PAPERS READ BEFORE THE CHEMICAL SOCIETY.

V.—On the Presence of Liquid Carbon Dioxide in Mineral Cavities.

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IN 1822 Sir Humphry Davy (*Phil. Trans.*, 1822, p. 367) investigated the contents of fluid-cavities in rock-crystals from different localities. His researches showed that in almost every case the liquid was nearly pure water, that the gas-bubbles were in two cases nitrogen in a greatly rarefied condition, but in one cavity the contents were retained under a pressure of about ten atmospheres; the composition of this gas has not, however, been recorded. In one single instance a quartz cavity was found to hold mineral naphtha, but no trace of any gas. Since that time fluid-cavities have generally been considered as holding pure water or weak saline solutions. About four years ago I bought from Mr. Norman, of the City Road, a microscopic slide of quartz, with fluid cavities. One good sized cavity was readily seen with a 2-inch objective; it exhibited when under the microscope the shape and appearance of Fig. 1. Its entire length was $\frac{1}{2}\frac{2}{3}$ of an inch, and its average breadth $\frac{1}{2}\frac{1}{30}$ inch. The liquid at once recognised is indicated by *b*.

Curious to see the effect of heat, I warmed the specimen over a lamp, until it was just too hot to be touched with comfort. On examin-

× 46 diameters.

FIG. 1.

FIG. 2.

ation, the liquid, to my surprise, was not to be seen, and the cavity under these circumstances, appeared like Fig. 2. As the temperature

to which the fluid had been subjected was but little above that of boiling water, I concluded that it had escaped from some minute and invisible opening; continuing, however, to observe the object until it became cold, I was gratified to see a sort of flickering movement within the apparently empty space of the cavity, followed by the replacement of the liquid, as at first. The extremely low temperature at which only the substance assumes the liquid state, made me at once desirous of ascertaining the exact conditions under which the liquid is dissipated and reproduced, for the researches of Prof. Andrews (*Chem. Soc. J.*, 1870, p. 74), "On the Continuity of the Gaseous and Liquid States of Matter," have told us that at a temperature of 88° F., or $30\cdot92^{\circ}$ C., liquid carbonic acid becomes a gas, and a pressure of even 300 or 400 atmospheres will fail to condense it to liquidity. I had almost completed my experiments, and had drawn my own conclusions, before finding that in 1823, Sir David Brewster (*Trans. of the Roy. Soc. of Edin.*, vol. x, p. 1) investigated the matter, and announced the discovery of some new liquids in the cavities of several minerals, which were characterised by the following properties: great mobility, slight adhesion to the walls of the cavities, especially their great expansion on warming, and their small refractive power. These liquids were colourless and transparent. When a cavity containing such a fluid was warmed, that which might be either a vacuity or an air-bubble, and was usually present, became smaller and smaller, by reason of the rapid expansion of the liquid, and at last finally disappeared. Brewster measured the temperatures at which this expansion of the fluid and disappearance of the bubble occurred, and it is desirable that these numbers should be quoted:—

1. Topaz, from New Holland	$74\cdot5^{\circ}$ F.
2. Blue topaz, from Aberdeenshire	74° to 82° F.
3. Colourless topaz, Brazil	$79\cdot5^{\circ}$ F.
4. Topaz, New Holland	$79\cdot75^{\circ}$ F.
5. Topaz, New Holland	$81\cdot75^{\circ}$ F.
6. Colourless topaz, Brazil	$83\cdot75^{\circ}$ F.
7. Chrysoberyl, Brazil	$83\cdot25^{\circ}$ F.
8. Quartz, from Quebec, different cavities	76° – 80° – 125° F.
9. Amethyst, Siberia	$83\cdot25^{\circ}$ F.

With but one exception it will be seen that these temperatures are all below 88° F. From the mean of many experiments it was found that the expansion of the liquids between 50° and 80° F. was 32 times greater than that of water, and that the refractive power was much less. Thus taking the refractive index of water at 1·3358, the liquid in topaz gave an index of 1·2946, and that in amethyst, 1·2106.

Now Simmler (*Pogg. Ann.*, vol. cv, p. 460), in 1858, offering an

interpretation of Brewster's observations, concluded that in some cases at any rate, the expansible liquid was carbon dioxide, and comparing Thilorier's co-efficient for this liquid with that which Brewster estimated from the expansion of the liquids in crystals, he found them to be almost identical; but it is doubtful, as will be seen presently, whether this can be regarded as satisfactory evidence of the nature of the liquid. In 1869, Sorby and Butler published conjointly an account of their researches on the structure of rubies, sapphires, diamonds, and other minerals. Further observations were made by them on fluid-cavities; the rate of expansion between 0° and 30° C. of the liquid contents of a cavity in sapphire was measured, and compared with that of liquid carbon dioxide, as determined by Thilorier, between these two temperatures, and found to agree so closely, that they believed the error might easily be due to a difference between the thermometers, and they concluded that their liquid was carbon dioxide (*Proc. Roy. Soc.*, vol. xvii, p. 299).

