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### XII.—Action of Hydrogen Sulphide on Arsenic Acid.

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(Communication from the Chemical Laboratory of the Bohemian University, Prague.)

THE treatment of solutions of arsenic acid, or acid solutions of arsenates with hydrogen sulphide, is an operation which is carried out daily in chemical laboratories, but there is a difference of opinion as to the reactions which take place under these circumstances.

### Historical Introduction.

According to Berzelius (Ann. Phys. Chem., 1826, 7, 2) arsenic pentasulphide is formed when hydrogen sulphide acts on a moderately concentrated solution of arsenic acid. Gmelin (Handb., 5, ed. ii, 690 [1853]) gives the following equation,  $AsO_5 + 5HS = AsS_5 +$ 5HO, as expressing the reaction. H. Ludwig (Arch. Pharm., 1859, 147, 32-34) quotes Wackenroder's "Dictate of Forensic Chemistry," in which the latter says that the arsenic acid is first reduced by hydrogen sulphide to arsenious acid, even in the presence of hydrochloric acid, and that then a mixture of arsenic trisulphide and sulphur is precipitated. H. Rose (Handbuch, 1851, 383) finds that on dissolving this precipitate in ammonia and adding silver nitrate, brown silver arsenate is thrown down, whereas arsenic trisulphide, free from sulphur, when similarly treated, yields yellow silver arsenite. Otto (Lehrbuch, 2 ed., 1019), Fresenius (Anleitung, 1856), Will (Anleitung, 1857), and Wicke (Analyse, 1857) express the opinion that the precipitate formed by the action of hydrogen sulphide on arsenic acid solutions is arsenic pentasulphide. Ludwig (loc. cit.) finds that in the above reaction pale-yellow (!) sulphur is precipitated at first, and later on lemon-yellow arsenic trisulphide is thrown down; he expresses the reaction as follows :---

# $AsO_5 + 5HS = AsS_3 + S_2 + 5HO.$

H. Rose (Ann. Phys. Chem., 1859, 107, 186), after passing hydrogen sulphide into a solution of arsenic acid, heated the solution and filtered off the separated sulphur. On adding silver nitrate to the filtrate, both the yellow silver arsenite and brown silver arsenate

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were thrown down; this afforded a proof that a partial reduction to arsenious acid had taken place. The precipitate formed by the continued action of hydrogen sulphide on arsenic acid is regarded by Rose as a mixture of arsenic trisulphide with sulphur, and from analogy the conclusion is drawn that antimony pentasulphide as well as arsenic pentasulphide may exist in combinations as double sulphides, but not in the free state. Since that time, the reaction in question is represented in Manuals of Chemistry, as follows :--

$$2H_3AsO_4 + 5H_2S = As_2S_3 + S_2 + 8H_2O.$$

We cannot but remark that all the experiments quoted above have been *qualitative* merely, the products of reactions were not analysed, neither was the reaction in any way studied quantitatively.

In the year 1878, Bunsen (Annalen, 192, 305—328) showed that on passing a rapid current of hydrogen sulphide into a solution of an alkaline arsenate, acidified with hydrochloric acid, and heated in a water-bath, arsenic pentasulphide was formed, and that this was the best mode of determining arsenic acid quantitatively. L. M. McCay (Chem. News, 54, 287, and Abstr., 1887, 213) confirms Bunsen's results.

In spite of Bunsen's work, only a very few Manuals of Chemistry published since (especially analytical ones) seem to have taken notice of the possibility of a different action of hydrogen sulphide on arsenic acid.

Having regard to the discrepancies existing between the statements of Berzelius and Bunsen on the one hand, and those of Wackenroder, Ludwig, and Rose, on the other, we have investigated this subject more thoroughly.

# First Series : Acid Solutions of Arsenates.

Three grams of arsenic trioxide were weighed exactly, dissolved in an aqueous solution of 100 grams of potassium hydroxide, and treated first with chlorine, and then with hydrochloric acid as described by Bunsen. The acid solution thus obtained was made up to one litre with distilled water (hereafter called "solution A"). The hydrogen sulphide used for the precipitation was prepared either from a material containing no arsenic, or by Jacobsen's method (*Ber.*, **20**, 1999), passing the gas through glass-wool impregnated with iodine, and washing with water (or still better with potassium sulphide solution), so as to purify the gas.

