EQUILIBRIUM IN ELECTRODELESS DISCHARGE.

PART V. EQUILIBRIUM IN THE DISSOCIATION OF OXYGEN AND IN THE FORMATION OF OZONE IN SILENT ELECTRIC DISCHARGE.

By R. Krishnan and S. K. K. Jatkar.

INTRODUCTION.

In Parts I–IV (*This Journal,* 1937, **20A**, 25–48) Bhatt and Jatkar showed that water vapour was dissociated to the extent of 70% in electrodeless discharge at high frequencies. It was also shown that carbon dioxide was dissociated to the extent of 25%, which increased to 70% in presence of water vapour. It was further pointed out that these reactions were equilibrium reactions which could be shifted to either side of the reaction, by cooling a portion of the apparatus in liquid air and by removing the liquid air with the discharge on. These results and the apparent disappearance of hydrogen in a discharge tube were shown to be due to the reversible chemical reactions of the molecules excited to higher states of energy by the electronic impact. In the case of oxygen no ozone formation could be detected, because the experiments were carried out at pressures below the vapour pressure of ozone at liquid air temperature (< 0.2 mm.). Any fall in pressure due to formation of ozone might have been counterbalanced by rise in pressure due to dissociation of oxygen.

The above investigations were carried out at very high frequencies ($\lambda = 1.8$ m.) and low power, so that it was essential to work at very low pressures. There is another method of exciting gases at high pressures by electrodeless discharge, namely, by subjecting the gases to silent electric discharge in a Siemen's ozoniser. As this apparatus was developed originally for the preparation of ozone from oxygen, we have taken up a systematic study of the equilibrium conditions obtained for this reaction under varying conditions of pressure and voltage.

The formation of ozone under static conditions had been the subject of investigation by many authors. The methods adopted for the production of ozone are (1) thermal, (2) exposure to ultra-violet light, and (3) by silent electric discharge. Warburg and Leithauser (*Zeit. Anorg. Chem.,* 1906, **48**, 260–293) have studied the equilibrium of ozone-oxygen mixtures at higher temperatures by passing the mixtures through a heated tube. Antoney Chassey (*Compt. Rendus,* 1906, **143**, 220–2; 1924, **128**, 1484–5) and Warburg and Rump (*Zeit. Physik,* 1925, **32**, 245–57) studied the kinetics of the formation of ozone in silent electric discharge at different frequencies. In all these experiments the pressure changes that occurred during ozonisation do not appear to have been closely followed. In spite of a large number of papers on corona pressure phenomena [*cf.* Farnweld, Kunz and Warner (*Phys. Rev.*, 1914, 4, 1770; 1916, **8**, 28; 1917, **10**, 483); Townsend and Warner (*Ibid.*, 1916, **8**, 285); Arnold, Tyndall and Searle (*Ibid.*, 1917, **9**, 93; 1918, **35**, 261); Fazel (*Ibid.*, 1922, **19**); and Joshi (*Malaviya Commemoration Volume*, 1932)], nobody has so far found an increase of pressure in silent electric discharge in oxygen.

In the present investigation, we have studied the effect of silent electric discharge in oxygen and we observed both a rise in pressure which was gradual and was not due to any temperature effect, and a fall in pressure which was due to the formation of ozone. We have shown that the formation of ozone under static condition is due to the simultaneous establishment of two equilibria $O_2^* \rightleftharpoons O + O$ $O_2^* + O \rightleftharpoons O_3$.

We have also studied the formation of ozone by the dynamic method and we have made several new observations which will be described in the next part (VI) of this series.

In this paper results of experiments done to study the ozone formation by silent electric discharge under static conditions have been reported. Care was taken to eliminate mercury vapour from the system. The pressure changes were followed by a glass Bourdon gauge sensitive to 0.25 mm. The use of mercury manometer was avoided, as it was intended to study the reaction in presence and absence of mercury vapour. Sulphuric acid has been used as manometric liquid by previous workers but it was considered to be unreliable owing to appreciable quantity of ozone absorbed.

EXPERIMENTAL.

The apparatus used is shown in Fig. 1.

