XXXIII.—*Notes on the Estimation of Gaseous Compounds of Sulphur.*

By EDWARD JOHN RUSSELL.

THERE are two chief difficulties attending the estimation of gases containing sulphur when only small quantities of the mixtures are available: one arises from the fact that, during explosion with oxygen, sulphur trioxide is invariably formed in addition to the dioxide; the other from the fact that, when absorption methods are used, other gases, and particularly oxygen, are absorbed. The first of these difficulties can be entirely overcome by introducing an equation allowing for the formation of sulphur trioxide; the second can, in certain cases, be partially obviated by modifying the conditions of absorption.

In this paper, an account is given of methods which have been found to work satisfactorily for the estimation of the four common gases containing sulphur, namely, sulphur dioxide, hydrogen sulphide, carbonyl sulphide, and carbon disulphide, when only one of them is present in the gas mixture. If two or more are present at the same time, the methods will not always work well.

I. SULPHUR DIOXIDE.

At the ordinary temperature and pressure, this gas does not obey Boyle's law, and hence volumetric methods are not available if its partial pressure is great. When, however, its partial pressure is less than one-third of the total pressure, good results can be obtained.

Sulphur dioxide being very soluble in water, all water in excess of that required to saturate the gases in the eudiometer must be removed. This is most conveniently effected by allowing the moistened eudio-

meter, filled with mercury, to stand for some time, and then running off the drops of water which accumulate at the top. The gaseous mixture can now be introduced.

Absorption by Caustic Potash, Carbon Dioxide being absent.—This method can be used in presence of oxygen when the amount of sulphur dioxide is not more than 20 per cent. of the whole volume, and the oxygen is well diluted with an inert gas. The following examples show the accuracy attained :

	Present.	Found.	Present.	Found.
SO ₂	13·03	12·89	20·00	19·98
O ₂	18·18	18·29	17·02	17·04
N ₂	68·78	68·80	62·98	62·98 (by diff.)

If larger quantities of sulphur dioxide are present, good results are not obtained. The solution used for absorption contains one part of caustic potash to two of water. Absorption is rapid and, after agitating two or three times, complete. Even when the gas remains in contact with the reagent for some time, there is no absorption of oxygen provided sufficient inert gas is present.

Absorption by Lead or Manganese Peroxide.—Berzelius and Marcet (*Phil. Trans.*, 1813, 103, 186) first used lead peroxide to separate sulphur dioxide from carbon dioxide, and found the separation to be quantitative and complete in one hour. Bunsen ("Gasometry," Eng. Edition, 1857, 84) recommends a bullet of manganese peroxide. Both act very well, but Norman Smith and I have found (this vol., p. 342) that, if oxygen is present, some of it combines with part of the sulphur dioxide to form sulphur trioxide owing to the surface action of the peroxide, and thus the dioxide comes out too high. Lead peroxide exerts much less surface action than the manganese compound, and is therefore to be preferred. By carefully observing the following details, the surface action can be reduced to a minimum, and under favourable circumstances is negligible.

Commercial lead peroxide, after digestion for some time with warm dilute nitric acid, is well washed with water and dried between folds of filter paper. A cake is thus formed from which small pieces are easily broken off; these constitute the "pellets" and act much better when obtained in this way than if prepared by heating the peroxide in a mould. It is essential that the peroxide should be used within a few days of this treatment. The pellet must be small and must be moistened with a drop of water, but it should remain quite firm and not be pasty. Absorption should be complete within five or

ten minutes; if it takes longer than this, the analysis should be rejected.

Another difficulty lies in the tendency of the pellet to occlude other gases within its pores. In order to overcome this difficulty, Bunsen recommends pouring syrupy phosphoric acid over the pellet, but this very much retards absorption, many hours or days often being necessary before it is complete. The same result can be attained without the use of phosphoric acid by sending over a small portion of the gas into the laboratory vessel and introducing the pellet; in a short time, equilibrium is set up between the pellet and the gas from which the sulphur dioxide is to be abstracted. This portion is now drawn off and the main portion sent over. In order to be certain that all the sulphur dioxide is removed from the eudiometer, the gases should be returned to the eudiometer and again passed into the laboratory vessel. The following experiments were made with lead peroxide :

	Present.	Found.	Present.	Found.
SO ₂	19·7	19·8	34·5	34·4
CO ₂	80·3	80·2	65·5	65·6
SO ₂	12·90	13·10	55·72	56·02
O ₂	37·75	37·75	9·27	8·94
N ₂	49·35	49·15	35·01	35·01

Absorption by Chromic Acid Solution.—This operation is carried out in a Hempel's pipette. 10 grams of chromium trioxide are dissolved in 150 c.c. of a saturated solution of calcium chloride and the whole introduced into the pipette. The gases are allowed to stand over it for 10 minutes, absorption being then complete. The calcium chloride is necessary in order to diminish the solubility of the carbon dioxide. The following results have been obtained :

	Present.	Found.	Present.	Found.
SO ₂	18·5	18·3	46·0	46·2
CO ₂	37·3	37·5	40·2	40·0

Of these three methods, absorption by lead peroxide is by far the best.