I. 100 c.c. of the "solution A" (= 0.3 gram  $As_2O_3$  in the form of arsenic acid) was precipitated as arsenic pentasulphide in order to test the exactness of Bunsen's method; all the precautions described by Bunsen were carefully observed. The solution was diluted with

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50 c.c. of water, and the small beaker containing it was placed in a large one filled with water at  $60^{\circ}$ . Hydrogen sulphide, the velocity of which was limited in this and the subsequent experiments to 5—6 bubbles per second, was passed through the liquid for three hours at  $60^{\circ}$ , and then, while the liquid cooled, for 12 hours. The first turbidity appeared after 3 minutes, the first precipitate after 5 minutes. After 24 hours, the precipitate was collected on a weighed filter, and washed well with water, alcohol, and carbon bisulphide,\* it was then dried at  $107^{\circ}$ , and weighed until the weight became constant.† The weight of the precipitate was 0.4701 gram. Theory requires from 0.3 gram  $As_2O_3: 0.47014$  arsenic pentasulphide.

Calculated. Found. Pentasulphide.... 0.4701 gram. 0.4701 gram.

II. "Solution A" = 100 c.c. Water 50 c.c. Temp. 17°. First turbidity in 15 minutes, first precipitate in 30 minutes. Hydrogen sulphide passed for 24 hours. Weight of precipitate, 0.4599 gram. Theory requires 0.4701 gram; the precipitate, therefore, either consists partly of trisulphide, or the precipitation is incomplete. The last was shown to be the case, for, on continuing to pass the gas at  $60^\circ$ , 0.0106 gram more of pentasulphide was obtained. The sum of both weights equals the theoretical quantity calculated for the pentasulphide:—

	Calculated.	Found.
Pentasulphide	0.4701 gram.	0.4705 gram.

From this experiment, it will be seen that arsenic pentasulphide is precipitated by hydrogen sulphide, not only from a hot but also from a cold solution of an alkaline arsenate containing an excess of hydrochloric acid. But precipitation in the cold is not practicable for analytical purposes, as it requires much time, and, moreover, is incomplete even after the gas has been passed for a long time; it was found here that, after 24 hours' treatment, 2.25 per cent. of the pentasulphide remained in solution.

\* The filter was weighed in a thin glass bottle, but as its weight continually changes while in the desiccator and on the balance, another thin glass bottle containing a filter which had been treated precisely like the first one, was used as a counterpoise. The action of humidity on both filters being the same, this source of error was eliminated.

<sup>+</sup> Arsenic pentasulphide is, according to Bunsen, quite insoluble in water, alcohol, and carbon bisulphide, but sometimes, on pouring alcohol on the finely divided precipitate, slight traces are carried mechanically through the filter, as can be shown by evaporating the alcoholic filtrate and testing it for arsenic by Babo and Fresenius' method. In all cases, however, the quantity lost is less than the inevitable experimental errors. III. This experiment was made like No. II. Temperature 24°. Volume of "solution A," 130 c.c., of water, 50 c.c. After 24 hours, 0.4719 gram was precipitated, and from the filtrate at  $60^{\circ}$ , 0.003 gram of pentasulphide = 0.63 per cent., was obtained.

IV. In order to prove that the precipitate obtained at the ordinary temperature is really arsenic pentasulphide (from a mixture of trisulphide and sulphur, the latter can be extracted by means of carbon bisulphide), 500 c.c. of the "solution A" was treated for 36 hours at  $17^{\circ}$ , with an excess of hydrogen sulphide, the precipitate obtained washed completely with cold water, and then most carefully with large quantities of freshly distilled carbon bisulphide, so as to remove every trace of free sulphur; it was finally dried at  $107^{\circ}$ . Arsenic pentasulphide as thus prepared in the cold is of a pale lemon-yellow colour, and more finely divided than that precipitated from a warm solution. The dry sulphide cannot be powdered, since it becomes so strongly electric by friction that it is thrown about on all sides.

