90. *The Separation of Ozone from Other Gases.*

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A method is described for the determination of ozone in a concentration of only a few parts in a hundred million parts of other gases. It is based on the condensation of ozone on the surface of specially prepared silica gel, and its separation from other gases by fractional distillation.

THE experiments to be described were undertaken with the intention of developing a reliable chemical method for the determination of atmospheric ozone. The main difficulty of this problem is the high degree of dilution in which ozone occurs in air—only a few parts in a hundred million. Previous methods brought the ozone in this low concentration into contact with the reagents. Such a procedure is, however, inaccurate as the contradictory results found by different observers indicate; the recent careful work of Guéron and Prettre (*Bull. Soc. chim.*, 1936, **3**, 295, 1841; *J. Roy. Met. Soc.*, Supp. to Vol. **62**, 2, 1936) has revealed the reasons for this failure. Sometimes it even remained doubtful whether the oxidising atmospheric agent thus measured was actually ozone, since the identification, at its best, was confined to the proof that this agent could be destroyed by substances known to react with ozone. It was obvious that much greater reliability would be achieved if the ozone were first concentrated by separating it, without loss, from the other constituents of the atmosphere and only using it for a quantitative chemical reaction after it had been thus isolated.

It was found that by passing ozone, in any degree of dilution, over silica gel cooled in liquid oxygen, the ozone can be frozen out quantitatively; that it can be recovered, without decomposition, by afterwards raising the temperature of the silica gel; that this distillation offers a method of separating it from nitrogen dioxide and hydrogen peroxide, the other oxidising agents that might be present in air; and, finally, that the concentration of ozone thus obtainable from the atmosphere is sufficient for its safe identification by chemical and spectroscopic methods, and for its exact measurement (cf. *Nature*, 1938, **142**, 112, 571).

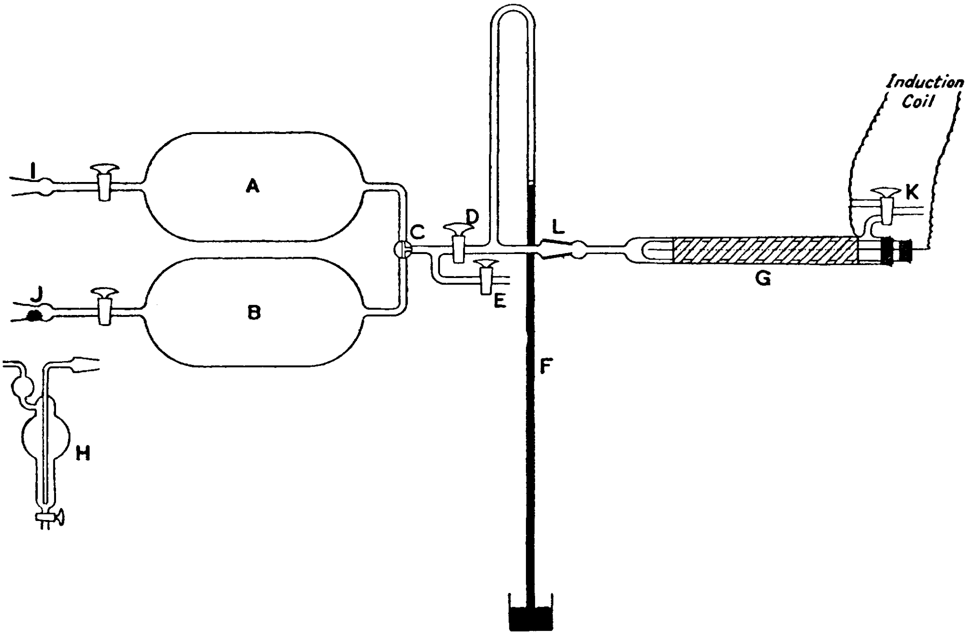
EXPERIMENTAL.

(1) *The Determination of Ozone.*—Before any investigation on the quantitative separation of highly diluted ozone from other gases could be started, it was necessary to ascertain whether the method applied for its determination was giving results strictly comparable within a wide range; the question of the correctness of the absolute values of the measurements could, for the time being, be neglected.