The ozoniser was made of pyrex glass (4 mm. gap, 30 cm. length) and was cooled in a tank of water. The high potentials were obtained from an ordinary Neon Sign transformer run on 60 cycles mains. Only half the section of the secondary was used, as the mid-point of the transformer was connected to the body. The voltage was regulated by a resistance in series with the primary and by connecting high voltage condensers across the secondary. The changes in pressure were followed by the Pyrex Bourdon gauge, the position of the pointer being read by a microscope with scale in the eye-piece The rest of the apparatus is clearly shown in the figure. The whole of the apparatus was thoroughly evacuated by means of Hyvac pump and the reaction tube was degassed by repeatedly subjecting it to 15,000 volts discharge without cooling the apparatus. Oxygen was prepared by heating potassium permanganate and was passed over calcium chloride and phosphorous pentoxide before entering the ozoniser. The apparatus was rinsed with pure oxygen several times and thoroughly evacuated

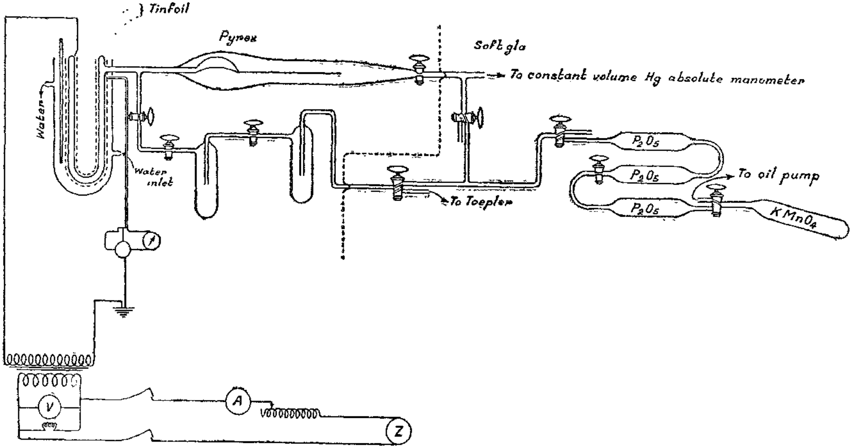
Tinfoil
Pyrex
Soft gla
To constant volume Hg absolute manometer
Water
Water inlet
To Toepler
P_2O_5
P_2O_5
P_2O_5
To oil pump
$KMnO_4$
V
A
Z

FIG. 1.

with 'hot' discharge on. During each experiment the gas was admitted at a known pressure which was read on a constant volume mercury manometer, the Bourdon gauge being used as a null instrument. When the discharge was on, water at a known temperature was circulated in the cooling tank. The pressure changes in the system were read from the positions of the gauge pointer on the micrometer scale. The readings were taken at frequent intervals until no further change was noticed.

The results of the pressure readings are given in the following tables.

TABLE I.

9 K.V.

Expt. 1 Pressure 725 mm.		Expt. 2 Pressure 713 mm.		Expt. 3 Pressure 608 mm.	
Time minutes	Pressure mm.	Time minutes	Pressure mm.	Time minutes	Pressure mm.
	700 +		700 +		600 +
0	25·0	0	13·0	0	8·0
5	24·25	5	12·5	5	6·75
10	,,	10	11·75	10	6·5
15	24·0	15	11·25	30	6·75
20	23·75	20	10·75	40	6·75
25	23·25	25	10·25	*	6·25
35	23·0	30	9·75		
45		35	9·5		
55	22·75	40	9·25		
60	22·5	50	8·75		
70	22·5	60	8·5		
80	22·0	*			
90	21·5	70	,,		
100	21·25				
110	21·0				
120	20·5				
*					
130	20·25				
140	20·25				

* Indicates the changes in pressures after the discharge was switched off.

TABLE I (*Contd.*)

Expt. 4 Pressure 521 mm.		Expt. 5 Pressure 411 mm		Expt. 6 Pressure 3 9 mm.	
Time minutes	Pressure mm.	Time minutes	Pressure mm.	Time minutes	Pressure mm.
	500 +		400 +		300 +
0	21·0	0	11·0	0	9·0
5	23·5	5	11·75	5	9·75
10	24·0	10	13·50	10	10·75
15	24·25	15	14·25	15	11·0
20	24·75	20	,,	20	,,
25	,,	25	,,	25	,,
30	,,	30	,,	30	,,
35	,,	35	,,	35	,,
40	,,	40	,,	40	,,
*		45	,,	45	10·25
41	23·75	*		50	,,
43	23·0	46	12·5	*	
45	22·5	47	11·75	51	9·0
50	21·5	48	11·25	52	8·5
60	21·0	49	11·0	53	8·0
		51	10·5	54	7·5
		53	9·75	57	6·5
		55	9·0	70	6·0
		60	8·5	80	6·0
		70	7·75		
		80	7·75		

* Indicates the changes in pressures after the discharge was switched off.

