XXXII.—*On the Decomposition of Water by Certain Metalloids.*

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Sulphur.—The statements of chemists with respect to the action of sulphur on water are conflicting. According to Mulder (*Jahresber.*, 1858, 84) the vapours of water and sulphur (at high temperatures) react to form pentathionic acid; Meyer, on the other hand (*Compt. rend.*, **74**, 195), states that thiosulphuric acid is formed. Girard (*Compt. rend.*, **61**) found that on boiling pure sulphur with water, a large quantity of hydrogen sulphide was evolved, but his observation is questioned by Gélis (*Compt. rend.*, **56**, 1004), who ascribes the evolution of hydrogen sulphide, which is, he admits, sometimes observed under these conditions, to the presence of impurities in the sulphur.

We have investigated the question by methods similar to and different from those adopted by the above-named observers, the results of which we proceed to detail.

Our first observations were made with lead acetate upon the steam from water, holding sulphur (flowers) in suspension and kept boiling under ordinary conditions in a glass flask; the lead salt was continuously decomposed with formation of sulphide. A tube, bent twice at right angles, was then fitted to the flask, and the steam passed thereby into a solution of lead acetate. Traces only of sulphide were precipitated, but we found that sulphur was present in some quantity; this apparent distillation of sulphur was unaffected by causing the steam to pass through cotton wool. On raising the boiling point of the water to 101·5°, by the addition of pure sodium sulphate, the quantity of lead sulphide precipitated in an experiment of $3\frac{1}{2}$ hours' duration, was ·0037 gram. In a second experiment, under the same conditions, ·0023 gram of the sulphide was precipitated, whereas the sulphur separated amounted to ·020 gram. In a third, water only was placed in the condensing flask; this rapidly became milky with suspended sulphur, ·0093 gram being present at the end of two hours. On substituting a retort and condenser, the formation and deposition of sulphur could be easily watched in the tubulus, on the sides of which it was curiously aggregated into stellate masses. After distilling 900 c.c. from 5 grams of sulphur, a fourth distillate of 300 c.c. was boiled down with nitric acid and the sulphur present, estimated as $BaSO_4$, was found to amount to ·0194 gram. Observations on a further 300 c.c. satisfied us that the phenomenon was uniform and continuous. In all cases the distillate contained a certain quantity of hydrogen sulphide, of which the odour was very perceptible; this was estimated (by iodine) in 100 c.c. as ·0017 gram. No trace of oxy-acids could be detected. The water which remained in the retort, filtered from the sulphur, yielded with barium chloride a precipitate of sulphate, representing ·0077 gram sulphur; the sulphur which has thus undergone oxidation is approximately equivalent to that escaping as hydrogen sulphide, supposing the decomposition to occur according to the equation,

$$2H_2O + S_3 = 2H_2S + SO_2,$$

and the sulphurous acid to be oxidised by atmospheric oxygen. The probability of the latter supposition was increased by the experiment of conducting the distillation in an atmosphere of carbonic anhydride, in which case no trace of oxyacid could be detected in the residual water. The former is supported by the observation that when the condenser was placed in an upright position, no traces of hydrogen sulphide escaped during a period of six hours' heating, whereas sulphur was continuously separated and carried back into the flask. Further, on extinguishing the flame and pouring a solution of lead acetate down the condenser, the lower portion, together with the flask, was instantly blackened by a considerable precipitation of lead sulphide, which is, we think, referable to hydrogen sulphide rather than to a decomposition by sulphur vapour—the alternative explanation.

While the reversal of the above decomposition, which would be determined by a change in the physical condition of the products from that which we may suppose to cause their dissociation, affords an explanation of the apparent distillation of sulphur, the view which we have advanced rests rather upon the indirect evidence than on any actual proof afforded by our experiments. We attempted to demonstrate the presence of sulphurous anhydride, by adapting to the flask a specially constructed diffusion apparatus, but the steam which accompanies the products proved an insurmountable obstacle to their separation by this method.* We therefore reverted to indirect experiment, and obtained the following additional results. Sulphur was boiled with aqueous lead acetate in an open flask; after 14 hours' boiling the precipitate (lead sulphide and sulphate) was analysed and found to contain for every 100 c.c.:

		Ratio.
S as PbS	·0198 gram	1 to
S as $PbSO_4$......	·0152 „	·76

Sulphur was then sealed up in glass tubes with aqueous lead acetate and heated to 150—160° for 6—8 hours. In the first instance sulphur was taken in excess, and the whole of the lead was precipitated from solution as sulphide. The lead salt was then taken in excess; the resulting precipitates were mixtures of sulphide and sulphate, of the following composition respectively (the quantities are calculated for 100 c.c.).

