XL.—*Notes on the Explosion of Sulphuretted Hydrogen and of the Vapour of Carbon Bisulphide with Air and Oxygen.*

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IN carrying out certain gas analyses, it was found desirable to attempt to determine the amounts of sulphuretted hydrogen and of the vapour of carbon bisulphide in the presence of air by explosion with oxygen.

In the case of explosion of sulphuretted hydrogen with oxygen, Dalton has stated, "1 vol. of hydrosulphuric acid exploded with half a vol. of oxygen is completely converted into water and sulphur, because half a vol. of oxygen is exactly sufficient to convert the 1 vol. of hydrogen contained in 1 vol. of hydrosulphuric acid gas into water; with $1\frac{1}{2}$ vols. of oxygen it is completely converted

into water and 0·87 vol. (in reality 1 vol.) of sulphurous acid gas. In this case, 1 vol. of oxygen combines with one-sixth vol. of sulphur vapour to form 1 vol. of sulphurous acid gas; part of this, however, is absorbed by the water which is formed at the same time" ("Gmelin's Chem.," 2, 197). But beyond these brief statements no details of such explosions appear to have been published. Similarly, in the case of explosions of carbon bisulphide vapour with oxygen, although the general phenomena are well known, the published results are almost wanting. Berzelius and Marcet say: "Its vapour (carbon bisulphide), mixed with oxygen gas, produces a most violent explosion The products of the combustion are always sulphurous and carbonic acids, or carbonic oxide if the supply of oxygen is too small to form carbonic acid" ("Gmelin's Chem.," 2, 203).

The usual practice hitherto in gas analysis has been to determine the sulphuretted hydrogen, either by a bullet of manganese dioxide, moistened with phosphoric acid, or by the action of solution of cupric sulphate, whilst in the case of carbon bisulphide the best available method has perhaps been to absorb with alcoholic potash.

The results of explosions of these two sulphur compounds with air and oxygen, however, at once showed that besides the simple oxidation of the sulphur, hydrogen, and carbon to be expected by theory, there were secondary reactions going on, and the following experiments were made to endeavour to ascertain what was their nature. As the result of these experiments was rather exceptional, it is thought desirable to place the main facts on record. It may be here mentioned that all the experiments to be described were performed in one of McLeod's gas analysis apparatus, and all the gases were used in the moist state.

The cause of the secondary reactions was at once shown not to exist in the reaction between sulphuretted hydrogen and air and oxygen. This was proved by taking 2·63 vols. of air with 3·42 vols. of pure sulphuretted hydrogen and 12·59 vols. of pure oxygen. On explosion, the contraction equalled 5·13 vols., the sulphur dioxide 3·38 vols., and the residual nitrogen 2·19 vols. The equation $2\text{H}_2\text{S} + 3\text{O}_2 = 2\text{SO}_2 + 2\text{H}_2\text{O}$ requires that the contraction should be one and a half times as great as the volume of sulphuretted hydrogen used, and $3·42 \times \frac{3}{2} = 5·13$. It may, therefore, be assumed that, if necessary, this process for the estimation of gaseous sulphuretted hydrogen can be used with fair accuracy.

The case is, however, very different with the vapour of carbon bisulphide. The method of procedure in the experiments about to be described was as follows:—A volume of air was taken and measured in the endiometer tube. It was then passed back to the laboratory tube, where it was saturated with the vapour of some carbon bi-

sulphide which had been specially purified. After measuring the volume of air, plus the carbon bisulphide vapour, it was mixed with a considerable excess of oxygen, and exploded at a tension which was measured. The contraction, the volume of sulphur dioxide, the carbon dioxide, and the residual nitrogen were then, in most of the experiments, measured. By the equation $\text{CS}_2 + 3\text{O}_2 = \text{CO}_2 + 2\text{SO}_2$, the amount of contraction should equal precisely the volume of the carbon bisulphide vapour used, whilst the volume of carbon dioxide should be equal to that of the carbon bisulphide, and that of sulphur dioxide should be twice as great as the carbon bisulphide vapour.

The following is a typical result of the explosion of vapour of carbon bisulphide with air and excess of oxygen:—2·42 vols. of air were mixed with 3·02 vols. of carbon bisulphide vapour, and then with 9·96 vols. of pure oxygen, and the mixture exploded. The contraction on explosion was 3·61 vols., the sulphur dioxide and carbon dioxide together equalled 9·00 vols., and the amount of nitrogen left behind was 1·67 vols. Now, the original volume of air would have contained 1·914 vols. of nitrogen, so there had been a very distinct disappearance of this gas during the explosion; on the other hand, the volume of $\text{CO}_2 + \text{SO}_2$ together should have equalled 9·06 vols., and only 9·00 vols. were found. The contraction should have equalled 3·02 vols., or the volume of the carbon bisulphide vapour, whilst it actually measured 3·61 vols. There had thus clearly been a disappearance of nitrogen and of either sulphur dioxide or carbon dioxide, and, probably, of oxygen as well, in this experiment.