A survey of the literature made it seem likely that the method of Ladenburg and Quasig *Ber.*, 1901, **34**, 1184; 1903, **36**, 115, 1903) could be trusted. These authors recommend the absorption of ozone in a neutral solution of potassium iodide, whereby part of it liberates iodine, $2KI + O_3 + H_2O = I_2 + O_2 + 2KOH$, while another part produces iodate, $KI + 3O_3 = KIO_3 + 3O_2$. If, after the complete absorption of the ozone, sulphuric acid is added, the iodate produced by the second reaction is decomposed by the excess iodide and again liberates iodine, $KIO_3 + 5KI + 3H_2SO_4 = 3K_2SO_4 + 3H_2O + 3I_2$, so that the total amount of iodine titratable with sodium thiosulphate corresponds exactly to 1 mol. per mol. of ozone.

In order to test the reliability of this and other methods the apparatus shown in Fig. 1 was used. The bulbs *A* and *B* were of equal volume. They were first evacuated; then, by means of the three-way tap *C*, a mixture of ozone and oxygen prepared in the ozoniser *G* was admitted, and finally both bulbs were filled with air up to atmospheric pressure; the surface of the mercury of the controlling manometer *F* was protected by a layer of sulphuric acid. Absorption pipettes of the design shown at *H* could be attached by means of ground glass joints to each of the bulbs, and their gas content blown through the pipettes by passing oxygen through the tap *E* into the bulbs.

FIG. 1.



If, following the procedure of Ladenburg and Quasig, the pipettes were filled with neutral 4% aqueous solutions of potassium iodide, and sulphuric acid was added before titrating the liberated iodine with sodium thiosulphate, the results obtained for the ozone contents of the two bulbs agreed usually to within 1%, and the deviations were never greater than 2—3%, an accuracy sufficient for the purpose of the experiments. Buffered solutions of diverse composition were also tried, but it was more difficult to obtain constant results with them. This is in complete accord with the statements of Powell (*Chem. Analyst*, 1916, **16**, 7) and of Riesenfeld and Bencker (*Z. anorg. Chem.*, 1916, **98**, 167) that for low concentrations of ozone—the only ones used in this work—the simple Ladenburg–Quasig method is at least as good as any other.

In order to test whether this method could be relied upon for the comparison of largely varying quantities of ozone, a streaming method was used; the apparatus is shown in Fig. **2**. A current of ozygen was passed first through the ozoniser *G* and was then divided, by setting the stopcocks *C* and *D* in an appropriate manner, into a fast and a slow stream; the velocities could be read on the glass flow-gauges *A* and *B* which, according to the varying width of their capillaries, were suitable for the measurements of different gas velocities; a number of such gauges were constructed in order to be able to cover a wide range. The absorption pipettes *E* and *F*, the solution with which they were filled, and the method of titration were the same as described above. The results obtained are shown in Table I. From the amount of thiosulphate necessary for the titration of the iodine liberated in pipette *E* and the ratio of the velocities of flow, the quantity of thiosulphate which ought to be necessary for the titration of the iodine liberated in pipette *F* can be calculated. The comparison of this figure with the one found experimentally showed that the agreement was good to within 2%. Since the readings of the gas velocities by the gauges were not accurate to more than that, the result was quite satisfactory and proved that the amount of iodine liberated was directly proportional to the ozone, even when there was in one case more than 25 times as much ozone as in the other.

FIG. 2.