II. HYDROGEN SULPHIDE.

The gas was generated by acting on ferrous sulphide with sulphuric acid, and was passed through water and through calcium chloride into

a bulb surrounded by solid carbon dioxide, where it very rapidly condensed to a clear and colourless liquid, any hydrogen present being thus removed. When several c.c. had collected, the bulb was removed, and the liquid allowed to volatilise. It was noticed that the earlier fractions of the gas caused the surface of mercury over which it was stored to become tarnished in a day or so, but that with later fractions, the surface remained bright for weeks. It appears then, that, contrary to the usual statement, pure hydrogen sulphide does not cause the surface of mercury to become blackened.

Absorption by Lead Peroxide.—Precipitated lead peroxide (washed with nitric acid), when not too dry, absorbs the gas very quickly,* but cannot be used in presence of oxygen or of carbon dioxide, either of these being absorbed simultaneously with the hydrogen sulphide. The reaction, according to my results, is apparently :

The lead oxide thus formed readily absorbs carbon dioxide and hydrogen sulphide :

18.4 vols. H_2S and 33.6 vols. CO_2 gave an absorption of 25.4 vols.

28.8 „ H_2S „ 48 „ CO_2 „ „ 46.8 „

when lead peroxide was used. This absorption of carbon dioxide does not take place if the pellet is moistened with phosphoric acid, but, as already remarked, the absorption in any case becomes so slow that the method is totally inapplicable whenever time is any object.

Manganese peroxide behaves in a precisely similar manner.

Absorption by Caustic Potash.—Caustic potash, also, is not a useful absorbent for hydrogen sulphide, owing to the ease with which potassium sulphide takes up oxygen. If sufficient zinc sulphate has been added to the caustic potash, this absorption of oxygen is very much reduced, but the reagent cannot be relied upon to give very satisfactory results, as the following analyses made with it show :

	Present.	Found.	Present.	Found.
H_2S	27.2	28	27.7	27.7
O_2	19.2	18.4	63	63
N_2	72.6	72.6	—	—

The action of lead hydroxide suspended in potash is even less accurate.

Estimation by Explosion with Air and Oxygen.—This is the method

* Apparently absorption is retarded when too much water is present.

most generally applicable. In the explosion, some sulphur trioxide is nearly always formed; we have therefore to deal with two reactions:

If x is the part burning to H_2O and SO_2 ,

and y „ „ „ H_2O „ SO_3 ,

Then the contraction = $3x/2 + 3y$,

oxygen used = $3/2x + 2y$,

and SO_2 formed = x ,

x and y can thus be found, and their sum gives the quantity of hydrogen sulphide present. If the mixture will not explode, carbon monoxide and oxygen may be added.

Mixtures of hydrogen sulphide and oxygen (diluted with air), on explosion, gave the following percentage results:

H_2S present.....	4.57	8.02	9.8	14.6	18.67
H_2S found.....	4.74	8.04	9.6	14.8	18.43

In the first three cases, explosion was brought about by adding carbon monoxide and oxygen.

Combustion proceeds quite smoothly when the gas is sufficiently diluted. There must, of course, be an excess of oxygen, and to every volume of explosive mixture there should be $1\frac{1}{2}$ —2 volumes of inert gas. With a view to further testing the method, mixtures of hydrogen sulphide, carbon dioxide, oxygen and nitrogen were analysed:

	Present.	Found.	Present.	Found.
H_2S	13.40	12.91	20.94	21.12
CO_2	25.13	25.39	33.56	33.41
O_2	32.82	33.28	23.56	23.37
N_2	28.63	28.42	21.94	22.10

III. CARBONYL SULPHIDE.

Absorption by Alcoholic Potash.—Alcoholic potash is usually quoted as the best absorbent, but is not of wide application since many gases, although not absorbed by caustic potash, are soluble to some extent in the alcohol present. Thus the method cannot be used for separating carbonyl sulphide from carbon monoxide. Again, as potassium sulphide is formed when carbonyl sulphide reacts with either aqueous or alcoholic potash, the method cannot be used in presence of oxygen, this being rapidly absorbed by alkali sulphides. If oxygen is absent,

a solution of 1 part of caustic potash in 4 parts of water absorbs the gas rapidly, and gives good results; addition of more potash retards absorption:

	Present.	Found.	Present.	Found.
COS	27·6	27·5	52·53	52·67
CO	72·4	—	47·47	47·33

In presence of oxygen, very fair results can be obtained by using a solution of 1 part of caustic potash in 4 of water, containing excess of freshly precipitated zinc hydroxide in suspension.

