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XXXIII.—*On the Action of Bromine upon Sulphur.*

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IN a former paper (*Chem. Soc. Journ.*, vol. xi, 1873, p. 823) I endeavoured to show, by an examination of the properties and decomposition of sulphur bromide, that, if such a compound existed, the elements were united by the faintest possible ties, and were not, as in sulphur chloride, united in their combining proportions to form a definite stable compound. The small quantity of heat evolved on mixing the two bodies is in itself sufficient to show that the chemical action is very slight, when we consider the energetic nature of either of the two elements. It was also mentioned in the above paper, that, on adding metallic arsenic to the mixture of bromine and sulphur, a new com-

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pound was formed, and as my observations on this point are now complete, and as I have collected a considerable mass of data relating to the action of bromine upon sulphur, I beg to lay the results before the Society.

First, as to the general action of bromine. On treating ordinary flowers of sulphur with bromine, it was noticed that a portion of the sulphur remained insoluble (that is why in my former paper I said the liquid was filtered), and on examining this insoluble portion, it was found to be entirely composed of prismatic or insoluble sulphur, which is always present in small quantities in flowers of sulphur. With roll sulphur this insoluble substance did not occur. To determine whether the amount left undissolved by bromine was the same as that by carbon disulphide, the following experiment was tried:—5 grams of flowers of sulphur were weighed out, and added in small quantities at a time to about 20 grams of bromine, in order to prevent any great rise of temperature, as it was found that hot bromine dissolved the insoluble sulphur; the liquid was filtered, the filter washed with carbon disulphide, and the sulphur weighed. Its weight was found to be ·0040 gram, equal to ·08 per cent. of the sulphur used. On treating 5 grams of the same sulphur with carbon disulphide, it was seen that very much more would be left insoluble, but it was found that on pulverising in an agate mortar and washing repeatedly with the disulphide, the amount became much smaller. It appears that some of the globules in ordinary flowers of sulphur are coated with insoluble sulphur, which retards or prevents the solvent action of the disulphide, the pulverisation allowing the disulphide to penetrate into the little spheres. When it appeared that no further solvent action was going on, the insoluble sulphur was filtered off and weighed, and was found to weigh ·006 gram, or 0·12 per cent. of the sulphur used. This result is, as would be expected, higher than the bromine result, but it shows that in the cold the action of bromine upon sulphur partakes more of the nature of solution than of chemical action. When it was thus found that insoluble sulphur was not readily acted upon by bromine, it seemed important to determine by some physical method whether or not the bromine in sulphur bromide were really combined or free. My former experiment showed that at temperatures above 80° the bromine was free, but at temperatures below the boiling point an experiment with phosphorus seemed to show that some kind of combination was in force, but there was no definite information on the subject. I found, however, that if a beam of light be passed through the stratum of vapour and air overlying the surface of the liquid, and this beam be examined spectroscopically, the absorption spectrum of bromine vapour (lately mapped by Professors Roscoe and Thorpe, *Phil. Trans. Roy. Soc.*, vol. clxvii), was distinctly visible. On lowering

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the temperature, the spectrum was still visible, though much fainter. When the temperature was lowered to 0°, the spectrum failed to appear; but on placing some other liquid in a long tube, closed at both ends with glass plates, laying it on its side, and passing the beam of light, the absorption spectrum again became visible. This plainly shows that the disappearance of the spectrum was owing to the lowered vapour-tension of the bromine, and not to its complete absence. On adding an excess of sulphur to the liquid and heating till it was all dissolved, the mixture failed to show the absorption spectrum of bromine at ordinary temperatures, except with a very thick stratum, and at lower temperatures it was invisible, even when a tube 1 meter long was employed. It appeared that a comparison of stability might thus be instituted between different mixtures of sulphur and bromine, and the following method was used. A tube 0·5 meter long and closed with plates at the ends was encased in an outer iron tube, leaving a space between in which was the bulb of a thermometer. The iron tube could be surrounded by a freezing mixture or placed in a bath, and it served to protect the glass and also to ensure an equable distribution of temperature. A beam of light was passed through the glass tube, which had a layer of liquid occupying about one-fourth of its volume on its lower side. An hour was always allowed to elapse before taking an observation, so that the air was thoroughly saturated at the temperature. The following table embodies the results:—

Percentage composition of mixture.		Formula (about).	Absorption spectrum failed to be visible (about).
Sulphur.	Bromine.		
56	44	S_3Br	+ 42°
50	50	S_5Br_2	+ 33
44	56	S_2Br	+ 25
35	65	S_4Br_3	+ 13
28·57	71·43	SBr	+ 3
22	78	S_2Br_3	− 7
17	83	SBr_2	visible at − 18.