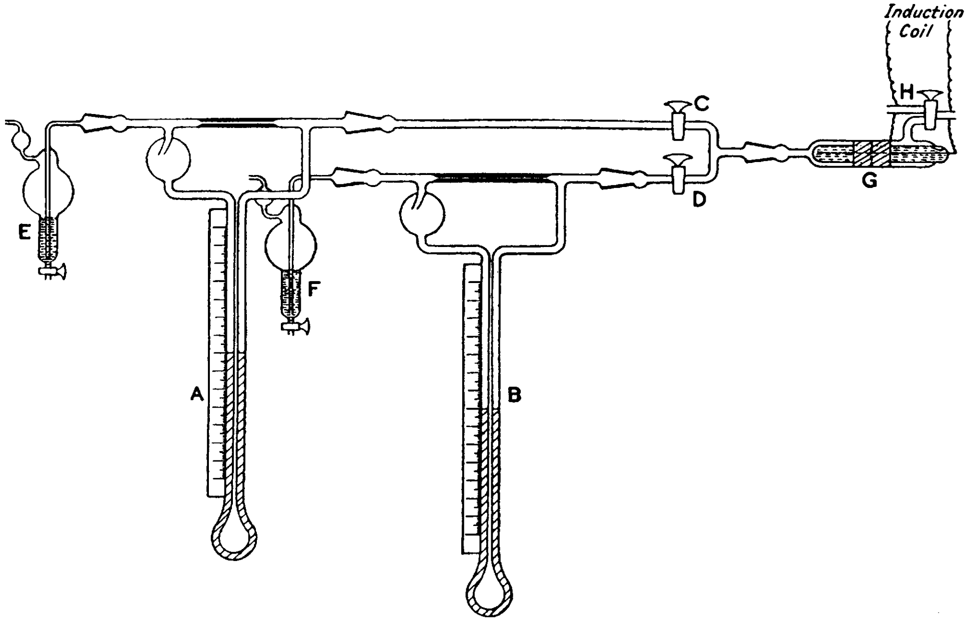


TABLE I.

Velocity of flow, ml./min.		Ratio of velocities, V_B/V_A.	Vol. of N/500-$Na_2S_2O_3$ solution, ml.			
				Pipette F.		
Gauge *A*.	Gauge *B*.		Pipette *E*.	Obs.	Calc.	Diff., %.
33·8	18·4	0·545	3·29	1·77	1·79	+1·1
24·1	22·5	0·934	9·80	9·02	9·15	+1·4
25·1	45·8	1·82	8·52	15·46	15·54	+0·5
16·9	34·2	2·02	3·92	7·91	7·93	+0·2
43·7	925	21·2	2·32	50·2	49·2	−2·1
37·9	900	23·7	1·63	38·7	38·7	0
38·1	947	24·8	1·91	46·7	47·2	+1·2

It should be emphasised, however, that even the lowest ozone concentrations used in this series of experiments were several orders of magnitude higher than that of atmospheric ozone (10^{-3} ml. of ozone/ml. of oxygen, as compared with 10^{-8} ml. of ozone/ml. of air), and the satisfactory analytical results in no way contradict the finding of Guéron and Prettre that below a concentration of 10^{-5} ml./ml. the direct absorption of ozone in potassium iodide becomes unreliable, thus necessitating the previous concentration of ozone as attempted by the method described in the following experiments.

(2) *The Condensation of Ozone.*—It is known from the work of Riesenfeld and his co-workers (Riesenfeld and Beja, *Z. anorg. Chem.*, 1923, **132**, 179; Spangenberg, *Z. physikal. Chem.*, 1926, **119**, 419) that at − 183° the vapour pressure of ozone is still 0·20 mm. and is thus too high to enable ozone to be condensed by passing it through a glass vessel cooled in liquid oxygen. In order to be able to concentrate atmospheric ozone by condensation at this temperature it was therefore necessary to find an adsorbent which would quantitatively retain ozone passed over it, and would release it without loss by decomposition if the temperature was raised afterwards. The first condition makes a large surface imperative, the second excludes all

oxidisable substances; the following surfaces were therefore tried : copper (on account of its good conductivity), glass beads, and silica gel.

The copper was used in the form of turnings which were washed successively with ether, alcohol, concentrated nitric acid, and water, and finally treated with ozonised oxygen. The glass beads were washed in hot chromic acid and water and were then slightly etched with hydrofluoric acid; they were then again washed with water and exposed to ozonised oxygen. Silica gel was prepared in three different ways : commercial silica gel was thoroughly treated with ozone to remove oxidisable impurities from its surface; another sample was obtained by the hydrolysis of silicon tetrachloride in an apparatus similar to that used by Ebler and Fellner (*Ber.*, 1911, **44**, 1915), and subsequent ozone treatment; a third sample was prepared by adding hot hydrochloric acid to a solution of pure silica in sodium hydroxide, the silica gel thus precipitated being filtered off, washed, and a part of it subjected to a stream of ozonised oxygen in a flask kept at 160°.

All these adsorbents were tested in the following manner. The apparatus with the two bulbs described above (Fig. 1) being used again, the total quantity of ozone employed in each experiment was measured by emptying bulb *A* directly into standard potassium iodide solution. The ozone from bulb *B* was passed through a trap packed with the adsorbent and then into potassium iodide, the trap being cooled in liquid oxygen; in this way the quantity of ozone escaping condensation was found. Then by removing the liquid-oxygen bath the condensed ozone or, in the case of decomposition having taken place, part of it, was evaporated and driven through potassium iodide solution. By comparing the sum of the titrations for the ozone coming through the cooled trap and the ozone condensed and evaporated, with the titration obtained directly from the bulb *A*, the amount of ozone that had been destroyed either catalytically or chemically was found.

The results of these experiments are compiled in Table II. It shows the velocity with

TABLE II.

