THE CRYSTALLIZATION OF CARBON-DIOXIDE, NITROUS OXIDE AND AMMONIA.

BY H. E. BEHNKEN.

A DISCUSSION by Professor Gill, of the similarity of the chemical compounds of carbon and silicon, during a study of the quartz crystal, suggested the problem of determining the crystallization of the dioxide of carbon.

Several methods for securing crystals were considered and tested.

1. The solution of the gas in a liquid of low freezing point and a microscopic study of the crystals formed on reducing the temperature below that of the sublimation of CO_2 crystals. This was tried with petroleum ether as the liquid, but no satisfactory study of the resulting cloudiness was made.

2. The freezing of the liquified gas.

3. The solution of the gas in some cold liquid of low boiling point and the production of crystals on evaporation.

4. The production of crystals by direct freezing. Two schemes were proposed; either to pass the gas through a very cold liquid, or to allow it to come in contact with a cold solid surface. The latter proved successful.

The chief difficulty was met in the elimination of water vapor, the crystals of which might not be distinguishable or whose presence in quantity would make results uncertain. While this would appear a simple matter, with the powerful dehydrating reagents available, it was not found possible to prevent the formation of some ice crystals.

The essentials of the apparatus, as suggested by Professor Shearer, consisted of a metal cup into which the gas was directed, a microscope for studying the crystals, and a Dewar cylinder of liquid air to be used as the freezing agent; the cooling was controlled by means of a copper rod attached to the bottom of the cup and immersed in the liquid air. By varying the distance between the surface of the cold liquid and the cup, the temperature of the freezing space could be regulated.

Difficulty in illuminating the field on an opaque surface in a Dewar tube caused the substitution of a glass freezing plate. By means of a series of reflections, the light could be sent up through the plate.

An arc light (*A*), Fig. 1, was used as the source of illumination, the heating effect of which was avoided by passing the light through the water cell (*W*). The light was then converged (*C*) and reflected down into the Dewar by the mirror (*M*).

The light in the Dewar (*D*) was reflected at right angles by a prism (*P*) to a small concave mirror (*R*) set in the freezing tube (*T*). This mirror was not actually made, being in fact a piece cut out of a broken silvered Dewar bulb. It was set at approximately 45° as shown, being held in place by pieces of tubing, cut at an angle, and slipped inside the main tube. After this reflection, the light passed through the freezing stage (*S*) to the microscope.

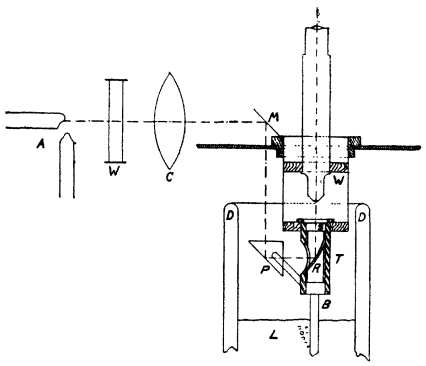

Fig. 1.

A, arc; *W*, water; *C*, condensing lens; *M*, mirror; *DD*, Dewar cylinder; *P*, reflecting prism; *L*, liquid air; *T*, freezing tube; *R*, concave mirror; *S*, glass freezing stage; *W*, wooden disk piston on microscope.

What has been spoken of as the "freezing tube" is a short length of Tobin bronze tubing, about 7/8 inch outside and 5/8 inch inside measure. A rabbet was cut around the top to hold the piece of glass on which the crystals were to form; this was a microscope cover glass, cut down to fit. To this tube was connected a brass rod (*B*) which dipped into the liquid air (*L*) and by means of which the temperature could be controlled. A hole was bored in the side of the freezing tube to admit the light to the mirror inside.