The following results were obtained on analysis :---

(a.) 0.6094 gram treated with nitric acid and potassium chlorate, and then evaporated with hydrochloric acid, gave 0.0297 gram sulphur (= 4.874 per cent.), and after the usual purification of the calcined impure barium sulphate, 2.0717 gram of the pure sulphate (= 46.746 per cent.).

(b.) 0.5303 gram of the sulphide, treated in a similar way, yielded 0.0472 gram sulphur (= 8.901 per cent.) and 1.6469 gram barium sulphate (= 42.702 per cent.).

The quantity of arsenic contained in arsenic pentasulphide, prepared at the ordinary temperature, may be calculated directly from Experiment II, representing a partial synthesis of that compound.

(c.) 0.3 gram As<sub>2</sub>O<sub>3</sub>, containing 0.2272 gram arsenic, yielded 0.4705 gram of arsenic pentasulphide.

				Found.		
	Calc	ulated.	<i>a</i> .		<i>c</i> .	Mean.
$As_2$	150.0	48.34	<b>(4</b> 8·38)	(48.40)	48.30	48.36
$S_5\ldots$	160.3	51.66	51.62	51.60	(51.70)	51.64
	100.0	100.00	100.00	100.00	100.00	100.00

In a similar way, the composition of arsenic pentasulphide obtained from a *warm* solution, may be calculated from the data of Experiment I.

0.3 gram of As<sub>2</sub>O<sub>3</sub> gave 0.4701 gram arsenic pentasulphide.

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	Theor	y and experiment
Arsenic		. 48.34
Sulphur		.51.66
		100.00

From this, it will be seen that under the aforesaid conditions arsenic pentasulphide is thrown down by hydrogen sulphide from a solution of potassium arsenate containing an excess of hydrochloric acid, both at low and high temperatures, and that no reduction takes place.

## Second Series. Solutions of Pure Arsenic Acid.

Pure arsenic acid was next investigated. This was prepared by the action of nitric acid on pure arsenic trioxide; the oxidation was carried on in such a way that all loss by spirting was avoided, a small flask being used, which was closed by a glass tube bent several times and furnished with three bulbs; these were filled with nitric acid, through which the evolved gases escaped. The solution was then repeatedly evaporated down with water until all traces of nitric acid were expelled; 5.0 grams of vitreous arsenic trioxide, treated in this way and diluted with water, yielded 500 c.c. of "solution B."

The behaviour of the aqueous solution of arsenic acid towards reducing agents in general was next investigated.

Bunsen (loc. cit., 321) took an arsenic acid solution, prepared from 0.1913 gram arsenic trioxide by the action of potassium hydroxide, chlorine, and hydrochloric acid, mixed it in a covered beaker with 100 c.c. of saturated sulphurous acid, and heated moderately for 20 hours. After removing the excess of sulphur dioxide by a current of air, the solution was precipitated with hydrogen sulphide. The precipitate was found to contain 51.27 parts of pentasulphide for 48.17 parts of trisulphide. In spite of the continued action of sulphurous acid, only about half of the arsenic acid was reduced.

We have repeated the experiment with a solution of pure arsenic acid.

V. 50 c.c. of "solution B" (= 0.5 gram As<sub>2</sub>O<sub>3</sub>) was treated exactly in the manner described, at 60° C. for 20 hours. The weight of the orange-yellow precipitate obtained was 0.6209 gram. Arsenic pentasulphide obtained from the above quantity should weigh 0.7836 gram; the trisulphide, 0.6216 gram. As the filtrate was free from arsenic, the precipitate was pure trisulphide.

	Calculated.	Found.	
Arsenic trisulphide	0 <sup>.</sup> 6216 gram.	0 <sup>.</sup> 6209 gram.	

It can readily be seen from a comparison of Bunsen's experiment

with ours, that under the conditions described free arsenic acid is completely reduced by sulphurous acid, and that the quantity reduced is much larger than in the case of a hydrochloric solution of an arsenate.