		Bulb *A* (not condensed).		Bulb *B* (condensed).				% of O_3.	
Expts. No.	Velocity of gas, ml./min.	Vol. of $Na_2S_2O_3$ ml.	Equiv. vol. of O_3, ml.	Vol. of $Na_2S_2O_3$ for O_3 evaporated, ml.	Vol. of $Na_2S_2O_3$ for O_3 escaping, ml.	Vol. of $Na_2S_2O_3$ for total O_3, ml.	Equiv. vol. of O_3, ml.	Condensed.	Destroyed.
1	105	8·93	0·97	7·26	0·94	8·20	0·90	89·5	8·2
2	100	6·80	0·74	5·46	1·00	6·46	0·70	85·3	5·0
3	105	8·08	0·88	6·56	0·92	7·48	0·82	88·6	7·4
4	120	8·46	0·92	6·14	2·30	8·44	0·92	72·8	0·2
5	54	7·44	0·81	6·54	0·90	7·44	0·81	87·8	0·0
6	54	9·05	0·99	8·64	0·42	9·06	0·99	95·4	0·0
7	105	10·92	1·19	9·48	1·46	10·94	1·19	86·7	0·0
8	35	9·22	1·01	8·54	0·58	9·12	0·99	93·7	1·1
9	105	11·42	1·24	8·10	0·00	8·10	0·88	100	29·0
10	175	9·48	1·03	6·84	0·00	6·86	0·75	100	27·6
11	175	14·70	1·60	11·50	0·00	11·50	1·25	100	21·8
12	175	8·42	0·92	6·74	0·00	6·74	0·73	100	20·0
13	305	9·15	1·00	7·38	0·00	7·38	0·80	100	19·4
14	300	16·20	1·76	11·88	0·00	11·88	1·29	100	26·6
15	300	15·98	1·74	12·72	0·00	12·72	1·39	100	20·4
16	460	15·75	1·72	13·84	0·00	13·84	1·51	100	12·1
17	300	19·86	2·16	17·42	0·00	17·42	1·90	100	12·3
18	380	13·88	1·51	10·96	0·00	10·96	1·19	100	21·0
19	370	11·38	1·24	10·24	0·00	10·24	1·12	100	10·0
20	498	10·06	1·09	8·70	0·00	8·70	0·95	100	13·5
21	385	11·16	1·22	9·88	0·00	9·88	1·08	100	11·5
22	1940	9·43	1·03	7·80	0·48	8·28	0·90	94·9	12·2
23	1920	6·83	0·74	5·86	0·60	6·46	0·70	91·2	5·4
24	510	10·78	1·18	10·32	0·00	10·32	1·12	100	4·3
25	500	14·80	1·61	14·04	0·00	14·04	1·53	100	5·1
26	500	12·18	1·33	11·62	0·00	11·62	1·27	100	4·6
27	490	12·02	1·31	11·58	0·00	11·58	1·26	100	3·7
28	357	11·28	1·23	11·00	0·00	11·00	1·20	100	2·5
29	2020	5·58	0·61	5·68	0·00	5·68	0·62	100	−1·7
30	2060	7·04	0·77	7·02	0·00	7·02	0·77	100	0
31	2010	6·84	0·74	8·84	0·00	6·84	0·74	100	0
32	4700	6·74	0·73	6·78	0·00	6·78	0·74	100	−0·6