To exclude the outside air with its attendant moisture, the freezing plate was enclosed in a chamber made of a four-inch length of 2½ inch thin glass tubing. The bottom of this chamber consisted of a wooden disk, cemented in with shellac, and thoroughly coated with the same. Through this disk, a hole was bored which admitted the freezing tube, a collar soldered to it holding it up. This hole being eccentric, allowed a limited horizontal shifting of the field under the microscope by turning the chamber. To allow of the focusing of the microscope, it was equipped with a fitted wooden disk covered with vaseline (*W*) which, by acting as a piston in the chamber, kept out the air completely. The CO_2 was admitted by a glass tube passing through a hole cut in the glass wall of the freezing chamber; all the space in this hole not occupied by the tube was filled with a lump of vaseline. To aid in keeping this chamber dry, a small boat filled with P_2O_5 was introduced.

Some difficulty was encountered in keeping the reflecting prism and other surfaces free of frost. This was partially overcome by enclosing the entire system so that the evaporated liquid air, which was practically dry, filled the enclosure. Even with this, frost slowly gathered and the prism must be warmed at intervals.

To allow the raising and lowering of the Dewar without admitting outside air, a square telescope box was used. The entire arrangement

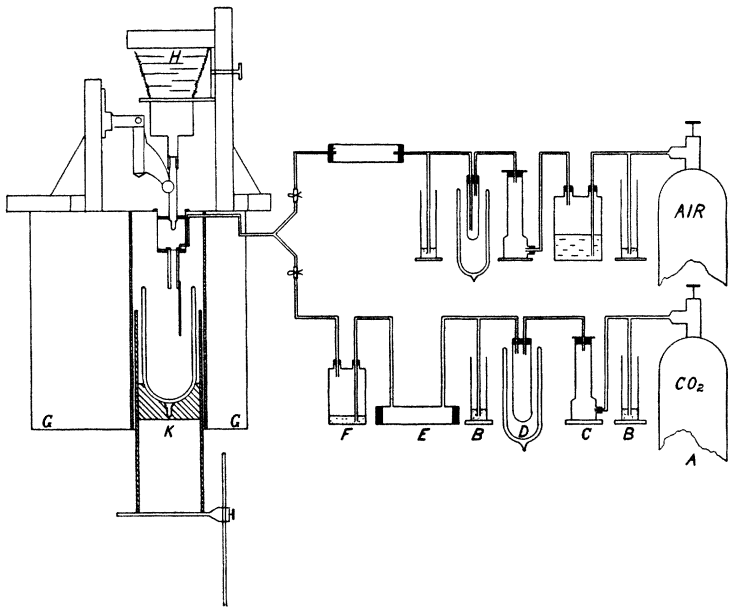

Fig. 2.

(*A*) Tank of liquid CO_2. (*B*) Safety by-passes, T tubes with end dipping below surface of mercury in cylinder. The depth of immersion determines safety point. (*C*) Calcium chloride drying tower. (*D*) Test-tube with Dewar tube of liquid air in which it can be immersed to various depths. Dewar tube is on adjustable stand. (*E*) Drying tube filled with glass wool dusted with P_2O_5. (*F*) Bottle with small amount of mercury by means of which the rate of flow of the gas could be watched. (*G*) Large glass case serving as enclosure and as support for bulk of apparatus. (*H*) Camera on adjustable stand. (*K*) Telescoping box holding large Dewar cylinder; supported by stand under table which rests on floor. Inner box of telescoping box passes through hole in table.

was enclosed in a large glass case, which, beside serving as an enclosure, supported the microscope, camera, freezing chamber, and reflector as shown in Fig. 2. The outer, fixed tube of the telescoping box extended from the top of the table to the top of this case, and was equipped with a strip of glass through which to observe the height of the Dewar. The inner, sliding tube, which was closed by the base carrying the Dewar,

passed through a hole cut in the table to fit it, but allow it to slide up and down. A quantity of $CaCl_2$ in the outer case helped to keep the moisture down. The tube carrying the Dewar was supported by an adjustable iron stand resting on the floor.

Liquid CO_2 in cylinders was allowed to vaporize and the gas was purified by freezing it in a tube immersed in liquid air, on allowing the solid to sublime slowly, the rate being controlled by the depth of immersion, a high degree of purity was secured.