In a second experiment, 2·14 vols. of air were mixed with 4·22 vols. of carbon bisulphide vapour, and 19·99 vols. of oxygen were added. The mixture was exploded at a tension of 150 mm., when a bright blue flash and very decided explosion occurred, and a small, white deposit occurred in the tube. The contraction, which was measured about five to ten minutes after the explosion, equalled 5·29 vols., while the amount of sulphur dioxide was 7·83 vols., that of carbon dioxide was 4·09 vols., and 1·57 vols. of nitrogen were left.

In this experiment, it will be seen that the contraction was 1·07 vols. in excess of theory, the volume of sulphur dioxide found was less than the theoretical amount by 0·61 vol., and 0·123 vol. of nitrogen had disappeared.

In another experiment, which gave results differing even more exceptionally from theory than the last two, 2·19 vols. of air were mixed with 5·88 vols. of carbon bisulphide vapour, 24·71 vols. of oxygen were added, and the tension of the gases was brought to about 165 mm., when the explosion was made, giving a bright, sharp, purple-coloured flash. After the explosion, a small amount of white deposit was seen in the tube, and the contraction, instead of ceasing

when the temperature of the gas became constant, went on continuously for about 50 minutes, when it became exceedingly slow. A single drop of water was then allowed to enter the eudiometer tube, when at first a distinct expansion took place, showing probably either that the gases had become free from moisture, and were expanding from the tension due to the aqueous vapour, or that there was some substance present in the eudiometer tube which was decomposed by the action of water evolving gases, or some substance that evolved heat on the addition of the water. After this, contraction recommenced, and, even after the lapse of considerably more than an hour, the contraction of the volume of the gas or absorption was still going on, though very feebly. This continued contraction, which was so very largely developed in this case, was found not to be an isolated phenomenon, and in several other similar experiments, contraction has gone on for very considerable periods after the explosion—even after allowing ample time for the gases to cool down to their original temperature after the explosion.

The total contraction which was measured in this experiment was 16·25 vols., whilst the sulphur dioxide produced measured 4·74 vols., and the carbon dioxide 5·50 vols. Here it will be seen the amount of contraction was 16·25 vols. instead of 5·88 vols., or nearly three times as great as theory; the sulphur dioxide was 4·74 vols. instead of 11·76 vols., or about one-third of the theoretical amount, whilst the carbon dioxide was 5·50 vols. instead of 5·58 vols. There was thus a comparatively excessive contraction, and a similarly large loss of sulphur dioxide.

The behaviour of the gases in this experiment, after explosion, at once suggested a possible explanation of the unusual phenomena obtained in these experiments. In the first two cases it will be seen that less nitrogen was found at the conclusion of the experiment than there was at starting—proving that, as one of the results of the explosion, nitrogen had been oxidised. This oxidation appears to be similar to that found to be the case many years ago by Bunsen, when nitrogen in presence of oxygen was exploded with considerable volumes of detonating gas ("Bunsen's Gasometry," English Edition, p. 58). The oxide or oxides of nitrogen formed being, then, in presence of the sulphur dioxide, produced from the carbon bisulphide and of the moisture in the eudiometer tube (for the gases were always measured in a moist state in these experiments, and the eudiometer was kept moist) and also of free oxygen, it will be seen all the materials necessary for the preparation of sulphuric acid, on a small scale, were present in the tube. It was noticed that during the contraction, which extended over more than an hour in the last case, there was evidently some substance produced which was deposited on

the sides of the tube, and also, after the analysis, it was found that the eudiometer tube, when washed out with water, had a very decidedly acid reaction. The possible explanation, therefore, which is suggested is that a slow formation of sulphuric acid was going on in the tube; and this would also account for the very acid reaction possessed by the washings from the eudiometer tube. In the second and third experiments, it will also have been noticed that a white deposit occurred in the tube; this was quite an ordinary occurrence in these experiments, and, so far as could be judged, the only possible explanation of the deposit is that this consisted of a small amount of some such compound as the so-called lead-chamber crystals, which, in the comparative absence of moisture, had not decomposed.

