can activate oxygen molecules from the normal state  ${}^3\Sigma_g^-$  to the electronically excited

state  ${}^3\Sigma_u^-$  (Fig. 5). We may suppose that the probabilities of such transitions are greater than for the type  ${}^3\Sigma_g^- \rightarrow {}^1\Sigma_g^+$  since the energy transfer is to a state which is not metastable. We actually find that the number of molecules reacting per electron impact increases markedly as would be expected on the above argument.

As above we will discuss the reaction "on the average" in this voltage range. Oxygen molecules in the  ${}^3\Sigma_u^-$  state can decompose spontaneously into a normal and an excited atom. If further impacts ( $\gamma$ ) have no influence then

$$M = ZEee'$$

and with  $M = Z \times E \times 0.06$  we find  $ee' = 0.06$ . Again we note that this product of probabilities is small in magnitude as expected. We may next consider various possibilities of reaction including other normal molecules and their impacts ( $\gamma$ ) with the excited molecules during their average life ( $\tau$ ). Although we have not studied the reaction in sufficient detail to carry out such an analysis, we can however give a picture of the activation reaction in this voltage range as follows: "*Electrons of energy 8-12 e. volts can cause activation of oxygen molecules with greater efficiency than can be obtained with slower electrons. The combined probability of excitation followed by reaction is 6%.*"

#### Reaction above Ionization.—

When 12.5 volt electrons impact with oxygen molecules they have enough energy to ionize them. We find that reaction does occur but that the rate of pressure drop does

*not increase markedly* when ionization voltage is reached. The number of molecules removed per electron crossing the tube is the same as in the lower voltage range (8-12 e. volts). This must mean that ions are not very much better activating centers for reaction than are excited states. At our low

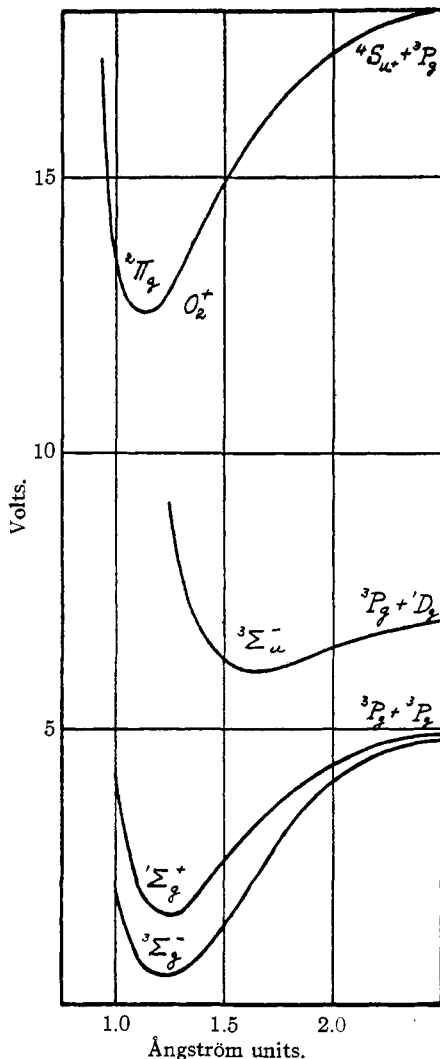


Fig. 5.—Energy diagram of oxygen molecule.

pressures the oxygen mole-ions make many collisions ( $Z^*$ ) before recombination  $R(t)$  (Table II). It may easily be possible to have several molecules removed per ion because there is sufficient energy available for activation or dissociation when the electron returns. Again we must consider an average situation and taking

$$M = (Z E e)(y e')$$

we have  $M = 0.06 Z E$  and  $M/N = M/(Z E e) = 4$  so that  $y e' = 4$  and since the number of impacts an ion makes before a recombination occurs is of the order of 100 we have  $e' = 0.04$ . The only conclusion is that  $e' < 1$ . Further detailed analysis is not possible at present: however, we have pointed

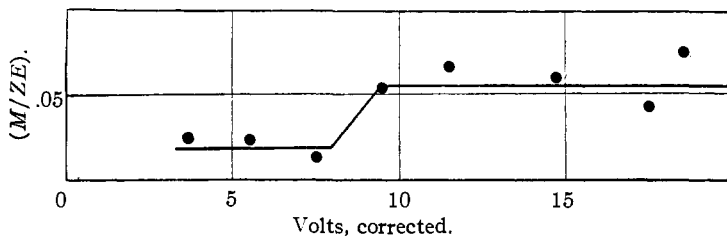


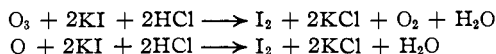
Fig. 6.—Molecules reacting per electron impact as a function of electron speed.

out the proper method of analysis and especially is it of importance to realize that such activation reactions should be interpreted in terms of efficiencies. We can summarize our findings as follows if we assume a certain mechanism predominant in a given voltage range.

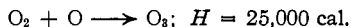
Volts	Reaction	Combined efficiencies of energy transfer and reaction ( $y e'$ )
3-8	$E_{fast} + O_2(^3\Sigma_g^-) \longrightarrow E_{slow} + O_2(^1\Sigma_g^+) + 2Hg \longrightarrow 2HgO$	0.02
8-12	$E_{fast} + O_2(^3\Sigma_g^-) \longrightarrow E_{slow} + O(^3P_g, ^1D_g) + 2Hg \longrightarrow 2HgO$	.06
12-20	$E_{fast} + 2O_2(^3\Sigma_g^-) \longrightarrow E_{slow} + [O_2^+, O_2] + 4Hg \longrightarrow 4HgO$	.06

Further research may enable us to determine these efficiencies separately and we expect to study these activation reactions on the basis of the considerations outlined here.