The greatest problem was the elimination of moisture from the gas. This has not been entirely mastered, for ice made its appearance in spite of all precautions. The CO_2 from the tank was first passed slowly through a $CaCl_2$ drying tower 12 inches high. It was then frozen in liquid air as described above. Before the gas secured by sublimation was admitted to the freezing chamber, it was passed through a 14-inch condenser tube filled with glass wool well filled with P_2O_5. As an additional precaution a small boat of P_2O_5 was placed in the freezing chamber. But in spite of all precautions, fairly large ice crystals were formed after passing the gas into the chamber for a half hour at a temperature too high to form CO_2 crystals. The fact that long crystals (needles) of this ice grew on top of the layer of phosphoric acid formed over the P_2O_5 in the boat showed the inefficiency of this agent under these circumstances, or when long runs are made. As the temperature rose, the unchanged P_2O_5 absorbed this moisture. Of course this did not occur in the short runs necessary for the production of the CO_2 crystals.

To test the efficiency of the drying arrangement and to make sure that CO_2 was not necessary to the production of this form, a duplicate freezing and drying train was built, through which air purified by lime, solid KOH, and KOH solution was passed. This pure air produced the same crystals, indicating that moisture alone was the source. This train was connected to the other by a Y tube and was useful in flushing the freezing chamber and also, by supplying air during cooling, preventing the drawing in of atmospheric air by contraction of the gas in the chamber.

In forming the crystals, different procedure was found to give great difference in results. If a considerable stream of CO_2 was allowed to flow into the chamber before and during the cooling, the plate would be covered rapidly, when the right temperature was reached, by crystals in fern leaf forms. These would quickly unite and produce a solid covering. If the plate were barely cold enough, they would begin to sublime on shutting off the CO_2. If the plate was first well cooled, and the stream was turned directly on it, the same forms were produced.

The best results were obtained by delivering the gas tangentially at the edge of the cooling stage. In this way, the gas would be delivered on the plate gradually, although it might come out of the tube at a greater rate. Much of it was frozen on the brass, sometimes producing a transparent glaze. This procedure caused the gas reaching the glass plate to be gradually cooled, maintaining more even conditions and tending to better crystal formation.

The best crystals were obtained by reducing the plate to a moderately cold condition and then admitting the gas in *limited* quantities. A quantity of solid CO_2 was first collected, the non-freezing portions being allowed to escape to the air by one of the safety vents. The solid CO_2 was then allowed to sublime slowly, flushing out the apparatus. The CO_2 was then shut off and the pure air turned into the chamber, sweeping out all residual gas. The Dewar cylinder having been filled with liquid air by means of a tube passing through a hole in the box, was then raised to bring the level of the liquid air about three inches below the freezing plate. The passing of the dry air prevented the drawing in of the outer air on cooling. The air is now shut off, the CO_2 being turned on at the same time. Only a small amount must be admitted at this time, as otherwise too many crystals are formed. They seem to flash into existence. By feeding the CO_2 very slowly or in a series of very small puffs, crystals could be grown to any size. If it is fed too rapidly, crystals with re-entrant angles are produced. After the formation of the crystals, the CO_2 is shut off and the Dewar is raised to cool the plate still further and so prevent sublimation. Often a "snowstorm" of small CO_2 crystals occurs, covering and obscuring the larger crystals and causing a mottled appearance of the pictures. After the temperature had risen high enough to vaporize the CO_2, small heaps of ice remained which, on further warming, ultimately sublimed in the dry atmosphere or melted when large. None of such size, however, were produced in making the regular runs, as the quantity of gas used was small and the water accordingly minute. Considerable time elapsed between the evaporation of the CO_2 and the disappearance of the water, showing the difference in temperature.

If the entire chamber is too cold, and the CO_2 is turned on, a veritable CO_2 snowstorm occurs which is worthless for our purpose. If the plate alone is very cold and a great puff of gas is turned in, "spiderweb" forms may be produced.