	Present.	Found.	Present.	Found.
COS	31	31·1	43·4	43·6
Air	81·8	—	198·6	—

Unless the oxygen is as much diluted as in air, some of it is always absorbed and the result is too high.

Other oxides (for example, lead oxide), suspended in caustic potash, potassium hypobromite, &c., do not act so well.

Manganese peroxide and *lead peroxide* do not absorb carbonyl sulphide, but in presence of moisture partial hydrolysis takes place with formation of carbon dioxide and hydrogen sulphide. Attempts to separate sulphur dioxide or hydrogen sulphide from carbonyl sulphide by means of these reagents did not usually give satisfactory results.

Estimation by Explosion with Oxygen.—This method is the one most generally applicable, being in fact the only one which can be used in presence of carbon dioxide.

When carbonyl sulphide is exploded with excess of oxygen in a long tube so that the explosion wave is set up, the products are of a complicated character, and contain carbon monoxide, unchanged carbonyl sulphide, and sulphur, as well as carbon dioxide, sulphur dioxide, and sulphur trioxide.

If, however, the explosion takes place in a eudiometer under diminished pressure, the only products are sulphur trioxide, sulphur dioxide, and carbon dioxide, unless the explosion is violent, in which case some sulphur escapes combustion and is deposited, and part of the nitrogen unavoidably present is oxidised. Whilst oxidation of the nitrogen and deposition of sulphur can be prevented by sufficiently diluting the explosive mixture with air, it has not been found

possible to avoid the formation of sulphur trioxide;* a separate equation must therefore be introduced as in the case of hydrogen sulphide. The method of calculation is as follows:

Let x be the part of the carbonyl sulphide burning to CO_2 and SO_2 ,
and y " " " " CO_2 " SO_3 .

$$\begin{array}{rcl} \text{Then contraction} & = & x/2 + 2y, \\ \text{SO, found after explosion} & = & x. \end{array}$$

These two being known, both x and y can be found, and thus $x+y$, the total carbonyl sulphide present, is known. Since this produces its own volume of carbon dioxide, the amount of carbon dioxide originally mixed with the carbonyl sulphide can be found by subtraction.

If oxygen is also present, its amount is found by adding to the oxygen left after explosion the amount required for combustion of the carbonyl sulphide (namely, $3/2x + 2y$), and of any other combustible gases present, and subtracting from this total the amount of oxygen added.

When the amount of carbonyl sulphide is small, an explosion can be brought about by adding a mixture of carbon monoxide and oxygen. The best results are obtained when at least two volumes of inert gas are present for every volume of combustible gas. On sparking, the flame travels slowly down the tube, and dense white clouds are seen. After allowing the gases to cool for half an hour, the contraction is read, the sulphur dioxide estimated by means of a pellet of lead peroxide, and the carbon dioxide and oxygen in the usual way.

Mixtures of carbonyl sulphide and oxygen, on explosion with air, gave respectively 11.79, 14.2, 26.9 per cent. of carbonyl sulphide, instead of 11.85, 14.5, 27.3 per cent.

Some more complex mixtures were made up and analysed:

	Present.	Found.	Present.	Found.
COS.....	9·6	9·7	13·16	13·48
CO ₂	16·2	16·0	13·42	12·77
SO ₂	—	—	8·71	8·73
CO	8·5	8·6	12·59	12·61
O ₂	44·4	44·1	10·88	10·82
N ₂	21·3	21·7	41·24	41·61

The nitrogen was estimated by difference, and the carbon monoxide

* The analogy to the combustion products of carbon disulphide (Dixon and Russell, Trans., 1899, **75**, 600) should be noted. Carbonyl sulphide further resembles carbon disulphide in that it undergoes phosphorescent combustion before actually igniting.

IV. CARBON DISULPHIDE.

The only useful absorbent for the vapour of this substance is alcoholic potash, and the application of this reagent in gas analysis, for reasons already stated, is very limited.

If x represents the part burning to CO₂ and SO₂
and y " " " " CO₂ " SO₃
then contraction = $x + 4y$
SO₂ = $x/2$
Total CS₂ = $x + y$.

Pedler (Trans., 1890, 57, 625) attempted to estimate carbon disulphide by explosion with oxygen, and found his figures did not at all agree with those calculated from the equation :

Fortunately, Pedler published all his analytical data, and I have calculated from these the composition of the mixture, using the equations given above. The agreement between the values found and the quantities originally taken show that his suggestion is probably wrong, and that his results are consistent with the equations given above.

