

that, from experiments made with this tube with Mr. De La Rue's chloride of silver battery on a former occasion, and quite independently of the present question, it was estimated that a current having an electromotive force of 400 volts was necessary to effect a discharge.

Other tubes were tried, and were illuminated in the same way.

When the tube was placed in the magnetic field, the discharge underwent the modifications described by Plücker, by Hittorf, and by others. But it may be mentioned as a result of the extraordinary strength of the field here employed that, whenever the tube was so placed that the direction of discharge made any considerable angle with the lines of magnetic force passing through it, the discharge was completely extinguished. When the tube was removed to a weaker part of the field, the discharge reappeared distorted in form, and altered in colour, in a manner known to those who have experimented in this direction.

February 26, 1880.

THE PRESIDENT in the Chair.

The Presents received were laid on the table, and thanks ordered for them.

The following Papers were read :—

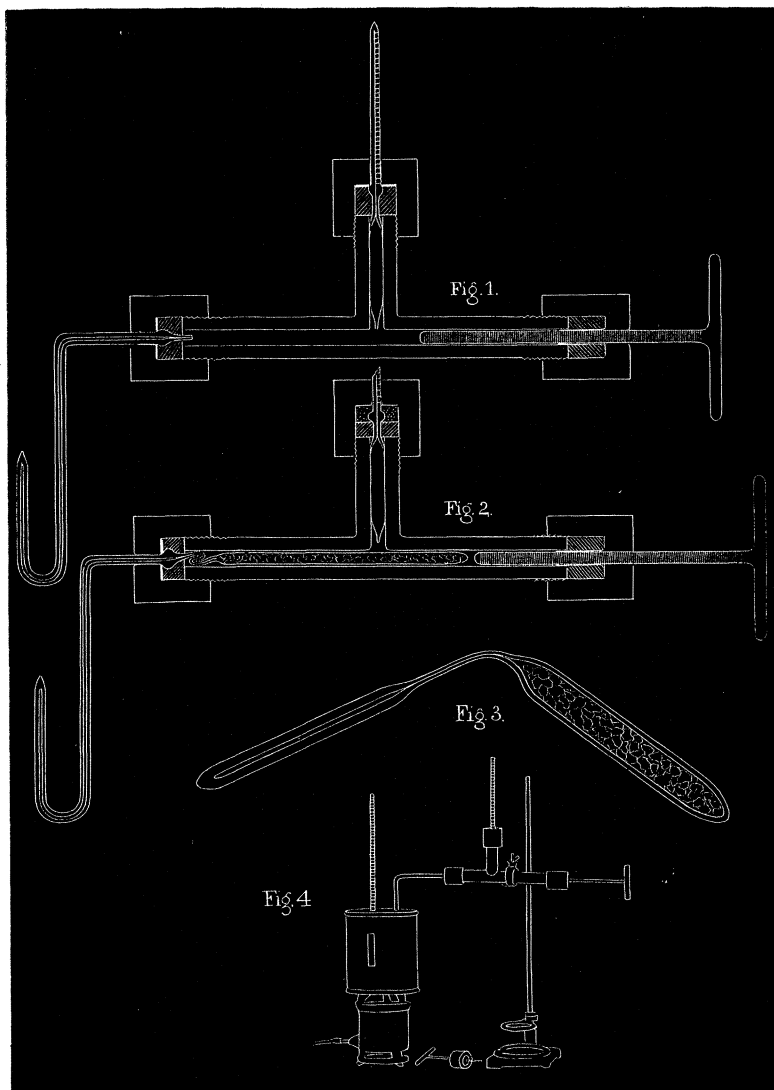
- I. "On the Solubility of Solids in Gases." By J. B. HANNAY, F.R.S.E., F.C.S., and JAMES HOGARTH, F.C.S. Communicated by Professor G. G. STOKES, D.C.L., LL.D., Sec. R.S. Received February 14, 1880.

The research which we now have the honour of submitting to the Royal Society, and of which a preliminary notice was published in the Society's Proceedings,* was instituted with the view of throwing some further light upon what Dr. Andrews calls the "critical state" of matter. In his famous Bakerian lecture, after a very careful discussion of the question, Dr. Andrews says :† "Carbonic acid at 35·5° C., and under a pressure of 108 atmospheres, stands nearly midway between the gas and the liquid, and we have no valid grounds for assigning it to the one form of matter any more than to the other."