The object of the following experiments was to ascertain whether free arsenic acid is reduced by hydrogen sulphide, and whether it is precipitated more easily than hydrochloric solutions of an arsenate. If a current of hydrogen sulphide is passed, not too slowly, into an aqueous solution of arsenic acid at the ordinary temperature, it becomes opalescent after 5-15 minutes, according to its concentration, and then turns milky, but the precipitate, which at first resembles finely-divided sulphur, very soon becomes pale lemon-yellow, and is sometimes semitransparent, especially if the reaction takes place at a temperature only a few degrees above zero; the same phenomenon is observed on adding a large quantity of saturated aqueous hydrogen sulphide to a dilute arsenic acid solution. This lemon-yellow, milky solution passes completely through a filter, and every trace of it may be washed out by water. As the precipitate is of the same colour, and as will be seen below, is also of the same composition as arsenic pentasulphide, it may be assumed that a new colloidal modification of arsenic pentasulphide is formed, especially at a low temperature, the formation of colloïdal trisulphide taking place under similar conditions. At a certain degree of dilution, there is no perceptible distinction between liquid and precipitate in the pale greenish-yellow milky fluid, even after it has been allowed to remain for many days at a low temperature  $(2-4^{\circ})$ . At the ordinary temperature, however, a separation of the precipitate from the liquid sometimes takes place a little less slowly, but the two cannot be separated by filtration. On adding an acid or a salt solution, a flocculent precipitate separates, especially on gently warming; it is now insoluble in water, and may be collected and washed in the ordinary way.

The following experiments show what products are formed by the continued action of hydrogen sulphide on arsenic acid :—

VI. 50 c.c. of arsenic "solution B" (= 0.5 gram As<sub>2</sub>O<sub>3</sub>) was diluted with 50 c.c. of water and a rapid current of hydrogen sulphide passed into it at 16—18°. The lemon-yellow colour of the precipitate after several hours changes to orange, showing that it is partly converted into arsenic trisulphide. After 48 hours, the action of the gas was interrupted, and then 10 c.c. of strong hydrochloric acid and 100 c.c. of ammonium chloride solution (10 parts to 100 H<sub>2</sub>O) were added, in order to cause the aggregation of the precipitate and render it capable of being collected on a filter; after gently warming, the precipitate separates completely. As it contains a comparatively large amount of free sulphur, it must be washed most carefully and repeatedly with

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carbon bisulphide; for this purpose, the lower part of the funnel is temporarily closed, then carbon bisulphide is poured on to the filter and allowed to run through; this operation is repeated six to eight times, so that on the whole the precipitate remains in contact with the carbon bisulphide for about half an hour. The results of incomplete washing with carbon bisulphide on the precipitate are seen from Experiments VII and VIII.

The weight of the precipitate obtained in the manner described above, was 0.7606 gram. From the filtrate, 0.001 gram of pentasulphide was obtained; this shows that, even after 48 hours, the precipitation of the free acid is incomplete, 0.13 per cent. remaining in solution.

The total quantity of the precipitate was 0.7616 gram (a). 0.5 gram arsenic trioxide should furnish 0.78358 gram (b) pure pentasulphide, but only 0.62165 gram (c) trisulphide. A simple calculation\* shows that both sulphides are contained in the precipitate in the following proportion:—

Arsenic pentasulphide	86.43
Arsenic trisulphide	13.57
	100.00

The two following experiments show that simple washing with carbon bisulphide—which may be used with advantage for the extraction of the small quantity of sulphur precipitated along with the pure pentasulphide—is insufficient when the precipitate consists partly of a mixture of trisulphide with sulphur or when the quantity of free sulphur is somewhat larger.