The numbers here given are the average of several experiments, which show a variation of at most two degrees for the disappearing point. A curve might be constructed showing the varying force with which bromine is held by different quantities of sulphur; but as the above table is not absolute, and is sufficient to show that the question is a physical and not a chemical one, a graphic representation would not teach us much.

It was stated in my former paper, that on heating the liquid it began to boil at about 80°, and the thermometer rose without one *continued pause* till the boiling point of sulphur is reached. I find that on

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taking a large mass of the mixture, it begins to boil as low as 72°, but it very quickly rises—only a very small distillate containing a very large percentage of bromine (about 96 per cent.) being obtained below 80°. By taking portions boiling between any two temperatures, any compound of sulphur and bromine may be said to have an existence; but although a large portion of the liquid distils over between 190° and 230° (and this contains the calculated boiling points of mixture of SBr and SBr_2), if this portion be redistilled, it will be found to yield no definite compound and to have no fixed boiling point. Thus, a quantity of about 50 c.c. of SBr was placed in a distillation-bulb and heated on the water bath for two days, when it was found that 15 c.c. of a distillate were obtained, having a composition approaching S_3Br_5, containing 20·62 per cent. sulphur and 79·38 per cent. bromine. This was put back and the liquid heated repeatedly up to 120°. It was found that, after cooling each time, the thermometer invariably showed 80° as the primary boiling point, and rose up to 120° just as before; 24·8 c.c., or about one-half of the liquid, came over, after five distillations, having the composition of about S_2Br_3, containing 23·5 sulphur and 76·5 bromine. This was again put back and the liquid made up to SBr, as it had suffered a small loss of bromine. Another series of distillations was undertaken, allowing the temperature to rise to 180°. After the fourth distillation, 34·2 c.c. of liquid were found in the receiver, constituting rather more than two-thirds of the original liquid, and having a composition approaching S_3Br_4, containing 23·8 per cent. of sulphur and 76·2 per cent. of bromine. I do not give the analytical numbers, as none of the analyses I have made agree well with any formulæ, and I am sure no bodies of these formulæ exist, the experiments being detailed to give an idea of the way in which the mixture can be manipulated. In every one of these distillations there was dissociation, as on looking at a source of light through the vapour, the spectroscope showed at any moment the characteristic bands of bromine. Thus, although SBr was supposed to distil at about 200°, two-thirds may be distilled over below 160°, leaving a body containing 39 per cent. of sulphur and 61 per cent. of bromine, or about S_3Br_2. We thus see that, as in ordinary mixtures, the body with the higher boiling point retains that which boils at a lower temperature with increasing tenacity the larger the proportion of the former in the liquid. If we say that it is a case of weak chemical combination, we must admit that no sudden dips occur at the multiple proportion points; that is, that there is an infinite number of compounds arranged along a curve.

Then as to the heat of formation. On mixing 40 c.c. of bromine with the requisite amount of sulphur, the thermometer rose 21°; that is, from 14° to 34°, so that the amount evolved is really inconsiderable.