* "Proc. Roy. Soc.," vol. xxix, p. 324.

† "Phil. Trans.," 1869, p. 588.

This conclusion is based on the relation of volume to pressure for different temperatures, and on the failure of optical tests to show any distinction between gas and liquid when pressure is applied above the



critical temperature. It occurred to us, that some knowledge might be gained by examining the solvent properties of some fluid for a non-volatile solid, in the passage of the solvent from the liquid to the

gaseous state. The property of dissolving solids being supposed peculiar to liquids, it seemed to us that on passing through the critical state there would be a precipitation of solid, or if on the other hand no separation occurred, a further proof of the perfect continuity of the gaseous and liquid states would be presented. To put the matter to the test, a solution of potassic iodide in alcohol was prepared, and a strong tube filled to about one-half with the solution. After sealing, the tube was placed in an air-bath, and heat applied. No precipitation of solid could be seen even at a temperature of 350° C., more than 100° C. above the critical point of alcohol.

For the examination of the phenomena of solution some form of pressure apparatus was necessary, so that the volume of the fluid experimented on might be altered at pleasure. After several experiments we adopted a modified form of Dr. Andrews' apparatus, which allowed us to change an experimental tube in a few minutes, and showed no sign of leakage at the highest pressure reached (fig. 4). A section of the apparatus is shown in the annexed engraving. It is made of wrought iron tubing such as is used in hydraulic machinery, about $\frac{1}{2}$ inch internal, and 1 inch external diameter. The length of the apparatus is 9 inches, and there is a side tube welded on, measuring about 3 inches, for the insertion of the manometer tube. On the ends of the tube are screwed strong caps, also of wrought iron; Through one of these the pressure screw works, the others serve for the admission of the experimental and manometer tubes. The distinguishing feature of the apparatus is the packing for the screw and tubes. It consists of a solid plug of india-rubber, about $\frac{1}{2}$ inch thick, placed in the hollow cap, so that it serves both for packing the screw or tube, and for making the joint between the cap and the iron tube tight. To prevent the pressure screw from cutting the india-rubber, a lining of thin leather, well soaked in lard, was placed between it and the rubber. The tubes were similarly packed, and to keep them from being forced out through the aperture in the cap, a thickening was made in the glass by fusing and pressing together, and between this bulbous part and the iron a strong leather washer was placed. In some cases, when a very high pressure was wanted, the tube was cemented in with oxychloride of zinc, which effectually prevented it from coming in contact with the iron cap. With this mode of packing the pressure screw did not require to be very fine, the one commonly used being $\frac{3}{4}$ inch in diameter and screwed 30 threads to the inch. The only limit to the pressure was the frailty of the glass tubes; we have, however, attained a pressure of 880 atmospheres as shown by an air manometer, and even at this enormous pressure the screw could be freely moved in either direction without leakage. The apparatus was as tight with mercury as with water, so that there was no necessity for using two liquids as in Dr. Andrews' machine. When

a high temperature was required, the experimental tube was bent over as shown in the drawing, and passed into an air-bath formed of two concentric iron cylinders. The cylinders had mica windows, through which the experiment could be observed, and to ensure perfect regularity of temperature, the inner one was lined with cement about $\frac{1}{2}$ inch thick. As in most of our experiments it was quite unnecessary to know the pressure, a simple straight tube was used instead of the T-shaped one described. It was screwed to fit the same caps, and from its simplicity made a very convenient and efficient apparatus.

