

II.—*The Identification of Liquid Carbonic Acid in Mineral Cavities.*

By WALTER NOEL HARTLEY, F.C.S. (King's College, London).

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## PLATE CXXXII.

IN 1822 Sir Humphry Davy\* 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.

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, Pl. CXXXII. Its entire length was  $\frac{2}{3}$  of an inch, and its average breadth  $\frac{1}{30}$  inch. The liquid at once recognized is indicated by *b*.

Being acquainted with the experiments of Cagniard de la Tour, I resolved to repeat them with this specimen, and therefore, proceeding cautiously, warmed the slide over a lamp, until it was just too hot to be touched with comfort. On examination, 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 Professor Andrews,† “On the Continuity of the Gaseous and Liquid States of Matter,” have told us that at a temperature of 88° F., or 30°·92 C., liquid carbonic acid becomes a gas, and a pressure of even 300 or 400 atmospheres will fail to condense it to liquidity. This temperature is called the critical point. 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, and although other more promising methods have been tried, the results obtained have been less accurate.

1st Experiment. The liquid in the two cavities had disappeared completely at 36° C.; the cavities appeared empty, but the liquid

\* ‘Phil. Trans.’ 1822, p. 367.

† ‘Chem. Soc. Journ.’ 1870, p. 74.

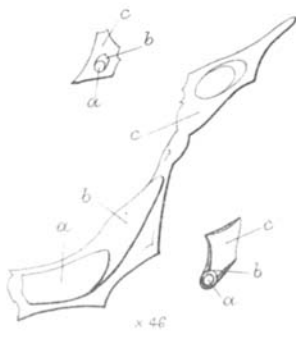


Fig. 1.



Fig. 2.

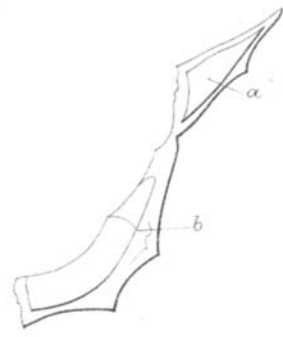


Fig. 3.



Fig. 4.

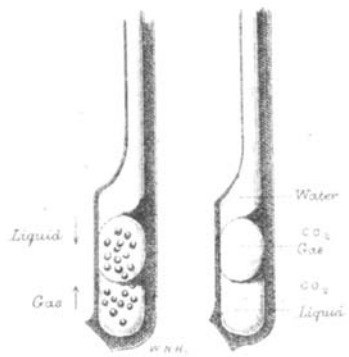


Fig. 6.

Fig. 5.



Fig. 7.

W. West 20° 1876.

Liquid Carbonic acid in micral Cavities.

returned after a short interval. 2nd. The liquid had totally disappeared at  $31^{\circ}\cdot5$ , and returned on cooling. 3rd. The liquid was invisible at  $31^{\circ}$ , but returned almost immediately after contact with the microscope stage. 4th. At  $31^{\circ}$  there was no liquid to be seen, but it was observed to be filling in immediately afterwards. 5th. Again at  $31^{\circ}$  did the liquid vanish. 6th. At  $30^{\circ}\cdot75$  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. On being warmed almost to  $31^{\circ}$ , the liquid was still visible, but the margin became more distinct immediately afterwards. 9th. At  $31^{\circ}\cdot5$ , liquid invisible. 10th. At  $31^{\circ}$ , upper portion of the liquid invisible; lower one not. 11th. The liquid invisible at  $31^{\circ}$ , in the upper cavity, but not in the lower. 12th. At  $30^{\circ}\cdot75$  the liquid was seen in the larger cavity; the quantity, however, increased to treble immediately afterwards. 13th. At  $31^{\circ}$  the upper cavity appeared empty; the lower one full. It is evident, then, that the critical point lies between  $30^{\circ}\cdot75$  and  $31^{\circ}$  C. The critical point of pure carbonic acid, as determined very precisely by Andrews, lies at  $30^{\circ}\cdot92$  C., or very nearly  $87^{\circ}\cdot7$  F. Hence I conclude that the identity of this liquid with carbonic acid 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 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 carbonic acid 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 vaporization of the liquid, as in Fig. 2. The appearance caused by the expansion and contraction resembled the dilata-