TABLE I (*Contd.*)

Expt. 7 Pressure 180 mm		Expt. 8 Pressure 108 mm.		Expt. 9 Pressure 33 mm.	
Time minutes	Pressure mm.	Time minutes	Pressure mm.	Time minutes	Pressure mm.
	100 +		100 +		
0	80·0	0	8·0	0	33·0
5	81·25	5	9·25	5	33·25
10	82·0	10	9·43	10	33·38
15	82·5	15	9·43	20	,,
20	,,	20	,,	30	,,
25	,,	25	,,	35	,,
30	,,	30	,,	*	
40	,,	40	,,	38	33·0
*		*		40	,,
41	81·75	41	9·25	50	,,
42	81·5	42	9·0		
45	80·75	45	8·5		
50	80·25	50	8·0		
55	80·0	60	8·0		
60	79·75				

* Switched off.

The results in Table I were obtained when the exciting potential was 9,000 volts, and are shown graphically in Fig. 2, which shows the variations of pressure in the ozoniser with time.

Experiment No. 1 (curve 1) was carried out with an initial pressure of 725 mm. in the ozoniser filled with pure oxygen. The equilibrium was reached after passing the discharge for two hours. The final readings were obtained by switching off the current.

Experiment No. 2 (curve 2) was conducted with an initial pressure of 713 mm. The equilibrium was reached within an hour and there was no difference in the pressure after switching off the current.

Experiment No. 3 (curve 3) was done with an initial pressure of 683 mm. in oxygen. The results show that the equilibrium pressure was attained within 10 minutes.

Experiment No. 4 (curve 4) was conducted with an initial pressure of 521 mm. Instead of the fall in pressure observed in previous experiments, we observed actually a rise in pressure which attained the equilibrium value within 10 to 20 minutes. The discharge was switched off after 40 minutes when the pressure gradually fell to the initial value.

Experiment No. 5 (curve 5) was carried out with 400 mm. starting pressure. There was a rise in pressure as in the previous experiment, the value of equilibrium being reached in a shorter time, namely,

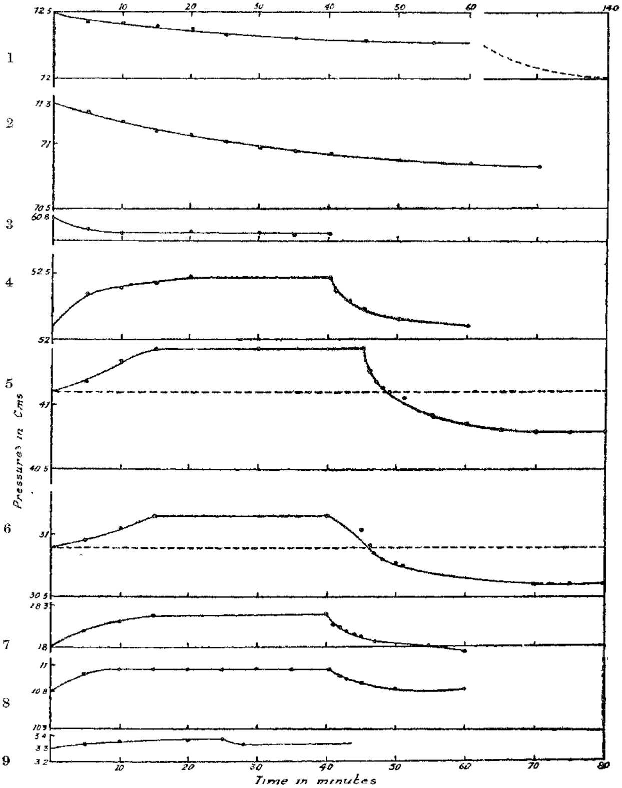

FIG. 2.

15 minutes, and after switching off the discharge at 45 minutes, there was a gradual fall in pressure which attained an equilibrium value at 70 minutes, the pressure being lower than the initial pressure.

Experiment No. 6 (curve 6) was conducted with an initial pressure of 309 mm. There was rise in pressure which attained its equilibrium value after 15 minutes. When the discharge was switched off there was a gradual fall in pressure with time, the final pressure reached being lower than the initial pressure of oxygen.

