PURE CARBON DIOXIDE.[1]

By W. P. Bradley and C. F. Hale.

Received March 26, 1908.

Pictet[2] has shown that the presence of a small quantity of impurity in solution in a liquid exerts many times as great an effect upon the critical temperature as it does upon the boiling point.

It is evident therefore that the highest attainable degree of purity is a matter of much greater significance for the prosecution of investigations in the neighborhood of the critical temperature than is elsewhere the case. Carbon dioxide has been and still is a favorite subject for such inquiries, in part because it is easily prepared and purified, and in part also because its critical phenomena may be observed at temperatures but little removed from that of the laboratory.

It is well known that carbon dioxide was the material used by Andrews in the prosecution of his classic inquiry regarding the nature of the critical state. It was generated from marble and sulphuric acid.[3] The amount of impurity recorded as present in the gas which he used was about 1 part by volume in from 500 to 1000.[4] Amagat redetermined the critical temperature of carbon dioxide with gas containing only 1 part of impurity in 4000.[5]

For quite a different purpose, Lord Rayleigh and W. Ramsay[6] obtained gas from hydrochloric acid and marble whose impurity was 1 part in 3000. The apparatus had rubber joints, and no special precautions were taken. The same materials yielded Moissan[7] a gas, of which 47 cm. left a bubble of impurity which was "almost imperceptible."

Zelaney[8] condensed the vapor of commercial liquefied carbon dioxide by means of liquid air and secured a product whose impurity was 1 part in 4,000. Kuenen[9] used gas whose ratio of impurity was 1 : 10,000.

A persistent source of error in critical temperature determinations with carbon dioxide is the presence of a trace of atmospheric gases, which are not liquefiable by pressure but dissolve in the liquefied carbon dioxide, and exert a considerable disturbing effect because of the fact that their own critical temperature is so low. Fortunately the amount of these gases when present may be determined easily by the aid of a solution of

---

[1] The studies upon the critical state of carbon dioxide, to which the subject matter of the present paper was in effect preliminary, may be found in the *Physical Review*, 19, 1904. 258-72, *et seq.*

[2] *Compt. rend.*, 120, 43-5, 64-7 (1895).

[3] *Phil. Trans.*, 166, 427 (1876).

[4] *Ibid.*, 159, 576, 582 (1869).

[5] *Compt. rend.*, 114, 1098 (1892).

[6] *Phil. Trans.*, 186, 209 (1895).

[7] *Compt. rend.*, 137, 367 (1903).

[8] *Physical Review*, 25, 490 (1907).

[9] *Phil. Mag.*, 40, 173-94 (1895).

potassium hydroxide. Of course it is evident that a determination of the unabsorbable constituents of the gas is not necessarily a measure of the total impurity, but as a matter of fact other sources of impurity may easily be avoided by the selection of suitable and sufficiently pure materials with which to charge the generator.