which the gas content of bulb *B* was passed through the cooled trap and, for both bulbs, the quantity of sodium thiosulphate, in ml. of the 0·01N-solution, necessary for the titration of the iodine liberated; the equivalent volumes of ozone, in ml. of the gas, are also given, and the last two columns give the amounts of ozone condensed and destroyed respectively. Expts. 1, 2, and 3 were carried out with copper turnings, expts. 4—8 with glass beads, and the rest with silica gel. It can be seen from the last but one and the last column of the table that the copper turnings, although employed in a quantity which was insufficient for condensing the total amount of ozone, destroyed part of it. Glass beads proved to be harmless but likewise failed to retain all the ozone, although in expts. 7 and 8 two cooled traps filled with beads were used instead of the one employed in all the other cases; condensation was above 90% at very low velocities but dropped to 73% at a velocity of no more than 120 ml./min. As to the efficiency of the various grades of silica gel, the table shows that in all the experiments with the exception of two they condensed 100% of the ozone. Expts. 9 and 10 were with coarse-grained commercial silica gel, and expts. 11, 12, and 13 were with the same gel after a strong current of ozonised oxygen had been passed over it for some time; it can be seen that this treatment decreased the amount of impurities in the gel. Expts. 14 and 15 were with a fine-grained commercial gel, and 16 and 17 were with the same gel but with about half the quantity of gel used in expts. 14 and 15; it seems that the amount of decomposition of the ozone depends on the amount of gel—and its impurities—present. Expts. 18—21 were with silica gel prepared by the hydrolysis of silicon tetrachloride. Condensation was 100% up to a velocity of 500 ml./min., but expts. 22 and 23 proved that at velocities four times as high a fraction of the ozone remained uncondensed; it is further seen from the table that this gel still contained oxidisable matter. Expts. 24—28 were with silica gel precipitated with hydrochloric acid from sodium silicate solution, a process which gave a very light and bulky gel with a much greater surface than that possessed by the gel obtained from the tetrachloride; it was not treated before use by passing ozonised oxygen and there was still a marked loss of ozone. In expts. 29—32 the same silica gel was used after it had been purified with ozone; after this treatment it not only condensed the ozone quantitatively at liquid-air temperatures up to velocities of 4700 ml./min., but it also released it without decomposition when its temperature was raised. This adsorbent was therefore satisfactory in both respects, and was adopted for all subsequent experiments.

(3) *The Determination of Ozone in Very Low Concentrations.*—All the preceding experiments had been carried out with ozone concentrations far exceeding those occurring in atmospheric air. It was therefore necessary to investigate whether the method of condensation could be utilised for the measurement of ozone in dilutions comparable to those found in the atmosphere. For the preparation of ozone in such extremely low, but nevertheless known, concentrations the apparatus shown in Fig. 3 was employed. It consisted essentially of three parts, separated by the three-way tap *F*; on the right-hand side there was a section in which to prepare a known quantity of ozone, on the left a section in which to dilute and condense this ozone, and below a section to give a current of purified air.

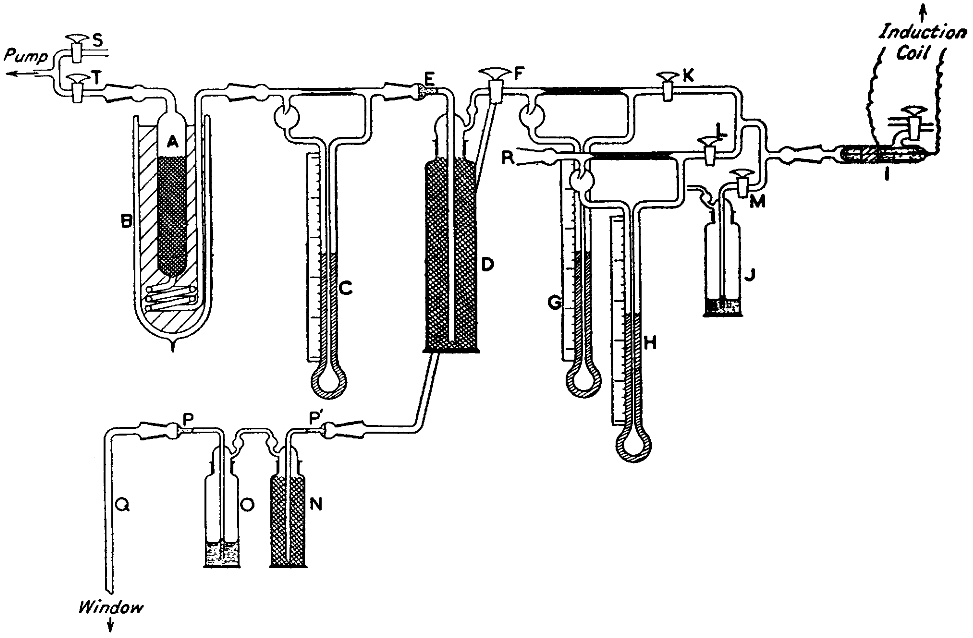
A was a special trap packed with silica gel with a glass spiral underneath for pre-cooling the gas before passing it over the gel; *C* was a high-velocity flow-gauge with a capacity of 2—3 l. of air per min.; *D* was a large calcium chloride drying tower, *E* a cotton-wool filter. All the taps and ground glass joints were very lightly greased with vaselin. It had been found in a series of experiments that neither vaselin, sparingly used, nor pure cotton-wool or calcium chloride had any effect on ozone; as a precautionary measure the calcium chloride was carbonated before use by passing a stream of carbon dioxide through it for a few hours, thereby fixing any free alkali that might have been present.