	Gram.	Ratio.	Gram.	Ratio.	Gram.	Ratio.
S as sulphide	·0975	1 to	·1464	1 to	0792	1 to
S as sulphate	·0678	·69	·1098	·75	·0420	·53
Total S in combination	·1653		·2562		·1212	

(The totals thus observed agreed closely with the numbers calculated from the weights of unaltered sulphur obtained.) These results afford further proof that sulphur in decomposing water unites both with its oxygen and hydrogen; the discrepancy between the ratios observed and that corresponding with the hypothetical equation, may be referred to atmospheric oxidation, the amount of oxygen present in our tubes being, as we found by calculation, sufficient for this effect. At the same time this primary decomposition is independent of atmospheric oxygen, as the following experiment clearly shows: Lead acetate solution which had been previously boiled and allowed to cool out of contact with the air, was placed in a tube together with sulphur; the tube was then narrowed, the residual air expelled by a rapid stream of carbonic anhydride, during the passage of which the operation of

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* On adding alkaline permanganate to the milky distillate (p. 250), a bright green colour was instantly developed. The thiosulphuric acid, whose presence is thus indicated, may be regarded as formed by the action of SO_2 on S (Flückiger). This seems to us the more probable explanation of Meyer's observation (p. 249).

sealing was continued. In this tube the formation of sulphide was observed to occur at a temperature as low as 95°.

It was now necessary to examine the ground upon which Gélis denies the decomposition of water by sulphur. The evolution of hydrogen sulphide, which he admits is often observed on boiling sulphur with water, he ascribes to the presence of impurities in the sulphur, on the following grounds: (1.) That it does not occur in the case of sulphur which has been treated with potassium permanganate or iodine, and washed; and (2.) on heating sulphur with water to 150—190° in sealed glass tubes, in three out of four experiments, no hydrogen sulphide was perceived on opening the tubes.

We have repeated these observations, but with different results. A portion of the sulphur used in our experiments was allowed to remain for some time in contact with a strong solution of permanganate. Manganic oxide was deposited upon the sulphur and removed by boiling with hydrochloric acid, the sulphur undergoing further oxidation by the chlorine thus liberated. After thorough washing it was boiled with water, which it decomposed as before with liberation of hydrogen sulphide. We also observed that, on boiling sulphur with permanganate solution, it appears to distil precisely as when water alone was used (we found by direct experiments on hydrogen sulphide and sulphurous oxide that either gas, when passed into boiling permanganate, escapes to a large extent unoxidised). With respect to the second point, the absence of hydrogen sulphide in the experiments cited, it is scarcely necessary to say that it in no way proves that which it assumes to do; on the contrary that a similar observation is the basis of our hypothesis. We must, therefore, regard Gélis' statements as unfounded. Flückiger has stated that all preparations of sulphur contain traces of thiosulphuric acid; we could not detect such in that employed by us, and the experiments just detailed prove that our observations are not subject to this source of error. Lastly the alkaline constituents of the glass vessels in which our solutions were boiled appear to be without influence; for in most cases an acid reaction was obtained, and the evolution of hydrogen sulphide occurred when dilute sulphuric acid was substituted for water.

We next examined the sulphur in the retort and in the distillate for solubility in carbon disulphide. In its original state (flowers) it contained 20·2 per cent. of the insoluble variety; after boiling with water it was found to be wholly soluble, whereas on the other hand, that which was present in the distillate was white, and insoluble in carbon disulphide, and probably therefore a product of decomposition.