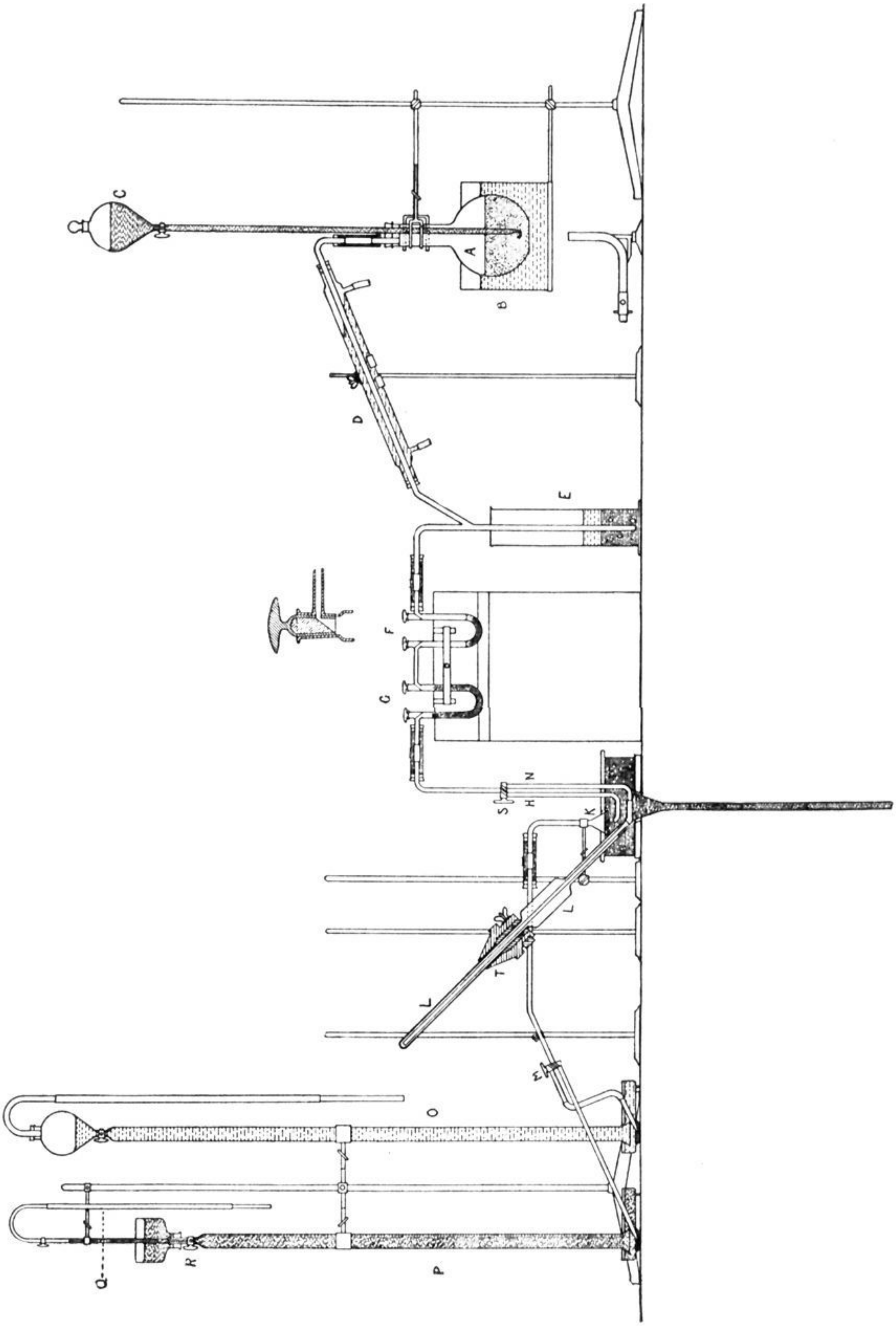
In the work the results of which follow, attention was given not merely to the selection of suitable materials for the generation of the gas but especially to such a construction and arrangement of the generating apparatus as would secure the most rapid and complete expulsion of the air which it contained.

The Materials.—It is well known that one cannot expect to obtain very pure carbon dioxide from mineral carbonates such as marble, magnesite and the like. These substances contain occluded gases of the sort referred to above. Moreover it is practically impossible wholly to remove these gases in advance by reducing the mineral to a fine state of subdivision or even by subjecting the powdered mineral to the continued action of boiling water or of a vacuum. Portions of occluded gas still remain and are liberated later with the carbon dioxide. Better results are obtained by the action of pure acid upon artificial carbonates, preferably those which are soluble in water and which can be obtained in micro-crystalline form.

After a rather careful canvass of the situation, and some experimentation, we finally settled upon acid sodium carbonate as being on the whole the most suitable material. It has already been used with a similar object by Dewar and others. Chemically pure concentrated sulphuric acid served to liberate the gas. The acid was invariably boiled for a short time before use, in order to expel all traces of air.

The Apparatus.—Rapid expulsion of air from a generating apparatus can be effected either by the production of the pure gas in large quantity or by constructing the apparatus itself in tubular form and with as small a diameter as possible. If the gas whose flow expels the air is to be dried or otherwise purified before delivery, both of the conditions just mentioned are in some degree limited.