The experiments with the sealed tube showed us that no deposit of solid occurred above the critical point. With the assistance of the apparatus just described, we were able to show a crystal of potassic iodide dissolving in alcohol gas (using the word gas as Dr. Andrews proposes for a fluid at any temperature above its critical point). Having fixed a tube (internal diameter .75 mm., external 7 mm.), in the apparatus previously filled with mercury, some alcohol was sucked in by gradually withdrawing the pressure screw. By a further withdrawal of the screw, the little thread of alcohol was moved inwards past a constriction made in the glass tube near the end, and a small fragment of fused potassic iodide dropped in so as to rest on the narrow neck. Sufficient heat was now applied to boil the alcohol and expel the air, and the end of the tube strongly sealed with the blow-pipe. The tube being placed in its position in the bath, heat was applied and the pressure regulated so as to keep the alcohol from passing round the bend into the other limb of the U tube. The tube and its contents were thus raised to a temperature of 300° C. (the critical point of alcohol as will be shown is 234°·4 C.), the crystal never having come in contact with the liquid alcohol. Pressure was now applied until the alcohol was reduced to about the volume occupied by it while still liquid, when the fragment of iodide was seen to dissolve gradually and completely. On withdrawing the screw slowly no deposit occurred even when the volume was very considerably increased, but by taking off the pressure very rapidly a crystalline film appeared on the glass, and in some cases, a cloud of fine crystals floating in the menstruum. These crystals could be easily redissolved by again increasing the pressure. The deposit most frequently occurred just at the surface of the mercury, and this we ascribe to a local rarefaction caused by the slightly higher temperature of the mercury. The fact of the existence of solvent power above the critical point being established by this experiment, we next sought to examine the phenomenon by using other solvents and solids. The sealed tube method was found most convenient for this purpose, an experiment with the pressure apparatus being resorted to when we wished to vary the volume. The tube was filled from half to two-thirds with the

solution to be tested, and by a few experiments the strength of the solution was so adjusted that no separation of solid took place, when the tube was completely filled by expansion.

The behaviour of a solution of potassic iodide we have already described. Bromide of potassium gave a similar result. The solubility of chloride of calcium in alcohol was found to be uninterrupted by the passage of the alcohol through the critical state. Cobaltous chloride (anhydrous) remained in solution at 320°C . the highest temperature reached in this experiment, and the beautiful blue colour of the solution was unimpaired. Ferric chloride (sublimed) gave a yellow fluid at a temperature of 260°C . This yellow colour rapidly disappeared, and a reddish-coloured powder separated out, which remained insoluble on cooling. On opening the tube a strong ethereal odour was perceived. This was most probably due to the formation of ethylic chloride. Some peculiar phenomena observed when heating the ferric chloride solution deserve description. At a temperature of 120°C . a very strongly coloured liquid layer appeared at the bottom of the tube, while the uppermost layer was perceptibly paler. As the temperature rose the two layers gradually mixed and the fluid was quite homogeneous at and above the critical point.

A solution of ferric chloride in ether was distinctly coloured at least 30°C . above the critical point, but the colour gradually faded, and did not return on cooling. The separation and redissolving of part of the ferric chloride occurred also with ether.

A solution of sulphur in carbon disulphide showed no separation of sulphur when raised 50°C . above its critical point. Of course sulphur at this temperature is a liquid, but its vapour tension is comparatively so small that its solution is worth recording. Selenium also remained in solution in carbon disulphide above its critical point, and separated out in part when the solution cooled. Chemical action evidently took place in this experiment, for on evaporating a portion of the solution after heating, a reddish-yellow residue containing selenium was obtained. The liquid had a distinct horse-radish smell, and on burning gave a dark stain on a piece of porcelain held in the flame. Sulphide of selenium was most probably formed. An attempt was made to dissolve cadmic sulphide in carbon disulphide, but without success. In an experiment with metallic arsenic and carbon disulphide the arsenic seemed to dissolve, but as an orange-coloured film appeared on the glass on cooling, we are inclined to doubt its solubility. When some sulphur was enclosed in the tube with arsenic and carbon disulphide, and the temperature raised above the critical point, solution occurred, and when the temperature was allowed to fall a separation of dense liquid drops took place at the critical point. At a lower temperature these solidify and form reddish-yellow crystals. The apparent solubility of arsenic was thus probably due to its con-

version into a sulphide, and the subsequent solution of the sulphide formed.

Carbon tetrachloride was also tried as a solvent, but as the number of substances soluble in this fluid is very small, we can only record a few negative experiments. Cupric chloride did not dissolve, but appeared to be acted on chemically above the critical point, its colour changing to brown. Chromic chloride showed no sign of solution. Zinc oxide did not dissolve, but at a temperature 20° or 30° above the critical point a sudden chemical change occurred, and as a result the critical point was found to be lowered from 280° C. to about 200° . On cooling some transparent globules were seen, and on opening the tube there was an outrush of gas. The transparent globules dissolved in water, and were found to be chloride of zinc.