The apparatus used for giving a stream of pure air consisted of a cotton-wool filter *P*, which removed the larger dust particles, a wash bottle *O* which contained potassium iodide solution to remove oxidising gases such as ozone and nitrogen dioxide, and a calcium chloride drying tower *N* with a second cotton-wool filter *P'* between this tower and the three-way tap; the air supply was admitted through the tube *Q*, which passed through a hole in the window into the open air.

The part of the apparatus used for producing the ozone consisted of a small ozoniser *I*, which was operated by means of an induction coil controlled by an adjustable spark-gap to give the amount of ozone required; the main bulk of the ozonised oxygen going through this passed through the tap *M* and was absorbed in a potassium iodide solution in the wash-bottle *J*; thus the concentration of the ozone produced could also be controlled by altering the velocity of the gas flow through the ozoniser. Small amounts of the ozonised oxygen stream were allowed to pass through the gauges *G* and *H*, both of which had very fine long capillaries and were thus very sensitive; the amounts of gas going through these were controlled by the taps *K* and *L*, and the relative proportions of ozone passed were measured on the scales of the gauges, these all having been previously calibrated.

The ozone passing through the gauge *H* was absorbed in standard potassium iodide solution in a pipette at *R*, but that going through *G* passed through the three-way tap, where it was met by the purified stream of air; thus a current of air carrying a known amount of ozone was passed through the calcium chloride tower and the cotton-wool filter and was then condensed in the trap *A* which was immersed in the liquid oxygen in the Dewar vessel *B*. The trap *A* was connected, by means of the tap *T*, to a water pump, a second tap *S* also being used; *S* was open to the air and was used as a throttle; between the pump and the tap *T* there was a very large (10-litre) bottle which stabilised the air flow.

FIG. 3.



To start the experiment, *T* was slowly opened and *S* was partly closed until the required velocity of air was passing through the apparatus, this being indicated on the gauge *C*; the induction coil was then switched on, only a small spark gap being left so as to produce the small amount of ozone needed. At the end of the experiment the ozoniser was switched off, but the air was allowed to be drawn through for a further short time to make sure that all the ozone in the ozone-producing part of the apparatus was taken into the air stream. The experiment usually lasted about 4—5 hours for the small concentrations, and the three gauge readings were taken every half hour; the averages of the readings were used for the calculations.

When the run was finished, the Dewar vessel containing the liquid air with the trap in it was removed; an absorption pipette containing standard potassium iodide solution was placed on the exit, and through the trap and the solution a slow stream of oxygen was passed at the rate of about 50 ml./min. The liquid-air bath was then removed, and the condensed ozone allowed to evaporate off.

This was then titrated with standard N/500-sodium thiosulphate solution in the usual way, as also was the ozone which had been absorbed directly in the pipette at *R*; from the latter titration and the ratio of the gauge readings of *G* and *H*, the actual amount of ozone sent into the apparatus could be calculated; from the gauge reading of *C* the volume of air, and thus the concentration of ozone used, could be found; finally, by the titration of the ozone which had been condensed, the percentage loss on dilution, concentration, and passage through calcium chloride and cotton-wool could be determined,

TABLE III.

Duration of expt., mins.	Velocity, ml./min., in			N/500-$Na_2S_2O_3$, ml.			Vol. of air, l.	Concn. of O_3, mg./ml.	% Diff. between O_3 found and added, %.
	C.	*G.*	*H.*	*H.*	*C*, calc.	*C*, found.			
100	2040	18·9	8·4	7·60	17·10	17·00	204	$4·0 \times 10^{-6}$	− 0·6
100	2040	6·3	5·6	6·10	6·85	6·83	204	$1·6 \times 10^{-6}$	− 0·4
150	2010	28·2	26·8	3·34	4·53	4·82	301	$7·5 \times 10^{-7}$	+ 6·0
60	2060	4·7	8·3	2·84	1·61	1·65	124	$6·4 \times 10^{-7}$	+ 2·4
100	2050	20·4	31·8	2·55	1·63	1·63	205	$3·8 \times 10^{-7}$	0
400	2060	3·9	4·8	5·35	4·35	3·87	824	$2·2 \times 10^{-7}$	−11
375	2000	0·6	3·7	10·90	1·77	2·68	750	$1·1 \times 10^{-7}$	+50
200	2020	24·2	17·2	0·39	0·55	0·53	242	$1·0 \times 10^{-7}$	− 3
330	2060	1·4	5·2	6·70	1·82	0·91	680	$6·4 \times 10^{-8}$	−50
280	2030	32·8	30·0	0·54	0·59	0·61	568	$4·0 \times 10^{-8}$	+ 3