**Production of Ozone.**—We have found that above the ionization potential the reaction product when adsorbed on glass showed chemical reaction with potassium iodide solution (iodine is liberated) but oxygen atoms may well cause this *same reaction as does ozone*



so no direct proof has been obtained for the presence of ozone. We may expect that ozone is not produced because triple collisions between oxygen atoms and oxygen molecules are needed to remove the energy of the reaction



in the gas phase. Although we do not have enough triple collisions to produce ozone, we must have taking place in our reaction tube the primary process (atom formation or production of an activated state) which would yield ozone had we the needed triple collisions. In further studies it will be necessary to distinguish between ozone and oxygen atoms.

**Photochemical Reaction.**—It is of interest to compare other activation reactions with our mode of activation by electron impact. While photochemical formation of ozone has not been observed below  $2537 \text{ \AA}$ ,<sup>23</sup> which is equivalent to 4.9 e. volts, we find reaction below this voltage. This situation can be understood when it is recalled that the transitions considered by us involve metastable states which cannot be reached by light absorption but can be excited by electron impact. No conflict exists between the photochemical action and our activation reaction. Photochemical actions are not studied below  $1800 \text{ \AA}$ . or 6.7 e. volts but activation by controlled electrons allows us to cover a much wider energy range than is available to the photo-chemist. A comparison of quantum yield and efficiency of our activations will be made when we have more detailed information.

**Radon Reactions.**—Oxygen has been studied by Lind and others<sup>9</sup> under the influence of ionization produced by the alpha particles of radon. The reaction process is expressed by the ratio of molecules reacted or formed ( $M$ ) to ions produced ( $N$ ) and it is found that the  $M/N$  ratio is variable since deoxygenation usually takes place under the conditions of the experiment. With a rapid flow Lind and Bardwell<sup>24</sup> obtained  $M/N = 2$ . We find  $M/N = 4$  if we assume that all of the reaction depends on the ions formed. This  $M/N$  ratio is not known with any accuracy from our experiments, but at least it can be seen that there is no disagreement with radon reactions. From our point of view we consider the further analysis of the  $M/N$  ratio into terms of efficiency necessary and we shall consider this question in another place.

### Summary

The activation of oxygen molecules by electrons of known speeds (3–20 e. volts) has been studied. The activated species have been removed by further reaction on a mercury surface. Activation is possible in the whole range of energies studied and is interpreted on the basis of the energy diagram of molecular oxygen derived from its band spectrum. In the low-velocity region (3–8 e. volts) metastable ( ${}^1\Sigma_g^+$ ) oxygen molecules serve as the activated state, in the region from 8–12 e. volts, electronically excited molecules ( ${}^3\Sigma_g^-$ ) are the activated species and above the ionization potential (12.5 e. volts) ions ( $O_2^+$ ) enter the reaction ( $M/N = 4$ ). These various

<sup>23</sup> Kistiakowsky, "Photochemical Processes," Chemical Catalog Co., Inc., New York, 1928, p. 221.

<sup>24</sup> S. C. Lind and D. C. Bardwell, *THIS JOURNAL*, **51**, 2751 (1929).

activations are discussed in terms of probabilities of energy transfer from electrons to normal molecules and of probabilities of further reaction between activated states and the mercury surface.

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## ENERGY EXCHANGE IN UNIMOLECULAR GAS REACTIONS

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### §1. Introduction

There is a large number of substances which decompose in the gas phase, and whose rate constants show a characteristic behavior in that they tend to approach a constant value as one goes to high pressures, but fall in value as one goes to low pressures.<sup>1</sup> According to the currently accepted theories, it is supposed that in these reactions the activated molecules receive their energy by collision with other molecules. As one goes to lower pressures the time between collisions becomes greater; when it becomes of the same order of magnitude as the average time necessary for an activated molecule to decompose, the falling off of the rate constant first becomes noticeable.<sup>2</sup>

Now it is found that it sometimes is possible to restore the rate constant to its high pressure value by the addition of an inert gas, which is able to exchange energy (without any chemical reaction taking place) with the molecules which are to decompose. Thus Hinshelwood and his co-workers have found that the rate constants for a number of ethers are increased by addition of a sufficient amount of hydrogen, the hydrogen being in most cases about as effective pressure for pressure as the reacting gas itself. They have also found that the rate constant is but little affected by the addition of helium, nitrogen, carbon dioxide and other gases composed of relatively heavy atoms;<sup>2</sup> also, strangely enough, in one or two cases, organic compounds have been reported ineffective.<sup>3</sup>

<sup>1</sup> As a matter of fact, in many cases, including those in which we shall be most interested here, this is a statement of a theoretical expectation rather than an experimental fact, since the limiting high pressure rate has not been reached experimentally.

<sup>2</sup> For a general discussion and references see Kassel, "Kinetics of Homogeneous Gas Reactions," Chemical Catalog Co., New York, 1932. It may be well to state explicitly that I assume the current explanations of the phenomena of unimolecular reactions, including the phenomena with inert gases present, although I am not certain but that further experimental work may show that some of the individual cases cited as illustrative of these principles really are more complex than they are now thought to be. In this connection note Rodebush and Copley, *THIS JOURNAL*, **54**, 2560 (1932), and Vernon and Daniels, *ibid.*, p. 2563.

<sup>3</sup> For example, Steacie, *J. Phys. Chem.*, **36**, 1562 (1932), reports that dimethyl and diethyl ether will not activate each other. These results have not been verified