ART. XXV.—*On the Gaseous Substances contained in the Smoky Quartz of Branchville, Conn.*; by ARTHUR W. WRIGHT, Yale College.

THE existence in quartz of numerous cavities containing a liquid substance is a matter of familiar occurrence, and great interest has attached to the investigation of the character of these inclusions. Although the presence of carbon dioxide and water had been well established, the difficulty of separating the contents of the cavities in sufficient quantity has hitherto prevented a direct examination of them. The quartz from Branchville is remarkable for the great size and number of the cavities, the peculiar characteristics of which are described by Mr. Hawes in the preceding article. The fortunate circumstance, noticed by him, that when exposed to a moderately high temperature it decrepitates and is speedily resolved into small fragments, made it possible to obtain with great ease and convenience enough of the enclosed substances for an extended examination. The material employed was derived from the collection of minerals from Branchville, of Professors Brush and Dana.

The temperature required for the disintegration of the quartz is much below that of red-heat, and the bursting of the solid material is evidently due to the increased tension of the gas, as it does not occur in those fragments which contain no cavities. The first trials were made with glass vessels, but the sharp fragments of the mineral were shot off with such violence as to destroy them immediately. Recourse was therefore had to a porcelain tube about one centimeter in diameter, glazed inside. This was carefully cleaned with pure distilled water, one end stopped with a plug cemented in, and the other provided with a perforated brass cap, into which could be screwed a piece through which passed a slender glass tube, the joint being rendered tight by a thin washer of india-rubber or paper. The closed end of the tube was filled for some 12 centimeters with pieces of clean glass rod, and upon these rested a loose plug of calcined asbestos. The quartz, broken into fragments of such a size as to permit their entrance, was dropped into the tube, filling it to within 10 or 12 centimeters of the mouth. When heated in a Bunsen flame, the whole of the material could be brought to the requisite heat without causing any perceptible elevation of the temperature of the cement joints. This receptacle, when charged, was connected by means of the glass tube with a Sprengel pump, all joinings of the glass tube being made by fusing, and the whole was easily rendered absolutely free from leakage.

The pump having been kept in action until no gas appeared to pass down, heat was cautiously applied to the tube, and gradually increased until a little gas was liberated from the quartz. When this had been thoroughly pumped out, removing thus the last portion of air, the heat was again applied and continued until the cessation of the decrepitation showed that no more gas could be obtained. The mercury was then set running in the pump carrying the gas into the measuring tube used for the analysis. A preliminary examination showed the greater portion of the gas to be carbon dioxide, the remainder apparently consisting chiefly or wholly of nitrogen. A considerable amount of water was also found to be present. In the succeeding operations this was collected for examination by causing the gas as it issued to pass through a U-tube of small caliber which was placed in a freezing mixture. As the temperature of the refrigerating mass was such as to reduce the tension of the vapor to less than one millimeter nearly the whole of the water was thus retained.

For the more careful analyses two portions of the rock were selected representing the greatest differences in the material. The first, No. 1, was of a light gray color, somewhat milky in appearance, and contained many cavities easily visible without

the aid of a lens. The weight of the material employed was 21.70 grams, which, divided by the specific gravity 2.63, gives for the volume 8.25 cubic centimeters. The second portion was of the darker variety, having a smoky brown color, appearing nearly black in large masses. The gas cavities in this were not so conspicuous, and apparently were less numerous. The amount of the material placed in the tube for examination was 19.49 grams, and the volume 7.41 cubic centimeters. This portion is designated as No. 2 in the following paragraphs. The total quantity of gas collected from No. 1 was 13.61 cubic centimeters, or 1.65 times the volume of the quartz. From No. 2, 7.20 cubic centimeters of gas were obtained, or 0.97 times the volume of the material employed. From the first portion examined in the preliminary work 1.33 volumes were obtained.

The eudiometer having been transferred to the mercury cistern, an absorption pellet moistened with solution of potassic hydrate was introduced into it, causing a rapid diminution of the volume of the gas. When this operation was complete the residual gas had been reduced to a small bubble in the top of the tube, which could not be measured directly with sufficient accuracy. To find its volume a little of the potash solution or of distilled water was admitted giving a meniscus concave toward the top of the tube. The position of this was carefully noted, and the tube emptied. Mercury was now introduced until the surface of the meniscus occupied exactly the former position of the surface of the water, and the metal was then weighed. The mean of five separate measurements being taken the volume of the gas was thus readily calculated. The results of the determinations with the two different portions of the material gave

I.		II.		Mean.
CO ₂	98.34	CO ₂	98.32	98.33
N	1.66	N	1.68	1.67
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100.00		100.00		100.00

Cuprous chloride produced no perceptible absorption, showing the absence of carbonic oxide. Potassium pyrogallate introduced into the tube with caustic potash solution produced a slight discoloration of the latter, but no change in the volume of the gas was visible, indicating that oxygen if present was not in recognizable quantity.