The use of water as a solvent was quite out of the question, both on account of its high critical point and the corrosion of the glass tubes, so that we were debarred from the use of the liquid whose examination promised most.

The mixture of light paraffins known as paraffin spirit was tried as a solvent for some organic substances. A solution of resin in this liquid remained perfectly bright and without sign of separation at a temperature of 350° to 360° , almost 100° above the critical point.

The examination of liquids to determine their critical temperature and pressure was not exactly in the line of our research, but as Cagniard de la Tour's numbers, so far as we are aware, are the only ones on record, we have made a number of experiments in this direction. To obtain accurate measurements of pressure is a matter of very great difficulty, and as for our purpose these were not required, it would have made our research unnecessarily tedious to attempt it. Our numbers are as follows:—

	Alcohol.	Carbon disulphide.	Carbon tetrachloride.
Mean temperature	$234^{\circ}\cdot6$	$272^{\circ}\cdot96$	$277^{\circ}\cdot9$
Number of experiments	47	12	4
Probable error of a single experiment	$2^{\circ}\cdot06$	$1^{\circ}\cdot34$	$0^{\circ}\cdot69$
Mean pressure	65 atmos.	77·9 atmos.	58·1 atmos.
Number of experiments	14	12	4
Probable error of a single experiment	1·0 atmos.	1·5 atmos.	·55 atmos.

The alcohol used had a specific gravity of $\cdot7949$ at $15^{\circ}\cdot5$ C. In the carbon tetrachloride experiments the mercury was attacked, but our numbers were taken as quickly as possible, and before chemical action had taken place to any great extent.

Cagniard de la Tour gives the following results for alcohol and carbon disulphide:—

Alcohol	258°·7 C.	119 atmospheres.
Carbon disulphide.	275°·0 C.	77·8 „

The differences between Cagniard de la Tour's numbers and our own in the case of alcohol are no doubt due to the difficulty of obtaining that body anhydrous. As will be seen from the density given, the alcohol used in these experiments contained only a very small quantity of water, and was indeed practically anhydrous.

To determine whether the presence of a solid in solution affected the critical temperature and pressure, a cold saturated solution of potassic iodide in alcohol was prepared. Experiments with this solution gave as the average of three trials—temperature 237°·1 C., pressure 71·1 atmospheres. The probable error of a single experiment is for the temperature 0°·37 C., for the pressure 0·5 atmosphere. The exact amount of solid present in solution when the readings were made it was impossible to determine; for in altering the volume, so as to observe the critical point, a small quantity was deposited on the glass just at the end of the mercury column. To make sure that some salt did remain in solution, we brought the mercury column up so as to cover the crystalline film, and after carefully examining to see that no solid particles were above the mercury, we allowed the fluid to cool under pressure. When cold, the end of the capillary was broken off, and the liquid, which had been shut off by the mercury from contact with the crystalline deposit, received in a watch glass. On evaporation it gave an appreciable residue. These experiments seem to show that a liquid has its critical point raised by the solution in it of a solid.

As the solubility of potassic iodide in alcohol is very slight (1 part in 40 at 13°·5 C.) we thought it advisable to try a solution of chloride of calcium in alcohol, so that the effect of solution on the pressure and temperature might be shown in a more marked degree. On heating a cold saturated solution of calcic chloride (anhydrous), a dense liquid layer was observed to form at the bottom when the temperature reached 230° C.; at 240° C. the line separating the lighter layer of liquid from vapour was very indistinct, and could not be distinguished at all above 250° C.; at 255° C. the dense layer dissolved, but re-appeared when pressure was taken off. When the volume was again reduced, it re-dissolved, and at 270° C. expansion caused a deposition of crystals. In this experiment there was no sharp critical point, and no pressure readings were taken. A dense layer, it will be remembered, was also noticed in the ferric chloride experiment. A combination of the chloride with part of the alcohol evidently occurs, and at a higher temperature diffusion takes place until the fluid is quite homogeneous.

