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XXXIII.—On Selenium Sulphoxide.

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In our paper on tellurium sulphoxide, published by the Society last year, we showed that this substance, $TeSO_3$, first obtained by Rudolph Weber, exists in two modifications, a red and a brown. We now give the results of an examination of selenium sulphoxide undertaken to determine whether this also does not exist under two forms, as it then appeared to us to do.

Selenium sulphoxide has been described by Weber (*Pogg. Ann.*, **156**, 531). On bringing liquid sulphur trioxide in contact with powdered selenium, union occurs with rise of temperature. The selenium changes, directly it is moistened with the trioxide, into a very thick dark green liquid, transparent in thin layers, while the excess of sulphur trioxide remains quite colourless and unaltered. In about 10 minutes the green liquid solidifies to a crystalline mass, which does not resume the liquid state when heated. We prepared it for analysis in precisely the same way as we prepared tellurium sulphoxide.

The analysis we have made of the green sulphoxide agrees with Weber's formula, $SeSO_3 :=$

Selenium taken	0.3282
Sulphur trioxide found	0.3588
Sum	0.717 0
Selenium sulphoxide found	0.7165
Difference	-0.0002

Calculated to percentages, we get-

	Obtained.	Theory.
Selenium	49.99	49.69
Sulphur trioxide	50.07	50.31

Very slowly green selenium sulphoxide undergoes change at ordinary temperatures, shown by its becoming discoloured. It may, however, be heated to 35° for some time without appreciable alteration. That at least has proved to be the case with us in several instances, whilst Weber remarks that it is not decomposed by gentle heating. But in one case it happened to us that decomposition set up at the ordinary summer temperature, before even the excess of sulphur trioxide had been removed. We can suggest no explanation of this difference of behaviour, but may point out that it is in accordance with what has been observed by Weber and ourselves in tellurium sulphoxide.

On heating selenium sulphoxide, decomposition begins to show itself at 40° by a change of the green colour to brown, and by the escape of sulphur dioxide, although this is exceedingly slow, even when 90° is reached. At 120° and upwards, however, sulphur dioxide is steadily evolved, the colour gradually changes to bright yellow, and the volume slightly shrinks. In that instance in which sulphur dioxide escaped freely at common temperatures, very little came off afterwards on heating the mass until it had turned yellow.

On continuing the heat the colour changes to orange, and then reddens and darkens until it becomes identical with that of selenium. Selenium, in fact, is here formed together with its ordinary oxide. Attempts to get the oxide corresponding to the tellurium monoxide, we have elsewhere described, failed.

By heating slowly and maintaining a moderate temperature for a long time, the sulphoxide changes, *in vacuo*, almost perfectly to a yellow amorphous mass. With more rapid heating, reddening occurs before the yellowing stage is completed, and the mass contains a much greater proportion of selenium than when the heat is better graduated.

We have analysed four preparations of the yellow mass, in the way we have described in our tellurium sulphoxide paper. They were heated more and more gradually, in the order in which they were prepared and now are numbered. The last one is that in which decomposition was active at common temperatures :---

	I.	II .	111.	IV.
Selenium	$0.5318 \\ 0.2612$	0 ·6210	0 ·6700	0 ·3764
Sulphur trioxide		0 ·3295	0 ·4137	0 ·3003
Sum	0 •7930	0·9505	1 ·0837	0 ·6767
Selenium sulphoxide	0 •8256	0·9885	1 ·1300	0 ·7040
Difference	0.0326	0.0380	0.0463	0.0273

These results do not agree among themselves, and, moreover, all of them show an excess of oxygen, appearing as the difference between the weight of the product and the sum of the selenium and sulphur trioxide contained in each. Nevertheless, we consider as almost certain that these preparations were mixtures of a yellow selenium sulphoxide with selenium and its dioxide, for reasons we proceed to state.