tion and contraction of the pupil of the eye. 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 vaporize, 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  $0^{\circ}$  C., it constitutes a *retrograde thermometer*, in which increase of temperature is shown by diminished volume, consequent on the vaporization of the liquid, and *vice versa*; 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.\*

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 vaporized 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. Professor Andrews has noticed such effects during the vaporization and condensation of liquid carbonic acid. In the same section of quartz there were observed upwards of fourteen smaller cavities, containing liquid carbonic acid, together with water in different proportions. There are two such cavities shown in Fig. 1; in each case the space marked *a* contains carbonic acid 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.

According to Thilorier, the specific gravity of liquid carbonic acid is 0.83 at  $0^{\circ}$  C., and 0.6 at  $30^{\circ}$  C., water being taken as unity. The constant position of this liquid in the cells being uppermost is in accordance with this.

Volatile fluids have been noticed in mineral cavities by Sir David Brewster,† by the late Mr. Alexander Bryson,‡ and by Messrs. Sorby and Butler, who came to the conclusion that the liquid in a particular cavity in a sapphire was really liquid carbonic acid, because it possessed a remarkable rate of expansion between  $0^{\circ}$  and  $30^{\circ}$  C. Thilorier has shown that the expansion of liquid carbon dioxide between  $0^{\circ}$  and  $30^{\circ}$  C. is such, that 100 volumes become 145. Sorby found that 100 volumes of the liquid he examined became 150 at  $30^{\circ}$  C., 174 at  $31^{\circ}$  C., and 217 at  $32^{\circ}$  C.§

Through the kindness of Mr. Butler, I have had the advantage of examining some of the best specimens from his unique collection of stones with fluid cavities, and I have no doubt that the con-

\* 'Ann. Chim. Phys.' [2], ix, 249.

† 'Trans. Royal Society of Edinburgh,' vol. x., p. 1, 1823.

‡ 'Proceedings of the Royal Society of Edinburgh,' 1860-1.

§ 'Proc. Royal Society,' vol. xvii., p. 299; also 'Transactions of the Royal Microscopical Society,' vol. i., p. 222.

clusion which he and Mr. Sorby arrived at was a just one. By a very simple contrivance I have been enabled to detect the presence of liquid carbonic acid in many very small cavities containing water. This consists of a glass tube about three-eighths of an inch in diameter and twelve inches long; it is drawn out to a jet at one end of about one-sixteenth of an inch aperture, the jet being bent at an obtuse angle. To prevent the glass being softened and bending when heated, it is covered for four inches in its central part by a piece of brass tube which slides on not too easily. The straight end of the tube is somewhat pointed, and passes through an india-rubber cork fitting into a universal joint upon a stand having a sliding motion in the upright so that it may be raised or lowered at will. This end of the glass tube which has passed through the cork has a piece of india-rubber tube slipped over it fifteen inches long, and to this is attached a ball syringe whereby air may be drawn in and discharged again. By heating the metal tube with a spirit lamp or Bunsen burner, the air discharged will be heated and may be directed on to the object while undergoing examination beneath the microscope without any displacement whatever, by which means a high power may be used for the examination of small cavities. By noticing the number of ballfuls of air necessary to vaporize a known specimen of carbonic acid, one may, if these be sufficient to vaporize the liquid in small cavities, be certain that the temperature is not greatly different. It is easy to demonstrate the presence of small quantities of carbonic acid mixed with water in cavities no larger than  $\frac{1}{1750}$  of an inch in their greatest diameter.

