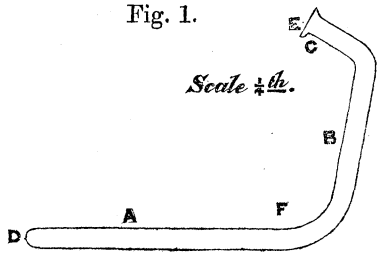
VI. *On the Properties of Liquid Carbonic Acid.* *By* G. Gore, *Esq.* *Communicated by Professor* Tyndall, *F.R.S.*

Received January 17,—Read January 24, 1861.

The following experiments were undertaken with a view of adding to the scanty stock of information which at present exists respecting the properties of liquid carbonic acid.

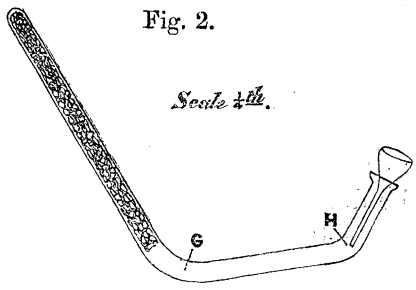
To ascertain the action of the liquid acid upon solid substances, the following method was in nearly all cases adopted. A piece of flint-glass tubing, 12 inches long, $\frac{3}{8}$ths of an inch external diameter, and $\frac{7}{32}$nds of an inch internal diameter, was bent to the annexed figure; the part A being about $6\frac{1}{2}$ inches, the part B about 4 inches, and the part C about $1\frac{1}{2}$ inch long. In pieces of glass tubing the bore is rarely of one uniform diameter, and in these experiments the smaller diameter was always employed for the end C, otherwise the tubes were liable to burst at that part. The end D was closed by fusion, and the end E was formed with a flange and left open. It is essential that the ends and bent parts of the tubes be well annealed immediately upon their formation.

Fig. 1.



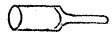
The lower limb A of the tube was filled to the point F with moderately small fragments of sesquicarbonate of ammonia, and the last fragments fixed firmly in their position by pushing a slender rod of gutta percha into the tube forcibly against them. If the carbonate was employed in a state of powder or very small fragments, the tubes frequently became choked by sulphate of ammonia, and the generation of carbonic acid was soon completely arrested. The tube being now placed in the position of figure 2, was filled from G to H with pure sulphuric acid by means of a small glass funnel.

Fig. 2.



A taper plug $\frac{3}{4}$ths of an inch long was made by softening the end of a solid rod of gutta percha, $\frac{7}{32}$nds of an inch thick, in boiling water, and allowing it to cool. Two notches were cut transversely to each other across the larger end of the plug to receive binding wires, and the smaller end of the plug was coated with melted paraffin to protect the gutta percha from contact with the liquid carbonic acid. A small glass cup, of the form and dimensions of figure 3, was made of thin glass tubing, and fixed (by previously heating the small and solid end) in a small hole previously made in the centre of the small end of the plug.

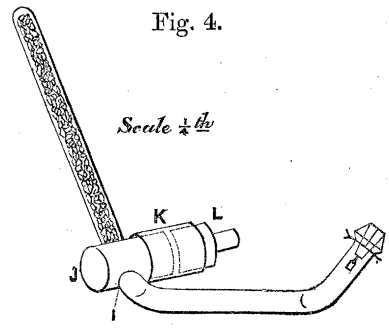
Fig. 3.



A small quantity or fragment of the solid substance to be subjected to the action of the liquid acid was placed securely in this tube, the sides of the plug welted with a saturated solution of paraffin in chloroform, and the stopper strongly forced while slippery into the mouth of the tube, taking care not to jerk or force any of the sulphuric acid into contact with the alkaline carbonate. The plug was then fastened down tightly by means of the two transverse binding wires, each of which was composed of a twisted strand of four "No. 30" copper wires. It is important that a plug of the exact diameter be carefully selected.

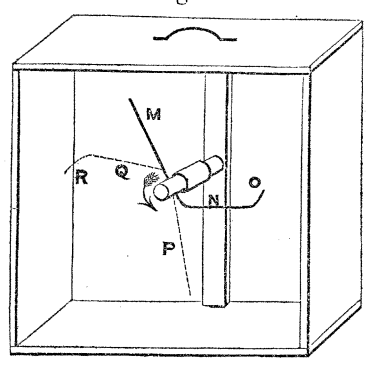
For convenience of manipulation, the tube was placed in the hole of a transversely perforated cork; the cork fitted rather loosely in a short piece of brass tube; the tube fixed upon a wooden peg, as shown in figure 4, in which I is the hole, J the cork, K the brass tube, and L the wooden peg with a prolongation of less diameter. The cork could thus be readily turned upon its axis, and the glass tube placed and retained in various positions.

Fig. 4.