VII. 50 c.c. of the acidified arsenate "solution A" was mixed with a solution of 1 gram of crystallised ferric chloride, and precipitated with hydrogen sulphide at 60°. The ferrous chloride formed had no reducing action on the arsenic acid. The precipitate of arsenic pentasulphide and sulphur was washed four times with carbon bisulphide in the ordinary rapid way. After drying, its weight was 0.2604 gram instead of 0.2350 gram, and after renewed extraction

\* The percentage of the trisulphide is  $\frac{100(b-a)}{b-c}$ , the difference between that

and 100 being pentasulphide. This method of calculation, as also that founded on the estimation of sulphur in the mixed sulphides, are the only trustworthy methods of deciding whether the precipitate consists of trisulphide, pentasulphide, or a mixture of both, supposing that the sulphur formed by the oxidation of hydrogen sulphide does not contain the "insoluble" modification. Rose's test mentioned above does not answer the purpose so well, for when small quantities of trisulphide are present, as is shown by the synthesis or analysis, no precipitate of silver arsenite is formed. 0.2548 gram: so that of the 0.0591 gram sulphur, formed by the action of hydrogen sulphide on the ferric chloride, 0.0198 gram remained undissolved, probably in the form of "insoluble" sulphur, which, according to Selmi (*Gmelin-Kraut's Handbuch*, 6th edition, 1, Part II, 166) is formed by the action of hydrogen sulphide on ferric chloride.

VIII. 50 c.c. of "solution B" was precipitated at 80° in exactly the same manner as described below in Experiment X. After rapidly washing with carbon bisulphide (four times), the weight of the precipitate was 0.7792 gram instead of the 0.7618 gram obtained in Experiment X, when extraction was complete; 0.0174 gram of sulphur, therefore, remained undissolved.

IX. The preparation of the mixed sulphides was carried on at 4°, The precipitate, washed and dried, was analysed.

- (a.) 0.3322 gram gave 1.212 gram  $BaSO_4 = 50.173$  per cent. sulphur.
- (b.) 0.7675 gram gave 2.8 grams  $BaSO_4 = 50.176$  per cent. sulphur.

Mean = 50.175 per cent. sulphur.

Arsenic trisulphide contains 39.069 per cent. sulphur: the pentasulphide 51.66 per cent. The percentage composition of the mixture of sulphides as calculated\* is—

Pentasulphide	85.57
Trisulphide	14.43
	100.00

It will be seen that both methods of calculation give one and the same result.

X. 50 c.c. of the arsenic "solution B," mixed with 50 c.c. water, was precipitated in the usual manner at 40°. After adding 10 c.c. hydrochloric acid and 100 c.c. of ammonium chloride solution (1:10), the last traces of pentasulphide remaining in solution were thrown down at 40°. Weight of precipitate, 0.7589 gram; composition—

Pentasulphide	84.76
Trisulphide	15.24
	100.00

XI. Solution B, 50 c.c.; water, 50 c.c.; temperature,  $80^{\circ}$ . First of all a lemon-yellow precipitate of pentasulphide was formed, then the trisulphide separated out on the surface of the liquid in the form of

\* See footnote, p. 151.

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orange, crystalline crusts. Hydrogen sulphide was passed for six hours at 80°, and for 24 hours at 18°. After the addition of 100 c.c. ammonium chloride solution, the precipitate was collected; its weight was 0.7575 gram. The filtrate was mixed with 25 c.c. hydrochloric acid and precipitated at 80°, when 0.0043 gram of pentasulphide was obtained. This shows that even after the continued action of hydrogen sulphide on the warm and cold pure arsenic acid solution, 0.56 per cent. of pentasulphide remained unprecipitated.

The total precipitate was 0.7618 gram; its composition-

Pentasulphide	86.56
Trisulphide	13.44
	100.00

It will be seen from the experiments VI, IX, X, and XI that the action of hydrogen sulphide on pure arsenic acid solutions between  $4^{\circ}$  and  $80^{\circ}$  is accompanied by a *partial* reduction of the arsenic acid to arsenious acid, and that by the further action of hydrogen sulphide a mixture of arsenic pentasulphide and trisulphide is formed, the quantity of trisulphide varying between 13.44 and 15.24 per cent. The variation of temperature does not seem to have any influence on the composition of the precipitate.