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The yellow mass hisses when thrown into water, just like the green sulphoxide and the tellurium sulphoxides, and is therefore a sulphuric oxide compound; it bears a heat of 120°, and therefore its sulphur trioxide is in combination; it does not contain any green sulphoxide, by which its properties might be explained; and its yellow colour cannot be regarded as due to free selenium. According to Weber, when the green sulphoxide is crushed, the powder is yellow. Further, on calculating to percentages, on the assumption that the preparations analysed were mixtures of the sulphoxide with selenious oxide and selenium, and arranging the results, these suggest, by their relations, the probable correctness of the assumption. Lastly, by the action of selenium selenochloride upon sulphur trioxide, there is produced, as we shall describe in a future paper, a bright yellow substance, which is apparently also selenium sulphoxide.

	I.	II.	III.	IV.
Selenium sulphoxide	$62 \cdot 8$	66 ·3	72 ·8	$84.8 \\ 13.3 \\ 2.0$
Selenium dioxide	13 $\cdot 9$	13 ·5	14 ·3	
Selenium in excess	23 $\cdot 3$	20 ·3	12 ·9	

We now give the calculated percentages :---

in which there are several things to attract notice. The more gradually the preparations had been heated, the more sulphoxide they contained, and, in the same order, the less free selenium they contained, while, throughout, the selenium dioxide was practically constant.

In the fourth preparation much of the selenium dioxide must have been produced from extraneous sulphur trioxide, since from selenium sulphoxide alone there would be as much selenium set free as that contained in the dioxide produced :---

$$2\mathrm{SeSO}_3 = \mathrm{Se} + \mathrm{SeO}_2 + 2\mathrm{SO}_2.$$

Now it was in this fourth experiment that sulphur dioxide was freely evolved before the excess of trioxide had been evaporated. In the other preparations, particularly the first and second, the free selenium is in greater quantity than is equivalent to the selenium dioxide.

The cause of the selenium dioxide being present in nearly constant proportions, is not very evident, and in the form in which we have cast our results, this constancy may appear a chance coincidence. But by referring the oxygen to a constant quantity of selenium, it still comes out nearly constant :--- 204

	I.	II.	III.	IV.
Selenium	100	100	100	100
Sulphur trioxide	49	53	62	79
Oxygen	6	6	7	7

The great excess of free selenium in the first two preparations proves that selenium sulphoxide must decompose, at least in part, to selenium and sulphur trioxide again. We are therefore led to adopt the view that selenium sulphoxide does not decompose at once, thus:---

$$2\mathrm{SeSO}_3 = \mathrm{Se} + \mathrm{SeO}_2 + 2\mathrm{SO}_2,$$

but exclusively into selenium and sulphur trioxide, and that then some of the trioxide acts upon undecomposed selenium sulphoxide to produce the two dioxides, thus:—

$$SeSO_3 + SO_3 = SeO_2 + 2SO_2$$

just as excess of trioxide must have acted in Experiment IV. With quick elevation of temperature much of the sulphur trioxide escapes, but with a gradual rise, only a little of it. Thus, in the third experiment, in which the free selenium and selenium dioxide are not far from equal in atomic proportion, only a little trioxide appears to have escaped without previous reduction.

With the sulphoxide of the more basic tellurium the reduction of the sulphur trioxide, when the sulphoxide is heated, is complete, a special oxide of tellurium being formed from the first. But it is probable that the fact we have pointed out in our paper on the tellurium compound, and could not then explain, respecting its decomposition by water, namely, that much more than half of the tellurium takes on the free state, is explicable as being the result of some of the tellurium sulphoxide reacting with water to form free tellurium and sulphuric acid.

Summary.—(1.) A yellow modification of selenium sulphoxide appears to exist, but has not been obtained pure. (2.) Selenium sulphoxide is resolved by heat into selenium and sulphur trioxide. (3.) Sulphur trioxide can oxidise selenium sulphoxide, producing selenium dioxide and sulphur dioxide. (4.) Tellurium sulphoxide, when decomposed by water, gives tellurium and sulphuric acid, and part of these then react to form sulphurous acid and tellurous acid.