As a protection from accidents by explosion, and for further convenience of manipulation, a moveable cage or box was constructed for each tube; its sides, top, and bottom were made of wood, and its front and back were of fine iron wire-gauze; its dimensions were 12 inches high, 12 inches wide, and 5 inches from front to back; the pieces of gauze were nailed to the wood on one of their vertical edges only, so that they served the purpose of doors. A small vertical strip or piece of wood was fixed at the back part of the box, with a hole at its middle part to receive tightly the small projecting part of the horizontal peg L, fig. 4. An inspection of fig. 5 will make more clear the whole arrangement.

Fig. 5.



The tube, charged with its acid and carbonate, is placed in the frame in the position shown by the lines M, N, O in fig. 5; and the operator having previously protected his hands by thick leather gloves, his eyes by a pair of spectacles, and keeping the wire-gauze door between his face and the tube, occasionally turns the supporting cork upon its axis in the direction of the arrow, so as to cause a little of the acid to flow upon the alkaline carbonate; this must be done with cautious watching and in very small quantities at the commencement, otherwise the bubbles of gas which ascend through the oil of vitriol will carry some of the latter acid into contact with the contents of the little glass cup. The process requires much watching; and if at any time the chemical action is allowed to progress too rapidly, the generating tube is liable to burst in consequence of the heat evolved.

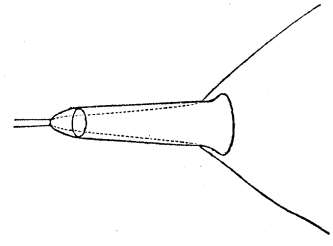
The tube is thus occasionally turned until after the lapse of several hours it has

acquired the permanent position indicated by the dotted lines P, Q, R in fig. 5, when a piece of cotton-wool should be placed upon the stoppered end and saturated with ether, so as to distil off the liberated carbonic acid, and the application of ether be repeated at intervals until nearly the whole of the carbonate is decomposed and the stoppered end of the tube is full of liquid carbonic acid. If the experiment has succeeded well, a length of the tube, equal to 1 or $1\frac{1}{4}$ inch, will, in cold weather, be filled with the liquid acid. By occasionally (once a day or less) applying the ether to the stoppered end of the tube, that part may be kept full, or partly full, of liquid acid for a long time; I have kept it in this manner during several months.

The most frequent cause of failure is clogging of the tube with sulphate of ammonia; it is rarely that a leakage occurs at the stopper; and the most frequent causes of explosion are, too rapid generation of the gas, and increased temperature of the atmosphere. It is highly advisable never to examine a charged tube without the wire-gauze intervening to intercept fragments of glass, and to use a large moveable screen of glass to protect the eyes from projected oil of vitriol. Nearly all the explosions which occur take place during the process of generating carbonic acid, or within a few days afterwards. The proportion of tubes fractured or burst at different stages of the process is about one-third.

In some experiments, where electric sparks were passed through the liquid acid, two longitudinal cuts, $\frac{1}{16}$th of an inch deep, were made by a knife on opposite sides of the gutta-percha plug, extending from its smaller nearly to its larger end, before inserting it in the tube; and two fine platinum wires inserted into the cuts and secured very carefully by means of a heated penknife; the inner end of the plug was then coated with melted paraffin, the plug wetted with paraffin solution, and inserted in the usual manner. The wires extended nearly $\frac{1}{2}$ an inch within the tube, and were imbedded for about $\frac{1}{4}$ of an inch next to the plug in paraffin, the remaining part served for the electrodes. (See fig. 6.) After inserting the plug and securing it by the binding wires, the whole of the outer end of the plug was freely coated with melted paraffin, to insulate more perfectly the electrodes from each other.

Fig. 6.



In a first experiment, with the electrodes $\frac{1}{12}$th of an inch asunder, and a sensitive galvanometer in the circuit, very feeble and variable conduction occurred with 30 SMEE'S batteries; but this was found to arise from absorption of a trace of sulphuric acid or saline liquid which had adhered to that end of the generating tube. In a second experiment, the electrodes being $\frac{1}{10}$th of an inch apart, and the liquid acid below 32° FAHR., not the slightest conduction occurred with 40 SMEE'S batteries; and sparks from a RUHMKORFF'S coil which passed through $\frac{3}{8}$ths of an inch of cold air would not pass through the liquid acid. In a third experiment, with electrodes about $\frac{1}{70}$th of an inch apart, sparks from the coil, which were passing freely through $\frac{9}{32}$nds of an inch of cold air, occasionally passed through the cold

liquid acid and exhibited a pale blue colour. And in a fourth experiment, the tube being charged with sulphuric acid diluted with an equal bulk of water, and with an anode of wood-charcoal $\frac{1}{8}$th of an inch distant from a cathode of platinum wire, and 40 SMEE's batteries, faint conduction occurred, probably in consequence of the presence of a trace of water from the dilute acid; the deflection of the galvanometer needles was 21°, but the conduction entirely ceased in twelve hours, and then, upon connecting the electrodes with the secondary wire of the coil, no sparks passed between them.