To ascertain the presence of hydrogen or other combustible gases a number of tests were made. A spark passed through the gas directly produced no effect, nor upon the addition of oxygen or air alone could any combustion be produced. When the proper quantity of pure electrolytic gas was added

the explosion produced no apparent change in the volume. This, if, from the small amount of gaseous substances operated with, it might not safely be concluded that hydrogen or hydrocarbons were entirely absent, shows that the quantity was exceedingly small. The residual substance then was nitrogen. In these operations, as already mentioned, the gas had passed through a tube placed in a freezing mixture. A later experiment, to be described in a succeeding paragraph, gave a somewhat different result.

The rock when broken or crushed with a hammer exhales a fugitive but unmistakable odor of hydrogen sulphide, but the proportion of the gas was too small to be directly detected with the ordinary lead-paper even when directly applied as a cover to a diamond mortar in which a considerable quantity of the material had been powdered. But when a slip of the paper was introduced into a tube filled with the extracted gases, a slight but distinct coloration was produced. The same was true in a somewhat more marked degree with a paper moistened with mercurous nitrate, indicating sulphurous oxide. To test this more fully separate slips of filtering paper were wet with plumbic acetate, sodium nitro-prusside, and mercurous nitrate. When dry they were introduced into a small tube through which gas freshly liberated was made to pass. Snow applied for a few moments to the tube ensured the presence of sufficient water to moisten the paper slightly. The first underwent a slight discoloration, which after a time disappeared, the second assumed a pinkish tint, while the third was distinctly blackened, thus proving the presence of a trace of both the gases in question, a conclusion moreover which was verified by other and independent trials.

As both hydrogen sulphide and sulphurous oxide are absorbed by potassic hydrate it was important to ascertain whether these gases were in sufficient quantity to affect the conclusion given above as to the amount of carbon dioxide. A portion of the gas collected in a clean tube was therefore submitted to a special examination. A pellet of ferric oxide formed upon the end of a platinum wire produced no effect at all, though kept in the gas for several hours. A similar pellet of manganese dioxide moistened with syrupy phosphoric acid likewise caused no perceptible effect, thus proving that these gases were not present in any measurable quantity.

An approximate estimation of the amount of water was made as follows: The U-tubes in which the water had been condensed were sealed after the gas had been thoroughly pumped out. The temperature of the freezing mixture was from -19° to -20° C., so that the tension of the residual vapor was less than one millimeter, which was confirmed by the reading of

the guage of the pump at the end of the operation. The connecting tubes were fused off and the portion containing the water withdrawn. The amount of liquid thus obtained was considerable. The tubes were carefully weighed, then opened, and after an examination of the liquid, thoroughly dried, and weighed again. The weight of the water in No. 1 was thus found to be 13.4 milligrams, in No. 2, 12 milligrams, corresponding respectively to 13.4 and 12 cubic millimeters at 4°. The volume of the quartz in the first instance being 8.25, and in the second, 7.41 cubic centimeters, we have for the amounts contained in one cubic centimeter of the mineral, 1.63 and 1.62 cubic millimeters respectively, no correction being made for temperature, as the results are only approximate. This would indicate a comparative uniformity in the distribution of the water, while the amount of the gas varies. But such a conclusion is at best doubtful, inasmuch as the darker quartz is not as thoroughly broken up by the heat as the lighter variety, and the refrigeration of the tube No. 1 was not made complete at first, so that some water doubtless escaped with the gas uncondensed.

A small portion of the water removed with a minute pipette was dropped upon red litmus paper, where it produced a strong but fugitive alkaline reaction, implying the presence of free ammonia. This was confirmed by adding Nessler's test solution to the remainder of the liquid in the end of the tube, in which it caused the characteristic yellow coloration, and, in one instance, a slight precipitate. Before the tubes were opened it had been noticed that the water, though to all appearance perfectly transparent and colorless, left a white deposit upon the glass where a drop of it had evaporated. When this was heated by the application of a small gas flame, it did not fuse, but appeared to shrink or to diminish in amount very slightly, while the glass around it and over it lost its transparency as if corroded. A similar but very slight action upon the glass where the moist gas had come in contact with it had previously been observed. This suggested the presence of fluorine. The glass of the tube in which the effect was most marked contained some lead, but the other showed it also to some extent. A special experiment with a tube free from lead, which had been most carefully cleaned, gave the same result, though in a somewhat less marked degree. Its appearance would be accounted for by the supposition that the water of the cavities contained some hydro-fluo-silicic acid in solution, resulting from the decomposition of silicon fluoride, or, as ammonia was also present, from an ammonium compound of the acid.