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Mr. Muir indeed stated in a paper published since mine, that a great deal of heat was evolved, but I have Mr. Muir's authority for stating that he was wrong in so stating the case. What he meant to convey was, that a considerable rise of temperature was observed. But still the fact remains that some heat is evolved, and this must be caused either by chemical action or by change of state. That some at least of the heat is due to the latter cause is, I think, shown by the following facts:—When nearly all the bromine is distilled off the mixture, the sulphur left is always viscid and very like plastic sulphur; and on adding the limpid liquid bromine to sulphur, it is not a limpid liquid which is formed, but a body as viscid as oil of vitriol, and not at all like sulphur chloride or a solution of sulphur in carbon disulphide. Now as we know that insoluble sulphur does not combine with bromine, and as the action of the latter on sulphur evidently partakes very much of the action of a solvent, it seems likely that sulphur dissolves, not as octohedral sulphur, but as the plastic variety, and that the heat evolved may be due to the conversion or change of state. A quantity of plastic sulphur was formed, and it was found to be much more readily soluble in bromine than the ordinary variety, and did not evolve so much heat in solution; in equivalent experiments the thermometer rose for ordinary sulphur 20°, and for plastic only 12°. The plastic sulphur is never pure, as there is always left a considerable amount of insoluble sulphur (in one experiment 15 per cent.). The plastic sulphur used was obtained by suddenly cooling fused sulphur in the ordinary way. As the thermal relations of those varieties of sulphur are still matters of dispute, no exact calorimetrical observations were made, but from the above it seems very probable that a portion of the heat evolved by the action of bromine upon sulphur is due to the change from octohedral to plastic sulphur.

Next as to the volumes of the various mixtures. I have given the sp. gr. of SBr in my former paper as 2·629, and five determinations made since at different times and at 4° give 2·629, 2·627, 2·627, 2·628, and 2·629; average, 2·628. It will be seen that as the mean of the sp. gr. of the constituents ($S = 2·050, Br = 2·980$) is 2·515, the mixture is denser by ·113 than mere mixture would give, showing a contraction of 4·34 per cent. on mixing the constituents. It occurred to me that an examination of the sp. gr. of various mixtures would elucidate the nature of this contraction, and show at what point it was greatest, and whether any multiple proportion-compounds could be discovered. The work was done with an apparatus I have described elsewhere (*Chem. Soc. Journ.*, vol. xii, 1874, p. 203), which, owing to the great ease with which it can be emptied and cleaned, enabled me to do sp. gr. determinations at the rate of six per hour. The following table embodies the result of the work, which for convenience was done

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with multiple proportion-mixtures. The column headed "calculated" is what the sp. gr. ought to be if it were a mere mixture:—

Mixture.	Found.	Average.	Calculated.	Difference.
1. S_3Br.	2·295 2·290 2·294	2·293	2·282	·011
2. S_2Br.	2·430 2·420 2·425	2·425	2·360	·065
3. SBr.	2·627 2·628 2·629	2·628	2·520	·108
4. SBr_2.	2·823 2·820 2·817	2·820	2·670	·150
5. SBr_3.	2·880 2·881 2·879	2·880	2·749	·129
6. SBr_4.	2·900 2·910 2·905	2·905	2·795	·125

It is plain from these numbers that the sp. gr. increases rapidly with the bromine up to the compound SBr_2, and this is brought out more clearly if we consider that the sulphur only is affected in volume, and that the bromine is constant. On such a supposition, the sp. gr. of the sulphur in the above mixture would be:—

Pure Sulphur	2·050
No. 1	2·065
„ 2	2·147
„ 3	2·266
„ 4	2·590
„ 5	2·570
„ 6	2·600

This plainly shows that up to No. 4 each increment of bromine doubles the increment in sp. gr., but beyond that we have very little effect. At SBr (or S_2Br_2 supposed) we have no sudden change, so that, pyknometrically, it has no existence. It is my intention to measure the amount of heat evolved on making the above mixtures, to find if, as would be expected, it is proportioned to the contraction. Thus we find that the effect of bromine upon sulphur increases till it has formed the same body as it does with chlorine, and that, as with chlorine, it has a feeble effect above SBr_2. If, however, we go upon the supposition that all compounds below SBr_2 are mixtures of that

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body with sulphur, we find that this does not hold. Let us take the case of $S_2Br.2S_2Br = SBr_2 + 3S$, which would give (2·050 × 3 + 2·820 ÷ 4 = 2·285, and we find the actual number to be 2·425, and so with any other of the series we find the observed sp. gr. higher than that calculated on the assumption of the existence of SBr_2. From this we see that *the action of any quantity of bromine upon any quantity of sulphur is an action on the whole mass, and not in multiple proportion.* Thus we find that the action of bromine upon sulphur is on the borderland between solution and chemical combination, the general action being that of a solvent, and the greatest contraction being at SBr_2, pointing to multiple proportion action.