While working with cobaltous chloride an interesting question presented itself to us—Is the absorption spectrum of a substance dissolved in a fluid above its critical point the same as in liquid solution or in

the solid state? To answer this question, a solution of anhydrous cobaltous chloride was sealed in a tube as before, and its spectrum observed while heat was applied. No change could be detected in its passage through the critical point, and a careful comparison of the spectra of the same solution at 15° C. and at 300° C. showed no difference beyond the fainter and more nebulous character of the bands caused by expansion. The position of the bands was not changed. Chloride of cobalt, however, was not well fitted for our purpose, the measurement of the bands being rather uncertain on account of the nebulous nature of their edges. At the suggestion of Professor Stokes, we turned our attention to the product of the decomposition of chlorophyll by acids. The beautiful spectrum of a solution of this body in alcohol was quite permanent, even at a temperature of 350° C., although when heated in air it decomposes below 200° C. A direct comparison of the hot and cold solutions failed to show any change in the position of the lines.

A good opportunity of testing the question further seemed to be offered by the blue solution of sodium in liquefied ammonia, described by Gore.* To prepare this, we first tried compression of the gas by the pressure apparatus, but the quantity of liquid got by this method was too small for experiment. We next tried a combination of Gore's method with the pressure apparatus. A tube, shaped as in the drawing, had the wide part charged with chloride of calcium saturated with ammonia, and the end sealed. By applying slight heat, the air was expelled by the liberated ammonia. A small piece of sodium was then placed in a pocket near the end of the experimental tube, and, after sealing, the tube was placed in the pressure apparatus and surrounded with mercury. The iron tube was now heated by flaming with a Bunsen, and the experimental tube cooled in a freezing mixture. Distillation of ammonia commenced, and when a sufficient quantity of liquid was obtained the pressure screw was advanced, until, coming in contact with the wide tube, it broke the narrow neck joining it with the experimental tube, and allowed the mercury to rush in and enclose the liquefied ammonia. Further pressure brought the ammonia in contact with the sodium and solution commenced, but an unforeseen difficulty caused the experiment to fail, for the sodium solution coming in contact with the mercury was rapidly decolorised by it. It was, therefore, necessary to dispense with the use of mercury. Several methods were proposed, and we finally arrived at the following simple and effective one. A piece of tubing, about $\frac{1}{4}$ inch diameter, was joined to a piece of marine barometer tubing, and just beside the join the latter was drawn out to an exceedingly fine bore. The wide tube was now charged with ammonia-saturated chloride of

* "Proc. Roy. Soc.," vol. xxi.

calcium and the end sealed. A small piece of solid paraffin was then dropped into the capillary tube so that it lay next the drawn out portion. When all air was expelled by heating slightly, a few fragments of sodium were placed in the tube and the whole sealed. The arrangement is shown in the Plate, fig. 3. The end containing the sodium being placed in a freezing mixture, the wide tube was carefully heated until sufficient ammonia was distilled over. When re-absorption commenced the fragment of paraffin was melted by the application of a very small flame, and capillary attraction caused it to run into the fine bore, where it solidified and prevented any passage of ammonia. The tube now containing a solution of sodium in ammonia, was next cut off near the join and the end sealed in the blowpipe flame, the paraffin plug preventing outward pressure. On heating the tube thus prepared in the air bath, the blue colour disappeared before the critical point was reached, and the loss of colour was accompanied by the deposit of a white powder. It was at first thought that this was due to the presence of water in the ammonia, but many experiments, in which every care was taken to have the ammonia perfectly dry, failed to give any other result. In one case only, when the temperature had been raised very rapidly, did the blue colour remain above the critical point, and this only for a few seconds. This chemical action most probably consists in the formation of sodamide, and this view is supported by the fact that one of the tubes opened under mercury gave a quantity of gas not dissolved by water.

As the solution of an alkali metal seemed best adapted for spectroscopic examination, we made an attempt to dissolve sodium in compressed hydrogen. For this purpose a tube with a very large expansion was made, and filled with carefully dried hydrogen. While the stream of gas was still passing, a small piece of sodium was placed in a pocket at the end of the tube, and the aperture closed before the blowpipe. In this experiment we used no manometer, our intention being to increase the pressure slowly and to make it as great as possible. After about half an hour, at a pressure so far as we could judge of about 300 atmospheres, the mercury, which had never come in contact with the solid sodium, was observed to become thick and pasty. At this point the tube burst (no further pressure had been put on) close to the iron cap, and on examining the broken piece small semi-solid globules of mercury were observed adhering to the glass, marking the highest point to which the mercury had reached. These were taken out and placed in water, when small bubbles of gas were observed rising from them. In another experiment a small rod of sodium, quite filling the capillary bore, was observed to be gradually corroded, until only a shell adhering to the glass remained. The very frequent bursting of the tubes, made more frail by the reduction of