These experiments show that liquid carbonic acid is a strong insulator of electricity, and that when prepared with concentrated oil of vitriol, and with the precautions stated, it is free from water, sulphuric acid, and sulphate of ammonia. As further proofs of the freedom of the liquid acid from oil of vitriol and water, it may be mentioned,—1st, that dry extract of litmus exhibited no signs of redness by immersion in the liquid acid; 2ndly, a small fragment of glacial phosphoric acid did not appear at all liquefied, nor lost the sharpness of its edges after being immersed several weeks; and 3rdly, anhydrous sulphate of copper did not become at all blue in the liquid acid.

The following are the results obtained with various solid substances immersed in the liquid acid; some were immersed during several months, many during several weeks, and a few only during several days. The temperature of the liquid acid was generally a little below that of the external atmosphere. Wood-charcoal remained undissolved and unaltered. Anhydrous boracic acid in powder slightly dissolved. White phosphorus slightly dissolved. Glacial phosphoric acid, green solid biphosphide of hydrogen, and ordinary yellow sulphur, undissolved and unchanged. (Bisulphide of carbon absorbs *gaseous* carbonic acid.) Sulphide of phosphorus, and selenium, undissolved and unaltered. Iodine, biniodide of phosphorus, and iodide of sulphur, all dissolved in small quantities (iodine the most freely), and formed red or reddish solutions. Anhydrous hydrochloric acid (prepared by first half-filling the limb A of the tube with sesquicarbonate of ammonia, and then filling the remaining half with hydrochlorate of ammonia) did not produce two strata in the condensed liquid, but imparted to the liquid a brownish colour in each of two experiments, probably by acting upon the gutta-percha stopper. Pentachloride of phosphorus dissolved slowly and formed a colourless liquid. Metallic potassium and metallic sodium slowly acquired bulky white coatings of alkali. Phosphide of sodium, fused chloride of sodium, phosphide of calcium, anhydrous chloride of calcium, bright metallic aluminium, crystals of silicium, anhydrous silica, silico-fluoride of potassium, and arsenic acid, all remained undissolved and unaltered. Terbromide of arsenic and terbromide of antimony, each dissolved slightly. Hydrated crystals of monosulphate of iron became dehydrated and fell to pieces as a white powder, and did not dissolve. Anhydrous sulphate of copper remained white and undissolved; the hydrated salt became white. Protochloride of mercury and nitrate of silver remained undissolved and unaltered.

Cyanide of mercury, oxalic acid, benzoic acid, succinic acid, pyrogallic acid, gallic acid, tannic acid, tannic acid and potash, paraffin, and cocostearic acid remained undis-

solved and unaltered in appearance. Pitch softened and partly dissolved. Napthalin dissolved in small quantity. Gutta percha; the liquid acid dissolved out the dark-brown colouring matter, and left the gutta percha undissolved, and much more white. India-rubber remained black externally, but became perfectly white through the whole of its thickness; on removing it from the acid it suddenly swelled to a large size, and then gradually shrank in a few hours to its original dimensions, and afterwards (in a few days) slowly regained its original colour. Common yellow resin dissolved slightly. Gum-copal remained undissolved. Camphor dissolved rapidly and formed a clear colourless liquid. (Spirit of turpentine dissolves more than its own volume of *gaseous* carbonic acid.) Spermaceti, indigo, pyroxylin, and solid extract of litmus remained undissolved and unaltered. Gamboge dissolved in minute quantity and formed a slightly-yellow liquid.

These experiments show that liquid carbonic acid is a chemically inert body, and is also a very feeble solvent of substances in general, and is not deoxidized by any of the ordinary deoxidizing agents except the alkali-metals.

The way to discharge the tubes of their contents is to support them over a gutta-percha vessel within the safety-cage, or behind a double screen of glass and wire-gauze, and, protected by gloves, cut off the binding-wires with a pair of nippers; then, if the stoppers are not blown out, pour boiling water upon them. Sometimes the explosion occurs immediately upon cutting the wires, but in most cases it requires the application of the hot water; this is a most convincing proof of the tightness of the stoppers, as the pressure of liquid carbonic acid (according to different authorities) varies from 500 to 1100 pounds per square inch, according to the temperature of the atmosphere. The tubes nearly always break by the violence of the recoil. In many instances a safer plan was adopted; the wires were not cut, but a current of steam was directed upon the stoppers until they were expelled; the discharge was then less sudden, and the tubes were less frequently broken. It would probably be a still further improvement if the lower end of the tube was closed by a stopper in a similar manner to the upper end; the contents of the tube might then be discharged at that end, and the substances operated upon would then be exposed to less risk of being lost, and of being brought into contact with the acid and saline matters by the discharge.

In an endeavour in one experiment to liberate the enclosed acid *gradually*, a small hole was made lengthwise through the stopper before inserting it; a piece of glass tubing, half an inch long and possessing a very fine bore, barely visible to the unassisted eye, was fixed in the hole at the small end of the stopper, and a small metal plug fixed in the outer end of the hole; and after generating the liquid acid the metal plug was withdrawn; nearly the whole of the liquid carbonic acid escaped through the fine aperture of the glass in about four seconds, and left the remainder in a solid state in the tube. In two instances, tubes with cracks in them half an inch in length, withstood the full pressure of the acid during several days.