The results obtained are shown in Table III. Col. 1 gives the duration of the experiment; cols. 2, 3, and 4 give the average velocities of the gas streams through the gauges *C*, *G*, and *H*. Cols. 5, 6, and 7 represent respectively the titration (in ml. of N/500-sodium thiosulphate) for the ozone which is directly absorbed from *H*, the theoretical titration for the ozone that is diluted and condensed from *C* (this being calculated from the previous one and the ratio of the two readings of the gauges *G* and *H*), and the actual titration for this ozone. Col. 8 shows the volume of air used, calculated from the time of duration of the experiment and the velocity of the air stream measured in *C*; col. 9, the concentration of ozone, calculated from the titration of the diluted ozone from *C* and the total volume of air. It should be noted that these experiments covered the range of concentrations from 4×10^{-6} down to 4×10^{-8} mg. of ozone per ml. of the gas mixture, or $1·9 \times 10^{-6}$ to $1·9 \times 10^{-8}$ ml. of ozone/ml. of air.

The last column of Table III gives the percentage differences between the amount of ozone actually found (col. 7) and the amount added (col. 6). It is seen that in the sixth, seventh, and ninth experiments these differences are big, but this apparent failure is obviously due to the extremely low velocities at which the gauges *G* and *H* were used in order to obtain small concentrations of ozone; their readings were accordingly very unreliable. In the last experiment the desired small ozone concentration was achieved by decreasing the spark gap while keeping the gauge readings reasonably high; here, the previous accuracy, limited by the accuracy of the titration, is restored. Since simple titration may be carried out accurately only to one drop (*ca.* 0·04 ml.), in none of the experiments can an agreement to within less than a few units % be expected. Neglecting, therefore, the three experiments in which the gauge readings could not be trusted, we believe that the reliability of this method may be taken to have an accuracy of about 6%, even when the ozone concentration is as low as 2×10^{-8} ml. per ml. of air.

(4) *The Separation of Ozone from Nitrogen Dioxide.*—The presence in atmospheric air of nitrogen dioxide has been frequently suspected, and was definitely proved by the work of Francis and Parsons (*Analyst*, 1925, **50**, 262) and by Reynolds (*Nature*, 1923, **112**, 396; *J. Soc. Chem. Ind.*, 1930, **49**, 168), who showed that its concentration—at least in big towns—can be of the same order as that of ozone. Since it oxidises potassium iodide in solution, this reagent cannot be used for the determination of ozone mixed with nitrogen dioxide unless special precautions are taken. Keiser and MacMaster (*Amer. Chem. J.*, 1908, **39**, 96) tried to remove the nitrogen dioxide by bubbling air through a solution of potassium permanganate, but this reaction is not quantitative, as revealed by control experiments. Reynolds, on the other hand, passed half the air over copper sulphate to destroy the ozone and compared it with the other half containing both the ozone and the nitrogen dioxide. It would be an improvement to use a safer reagent for the destruction of the ozone, since, according to experiments carried out, even in a slow current of air copper sulphate allows the passage of a considerable fraction of ozone whilst, for instance, manganese dioxide, as recommended by Usher and Rao (J., 1917, **111**, 799), or charcoal, can be trusted to decompose it quantitatively; but even then the method applied by Reynolds would not be reliable because the simultaneous titration of ozone and nitrogen dioxide with potassium iodide would be still less trustworthy in such low concentrations than the titration of pure ozone alone. The procedure adopted in this work of first condensing the gases made it possible not only to carry out the titration with concentrations of ozone for which the results are known to be reliable, but also to separate the ozone from the nitrogen dioxide by fractional distillation before its determination.