Some clear patches were often observed containing no crystals. These were caused by a sort of explosion. Unfortunately, the eye was drawn to a point only after the explosion was over, so that what had really taken

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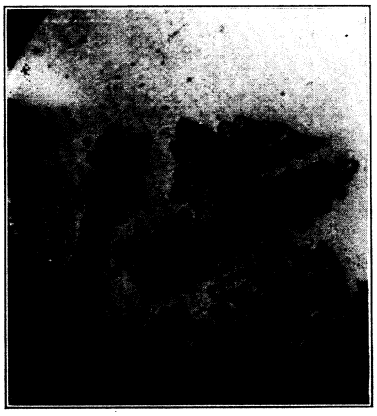
Fig. 3.



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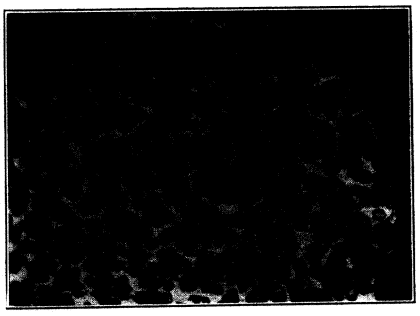

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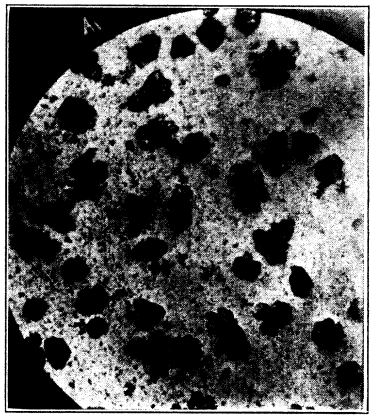

Fig. 6.

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PLATE I.

place could not be learned. It was probably caused by the cooling of a large CO_2 crystal causing its breaking due to contraction. It might be a change of crystal form taking place with a change of temperature. A comparison of three successive plates showed the result of these explosions. Clear spaces in locations where large crystals were shown on plates taken first were noted on the subsequent ones. The sharpest, best-formed crystals seemed most likely to rupture in this manner.

The CO_2 crystals appear to be combinations of cubes and octahedra. Many of the triangular faces with the corners off were clearly seen. Some square faces with the plain triangles are also observed.

On analysis, the gas purified in the way described showed an impurity of 0.16 per cent. unabsorbable in KOH. This percentage has been corrected for vapor tension of water, and calculated on the basis of zero water content of the gas analyzed. The unabsorbed residues of all the determinations were run together and the sum used in obtaining this result.

The work so far described was done in the summer session of 1909 and 1910. The following results were obtained in the summer of 1911.

It was deemed essential to use polarized light in the further study of the crystal forms. A polarizing nicol introduced into the freezing tube below the plate would, in all probability, have broken on cooling. Some compact device that would survive cooling, and if broken could be replaced readily, was needed. A pile of microscope cover glasses ground to fit replaced the concave mirror below the freezing plate. The reflecting prism was moved down and so set that the angle of incidence on the pile of plates was 57°; the plates being set at an angle of 33° in the tube so as to send the polarized beam directly upward. The rest of the lighting device was unchanged. The analyzer was a regular microscope nicol set above the ocular. A diaphragm made of black paper was used below the first reflector so as to prevent stray light and the inside of the Dewar was coated with dead black to prevent reflection. The freezing chamber and the end of the objective were blackened to avoid reflection of light upon the crystals. The small amount reflected from the object lens could however be noticed.

The darkening of field and CO_2 crystals was simultaneous, and no optical peculiarities could be noted. Some excellent crystals, perfectly clear and with perfect faces were produced.

Professor Gill was kind enough to visit the laboratory and to make a study of the CO_2 crystals. He declared them to be undoubtedly isometric and their forms to be combinations of cubes and octahedra.

USE OF THE APPARATUS FOR OTHER GASES.

Ammonia (NH_3) and nitrous oxide (N_2O)[1] were used because their freezing points were near that of CO_2.

The N_2O was dried by passing it through P_2O_5, the same agent being used in the boat in the freezing chamber. The NH_3 was dried by passing it through a tube filled with metallic sodium threads formed by squeezing the metal through a die. The boat was filled with scraped sodium. For this method of drying, I am indebted to Dr. H. B. Browne.