lead oxide, due to the action of hydrogen on the hot glass, makes the demonstration of the solubility of sodium in hydrogen exceedingly difficult, but the phenomena described, we are convinced, can only be explained on this hypothesis. In several experiments we have seen little pieces of sodium slowly disappear, leaving only the thin shell of oxide formed round them while they were being placed in the tube. There seemed in many cases to be a sudden chemical action, for the tube burst, not while pressure was being applied, but often several minutes after the pressure screw had been advanced. A beam of light passed through the tube showed no absorption when examined by the spectroscope.

Having described our experiments, it remains only for us to consider the state of the solvent at a distance above the critical point. We cannot do better than quote Dr. Andrews' consideration of the subject. He says,* "What is the condition of carbonic acid when it passes at temperatures above 31° C. from the gaseous state down to the volume of the liquid without giving evidence at any part of the process of liquefaction having occurred? Does it continue in the gaseous state, or does it liquefy, or have we to deal with a new condition of matter? If the experiment were made at 100° C., or at a higher temperature, when all indications of a fall had disappeared, the probable answer that would be given to this question is, that the gas preserves its gaseous condition during the compression, and few would hesitate to declare this statement to be true, if the pressures, as in Natterer's experiments, were applied to such gases as hydrogen or nitrogen. On the other hand, when the experiment is made with carbonic acid at temperatures a little above 31° C., the great fall which occurs at one period of the process would lead to the conjecture that liquefaction had actually taken place, although optical tests carefully applied failed at any time to discover the presence of a liquid in contact with a gas. But against this view it may be urged with great force, that the fact of additional pressure being always required for a further diminution of volume, is opposed to the known laws which hold in the change of bodies from the gaseous to the liquid state. Besides, the higher the temperature at which the gas is compressed the less the fall becomes, and at last it disappears." Leaving out of consideration the solubility of sodium in hydrogen, we have had iodide of potassium in solution in alcohol at temperatures much too high for measurement by the mercurial thermometer, and which may safely be estimated at 150° C. above the critical point ($=380^{\circ}$ C.). We think therefore we are justified in saying that at this high temperature the solvent was truly gaseous. An examination of Dr. Andrews' curves for carbonic acid shows us that at a temperature only 16° C. above the

* "Phil. Trans.," 1869, p. 575.

critical point, the sudden fall in volume corresponding to the boiling line has disappeared, and although the curve does not coincide with the air curve, it is regular and shows no sign of liquefaction having occurred. Our experiments were made at temperatures further removed from the critical point than this, and as no sudden change in solubility could be detected in passing from the liquid state to these high temperatures, we conclude that, in these experiments, we have further proof of the perfect continuity of the liquid and gaseous states, and also a complete proof of the solubility of solids in gases.

II. "On the Artificial Formation of the Diamond." By J. B. HANNAY, F.R.S.E., F.C.S. Communicated by Professor G. G. STOKES, D.C.L., &c., Sec. R.S. Received February 19, 1880.

(Preliminary Notice.)

While pursuing my researches into the solubility of solids in gases, I noticed that many bodies, such as silica, alumina, and oxide of zinc, which are insoluble in water at ordinary temperatures, dissolve to a very considerable extent when treated with water-gas at a very high pressure. It occurred to me that a solvent might be found for carbon; and as gaseous solution nearly always yields crystalline solid on withdrawing the solvent or lowering its solvent power, it seemed probable that the carbon might be deposited in the crystalline state. After a large number of experiments, it was found that ordinary carbon, such as charcoal, lampblack, or graphite, were not affected by the most probable solvents I could think of, chemical action taking the place of solution.

A curious reaction, however, was noticed, which seemed likely to yield carbon in the nascent state, and so allow of its being easily dissolved. When a gas containing carbon and hydrogen is heated under pressure in presence of certain metals its hydrogen is attracted by the metal, and its carbon left free. This, as Professor Stokes has suggested to me, may be explained by the discovery of Professors Liveing and Dewar, that hydrogen has at very high temperatures a very strong affinity for certain metals, notably magnesium, forming extremely stable compounds therewith.