Since the b. p. of nitrogen dioxide is as high as 22°, it should be a simple task to keep it in the condensed state on the surface of the silica gel while distilling off the ozone (b. p. — 112·3°). The vapour-pressure curve of pure nitrogen dioxide at low temperatures is well known from the work of Egerton (J., 1914, **105**, 647); his figures have been confirmed and his research extended in this work to the measurement of the vapour pressure of nitrogen dioxide condensed on the surface of the specially prepared silica gel described above. As expected, there was a marked depression of the vapour pressure, as can be seen from Table IV, which contains

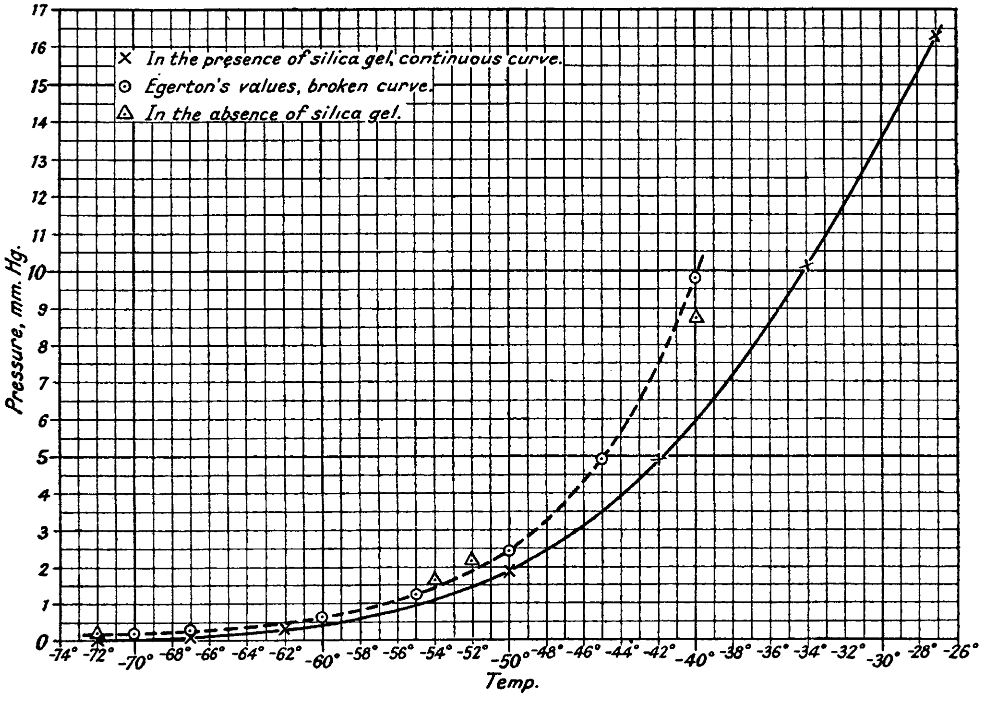
TABLE IV.

Vapour Pressure of Nitrogen Dioxode.

Condensed in glass vessel.				Condensed on silica gel.			
Temp.	V. p. (mm. Hg).	Temp.	V. p. (mm. Hg).	Temp.	V. p. (mm. Hg).	Temp.	V. p. (mm. Hg).
−72°	0·07	−52°	2·14	−72°	0·00	−42°	4·89
−54	1·61	−40	8·70	−67	0·07	−34	10·10
				−62	0·38	−27	16·35
				−52	1·76		

the results obtained by the authors, and from Fig. 4, which gives Egerton's figures as well as those obtained by the present measurements. The surface concentration of the nitrogen

FIG. 4.



dioxide was varied between 3 and 52 mg. per g. of gel without our being able to detect in this range any change in its vapour pressure.

In view of the fact that in the presence of silica gel the vapour pressure of nitrogen dioxide at — 72° was already too low to be measured with the butyl phthalate manometer used, it was expected that even a rapid current of air would not transport any traces of nitrogen dioxide through a trap filled with silica gel and cooled to — 120°. This was confirmed by experiment: a solution of potassium iodide remained perfectly colourless. On the other hand, by using once more the apparatus shown in Fig. 1, it was found that the same cooled trap did not condense any detectable amount of ozone. Finally, if both gases were first condensed on silica gel in a trap immersed in liquid oxygen, and the temperature was subsequently raised to — 120° while a current of oxygen gas passed over the gel, the total amount of the condensed ozone was quickly distilled off, and no traces of nitrogen dioxide could be detected in the gas current.

Condensation on specially prepared silica gel is accordingly a very satisfactory method, not only for concentrating ozone by freeing it from the bulk of the atmospheric gases, but also for separating it sharply from nitrogen dioxide. It is clear that hydrogen peroxide with a boiling point still higher than that of nitrogen dioxide, would also remain quantitatively in the cooled trap, should it ever be present in the analysed air. The method was therefore adopted for the determination of ozone and nitrogen dioxide in the atmosphere, as described in the following paper.

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