Experiment No. 7 (curve 7) was done with an initial pressure of 180 mm. There was a similar rise in pressure as in previous experiments and fall in pressure after switching off the discharge, which was only slightly lower than the starting pressure.

Experiment No. 8 (curve 8) shows the results obtained when the initial pressure was 108 mm. There was a rise in pressure which shows the equilibrium value on continuation of the discharge and a fall in pressure after switching off the current, the final pressure being nearly the same as that of initial pressure.

Experiment No. 9 (curve 9) shows similar results when the initial pressure was 33 mm.

Experiments were next conducted with 10,000 volts as the exciting voltage. The results are shown in Table II and Fig. 3.

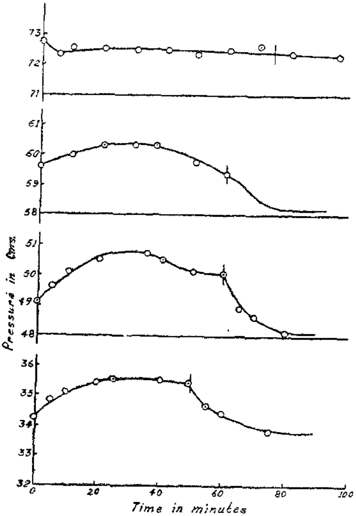

FIG. 3.

TABLE II.

10 K.V.

Expt. 10 Pressure 727 mm.		Expt. 11 Pressure 596 mm.		Expt. 12 Pressure 491 mm.		Expt 13 Pressure 342 mm	
Time minutes	Pressure mm.	Time minutes	Pressure mms.	Time minutes	Pressure mm.	Time minutes	Pressure mm.
	700 +		580 +		480 +		330 +
0	27·0	0	16·0	0	11·0	0	12·0
5	23·0	10	20·0	5	16·0	5	18·0
10	25·0	15	22·5	10	21·0	10	21·0
15	26·6	25	22·5	20	25·0	15	22·5
20	25·0	35	21·3	25	27·0	20	24·0
25	24·0	40	20·0	35	28·0	25	25·0
35	24·0	45	18·5	40	26·0	30	25·5
40	24·0	50	17·0	45	23·0	40	25·0
45	23·6	55	15·0	50	21·0	55	25·0
50	23·0	60*	15·0	55	20·0	60	24·2
55	24·0	61	11·2	60	20·0	*	
60	25·0	62	10·0	*		62	19·0
65	25·0	64	7·0	61·5	16·0	65	14·0
70	26·0	65	7·0	65	9·0	80	8·0
75	26·0	75	2·0	70	6·0		
85	25·0	85	1·0	80	1·0		
90	25·0						
*	25·0						

* Switched off.

Experiment No. 10 was done with an initial pressure of 727 mm. There was a gradual fall in pressure, the equilibrium being reached within 10 minutes.

Experiment No. 11 was carried out with an initial pressure of 596 mm. The pressure rose by 6.5 mm. within 15 minutes and on continuation of the discharge came to an equilibrium value which was only 1 mm. less than the original. After switching off the discharge the pressure gradually fell down by 15 mm.

Experiment No. 12 was conducted with an initial pressure of 491 mm. There was a rise in pressure for about half an hour and fall to an equilibrium value which was 9 mm. higher than the original. After switching off the discharge, the pressure gradually fell to a value which was 10 mm. less than the original pressure.

Experiment No. 13 was carried out with an initial pressure of 342 mm. There was a rise in pressure again which was 13 mm. higher than the original and remained constant when the discharge was continued for an hour. After switching off the discharge the pressure gradually fell to a value which was only 4 mm. lower than the original.

The next set of experiments were conducted with an exciting voltage of 10,500–11,000. The results are shown in Table III and Fig. 4.

TABLE III.

10·5–11 K.V.

Expt. 14 Pressure 621 mm.		Expt. 15 Pressure 741 mm.	
Time minutes	Pressure mm.	Time minutes	Pressure mm.
0	621	0	743
2	619	5	742
5	624	10	740
10	625	15	739
15	623	20	737
20	618	25	735
25	616	30	734
30	613	35	733
35	611	40	731
40	609	55	731
45	606		*
50	604	58	724
55	601	59	723
60	601	60	722
	*	65	720
65	591	70	717
75	588	75	716
85	588	80	716

* Switched off.