The N_2O crystals formed readily when no moisture was present. When moisture was present or when the gas was fed too rapidly, lint-like forms were produced. On close examination, the threads looked somewhat like coral; on the whole, a formless bunch.

The leaf forms were very easily obtained, but the separate forms photographed were produced only with very slow feeding of the gas after the plate was extremely cold.

Ammonia crystals were very hard to obtain. If the plate were not cooled to a very low temperature the gas first liquified, and then froze into a solid mass. It was found necessary to submerge the freezing tube until the prism and the polarizing plates were almost completely submerged in the liquid air, whose level was not more than 2.5 cm. below the freezing plate. As a result, the polarization was poor and could not be used.

When the pure gas was fed into the cold chamber, a great mass of "ammonia snow" looking much like a mass of cotton was produced. It was very much like the "coral" formed by N_2O. Its method of growth was interesting. A cloud of tiny crystals would appear and fall on the plate. Others would fly into the field and alight on the first comers as though attracted by electric charge. This piling up in single column would go on with occasional branching, each fiber meanwhile swaying about wildly in the field of the microscope.

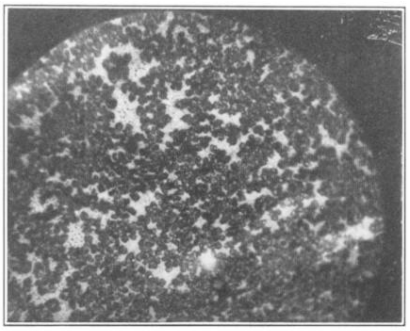
The crystals photographed were obtained by diluting the dry NH_3 with pure, dry air, obtained from the auxiliary system and feeding this diluted gas slowly into the cold chamber. In both NH_3 and N_2O isometric crystals were obtained. The photographs shown were selected from a considerable number to show the general appearance of the plates. The results obtained with these gases would indicate that with sufficient care in manipulation, the apparatus might be used for determining

[1] N_2O, melting point 102.3°, boiling point 89.8°; NH_3, melting point −75.5°, boiling point −38.5° (760 mm.). (Landolt-Bornstein's tables, third edition.)

the crystal form of many gases whose freezing points are only moderately low.

The writer is indebted to Professors Gill, Gage and Chamot for advice, and to Professor Shearer, under whose direction the work was carried out, he wishes to express his gratitude.

CORNELL UNIVERSITY,
August, 1911.



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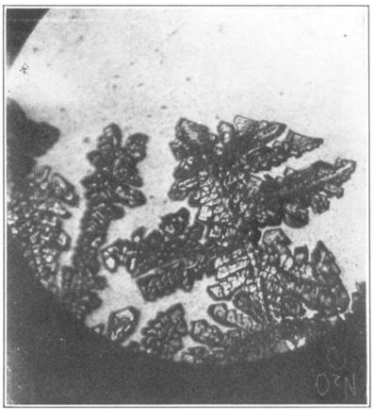

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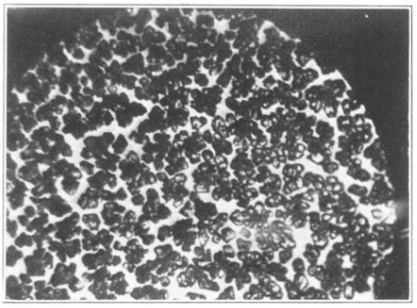

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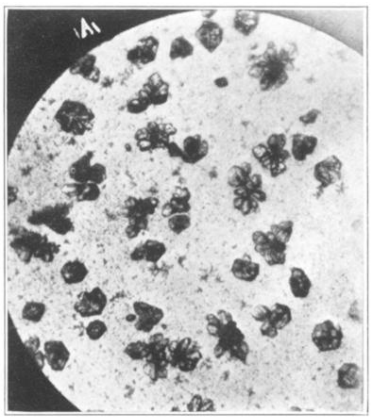

Fig. 6.