A series of experiments was made to see if there was any definite relation between the amount of contraction and certain varying conditions of the experiments, and the only general but rather rough result which could be obtained was that the amount of contraction became greater when the volume of oxygen was increased within certain limits, and, conversely, the volume of sulphur dioxide, which could be measured, decreased. This is shown in the following table, which contains several other analyses. The third of the above experiments gave such distinctly anomalous results, that it and some others made have not been included in calculating out the general results given on p. 630. In the table, the results are arranged according to the increase in the ratio of oxygen to the combustible gas.

These figures, it will be seen, indicate that the volume of carbon dioxide obtained by the combustion of carbon bisulphide in oxygen is, as might be expected, in accordance, practically, with theory; but, on the other hand, the contraction on explosion is always much greater than it should be, whilst the volume of sulphur dioxide is correspondingly smaller. The figures representing the excess of contraction on explosion and the sulphur dioxide are naturally not strictly complementary, for if the above suggested or possible explanation of the anomalous results be accepted, it will be seen in the formation of sulphuric acid, in addition to the sulphur dioxide, the volume of oxygen which disappears will form part of the contraction; the oxides of nitrogen which are formed may act also on the mercury in the eudiometer. In the second case of the possible formation of the lead-chamber crystals ($\text{HSO}_4 \cdot \text{NO}$), a similar effect will be obtained, for the contraction in this case should much more than exceed the volume of sulphur dioxide which condenses from the additional disappearance of both oxygen and the oxide of nitrogen and the vapour of water, whilst if both sulphuric acid and nitrosyl sulphate were formed as the result of any explosion, the actual cause of the whole contraction may be expected to become very complicated. In view,

Number of volumes of air.	Number of volumes of carbon bisulphide vapour.	Number of volumes of oxygen added.	Tension at moment of explosion in mm.	Contraction in volumes.	Volumes of sulphur dioxide.	Volumes of carbon dioxide.	Ratio of oxygen used to volume of carbon bisulphide (equal 1).	Ratio of contraction to volume of carbon bisulphide (equal 1).	Ratio of sulphur dioxide to vapour of carbon bisulphide (equal 1).	Ratio of carbon dioxide to vapour of carbon bisulphide (equal 1).
α. From 3 to 4 volumes of oxygen to 1 of carbon bisulphide.										
1·94	6·27	21·05	175	7·11	12·47	6·83	3·35	1·13	1·98	1·08
3·08	6·26	23·26	165	8·00	11·58	6·28	3·81	1·28	1·85	1·03
2·65	4·97	19·05	95	5·74	9·36	4·77	3·94	1·16	1·89	0·96
3·48	4·82	18·56	90	5·69	8·81	4·67	3·99	1·18	1·83	0·97
Mean ratios.....							3·77	1·19	1·89	1·01
β. From 4 to 4½ volumes of oxygen to 1 of carbon bisulphide.										
2·30	4·50	17·96	162	5·88	8·34	4·48	4·09	1·31	1·85	0·99
2·33	4·67	18·68	120	5·60	8·80	4·56	4·10	1·20	1·88	0·98
Mean ratios.....							4·10	1·26	1·86	0·99
γ. From 4½ to 5 volumes of oxygen to 1 of carbon bisulphide.										
2·40	5·70	25·63	160	7·57	10·85	5·85	4·57	1·33	1·90	1·02
2·14	4·22	19·99	150	5·29	7·83	4·09	4·83	1·25	1·85	0·97
2·05	4·05	19·28	175	5·32	7·79	4·86	4·86	1·31	1·92	1·01
2·13	5·17	25·08	175	6·70	10·00	5·12	4·94	1·30	1·93	0·99
Mean ratios.....							4·80	1·30	1·90	1·00
δ. From 5½ to 6 volumes of oxygen to 1 of carbon bisulphide.										
2·23	4·18	23·28	170	5·53	7·99	4·22	5·68	1·33	1·91	1·01

therefore, of these complications, it was not thought necessary to push the experiments any further than has been done.

The explanation of the oxidation of the nitrogen in these experiments, even though comparatively low tensions were employed in the explosions, is probably to be found in the fact that carbon bisulphide, in its combination with oxygen, yields such a large amount of heat, and, therefore, produces such an excessively high temperature. Carbon bisulphide is well known to be an endothermic compound, or one which is formed from its elements with the absorption of a large amount of heat. As a liquid, when formed from its elements, it absorbs, according to Thomsen, no less than 19610 calories, and, when exploded with oxygen, this amount of heat, in addition to the heat of combination of both carbon and sulphur with oxygen, will necessarily be liberated. Hence the temperature produced in these explosions with oxygen will be exceedingly high.