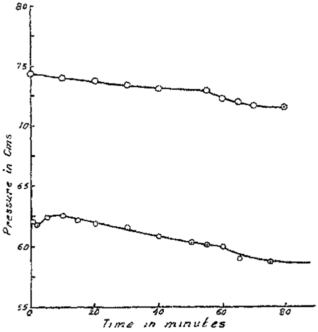

FIG. 4.

Experiment No. 14 was conducted with an initial pressure of 621 mm. There was a small rise in the initial pressure in 10 minutes and a subsequent fall which attained an equilibrium value after one hour which was 20 mm. less than the original. On switching off the discharge there was a further fall in pressure, *viz.*, 33 mm. less than the original pressure in the same time as in the previous experiments.

Experiment No. 15 was conducted at a higher initial pressure, namely, 743 mm. The table shows continuous fall in pressure which attained an equilibrium value in 40 minutes, the decrease being 12 mm. On switching off the discharge there was a further fall in pressure showing a total fall of 27 mm.

DISCUSSION.

The fall in pressure in an ozoniser is obviously due to the formation of ozone. The rise in pressure is more difficult to account for.

This rise cannot be the same as the so-called corona pressure, as the latter is obtained instantaneously on switching on the discharge, while in all our experiments we have found that the pressure rises slowly and takes 10 to 15 minutes to reach the maximum. It appears to us that the rise in pressure is due to dissociation of the oxygen molecules by the impact of the small number of ionised oxygen which is present in the tube. The observed pressure rise or fall is thus due to the simultaneous existence of two equilibria (1) $O_2^* \rightleftharpoons 2O$, (2) $O_2^* + O \rightleftharpoons O_3$.

The above mechanism is identical with that of Warburg (*Preuss. Akad. Wiss.*, Berlin, 1914, 872) who has shown that the formation of ozone in ultra-violet light is due to the two reversible equations given above. Thus the atomic oxygen in equation (1) may react with another atomic oxygen to form molecular oxygen, or it may react with excited oxygen molecule to form ozone (equation 2).. Ozone formation may, therefore, take place without ionisation of the gas. This was proved by the fact that light of shorter wave-length is required to produce ionisation of oxygen than that necessary to produce atomic oxygen.

The following table (IV) shows the values of the three equilibrium constants,

$$K_1 = \frac{[O]^2}{[O_2^*]}, \quad K_2 = \frac{[O_3]}{[O^*]_2\,[O]}, \quad \text{and } K_3 = \frac{[O]_3^{\,2}}{[O_2^*]^3} = K_1 K_2^{\,2}$$

calculated from the various results of the experiments. Po_2, Po and Po_3 represent the pressures of molecular oxygen, atomic oxygen and ozone which are apparently present in equilibria. P_i and P_f are respectively the initial pressure before switching on the discharge and the final pressure after switching off. δ_{p1} is the fall in pressure due to the formation of ozone (the actual pressure of ozone Po_3, being twice δ_{p1}); δ_{p2} is the rise in pressure due to the dissociation of oxygen including the small proportion of ionised oxygen, the actual pressure of the atomic oxygen being $2(\delta_{p1} + \delta_{p2})$; Po_2 is the pressure of molecular oxygen present in equilibrium. K_1 and K_2 were calculated from the partial pressures of molecular and atomic oxygen and of ozone. K_3 was calculated from the partial pressures of molecular oxygen and ozone in the system and was equal to $K_1 \times K_2^2$ except in experiments 1 and 2, where values of K_1 and K_2 could not be calculated owing to the fact that no rise in pressure was recorded.

The observed equilibrium constants for K_1, K_2 and K_3 are fairly concordant and well within experimental error.

It will be seen from Table IV that the dissociation constant (K_1) of oxygen, increases tenfold by changing the voltage from 9 to 10 K.V., there being no appreciable difference between 10 and 11 K.V. The equilibrium constant for the formation of ozone from atomic and molecular oxygen apparently passes through a minima at 10 K.V. The comparatively large value for this equilibrium shows that at 10 K.V. the rate of formation and decomposition of ozone are nearly the same. In the last column, the values of the equilibrium of oxygen with ozone in the silent electric discharge for different exciting voltages and different initial pressures have been shown. The mean value of the equilibrium at 9 K.V. is 0.027. The value of the equilibrium at 10 K.V. is nearly four times the above value and the one at 11 K.V. being fifteen times that at 10 K.V. The results obtained show that one molecule of ozone is present in equilibrium with one atomic oxygen and with about 12 molecules of oxygen.

