EQUILIBRIUM IN ELECTRODELESS DISCHARGE.

PART VI. INFLUENCE OF RATE OF FLOW ON THE FORMATION OF OZONE IN THE SIEMEN'S OZONISER.

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

INTRODUCTION.

We have shown in Part V (*This Journal,* **21A**, 223–36) that an equilibrium is established in the Siemen's ozoniser between atomic oxygen, molecular oxygen and ozone, at different exciting voltages, in static experiments. We showed that at 11 K.V., one atom of oxygen and one molecule of ozone, were in equilibrium with 12 molecules of oxygen. The results, in general, indicated that appreciable amount of atomic oxygen is present in the Siemen's ozoniser and that, atomic oxygen appears to have a life of about 10 minutes after the discharge is switched off.

Although Anderegg (*Jour. Amer. Chem. Soc.,* 1917, **39**, 2581) had pointed out that atomic oxygen was probably formed in all cases when ozone was formed, sufficient attention does not seem to have been paid to the reactions of atomic oxygen as compared with the reactions of ozone. There seems to be some indirect evidence to show that atomic oxygen has been responsible for the confusion in the literature regarding the existence of the molecule O_4. Harries [(*Liebig's Ann.,* 1912, **390**, 235); *cf.* Mellor, *Treatise on the Inorganic and Theoretical Chemistry,* 1922, Vol. 1] noted that the specific gravity of the gas from the last fraction of the liquid ozonised oxygen was *less* than that which corresponded with the amount of iodine liberated from potassium iodide solution. Harries, however, concluded that O_4 as well as O_3 was present, the former on decomposition furnishing two atoms of oxygen and the latter one such atom. This explanation is obviously in error, because the density of the gas should be higher and not lower, if O_4 was formed, than that calculated from the reactions with potassium iodide solution. The most important evidence which Harries put forward in favour of the theory of formation of O_4, is the formation of oxozonides $C_4H_8O_4$ instead of ozonide $C_4H_8O_3$, when *concentrated ozonised oxygen,* or oxygen ozonised by means of a *high voltage,* was passed through butylene. Similar results were obtained with tetrahydrobenzene and caoutchouc. If, however, the ozonised oxygen was passed through a solution of potassium hydroxide or sulphuric acid, there was *a loss of ozone* and the products obtained were ozonides proper. Harries, therefore, concluded that the so-called ozone in ozonised oxygen contained one-third oxozone. All these observations could now be easily explained by the fact that equal quantities of atomic oxygen and ozone are formed in the process of ozonisation at high voltages. The atomic oxygen is apparently destroyed by the alkali and acid, more rapidly than ozone is affected. The formation of oxozonides probably depends upon the reactions of ozonide with the atomic oxygen. The lower density of the ozone finds a ready explanation on the basis of the existence of atomic oxygen.

It is also now known that oxygen atoms in the outer atmosphere are almost permanently free, since the process of recombination into molecular oxygen is very slow at higher altitudes. This process is supposed to occur more frequently at lower altitudes, so that we pass from a region of atomic oxygen through a transition layer in which the proportion of molecular oxygen increases till we come to a region where atomic oxygen is rare because the oxygen atoms which are obtained by dissociation, form ozone by combination with oxygen.

In the present investigation it has been observed by the authors that atomic oxygen is far more stable in air than in oxygen at atmospheric pressure. Experiments have been made to find out (1) what proportion of atomic oxygen was formed when air was used in the ozoniser under static conditions, and (2) whether the experiments on the ozone formation by the dynamic method agreed with the limiting conversion of oxygen into ozone by the static method, in air and oxygen.

EXPERIMENTAL.

(1) *Static Method.*—The equilibrium in the formation of ozone from air by static method was studied by using the same apparatus as used in Part V (*loc. cit.*). The results for different exciting voltages are shown in Table I.

TABLE I.

Equilibrium in Silent Electric Discharge.

Experiments with Air.