### Third Series. Arsenic Acid in the Presence of a Salt.

XII. 50 c.c. of arsenic acid solution B was mixed with 100 c.c. of aqueous ammonium chloride solution (1:10), and treated with hydrogen sulphide at 17°. Heating to 70° did not cause complete precipitation, for 0.0271 gram was obtained from the filtrate by the action of the gas in presence of 10 c.c. of hydrochloric acid; the weight of the precipitate first obtained was 0.7221 gram. It will be seen that the precipitation in the presence of ammonium chloride is less complete than in the case of pure arsenic acid solution, 3.62 per cent. being left in the filtrate. From the total weight of the precipitate obtained = 0.7492 gram, the following percentage composition of the precipitate was calculated :—

Pentasulphide	78·77
Trisulphide	21.23
	100.00

XIII. This experiment was made in the same way with 0.5601 gram of arsenic trioxide oxidised to arsenic acid; temperature 40°. Only the portion precipitated after 24 hours was collected; its weight was 0.7625 gram. Assuming the same percentage composition of the precipitate as in XII, the quantity of the sulphides thrown down is 90.85 per cent., 9.15 per cent. remaining in solution.

XIV. The same quantity of arsenic acid as in XIII was treated at 8° with hydrogen sulphide in the presence of ammonium chloride for 24 hours. Weight of precipitate: 0.8085 gram = 96.33 per cent. of mixed sulphides, 3.57 per cent. remaining in solution.

XV. Arsenic acid solution B, 50 c.c.; ammonium chloride solution, 100 c.c.; temperature, 70°. Hydrogen sulphide after 15 minutes produced a pure white precipitate of sulphur which soon became lemonyellow, and after 30 minutes an orange precipitate was formed. From this moment the quantity of precipitate increased so rapidly that, after one hour, the voluminous precipitate settled well from the clear solution, and nothing more was thrown down by the further action of the gas. Five drops of hydrochloric acid were then added, and 10 c.c. after 15 minutes, in order that all the arsenic might be thrown down by the hydrogen sulphide. The passage of the gas was continued while the liquid was cooling, and after 12 hours it was interrupted. After completely extracting the free sulphur with carbon bisulphide, the weight of the precipitate, dried as usual at 107°, was found to be 0.7018 gram. Its composition is—

Pentasulphide	49.50
Trisulphide	50.50
	100.00

It is evident from these experiments, that in the presence of ammonium chloride hydrogen sulphide reduces the arsenic acid more than in the case of pure arsenic acid solution, and that the reduction increases with rise of temperature, 56.25 per cent. of the total arsenic present being converted into the trisulphide at  $70^{\circ}$ . On the contrary, the precipitation is far less complete than that of the pure acid.

## Fourth Series. Arsenic Acid in Acid Solution.

XVI. 20 c.c. of the arsenic acid "solution B" was mixed with 50 c.c. of water and 20 c.c. of hydrochloric acid. Hydrogen sulphide was passed in at 17°. After 24 hours, the traces of arsenic still remaining in solution were thrown down by heating the solution to  $70^{\circ}$ ; it was filtered after a lapse of two days. The colour of the precipitate was lemon-yellow, and identical with that of pentasulphide, and its weight was 0.7833 gram, that calculated for the pentasulphide being 0.7836 gram. From this partial synthesis, the composition of the pentasulphide is again calculated to be—

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	Calculated (theory).	Found.
Arsenic	48.34	48.36
Sulphur	$\dots 51.66$	51.64
	······	·
	100.00	100.00

XVII. Arsenic acid was prepared from 0.6970 gram trioxide, dissolved in water, 10 grams of ammonium nitrate, and 10 c.c. of hydrochloric acid were added, and the mixture precipitated at 75°. The weight of the precipitate was 1.0905 gram, that calculated for arsenic pentasulphide being 1.0923 gram.

XVIII. A solution of arsenic acid was precipitated with hydrogen sulphide at 10° in presence of ammonium nitrate and hydrochloric acid. The analysis of the precipitate, formed after 12 hours, and dried at 107° (after extraction with bisulphide of carbon), gave the following result :---

(a.) 0.2745 gram sulphide yielded 1.0305 gram barium sulphate.

- (b.) 0.4 gram sulphide yielded 1.4975 gram barium sulphate. The precipitation took place at 4°.
- (c.) 0.505 gram sulphide yielded 1.901 gram barium sulphate.