After carbonic acid has passed its critical temperature, if it be cooled suddenly it condenses with a motion resembling ebullition. This is best seen in deep cavities. Messrs. Sorby and Butler have observed this phenomenon.\* Having attentively studied it in different cavities, I have come to conclusions as to the meaning of it. When the gas is chilled, a sort of mist forms throughout the space; the individual spherules of this mist grow so large that they begin to touch each other, to coalesce, and to gravitate. They of course at the same time entangle gas, and as they descend to the lower part of the cavity the spherules of gas (bubbles) take an opposite direction; consequently when a portion of the liquid has collected at the lower end and gas at the upper, there are showers of liquid descending into and streams of bubbles rising out of the liquid. In two or three seconds the movements have ceased. In Figs. 5 and 6 are given representations of a fluid cavity in topaz belonging to Mr. James Bryson, of Edinburgh, to whom I am much indebted for allowing me to examine some of his valuable specimens. When at a temperature two or three degrees below the

\* 'Monthly Microscopical Journal,' vol. i., p. 222.

critical point, the liquid has the appearance seen in Fig. 5, but the boiling is shown in Fig. 6—the *spherules* called *gas* and *liquid* are passing in the direction of the arrows nearest them. The drawing, Fig. 7, represents a cavity seen in one of my specimens of quartz; the contents are undergoing the apparent boiling. The conditions favouring this singular mode of condensation seem to be, first, that the greater part of the carbonic acid shall be in the liquefied state at ordinary temperatures so that the liquid expands greatly on approaching the critical point; second, that the cooling shall be sudden.

Cavities containing liquefied carbonic acid may be divided into two classes, *wet* and *dry* cavities, according to the absence or presence of water. The appearance of the liquid in a dry cavity differs much from that in a wet one. Thus in a dry cavity the liquid presents a convexly curved surface to the gas, in a moist one a concave surface. While the carbonic acid in sapphires and rubies seems generally to be dry, that met with in quartz and other minerals is more frequently wet.

. Another means of ascertaining the critical temperature of the liquid in fluid cavities was resorted to. It consisted in making a water-tight cell with glass sides, which would contain besides the mineral under examination the bulb of a small thermometer three inches in length and graduated into one-tenths of a degree Centigrade, between 29° and 35° C. An inlet and outlet tube of india-rubber conveyed a stream of warm water, forced through the cell from a small flask by means of the pressure of a large india-rubber finger-pump or syringe. The entrance and exit for air to and from the syringe was by valves in different branches of a T tube.

The walls of the cell were made by boring a hole an inch in diameter through an india-rubber cork of the diameter of  $1\frac{1}{4}$  inch. Two perforations one-eighth of an inch in diameter were made in the side of this to admit the water tubes, and a third for fixing the thermometer in. The glass slides placed top and bottom of the ring were firmly fixed by passing stout india-rubber bands over them. When the cell was placed on the microscope stage, a powerful Coddington lens was so arranged in position near the thermometer that without the slightest movement the cavities could be watched through the microscope with the left eye, and simultaneously the mercury in the thermometer with the right. The cavity under examination was so arranged that it appeared just upon the edge of the lens. Admirable though this arrangement seems, it does not answer quite so well as one might expect. The volume of water in the cell is so small, that it changes temperature more readily than the slowly conducting mineral.

My original plan of immersing the mineral in a considerable volume of water at temperatures just above and below the critical

point, may be improved upon by placing the specimen in a glass cell with parallel sides and immersing this in water of known temperature; on removing this for examination, the sides of the cell may be wiped dry without fear of the mineral losing an appreciable amount of heat. Being now engaged in the study of other rocks and minerals, details regarding these had better be left for another communication. I have elsewhere shown\* the nature of the chemical reaction which would most probably yield quartz crystals with carbonic acid cavities, but this explanation could not be applied to the formation of topaz and sapphire.

\* 'Journal of the Chemical Society,' February 1876.

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