No.	K.V	P_i	P_f	δ_{p1}	δ_{p2}	P_0	P_{O_3}	P_{O_2}	$K_1 \times 10^2$	K_2	$K_3 \times 10^2$	% Conversion of O_2 to O
1	7·5	683	681	2	2	8	4	122·6	0·39	0·56	0·12	1·0
2	9	701	696	11·5	..	..	23	112·2	..	..	5·3	4·6
3	10	685	683	12	..	..	24	111	..	..	5·7	4·8
4	10·5	687	694·5	6	7·5	27	12	105·9	4·8	0·61	1·8	3·4

P = Initial pressure; P_f = final pressure on switching off the discharge; δ_{p1} = fall in pressure due to ozone formation (actual pressure of ozone being $2\delta_{p1}$); δ_{p2} = rise in pressure due to dissociation of oxygen, the actual pressure due to atomic oxygen being $2(\delta_{p1}+\delta_{p2})$; P_0, P_{O_2} and P_{O_3} are partial pressures of atomic and molecular oxygen and ozone present in equilibrium.

$$K_1 = \frac{[O]^2}{[O_2^*]},\ K_2 = \frac{[O_3]}{[O_2^*]\,[O]},\ \text{and}\ K_3 = \frac{[O_3]^2}{[O_2^*]^3} = K_1K_2^2$$

There was rise in pressure both at lower and higher voltages which attained an equilibrium value within less than ten minutes, and a fall in pressure which reached a limiting value in 30 to 50 minutes after switching off the discharge, indicating the increased stability of the atomic oxygen in air than in oxygen. The ratio of atomic oxygen to ozone is about 2: 1. The values of the equilibrium constants K_1, K_2 and K_3' are of the same order as found in the case of experiments with oxygen (*cf.* Part V of this series). The results indicate that the maximum conversion of oxygen in air to ozone, is about 1% at 7.5 K.V. and 4% at 10 K.V.

(2) *Dynamic Method.*—Experiments were conducted to find out the influence of rate of flow on the formation of ozone from air and oxygen. The apparatus used is shown in Fig. 1. The ozoniser consisted of double-walled pyrex or soft glass tubular vessel, 20 cm. in length, with an annular space of 3–4 mm., the thickness of the glass of the wall being about 0.8 to 1 mm. The gas after being dried and freed from carbon dioxide and dust, was streamed through the annular space of the ozoniser.

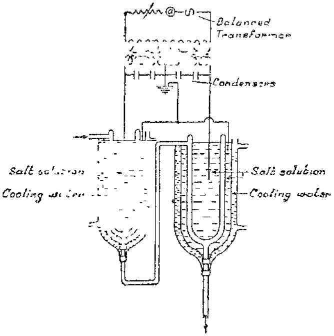

Fig. 1

In order to utilize the balanced windings of the transformer, two ozonisers were used as shown in the figure, the high potentials being applied to the inner electrodes through salt solution and the outer electrodes of both the ozonisers being earthed.

Ozone reacts with potassium iodide giving an atom of iodine, a molecule of oxygen, and an equivalent amount of potassium hydroxide. The solution is acidified with dilute sulphuric acid and then titrated with standardised thiosulphate solution.

The results showing the percentage conversion of oxygen at various rates of flow of air and oxygen through one ozoniser and through two ozonisers in series, each having 4 mm. annular gap, at different exciting voltages, are given in Table II and shown graphically in Figs. 2 and 3.

With oxygen, the maximum conversion was 4% at 10 K.V. which is very nearly the equilibrium conversion. At 11 K.V. the maximum conversion with both a single ozoniser and the double ozoniser, was about 8% which is far short of the theoretical value, 15%. The curves showing the influence of rate of flow on the

TABLE II.

Air—7·5 K.V.

Single Ozoniser			Double Ozoniser					
Rate	% Conversion	gms./hr.	Rate	% conversion	gms./hr.	Rate	% Conversion	gms./hr.
3·5	0·02	0·0006	4·6	1·17	0·038	7·2	0·73	0·037
4·4	0·13	0·004	5·5	0·65	0·025	10·4	0·48	0·035
5·5	0·13	0·005	7·3	0·21	0·011	10·7	0·48	0·036
10·0	0·26	0·018	10·0	0·00	0·000	15·8	0·45	0·050
12·8	0·43	0·039						

Air—10 K.V.