A less direct but similar case of decomposition of water by sulphur takes place on heating them in presence of iodine. In one experiment 1·27 grams iodine was treated with 25 c.c. of water, and excess of sulphur to 160°; the solution became colourless at the end of ten hours. The iodine existed in solution entirely as hydriodic acid, the sulphur as sulphuric acid. This reaction appears to be the reverse of the decomposition of aqueous hydriodic acid by sulphur (*Watts's Dictionary*, 1, Suppl., 739). Certain points of *à priori* evidence which favour our hypothesis remain to be mentioned. Thus carbon disulphide is resolved by the action of water at high temperatures into carbonic acid and hydrogen sulphide (Schlagdenhauffen, *J. Pharm.*, [3], **29**, 401). It was interesting to us, in its bearing upon our previous experiments, to investigate the influence of the presence of lead acetate upon this reaction. In one experiment, when this salt was in excess ·509 gram of the precipitate was found to contain ·3305 gram PbS and ·168 gram $PbCO_3$, quantities which closely satisfy the equation: $2H_2O + CS_2 = 2H_2S + CO_2$. In a second experiment, the disulphide being in excess, the contents of the tube were under considerable pressure, and the precipitate contained 94 p.c. of sulphide, 1·5 p.c. of carbonate, the residual 4·5 p.c. consisting probably of free sulphur, the formation of which is known to attend the decomposition of the disulphide by water alone. It appears, therefore, that the reaction is simplified by the presence of a body capable of uniting with the products. It is also to be remembered that sulphur decomposes both the aromatic hydrocarbons and the paraffins with formation of hydrogen sulphide and liberation of carbon.* We therefore conclude that sulphur decomposes water, and infer on the evidence indirect and *à priori* which we have discussed that it does so, by uniting with both its hydrogen and oxygen. At the same we are of opinion that the observed distillation of sulphur is chiefly referable, not to the reunion of the products of this decomposition—for we find that sulphur also accumulates in the distillate when a current of hydrogen sulphide or of sulphurous anhydride is continuously passed through the water (boiling in presence of sulphur)—but rather to the fact that sulphur is vaporised by steam, in same way as paraffin and other bodies of high boiling point, and that a portion of the vapour thus formed reacts with the vapour of water at the temperature of 100° (and even below 100°), forming a hydrogen and an oxygen compound.

Selenium and *tellurium* we found to exert an inappreciable action upon water at a temperature of 160°.

Phosphorus.—The amorphous variety does not appear to decompose water when boiled with it in an open flask. A slight reaction occurs at higher temperatures.† Thus on heating a small quantity with 25 c.c. of water to 160° for about 32 hours, the quantity of phosphorus in

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* In repeating these observations we obtained from toluene graphitic scales, while the carbon obtained from the paraffins resembled lamp-black.

† In presence of air.

solution amounted to ·0096 gram, of which ·0055 gram had been fully oxidised to phosphoric acid. On replacing the water by a solution of lead acetate, the reaction was much increased, and a bulky precipitate, consisting of metallic lead, phosphate, and an unstable phosphide, was formed. With copper sulphate we obtained a similar result: a considerable quantity of metallic copper was deposited, largely in the form of long needles, mixed with a phosphide which will presently be described, and sulphide, the solution containing sulphuric and phosphoric acids. (The reduction of the sulphuric acid is worthy of remark.)

The reduction of cupric chloride by phosphorus is more striking. On heating the aqueous solution of this salt also with the amorphous variety at 160° for eight hours, it underwent complete reduction to cuprous chloride, which crystallised on cooling in large foliated plates. On again heating at 160° for eight hours, the chloride was entirely decomposed, yielding a phosphide of definite composition, which was obtained as a semi-metallic powder of sp. gr. 4·874. Two analyses of this body gave the following results:—

(*a*.) ·388 gram gave ·3358 gram CuO and ·443 gram $Mg_2P_2O_7$.
* (*b*.) ·388 „ ·460 „ „ ·611 „ „

	(*a*.)	(*b*.)	Calc. Cu_nP_n.
Copper	68·98	68·36	67·2
Phosphorus ..	31·66	31·64	32·8
	100·64	100·00	100·0

