XCVIII.—*Notes on Ozone. Estimation, Solubility, and Interaction with Hydrogen Peroxide.*

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The experiments of Ladenburg (*Ber.*, 1901, **34**, 1184) have shown that ozone can be accurately estimated by means of its action on potassium iodide in *neutral* solution, the solution being acidified *after* the action is complete. In this case, a molecule of iodine is formed for each molecule of ozone present. If, however, the ozone acts on an acidified solution of potassium iodide, the amount of iodine set free is greater than would correspond with this ratio; for in this case if the iodide is very dilute three atoms of iodine are formed for each molecule of ozone. Now it has been shown that ozone forms some complex when dissolved in acids (*Zeit. physikal. Chem.*, 1903, **43**, 229), and it was thought that the nature of this complex could be determined by a study of the solubility of ozone in water and acids. The object of these experiments was (1) to find a reliable method for the estimation of ozone in acid solution and (2) to study the solubility of ozone in water and acids. At the suggestion of Sir W. Ramsay, some further experiments were made regarding the action of ozone on hydrogen peroxide.

I. *Estimation of Ozone in Acid Solution.*

When these experiments were begun, no data for the estimation of ozone in acid solution had been published. But in a recent paper Ladenburg (*Ber.*, 1903, **36**, 115) has shown that ozone can be estimated in acid solution by means of its action on sodium hydrogen sulphite and on arsenious acid. The results obtained by Ladenburg show, however, considerable variation, so that further work on the subject seemed desirable.

Since the extra amount of iodine formed in acid solution was probably due to the hydriodic acid being too easily oxidised by the ozone, it seemed likely that a less easily oxidisable substance, such as hydrobromic acid, would give more regular results. As it was possible that the action of ozone gas on hydrobromic acid would not be the same as that of an acid solution of the gas, Ladenburg's method could not be directly employed. Hence, in order to ascertain the amount of ozone taken the following procedure was adopted. A solution of ozone in water was prepared and equal volumes (50 c.c.) were added to 10 c.c. of (1) water, (2) an acid. To No. 1, potassium iodide was added, followed by a small quantity of acid; to No. 2, potassium bromide, and then, after a short time, potassium iodide. The iodine liberated was then titrated with *N*/100 sodium thiosulphate, and in this way the same amount of ozone was estimated by means of Ladenburg's method and by means of potassium bromide in acid solution. The water and acid used in these experiments were first of all treated with ozone to destroy any oxidisable matter, and then boiled to drive off the remaining ozone. Usually, five estimations were carried out together, the first and last according to Ladenburg's method and the remaining ones by the bromide method. Table I (p. 1012) shows the number of c.c. of thiosulphate required in each case.

A solution of ozone in *N*-HNO_3 gave the following figures:

(*a*) Estimation with iodide (in acid solution), 8·75 c.c. and 8·70 c.c.

(*b*) Estimation with bromide, 6·30 c.c., 6·40 c.c., 6·45 c.c.

These figures show that the iodide method gives a high result with an acid solution of ozone, and also that the estimation by means of bromide does not give very concordant results; but although every precaution was taken in order to increase the accuracy a closer agreement could not be obtained. Now, the differences between the iodide titres of Table I are not much less than those between the other three titres, and they are all probably due to experimental error, which is unavoidably high owing to the method which has to be adopted. Hence, the conclusion may be drawn that ozone in acid solution acts on potassium bromide according to the equation $O_3 + 2HBr = Br_2 + O_2 + H_2O$.

TABLE I.

Potassium iodide. neutral.	Potassium bromide in acid solution.				Potassium iodide neutral.
	Acid.	1.	2.	3.	
10·50	N-H_2SO_4	10·13	9·87	9·58	10·50
9·00	N-H_2SO_4	8·65	8·80	8·65	9·00
11·95	N-HNO_3	12·05	12·30	12·07	12·55
13·10	N-HNO_3	13·40	12·80	13·10	13·55
13·00	N-HNO_3	12·05	12·05	—	12·85
12·85	N-HNO_3	12·30	11·80	11·50	12·00
12·65	N-HNO_3	12·40	12·20	12·15	12·15

II. *Solubility of Ozone.*

In some experiments carried out by Schöne (*Ber.*, 1873, 6, 1224), it was shown that when ozonised oxygen was passed through distilled water a true equilibrium was not reached since, although the concentration of the dissolved ozone remained constant, the gas did not pass through the solution unchanged, one-fourth of the ozone being decomposed into oxygen. Schöne applied this result to correct Carius' determination of the solubility, not realising that in such a case there can be no question of a solubility, since the apparent solubility would depend on the rate of passage of the gas. It seemed advisable, therefore, to repeat Schöne's experiments in order to decide whether the solubility could be used to ascertain what complex is formed by the ozone in acid solution.