There is one important fact which cannot be reconciled with this conclusion, namely, that the fluid could be heated up to a temperature of 42° C. (108° F.). Thilorier has shown that the expansion of liquid carbon dioxide between 0° and 30° C., is such, that 100 volumes become 145. Sorby found that 100 volumes of the liquid he examined became 150° at 30° C., 174 at 31° C., and 217 at 32° C.

I will now return to my own observations. To determine the critical point of the new fluid, immersing the slide in water of known temperature, removing, wiping it hastily, placing it on the microscope stage, and instantly examining it, seemed preferable to any other mode of operating.

Specimen A. 1st Experiment.—The liquid in the two cavities had disappeared completely at 36° C.; the cavities appeared empty, but the liquid returned after a short interval. 2nd Experiment.—The liquid had totally disappeared at 31.5° , and returned on cooling. 3rd.—The liquid was invisible at 31° , but returned almost immediately after contact with the microscope stage. 4th.—At 31° there was no liquid to be seen, but it was observed to be filling in immediately afterwards. 5th.—Again at 31° did the liquid vanish. 6th.—At 30.75° the margin of the liquid was visible, but was not so sharply defined or so high up in the cavity as it afterwards became. 7th and 8th Experiments.—On being warmed almost to 31° , the liquid was still visible, but the margin became more distinct immediately afterwards. 9th.—At 31.5° , liquid invisible. 10th.—At 31° , upper portion of the liquid invisible; lower one not. 11th.—The liquid invisible at 31° , in the upper cavity, but not in the lower. 12th.—At 30.75° the liquid was seen in the larger cavity; the quantity, however, increased to treble immediately afterwards. 13th.—At 31°

the upper cavity appeared empty; the lower one full. It is evident, then, that the critical point lies between 30.75 and 31°C . The critical point of pure carbon dioxide, as determined very precisely by Andrews, lies at 30.92°C ., or very nearly 87.7°F . Hence I conclude that the identity of this liquid with carbon dioxide is established in a most convincing manner. It was noticeable that in whatever position the slide was placed, the liquid generally condensed on the same spot. Varying the method of heating the liquid by applying a hot wire to the surface of the quartz, I discovered what was at first by no means apparent, namely, that the upper and lower cavities were connected by a small fissure, and that water occupied the intervening space; the upper cavity was then seen to have the shape drawn in Fig. 3, and marked *a*. This presence of water, no doubt, determined the place of condensation, so that no matter what the position of the specimen, the carbon dioxide always condensed on the surface of the water, because of its adhesion to this fluid being greater than to the quartz. The concavely curved surface of the carbon dioxide is due to adhesion to

FIG. 3.

FIG. 4.

the moist sides of the cell; the convex curvature indicating where the two liquids are in contact is caused by the greater adhesion of the water to the same surface. Before the specimen had been heated in such a way as to drive the liquid from the smaller into the larger cavity, it contained more of the carbon dioxide than has collected in it since, and it was noticed on two or three occasions, that the action of heat was to diminish the gas-bubble very rapidly, by expansion of the liquid, until it had the appearance shown in Fig. 4; the bubble then as quickly increased in size, by *contraction of the liquid* to its original dimensions, when the source of heat was removed; likewise, when the heat was continued, the gas-bubble increased by *vaporisation of the liquid*, as in Fig. 2. The appearance caused by the expansion and contraction resembled the dilatation and contraction of the pupil of the

eye, and to this motion Brewster compares a similar effect of heat on the liquid in topaz.

Since the connection between the cavities has been made by excessive heating, the expansion and contraction cannot be shown; the liquid at once begins to vaporise, when warmed, and even boils, as is shown in Fig. 4. The following observation of Thilorier explains this. When a tube containing liquid carbonic acid is one-third full, at 0°C ., it constitutes a *retrograde thermometer*, in which increase of temperature is shown by diminished volume, consequent on the vaporisation of the liquid, and *vice versâ*, while if the tube be two-thirds full, a *normal thermometer* of great sensitiveness is the result, the liquid expanding by heat in this case (*Ann. Chim. Phys.* [2], lx, 249).

This furnishes some evidence against the liquid in sapphire, examined by Sorby and Butler, being carbonic acid, because the cavity was very considerably less than half-full at 0°C . hence, instead of the liquid expanding to fill the entire cavity, it should have vaporised, and become smaller in bulk.

Very careful observation several times repeated has shown that on the approach of a warm substance, causing the liquid in the larger cavity to be vaporised gradually, the curvature of the surface in contact with the gas becomes reduced very much, and at the same time rendered less plainly visible, as shown by *b*, Fig. 3.

There was also noticed a faint flickering shadow in the point of the cavity, when the liquid was about to condense.

I need scarcely remark that Professor Andrews has noticed such effects during the vaporisation and condensation of liquid carbon dioxide. In the same section of quartz there were observed upwards of fourteen smaller cavities, containing liquid carbon dioxide, together with water in different proportions. There are two such cavities shown in Fig. 1; in each case the space marked *a* contains carbon dioxide as gas; *b* the same substance liquefied and floating on the water, which being indicated by *c*, is seen to be occupying the remaining space.