When the carbon is set free from the hydrocarbon in presence of a stable compound containing nitrogen, the whole being near a red heat and under a very high pressure, the carbon is so acted upon by the nitrogen compound that it is obtained in the clear, transparent form of the diamond. The great difficulty lies in the construction of an

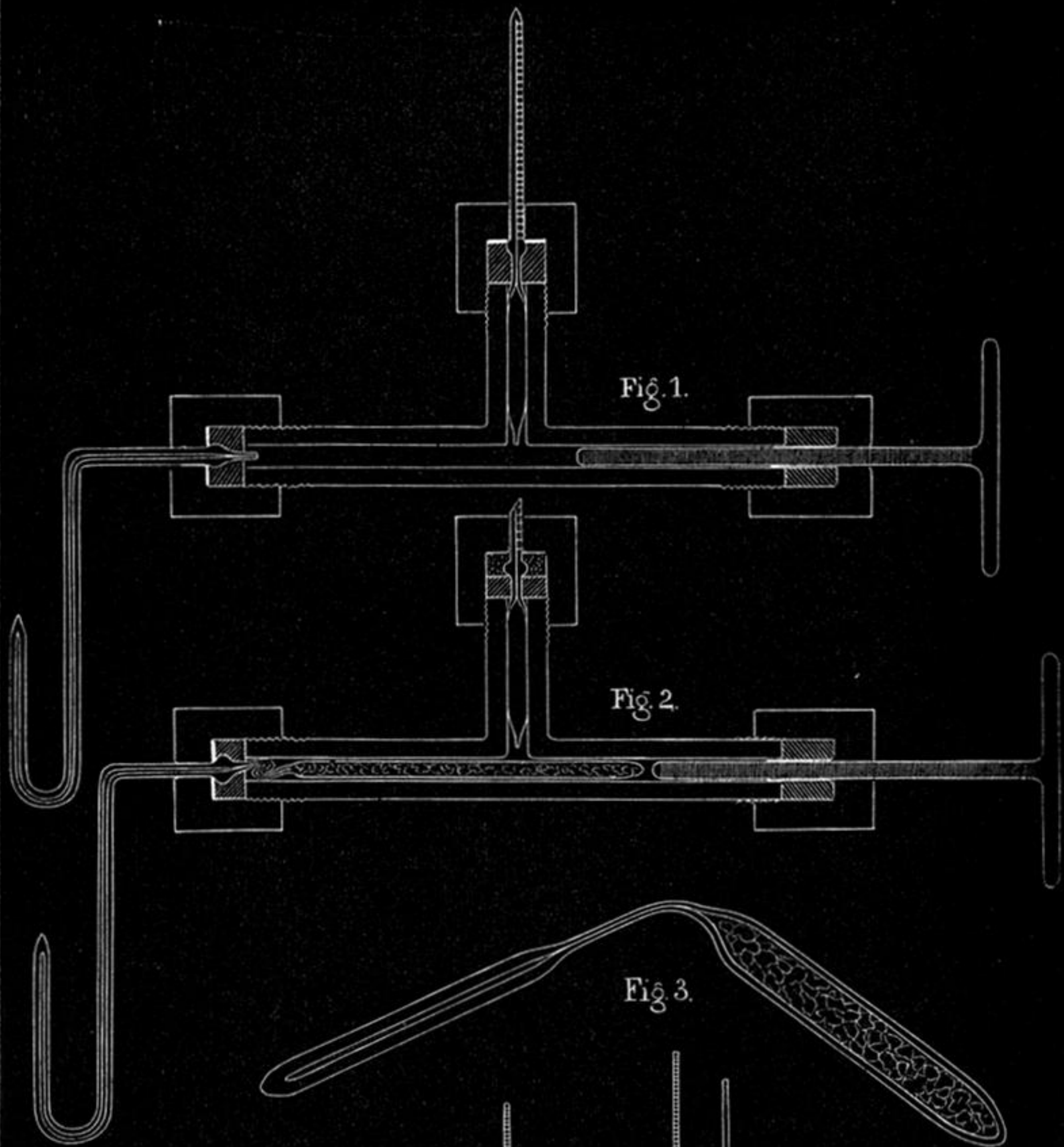


Fig. 4