Single Ozoniser		
Rate	% Conversion	gms./hr.
5·3	1·56	0·058
7·7	1·65	0·089
8·0	1·44	0·084
14·8	1·20	0·124

Oxygen—10 K.V.

Single Ozoniser			Double Ozoniser		
Rate	% Conversion	gms./hr.	Rate	% Conversion	gms./hr.
7·0	4·02	0·219	5·3	6·43	0·266
8·5	2·84	0·188	6·8	5·08	0·279
15·0	2·04	0·238	9·1	4·69	0·324
17·0	1·40	0·189	19·2	2·83	0·411

Oxygen—11 K.V.

Single Ozoniser			Double Ozoniser		
Rate	% Conversion	gms./hr.	Rate	% Conversion	gms./hr.
3·6	7·94	0·221	3·2	7·53	0·186
4·2	6·99	0·227	7·0	8·40	0·414
6·1	5·59	0·262	7·8	6·96	0·419
8·2	4·97	0·312	8·3	2·51	0·361
11·0	5·38	0·457	8·9	9·16	0·456
15·7	3·52	0·427	24·2	6·33	0·507

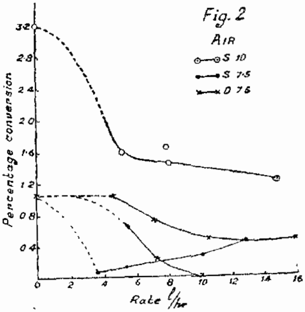
Fig. 2

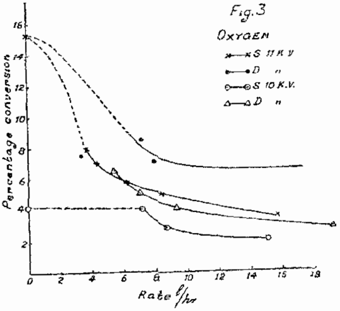
Fig. 3

S = Single Ozoniser ; D = Double Ozoniser conversion in a single ozoniser do not permit the extrapolation to be made with confidence, the dotted line having been drawn only to show the theoretical relationship of the equilibrium values obtained by the static and the dynamic methods. In the case of air, the maximum % conversion at 10 K.V. in a single ozoniser is about 1.6%, the value obtained by the static method being double this. The results with a single ozoniser at 7.5 K.V. showed a fall in the apparent % conversion with decreasing rate, which was practically zero at 3.5 litres/hour. With double ozoniser there is no conversion at the rate of 10 litres/hour and the conversion increases with decreasing rate, attaining a maximum value of 1%, which is in agreement with the value obtained by the static method.

From the results of the experiments by the static method, we have shown that in all cases there is formation of atomic oxygen which is stable under the conditions of the experiment. The latter may react with potassium iodide solution and indicate higher concentration of ozone than is actually present, or may react with ozone in presence of potassium iodide to yield oxygen. In the latter case there will be no apparent formation of ozone, which appears to be the case, because atomic oxygen is known to have reducing action (W. R. Rodebush and W. A. Nichols, *Jour. Amer. Chem. Soc.*, 1930, 52, 3864–68). Thus molybdenum trioxide combines with atomic oxygen to form the slate-blue oxide MO_3O_8, which was also obtained by the action of atomic hydrogen on the same oxide. Lead peroxide is also reduced by atomic oxygen. The results obtained in the present investigation can be explained on the basis of the *reducing* action of atomic oxygen on ozone to form molecular oxygen, especially in presence of moisture. Thus, in the case of experiments with the single ozoniser at 7.5 K.V. the atomic oxygen formed goes on increasing at lower rates of passage which neutralises the oxidising action of ozone, until at a rate of 3.5 litres/hour, there is no apparent reaction of ozone with potassium iodide solution.

In the case of experiments with the double ozoniser at the same exciting voltage, there was no apparent conversion at the rate of 10 litres/hour due to the same cause. With lower rates there is obviously increased amount of ozone formed until the equilibrium is reached at the rate of 4.5 litres/hour. At 10 K.V. and 11 K.V. the apparent maximum conversion observed both in air and oxygen, is half that obtained by the static method. The atomic oxygen formed, apparently interferes with the reaction of ozone with potassium iodide solution, by converting the oxygen atom liberated from ozone, directly into molecular oxygen.