			Found.	
	Calculated.	<i>a</i> .	<i>b</i> .	c.
Arsenic	48.34	<u> </u>	<u> </u>	
Sulphur	51.66	51.62	51.48	51.76
	100.00			

XIX. This experiment was made at  $10^{\circ}$ , in presence of ammonium nitrate, with a small quantity of hydrochloric acid only.

On analysis, 0.4757 gram sulphide gave 1.765 gram BaSO<sub>4</sub>; this corresponds with 51.02 per cent. sulphur, showing that the pentasulphide is not pure, but that it contains some trisulphide; its composition is—

Pentasulphide	93.66
Trisulphide	6.34
	100.00

The foregoing experiments were varied in different ways, but the quantity of hydrogen sulphide passing through the liquid was kept as nearly as possible constant, in order to obtain results comparable among themselves with regard to the quantity of that gas employed.

The number of gas-bubbles was regulated, so that about 300 passed per minute.

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The question now arose: How will a solution of arsenic acid, which yields *pure arsenic pentasulphide* when treated with an excess of hydrogen sulphide, behave, if the quantity of gas passing through the solution is *much smaller* in the unit of time? For the purpose of settling this point, the following experiment was made.

XX. To 100 c.c. of "solution A" (which served for experiments I— IV, and contains 0.3 gram arsenic trioxide in the form of potassium arsenate in a solution strongly acid with hydrochloric acid) 50 c.c. of water was added, and the mixture heated at 70°. A current of hydrogen sulphide was passed through the liquid as slowly as possible, that is, at the rate of 20—25 bubbles per minute. The precipitate formed after 20 minutes was nearly white, and after 30 minutes orange crusts of trisulphide were formed on the surface of the liquid. At the same time, a turbidity caused by the pale-yellow pentasulphide made its appearance in the liquid. After 5 hours, the precipitation was complete; the gas, however, was passed into the liquid for 12 hours more, while the liquid was cooling. The weight of the precipitate formed was 0.4413 gram; its composition was—

From this it follows that the hydrochloric solution of an arsenate (which is reduced less readily than a pure arsenic acid solution both by sulphurous acid and by hydrogen sulphide), when warmed is reduced by hydrogen sulphide more completely if the gas is present in small quantity.

It may be concluded from analogy, with regard to the *second* and *third* series of experiments, that the reduction of arsenic acid solutions, either pure or containing ammonium chloride, will be more complete the more slowly the hydrogen sulphide is passed through the solution.

It follows further from the whole four series, that arsenic acid is not reduced by hydrogen sulphide if the solution contains enough hydrochloric acid, or of this acid and a salt, the gas being present in excess, and that it behaves towards hydrogen sulphide exactly like a solution of an alkaline arsenate acidified with hydrochloric acid. When, however, the quantity of hydrochloric acid is small in proportion to the ammonium salt, a little arsenic acid is reduced, and some trisulphide is precipitated along with the pentasulphide. When no hydrochloric acid is present, the phenomena described in experiments XII—XIV take place.

The following is the result of the experiments described in the present communication :---

On acting with hydrogen sulphide on aqueous arsenic acid or acid solutions of arsenates, it is shown, cæteris paribus-

1. That more arsenic pentasulphide is formed—

- (a.) The larger the quantity of hydrochloric acid present;
- (b.) The larger the quantity of hydrogen sulphide passed in the unit of time; and
- (c.) The lower the temperature (between  $0-100^{\circ}$ ).

2. That arsenic trisulphide mixed with sulphur is formed in larger quantity (in consequence of the reducing action of the hydrogen sulphide)—

- (a.) The less hydrochloric acid there is present;
- (b.) The smaller the quantity of hydrogen sulphide; and
- (c.) The higher the temperature.

3. Arsenic acid, especially in presence of ammonium chloride, is reduced more easily than an acidified solution of an arsenate.