As was mentioned in a preceding paragraph, no evidence of the presence of a hydro-carbon compound was discovered in

the examination of the gas which had passed slowly through the cooled tubes. The tubes themselves, however, contained what appeared like minute drops of some oily substance, so small as to be scarcely visible without a lens, and quite insufficient for examination. In order to investigate this point more satisfactorily, as also to obtain a greater quantity of the residual gas left by absorption of the carbon dioxide, an experiment was made as follows: A bolt-head of porcelain, glazed interiorly, and having a capacity of about 300 cubic centimeters, was employed for the reception of the quartz, of which 196 grams, making 75.4 cubic centimeters, were used. It was arranged that after the air had been pumped out, the gas from the quartz should pass through a strong solution of potassic hydrate contained in a large U-tube, all connections being made with fused glass joints as before. The greater portion of the carbon dioxide was thus absorbed. Unfortunately just at the close of the operation a slight crack in the porcelain vessel admitted some air, but the tube leading to the pump was sealed immediately, so that the amount mixed with the gas was not too great to permit a quantitative examination of the gas to be made. A portion of the latter being transferred to the eudiometer, and just sufficient electrolytic gas being admitted to ensure combustion, the volume of the gas after explosion was found to be considerably increased, with the production of carbon dioxide. Repeated tests gave uniformly the same result, but the expansion was greater at first than after the gas had been kept for two days in the pump. This must be regarded as evidence of the presence of the vapor of some condensable hydrocarbon having a large number of carbon atoms in the molecule.

The quartz on heating entirely loses its color, the coarse powder which is left being almost snow-white. Now, in the experiment just described, a dark brownish deposit was formed in the tube leading from the bolt-head, and the potash solution after the passage of the gas had become brown, the color being almost exactly the same as that of the quartz before the heating. After standing a day or two a small amount of a dark brown, nearly black, substance separated out as a precipitate and the liquid lost its color. The potash solution was now decanted and the dark deposit examined. Treated with alcohol it dissolved but partially, communicating its color to the liquid, and taking on a tarry consistency. On evaporating the alcohol, the substance was volatilized by more intense heat, with a strong bituminous odor, very much like that given off by cannel coal when burning. The brown deposit in the tube also gave off the same odor when strongly heated. These results imply that the smoky color of the quartz is due to the

presence of a hydrocarbon of the nature of bitumen, which is driven off by heat, and the partial decomposition of which, at the high temperature reached, accounts for the heavy hydrocarbon found in the residual gas, or condensed upon the walls of the cooled tubes. These facts, moreover, are entirely in harmony with and confirm the conclusion of Forster* from an examination of the remarkable smoky quartz from the canton of Uri, that the color of the latter is due to the presence of some volatilizable hydrocarbon, though they do not directly connect the ammonia with the latter, as his observations appear to do.

After the operation just described had been concluded, some pure distilled water was introduced into the bolt-head, and after standing for some time was then withdrawn. Tested with argentic nitrate it gave a considerable precipitate of argentic chloride, while when examined spectroscopically it afforded satisfactory evidence of the presence of sodium, but of no other metal. The water previously examined was found to be free from both chlorine and sodium. The bolt-head had been scrupulously cleansed before use, and great care was taken in this, as in all the experiments, to prevent contact of the quartz with things that might communicate to it any impurity. This result would indicate that the cubical crystals observed by Mr. Hawes in some of the cavities were chloride of sodium. Search was also made for chlorine or chlorine compounds in the gas. A quantity of this freshly liberated was passed through distilled water. This, on the addition of argentic nitrate, was very slightly clouded, making the existence of a trace of some chlorine compound probable. Not unlikely a minute proportion of ammonium chloride is among the contents of the cavities.

The quantitative relation of the water to the gases obtained from the quartz may be made more evident if calculated for a temperature of 100° C. at which the former would be entirely converted into vapor. Taking the amount of water per cubic centimeter at 1.62 cubic millimeters as found above, this multiplied by 1694.3 gives 2.74 cubic centimeters for the volume of the water vapor at 100° . If we take the gaseous volume for one cubic centimeter of the quartz at 0.97 cubic centimeter, the result derived from No. 2 above, where the water determination was most satisfactory, the temperature of the room at the time of measurement being about 20° C., we have for the volume at 100° , neglecting the correction for the barometric pressure which was not greatly different from 760 mm., 1.23 cubic centimeters. Reduced to parts in 100 these volumes give

* Pogg. Ann., cxliii, 173, 1871.

CO ₂	30.48
N	0.50
H ₂ O	69.02
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	100.00

For the reasons mentioned above this must be regarded, so far as the water is concerned, as merely an approximate result.

For the gases alone, leaving out of view the bituminous matter, which is not known to be specially connected with the cavities in the material, and probably is not, we have the following summary :

CO ₂	98.33
N	1.67
H ₂ S	<i>trace</i>
SO ₂	"
H ₃ N	"
F	"
Cl?	"
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	100.00

The ammonia, if derived from the gas cavities, undoubtedly existed there in combination with the carbon dioxide, as ammonium carbonate. From the considerations mentioned above the fluorine and chlorine detected by the tests applied also represent compounds of these elements with some of the other substances present. The results of the investigation show that the contents of the cavities are chiefly water and carbon dioxide, with a small portion of nitrogen, thus essentially confirming the conclusions derived from microscopical examination.

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