The following table contains, in the first three columns, Pedler's experimental data, in the other three columns, my results calculated from them. The carbon dioxide and the carbon disulphide should be identical in volume; the difference represents Pedler's experimental error. The value of the method would, of course, be destroyed if it were necessary to make use of the carbon dioxide determination to calculate the amount of carbon disulphide present, but obviously a calculation of the amount of carbon disulphide from the sulphur dioxide alone gives results which are too low. The discrepancy becomes even greater when we bear in mind that Pedler estimated sulphur dioxide by means of a bullet of manganese peroxide, which

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causes some sulphur dioxide to combine with part of the excess of oxygen, thus producing a greater decrease in volume than is accounted for by the amount of sulphur dioxide present. On the assumption that 6 per cent. of oxygen is absorbed (which represents a very fair average, see preceding paper), the columns marked "corrected" have been calculated; these, of course, are simply given as an indication, as there is no means of finding out what was the amount of oxygen actually absorbed.

CS ₂ taken.	CO ₂ found.	$\frac{1}{2}$ SO ₂ found.	Corrected SO ₂ .	CS ₂ calculated.	Corrected CS ₂ .
$\alpha \left\{ \begin{array}{l} 6.27 \\ 6.26 \\ 4.97 \\ 4.82 \end{array} \right.$	$\left\{ \begin{array}{l} 6.83 \\ 6.28 \\ 4.77 \\ 4.67 \end{array} \right.$	$\left\{ \begin{array}{l} 6.23 \\ 5.79 \\ 4.68 \\ 4.4 \end{array} \right.$	$\left\{ \begin{array}{l} 5.88 \\ 5.44 \\ 4.38 \\ 4.2 \end{array} \right.$	$\left\{ \begin{array}{l} 6.45 \\ 6.34 \\ 4.94 \\ 4.72 \end{array} \right.$	$\left\{ \begin{array}{l} 6.19 \\ 6.08 \\ 4.72 \\ 4.57 \end{array} \right.$
$\beta \left\{ \begin{array}{l} 4.50 \\ 4.67 \end{array} \right.$	$\left\{ \begin{array}{l} 4.48 \\ 4.56 \end{array} \right.$	$\left\{ \begin{array}{l} 4.17 \\ 4.4 \end{array} \right.$	$\left\{ \begin{array}{l} 3.92 \\ 4.2 \end{array} \right.$	$\left\{ \begin{array}{l} 4.59 \\ 4.70 \end{array} \right.$	$\left\{ \begin{array}{l} 4.41 \\ 4.55 \end{array} \right.$
$\gamma \left\{ \begin{array}{l} 5.70 \\ 4.22 \\ 4.05 \end{array} \right.$	$\left\{ \begin{array}{l} 5.85 \\ 4.09 \\ 4.09 \end{array} \right.$	$\left\{ \begin{array}{l} 5.42 \\ 3.91 \\ 3.89 \end{array} \right.$	$\left\{ \begin{array}{l} 5.12 \\ 3.66 \\ 3.64 \end{array} \right.$	$\left\{ \begin{array}{l} 5.96 \\ 4.25 \\ 4.25 \end{array} \right.$	$\left\{ \begin{array}{l} 5.73 \\ 4.07 \\ 4.06 \end{array} \right.$
$\delta \left\{ \begin{array}{l} 5.17 \\ 4.18 \end{array} \right.$	$\left\{ \begin{array}{l} 5.12 \\ 4.22 \end{array} \right.$	$\left\{ \begin{array}{l} 5.0 \\ 3.99 \end{array} \right.$	$\left\{ \begin{array}{l} 4.7 \\ 3.75 \end{array} \right.$	$\left\{ \begin{array}{l} 5.42 \\ 4.38 \end{array} \right.$	$\left\{ \begin{array}{l} 5.10 \\ 4.12 \end{array} \right.$

Had Pedler used lead peroxide instead of manganese peroxide, the "corrected" columns would not have been necessary.

If we reject all cases where the experimental error was large, that is, where the numbers for the carbon disulphide taken and the carbon dioxide found do not nearly coincide, it will be seen that the values for the former come out fairly well.

Mixtures of several gases, each containing sulphur, cannot generally be analysed by explosion, unless the amounts of one or more of them are known. Each new gas introduces, of course, two new unknown quantities—its share of the sulphur dioxide and its share of the sulphur trioxide—and a sufficient number of equations may not be obtainable. For instance, mixtures of carbonyl sulphide, carbon disulphide, and carbon dioxide cannot be analysed by explosion. Absorption methods not being very reliable, no general scheme can be laid down for analysis, and each mixture must be treated as a special case.

Messrs. Norman Smith and Nicoll have made some of the analyses quoted in this paper, and I wish to tender to them my best thanks for their assistance.

THE OWENS COLLEGE,
MANCHESTER.