4. The second limit, namely, complete formation of trisulphide, is reached, if at all, with greater difficulty than the first limit, that is formation of pure pentasulphide. Probably the relation between the mode of formation of the two sulphides and the conditions described above may be represented by an asymptotic curve, but at present the principal function, the quantity of hydrogen sulphide coming into contact and reaction with the liquid in the unit of time, cannot be expressed mathematically.

# Discussion of Earlier Experiments on this Reaction.

Berzelius' statement that arsenic pentasulphide is precipitated from aqueous arsenic acid solutions by hydrogen sulphide, is correct only from the qualitative point of view, that is, only as far as it represents the main reaction, when no foreign substance is present. It is perfectly correct, however, as regards hydrochloric solutions of arsenic acid, or solutions of alkaline arsenates in presence of an excess of hydrogen sulphide. (This was not mentioned by Berzelius.)

The statements of Wackenroder and of Ludwig are correct only with respect to the secondary reaction between hydrogen sulphide and arsenic acid. Both these chemists, as was stated before, have investigated the reaction qualitatively only, and both have overlooked the fact that their "pale-yellow" (Wackenroder) or "light grey-yellow" (Ludwig) sulphur was nothing else than *arsenic pentasulphide*. The said secondary reaction is still less marked when hydrochloric acid is present.

H. Rose's observation that, when hydrogen sulphide acts for a short

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time only on aqueous arsenic acid, *partial* reduction of the latter takes place, is correct. But Rose overlooked the fact that his milky precipitate of sulphur (which, as he says, is never free from arsenic) consists to a great extent of (colloïdal) arsenic pentasulphide. We have several times repeated the experiment as described by Rose qualitatively, that is, under varying conditions, and we found that in all cases a mixture of arsenic trisulphide and pentasulphide was produced. Rose himself gives neither a qualitative nor a quantitative proof that the precipitate he obtained was actually arsenic trisulphide mixed with sulphur, and his conclusion that the pentasulphides of arsenic and also that of antimony cannot exist in the free state, may be regarded as untenable.

Regarded as an analytical operation, the following conclusions may be drawn from Bunsen's experiments and our own on the reaction between hydrogen sulphide and arsenic acid.

Solutions of arsenic acid or of soluble arsenates are tested qualitatively (by students), by precipitating with hydrogen sulphide, as a rule in the presence of hydrochloric acid. The following notes, therefore, might be inserted with advantage in Manuals of Analytical Chemistry :--

When a *rapid current* of hydrogen sulphide is passed into a solution of arsenic acid, *arsenic pentasulphide* alone is formed, although but slowly, if free hydrochloric acid is present, and the liquid is kept warm :—

$$2H_{3}AsO_{4} + 5H_{2}S = As_{2}S_{5} + 8H_{2}O.$$

When the gas is *passed slowly* into a solution of the free acid, or into warm acid solutions of arsenates, a secondary reaction takes place in two stages, along with the primary reaction mentioned above:—

(a.) 
$$H_3AsO_4 + H_2S = H_3AsO_3 + S + H_2O.$$
  
(b.)  $2H_3AsO_3 + 3H_2S = As_2S_3 + 6H_2O.$ 

For the quantitative estimation of arsenic acid in the form of a sulphide, it is best to convert it into *pentasulphide*, and for this purpose Bunsen's method must be *strictly adhered to*. In the case of free arsenic acid, the precipitation with hydrogen sulphide must be carried on in the presence of a sufficient quantity of hydrochloric acid.

We are unable to answer satisfactorily the question as to why, in the reaction studied in the present paper, arsenic pentasulphide alone is formed under one set of conditions, whilst under other conditions both pentasulphide and trisulphide are formed simultaneously, the proportion of the latter being sometimes very considerable. It is no explanation to say, for example, that if a *small* quantity of hydrogen

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sulphide is present, part of it is oxidised by the arsenic acid, but that this does not occur if the gas is present in *excess*, or that the oxidation of hydrogen sulphide by arsenic acid (or the reduction of the latter) does not take place as easily in presence of hydrochloric acid as it does in the case of pure arsenic acid, &c.; the above question, therefore, remains an interesting problem of chemical dynamics. It may be that the molecular state in which arsenic acid exists under the different conditions affects the reactions in some way.