As Thilorier has shown, the specific gravity of liquid carbon dioxide is 0.83 at 0°C ., and 0.6 at 30°C ., water being taken as unity. The constant position of this liquid in the cells being uppermost is in accordance with this. Its critical point was always within 0.5° of that of carbon dioxide.

The bubbles, or what appeared to be bubbles in water cavities were seen to be excited with a very lively motion on the approach of a hot wire, from which they were repelled to the farthest limits of their cavities. This movement was not seen when liquid carbon dioxide was present.

This curious motion has been observed by Mr. Sang, of Edinburgh, in the fluid cavities of calc-spar. A variety of experiments with thin layers of water and oil, and with capillary tubes containing these and other liquids, were conducted by himself and Dr. Hunter. They were unable to decide whether it is dependent on actual contact, and due to unequal heating of the adjacent solid, or owing to a true repulsion between the colder fluid and the warmer solid, independent altogether of contact. The instantaneous movement of the fluid, when a warm body is brought near to without touching the spar, favours the latter interpretation of the phenomena, but the former interpretation seems to be more in accordance with the other variations of the experiments.—(*Proc. Roy. Soc. of Edin.*, 1872-73, p. 126.)

Specimen B. Quartz. Many cavities were seen, containing water only.

Specimen C. The same.

Specimen D. Quartz. At first only three cavities containing two fluids were noticed; the lighter liquid was identified with liquid carbon dioxide. A closer examination showed an immense number of water cavities containing the two liquids, the carbon dioxide being often in extremely minute proportion.

Specimen E. A fine piece of quartz from Ceylon, cut by Mr. Norman for myself, proved to be crowded with fluid cavities, some of large size, but none containing anything beyond water.

Specimen F, quartz, kindly lent by Mr. Browning, contained a fine water cavity, with a bubble, which easily moved about as the microscope stage was rotated. There were noticed also several smaller cavities, three of which contained liquid carbon dioxide, as well as water.

Specimen G was a quartz crystal from Poretta, near Bologna, kindly placed at my disposal by Mr. Lettsom. It contained a large cavity, with only one liquid, and an easily movable bubble of air; this liquid was unaffected at 40° C., and therefore was not carbon dioxide. I was quite prepared to find the critical temperature of the liquid in mineral cavities varying a little from that of carbon dioxide, on account of admixture with atmospheric air, or some other incondensable gas: for on communicating with Professor Andrews, he kindly referred me to a recent continuation of his well known researches "On the Physical Properties of Matter," in which he has established the fact of the lowering of the critical point of carbon dioxide by such an admixture. I have not yet, however, found it necessary to refer to this.

Geissler has very ingeniously proved the presence of carbonic acid in quartz by breaking the specimen in a vacuum tube, and passing a spark through the liberated gas, which yielded the characteristic spectrum. I have come to the conclusion that the only practicable

method of identifying the liquid contents of mineral cavities is by means of the critical point, and I am inclined to believe that the liquid in some of Messrs. Sorby and Butler's specimens, though probably a liquid gas, is not carbon dioxide.* The refractive indices of such remarkably expansible liquids cannot serve to identify them, since they would alter so considerably by change of temperature: hence we cannot draw conclusions in the case of those liquids examined by Brewster, the temperature at which his observations were made being stated generally as about 60° F. Should I have the opportunity of examining other specimens of minerals, I am hopeful of being able to make some further observations of interest to the Society.

To explain the formation of these fluid cavities, the following evidence is of service. The silica is deposited from an aqueous solution, as shown by the water cavities found in great abundance in it, and moreover (following the reasoning of Mr. Sorby, applied to similar cases, *Phil. Mag.*, vol. xv, p. 153), at the time of its assuming the solid state, the solution endured a high temperature. The hot springs of Iceland and of New Zealand constantly give large deposits of silica; more particularly is this so in the latter country, where a considerable formation, resembling chalcedony, surrounds the hot lakes. Now Bischof's experiments (*Chemical Geology*, 1858; English edition, vol. i, pp. 6 and 7) have shown that even such intractable materials as granular limestone and powdered quartz yield carbon dioxide, in presence of boiling water. Hence the contact of a carbonate with a hot silica solution, would, under considerable pressure, liberate carbon dioxide, which would form cavities along with water, and on cooling condense to the liquid state. Judging from what takes place in the laboratory, when silica in solution is brought into contact with carbonates, namely, a gelatinisation of the substance, it requires no stretch of the imagination to believe that a similar action occurs in nature, causing the imprisonment of the liquid. The product in the one case is crystalline, and in the other colloid, but then this may result from the conditions of pressure under which the change takes place being different. It is indeed conceivable that the action of a carbonate on a silica solution under a high temperature and pressure may resemble in some degree the action of a crystal on a supersaturated solution.

* Since the reading of this paper, Mr. Butler has very kindly shown me his unique specimens collected from many thousands of sapphires and rubies. The observations I made led me at once to reverse this opinion. I hope to allude to this on another occasion.