The method employed was as follows: pure dry oxygen, prepared from potassium permanganate, was passed through an ozoniser and thence through (1) a bulb fitted with two taps and having a capacity of 80 c.c.; (2) a gas-washer containing distilled water; (3) a phosphorus pentoxide tube; (4) a second bulb similar to (1). The gas-washer contained a spiral through which the ozone was bubbled, this arrangement ensuring good stirring and thorough contact of the gas with the solution. The ozone was passed through the apparatus until the concentration of the ozone in the gas-washer was constant. The taps on the two bulbs were then closed, the apparatus disconnected (the different parts were connected by ground glass joints), and the contents of the two bulbs were then analysed by aspiration into neutral potassium iodide, &c., as in Ladenburg's method. If no decomposition had taken place during the passage of the ozone through the solution, the contents of the two bulbs should give identical results on analysis. In order to be certain that any differences found were caused by the action of the water and not by that of the connecting tubes or the phosphorus pentoxide, similar experiments were made in which the gas-washer was omitted. The results are given in Table II.

TABLE II.

	Gas-washer used.				Gas-washer omitted.	
Percentage of ozone in first bulb ...	10·5	12·7	11·4	11·8	8·67	6·00
Percentage of ozone in second bulb...	9·9	12·1	10·5	10·1	8·29	5·84

The above results confirm Schöne's experiments and indicate that ozone, when passed through water, is partly decomposed. Hence there can be no question of the solubility of ozone in water, and it is therefore impossible to study the molecular state of dissolved ozone by means of its solubility relationships.

III. *Interaction of Ozone and Hydrogen Peroxide.*

Ever since the time of Schönbein (see Dammer, *Handbuch der anorg. Chem.*, Vol. I, p. 434) it has been believed that ozone and hydrogen peroxide mutually destroy one another. Now the odour of ozone is not destroyed by passing it through hydrogen peroxide, and it has been stated recently (*Ber.*, 1902, **35**, 2905) that the substances have no action on one another. Sir W. Ramsay suggested to me that the action might possibly be a slow one, and that by mixing solutions of the two substances the rate of their reaction might be determined. A solution of ozone in water was therefore prepared, and equal portions (50 c.c.) were placed in a series of flasks. Each of these was treated with 5 c.c. of a dilute hydrogen peroxide solution (5 c.c. = 14·2 c.c. of $N/50$-$KMnO_4$), and then, after different intervals of time, dilute sulphuric acid was added and the amount of unchanged peroxide was estimated by means of permanganate solution, which has no action on ozone.

TABLE III.

Time	5 minutes.	20 minutes.	36 minutes.	50 minutes.
Permanganate used	11·2 c.c.	12·2 c.c.	12·6 c.c.	12·65 c.c.

These figures would seem to indicate that the amount of peroxide decomposed diminishes as the time increases, but the true explanation is as follows. Although ozone has no action on permanganate, it oxidises a manganous salt to the dioxide, and this dioxide is easily reduced by hydrogen peroxide. Now the permanganate used was so pure that it had no action on pure hydrogen peroxide until a small quantity of manganous sulphate was added (*Zeit. Elektrochem.*, 1903, 9, 226). Hence, during the titration, the manganous salt would act catalytically on the ozone and hydrogen peroxide and so diminish the number of c.c. of permanganate required, and as some of the ozone would undoubtedly slowly escape, the catalytic action, and therefore the apparent amount of decomposition of the peroxide, would diminish as the time increased. As a confirmation of this explanation, it was found that if manganous sulphate was added at once to the mixture of ozone and peroxide and the titration carried out after the lapse of a few minutes, the number of c.c. of permanganate used (10·5 c.c.) was still less than had been the case in the previous experiment.

Another method had therefore to be devised to show that the reaction really took place without a catalytic agent. A current of ozone (free from nitrogen and oxides of nitrogen) was passed through a solution of hydrogen peroxide and the amount of unchanged peroxide was estimated, as before, after definite intervals of time. The concentration of the peroxide chosen was so great that the greatest possible concentration of ozone would not be nearly sufficient to destroy the peroxide originally taken, so that the catalytic effect during titration would necessitate only a small correction. In this way, it was found that the titre of the peroxide diminished from 14·8 to 1·6 in 205 minutes, whereas a similar current of oxygen merely caused this value to diminish from 24·0 to 23·6 in 410 minutes. This result shows that the original experimenters were correct, and that ozone does act slowly on hydrogen peroxide.

In conclusion, I wish to express my thanks to Sir W. Ramsay for the kind interest he has taken in the above experiments and for the advice and help he has given me.

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