Experiments were next conducted to find out the effect of the reduced annular gap on ozone formation. The results are given in Table III.

TABLE III.

Air.

1 Pyrex ozoniser, annular gap 3 mm., length 50 cm., 8·5 K.V.

Rate	% Conversion	Yield gms./hr.
27·8	1·6	0·344
16·4	1·7	0·173
12·7	1·6	0·163
8·2	1·5	0·096
4·0	1·5	0·048

Oxygen.

1 Soft glass ozoniser, annular gap 3 mm., length 50 cm., 10 K.V.

Rate	% Conversion	Yield gms./hr.
24·5	5·3	1·248
17·0	5·9	0·948
14·0	6·9	0·924
8·0	9·6	0·732
6·0	11·5	0·660
2·0	6·2	0·112

Oxygen.

Pyrex ozonisers, annular gap 3 mm., length 50 cm., 10 K.V.

Single Ozoniser			Double Ozoniser		
Rate	% Conversion	Yield gms./hr.	Rate	% Conversion	Yield gms./hr.
28·5	3·4	0·918	28·5	4·6	1·248
24·0	3·2	0·738	18·25	6·5	1·134
22·0	4·0	0·834	17·0	6·2	0·996
7·9	4·5	0·339	10·8	7·3	0·748
4·9	6·3	0·295	9·3	10·2	0·882
2·6	9·7	0·240	2·6	9·7	0·236

It will be seen from the tables that the reduction of the annular space favours higher percentage conversion at the same voltage. Thus the maximum conversion with a single ozoniser having a 4 mm. gap was 4%, and with a double ozoniser, the conversion increased only to 6%. The maximum percentage conversion increased to about 10% with both single and double ozonisers when the gap was reduced to 3 mm. With a soft glass ozoniser of the same dimension, the maximum conversion was about 12%. The yields obtained with a single soft glass ozoniser were comparable with the yields obtained with two pyrex ozonisers in series. It will be interesting to conduct experiments under static conditions with both pyrex and soft glass ozonisers having 3 mm. gap, in order to find out to what extent the limiting percentage conversion obtained in the static and the dynamic method, is affected by the formation of atomic oxygen.

The results for the formation of ozone from air, with pyrex ozonisers having annular gaps of 3 mm. and 4 mm., showed apparent percentage conversions which were independent of the rate of passage, which were, however, only 50% of the value obtained by the static method. It appears that the reason for this discrepancy is due to the reactions of atomic oxygen, increasing quantities of which are formed at low rates of passage and which are far more stable in air than in oxygen, and which neutralize the effect of the increasing quantities of ozone formed at low space velocities.

Further work is in progress.

SUMMARY.

A simple design for an ozoniser has been described for utilizing the balanced windings of the cheap Neon Sign Transformer.

The results of experiments conducted with pyrex ozonisers having annular gap of 3 mm., at 8.5 K.V. yielded results which were comparable with a similar ozoniser having 4 mm. gap at 10 K.V., and with the latter exciting voltage, the results were as good as those obtained with two 4 mm. gap ozonisers put in series. The soft glass ozoniser was nearly twice as efficient as the pyrex ozoniser.

The results of experiments on the formation of ozone from air in silent electric discharge by both static and dynamic methods were found to be in general agreement with the previous findings of the authors regarding the formation of atomic oxygen. The equilibrium conditions were also found to depend upon the exciting voltage. The apparent percentage conversion of oxygen, however, was found to be less for lower rates of passage at lower voltages, and at a particular rate, apparently no ozone was obtained. Atomic oxygen is apparently

far more stable in air than in oxygen, the proportion of atomic oxygen to ozone being 2 to 1. The remarkable divergence in the values of equilibrium conversion observed between the static and the dynamic conditions at higher voltages, has been explained on the basis of the reducing action of atomic oxygen on the reactions of ozone.

Department of General Chemistry,
Indian Institute of Science,
Bangalore (India).

[Received, 4–11–1938.]

1852-38—Printed at The Bangalore Press, Bangalore City, by G. Srinivasa Rao, Superintendent.