This phosphide is insoluble in hydrochloric acid; it decomposes potassium cyanide in the cold, with evolution of hydrogen phosphide, and corresponds therefore with that described by Miller (*Elements*, **2**, 701) as resulting from the action of phosphorus, presumably vitreous, on a boiling solution of copper sulphate, and formulated as Cu_2P_2 under a note of interrogation. We have, however, been quite unable to prepare this body by the method there stated, the precipitate so obtained containing also metallic copper and an oxy-salt in varying proportions. Thus in four experiments under similar conditions the precipitates obtained were found to contain the following percentages of copper respectively, 31·66, 32·75, 34·68, and 36·08. In the first of these the sum of the percentages of copper and phosphorus was only 89·25. Further, these precipitates on exposure to the air underwent oxidation accompanied by deliquescence, and on subsequent treatment with water yielded a green solution, which on evaporation deposited

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* Ratio Cu : P only determined. The excess of copper over the calculated percentage is due to the unavoidable formation of a small quantity of the metal.

metallic copper as a bright red powder, whereas the phosphide described by us is perfectly stable in the air.

It will be seen from these observations that amorphous phosphorus decomposes water freely at high temperatures in presence of metallic salts capable of forming insoluble compounds with the products; the reaction appears to be similar to that which occurs with the alkalis, the precipitation of phosphide indicating the previous formation of hydrogen phosphide, and the separation of metal the formation of hypophosphorous acid as a stage in the reaction.

Vitreous Phosphorus.—The question of the decomposition of water by this variety was investigated by observations similar to those detailed in the case of sulphur. When boiled with water under ordinary conditions in a flask attached to a condenser, phosphorus accumulates in the distillate; phosphoric and phosphorous acids are formed and dissolved by the boiling water, and the distillate gives the reactions of hydrogen phosphide. If, on the other hand, the distillation is conducted in an atmosphere of carbonic anhydride, no traces of oxy-acids are formed, whereas the distillation of phosphorus is unaffected. We conclude, therefore, that phosphorus, like sulphur, is vaporised by steam, but does *not* decompose boiling water, except in presence of oxygen. This accords with a recent observation of J. Corne (*J. Pharm. Chim.* [4], **28**, 386), that moist phosphorus reduces iodic acid and the iodates at ordinary temperatures in presence of air, but is without action if oxygen be excluded.

On sealing a tube containing lead acetate solution and phosphorus, after expelling the air with a current of carbonic anhydride, and placing it in hot water at 80—90°, we observed that reduction took place; a black phosphide was formed, which when thrown on to a filter underwent rapid oxidation to phosphate. Phosphorus appears, therefore, to reduce metallic solutions, *i.e.*, to decompose water, in presence of metallic salts, even when oxygen is excluded.

Halogens.—Bromine was heated with many times its volume of water for eight days at 160°; no pressure was observed on opening the tubes, and the whole result of the experiment was the formation of a small quantity of alkaline salt. Iodine was found to be similarly dissolved in small quantity as alkaline iodide and iodate. On replacing the water by a solution of lead acetate, the addition of bromine caused the precipitation of a brown mass resembling lead dioxide. This compound, after washing and drying, was found to contain 13 per cent. bromine (12·92 and 13·17 in two analyses) and 73·3 per cent. lead. By washing with boiling water for some hours the percentage of bromine was reduced to 12·1. After then treating with hot dilute acetic acid and washing with water, a residue of the pure dioxide was obtained (Pb = 86·3 per cent., calc. 86·6). On heating the original precipitate with water at 160° (containing also acetic acid) we obtained, on cooling, a crystalline mass of lead bromide mixed with a small quantity of carbonate (Pb = 57·56 per cent., calc. PbBr = 56·4). We confirmed the latter observation by a direct experiment on the dioxide, which we find is dissolved by dilute acetic acid at high temperatures, a small quantity of the latter being simultaneously oxidised to carbonic acid. It is evident, therefore, that bromine decomposes water in presence of lead acetate, with formation of a hydracid (*i.e.*, lead bromide) and liberation of oxygen (*i.e.*, formation of lead dioxide).

Since writing the above we have made the following observations: Absolute alcohol was distilled from sulphur (flowers); the distillate contained no trace of sulphur. Aqueous alcohol was then substituted, and the "distillation" of sulphur found to begin at 92°. The bearings of these points upon the discussion of p. 253 are evident.