TABLE IV.

Equilibrium in Silent Electric Discharge.

Expt. No.	Volts K.V.	P_i mm.	P_f mm.	δ_{p1} mm.	δ_{p2} mm.	Po mm.	Po_2 mm.	Po_3 mm.	$K_1 \times 10^2$	K_2	$K_3 \times 10^2$
1	9	725	720	5	..	..	710	10	..	..	0·020
2	,,	713	708·5	4·5	..	..	699·5	9		..	0·017
5	,,	411	414·25	3·25	3·25	13	394·75	6·5	0·11	0·52	0·028
6	,,	309	311·5	3	2·5	11	294·5	6	0·13	0·58	0·044
									0·12	0·55	0·027
11	10	596	613·5	4	17·5	43	562·5	8	0·54	0·20	0·022
12	,,	491	508	10	17	54	434	20	1·32	0·43	0·248
13	,,	342	355	4	13	34	313	8	1·04	0·28	0·074
									1·18	0·30	0·115
14	11	741	743	27	2	58	631	54	0·72	1·09	0·860
15	,,	621	625	33	4	74	485	66	1·80	1·14	2·380
									1·26	1·12	1·62

Warburg and Leithauser (*Ann. Physik.*, 1909, **28**, 29) also found at equilibrium 1 molecule of ozone to 12 of oxygen for a static system in silent electric discharge at normal temperature and pressure. Our results are thus in agreement with previous observations and are further an advance over the older work in that we have shown that the equilibrium in the oxygen-ozone reaction is the resultant of two other equilibria, one being the dissociation of oxygen (K_1) and the other formation of ozone by combination of activated molecular oxygen with atomic oxygen (K_2).

The assumption of the presence of atomic oxygen is supported by the views of Anderegg (*Jour. Amer. Chem. Soc.*, 1917, **39**, 2581) who says that oxygen atoms are probably present in all cases of ozone formation.

In brush discharge the increase in pressure (δ_{p2}) due to breaking up of molecules by ionic collisions has been shown to follow the relationship $V \times i = v_0 \, \delta_{p2}$, where V is the applied voltage, i is the corona current and v_0 is the volume of the gas subjected to discharge (Townsend and Warner, *Phys. Rev.*, 1916, **8**, 285). In experiments 14 and 15 the steady current at equilibrium was 17.5 milliamps. Taking the pressures instead of volume (which was kept constant) as proportional to v_0, we find that the products of $\delta_{p2} \times$ pressure P_f are 20.05, 20.6 which compare with the value of voltage current, *viz.*, 19.25 within experimental error.

The statement that there is scarcely any rise in pressure in the discharge in oxygen (*cf.* Rideal, *Ozone,* 1920, Constable and Company, p. 95) must be revised in the light of our observations, which indicate conclusively that the increase in pressure due to dissociation has been obscured by the fall in pressure due to ozone formation.

The application of thermodynamics to the chemical equilibria observed in electrical discharge will be discussed in a subsequent part of this series.

SUMMARY.

We have investigated the reaction in the Siemen's ozoniser under static conditions and the equilibrium has been studied from the standpoint of the application of the law of mass action. Equilibrium was attained from one side only, using different initial pressures and different exciting voltages. At higher pressures there was a gradual approach to equilibrium when the exciting voltage was low. At lower pressures, there was a rise in pressure apparently due to the dissociation of oxygen molecule into oxygen atoms. When the exciting potentials were increased the equilibrium was reached in a shorter time and the dissociation of oxygen was observed at a higher pressure of oxygen than in experiments at a low exciting voltage.

The ozone produced is never proportional to ionization as the quantity of ozone formed is not at all related to the current flowing. Instead of assuming that a large number of secondary ions are produced by shock excitation and that these ions do not reach the electrode even under saturating conditions, it is much simpler to assume that dissociation of oxygen molecule occurs under the effect of silent electric discharge and that the atomic oxygen combines with the excited oxygen molecule to form ozone.

We have calculated the equilibrium constant for the two reactions $O_2^* \rightleftharpoons 2O$ and $O_2^* + O \rightleftharpoons O_3$, which occur simultaneously. The equilibrium constants are fairly concordant and well within the experimental error.

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