Since the proportion SBr_2 seemed to give the maximum of action, it was thought that an examination of the freezing points of various mixtures might throw some light on relations between them, but it was found that, except when the proportion of bromine was very large, the mixtures would not freeze, but became thick like tar. It seems strange that mixtures of bromine and sulphur should remain liquid below the temperature at which bromine freezes, yet this is the case: in fact SBr is quite liquid when bromine is solid. At temperatures approaching −30° the mixture only becomes more viscid. No information can be got in this way, except a confirmation of the changed state of the sulphur and of the *general* action of the bromine, as no multiple proportion hereby crystallises out. As shown further on, however, when other bodies are present capable of forming molecular compounds with SBr_2, the two crystallise together, thus affording evidence of a certain amount of chemical action. Since the temperature of boiling varied constantly, that is to say, the liquid always gave off portions of vapour containing more bromine than the residue, it appeared to be desirable to measure the vapour-tension at temperatures below the boiling point to find if it became constant for successive portions at temperatures where the vapour over the liquid did not show the absorption-spectrum of bromine. The "time method" which has been described in this Journal* was used, and the following experiments made. First an examination of the mixture SBr at the ordinary temperature of the laboratory (16°) was made. The following table embodies the results:—

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* Examination of substances by the time method (*Chem. Soc. Journ.*, 1877, No. II, page 381).

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Hours.	Pure air passed (litres).	Weight carried over.
1	·5	·0285
2	,,	·0282
3	,,	·0280
4	,,	·0275
5	,,	·0271
6	,,	·0263
7	,,	·0254
8	,,	·0246
9	,,	·0230
10	,,	·0218
11	,,	·0203
12	·4	·0175

Five grams of liquid were employed, and the total loss was ·2985, and the increase in the weighing tube was ·2982. On analysis the portion carried over had the composition 78·07 per cent. Br and 22·04 S, agreeing accidentally with the formula S_2Br_3, which requires 78·94 Br and 21·06 S. I say accidentally, for it is evident that as the vapour-tension was decreasing; had the time been lengthened, a formula higher in sulphur would have been obtained. On subtracting the bromine and sulphur from the original amount used, there is left a liquid in which the sulphur and bromine have the ratio S 427, Br 417. So that here again we see that an indefinite mixture is obtained and not a multiple proportion body. On passing air over the mixture at 0° for two days the specific gravity was reduced from 2·628 to 2·614, and in another three days to 2·604. The action was allowed to go on for four days longer, when it was found that the density was 2·571, which is much below SBr, and would agree roughly with a mixture of about S_3Br. Thus, even at 0°, there is no fixed composition.

In the paper before referred to I stated that when metallic arsenic is added to the mixture of sulphur and bromine (SBr) heat was evolved and a red liquid formed which contained a new compound. When sufficient arsenic is added to the liquid, arsenic bromide is formed, and even arsenic sulphide; but if the quantity be small and the liquid subsequently cooled to —18°, beautiful dark-red crystals of the new compound are obtained which may be separated from the excess of liquid compounds, and then melted and again crystallised and drained. They were found to melt at about —17° and form a red liquid containing arsenic, sulphur, and bromine. The liquid had the sp. gr. of 2·789, and was decomposed by water into arsenious acid, hydrobromic acid, and sulphur. On analysis it gave a composition equal to a body with a formula AsS_2Br_3 as shown by the following analyses:—

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	Found.			Calculated.
As......	20·43	20·07	18·52	19·79
S	16·00	16·23	17·04	16·88
Br......	63·51	64·24	63·70	63·33
	99·94	100·54	99·26	100·00

This body, which is evidently a multiple proportion compound, is most likely a compound of arsenic sulphobromide and sulphur dibromide after the following formula, $AsSBr.SBr_2$. The only other simple formula which would fit the above analyses is $AsBr_3.S_2$, which would mean, I think, a mechanical mixture, and this is not the case. I think that the evidence I have already adduced for the existence of SBr_2 renders it probable that when at low temperatures it meets a body with which it can form a molecular combination, it assumes the crystalline form in conjunction with such a body. In conclusion, my whole work seems to show that the action of bromine upon sulphur increases in a regular manner up to SBr_2, totally ignoring the point SBr, and that above SBr_2 we may have another curve to SBr_4, and then another fainter echo to SBr_8, and so on; but of the existence of S_2Br_2 we have at present no evidence.