Having provided therefore for the delivery of a quantity of carbon dioxide equal to about one-fourth of a liter per minute, we paid special attention to the form of the apparatus, with a view to the elimination of all needless volume. Tubes of narrow bore were used for connections. In particular, pains were taken to avoid all gas pockets, that is, angles and corners of every sort in which eddy currents are set up and the direct forward flow of the gas is hampered. With the single exception of the generating flask, practically the entire apparatus took the form of a continuous tube of small bore. Chiefly for the sake of flexibility, five rubber connections were retained, but these were surrounded by mercury jackets so as to prevent absolutely the entrance of any air. In the accompanying diagram, A represents the generator; F G, the drying tubes; L, the piece of apparatus to be filled with pure gas, which may be conveniently called the receiver; and O P, the burettes for testing the purity of the gas.



The drying apparatus consists of a pair of U tubes 105 mm. high, with glass stoppers. The one nearer the generator contains pure concentrated sulphuric acid, and glass beads in quantity sufficient to break the bubbles of carbon dioxide. This tube was recharged at the beginning of each run. The other contains asbestos fibers thoroughly dusted with phosphorus pentoxide. After half a dozen runs, each lasting about 3 hours, the phosphorus pentoxide showed no signs of deterioration except in a layer about 1 mm. in height at the point nearest the sulphuric acid. Even here the change could be detected only by close scrutiny. The hollow glass cocks of these drying tubes are carefully filled with melted paraffin down to the level of the lateral passage, as shown in the enlarged section above. Gas pockets are thus avoided at this point.

The generating flask has a capacity of 750 cc. For practical reasons it is impossible to bring this piece into conformity with the principle which governs the rest of the apparatus. The retention of a considerable space above the charge is quite unavoidable. To compensate for this the device is employed of generating the gas, at the temperature of 100°, from a thin paste formed by mixing the carbonate with a sufficient quantity of distilled water. This is merely a way of using water vapor in large quantity to assist the carbon dioxide in sweeping the air from the space above the charge. The employment of water vapor in this way accounts for the hot water bath B in which the generating flask is immersed; for the condenser D into which the mixture of gas and water vapor passes on leaving the generator; and in part for the mercury seal E.

The mercury seal serves a three-fold purpose. It provides an exit for the condensed water vapor; it furnishes an exit also for all of the impure gas delivered in the first stage of the operation, thus avoiding needless use of the drying tubes; and it serves as a pressure regulator through the operation of which a steady flow of gas is maintained in the system beyond, in spite of any irregularities in the speed of production. Best results have been obtained with a column of mercury about 50 mm. in height.

The maintenance of a gas pressure equivalent to this column of mercury requires a corresponding "head" of acid in the stem of the funnel C. The stem is accordingly made of greater length than usual. In the interest of steadiness of generation the stem should dip under the surface of the charge, and this arrangement in turn necessitates the crook which is shown at the end. Otherwise small gas bubbles would displace the acid in the stem so as gradually to reduce the "head."

The testing apparatus O P consists essentially of two burettes. One of these, O, contains water and is designed to record the rate at which the gas is being delivered. The other, P, contains a solution of potassium hydroxide for the purpose of absorbing the carbon dioxide, in the usual way. A 3-way cock, M, permits of switching the gas current at will into one or the other of these burettes.

It remains only to speak of the receiver L, and its connection with the rest of the apparatus. The receiver as here shown is simply the glass pressure tube of the Cailletet apparatus which we were employing in the studies already mentioned. This explains the presence of the large cylindrical bulb just below the steel cap T. Such a bulb requires a much larger time to fill with a current of pure gas than would be the case with the same volume in the form of a narrow tube. Moreover, for reasons which grew out of the nature of the work referred to and which need not here be mentioned, it seemed impracticable to fill this receiver with the upper end open, as is often done, and subsequently to seal off the top. On the contrary it was necessary that the current of gas should both enter and leave the tube at the lower end. This was accomplished by the narrow feeding tube which appears inside, and by the aid of the mercury bath into which the receiver dips. The tubular extension underneath the bath was added for the purpose of introducing and removing the feeding tube. The use of the funnel K, inverted in the mercury of the bath, is to catch the carbon dioxide as it escapes from the receiver and to deliver it to the testing burettes, in a manner sufficiently clear from the diagram. The cone of the funnel is short and is kept wholly immersed in the mercury to avoid a gas pocket.

The Manipulation.—We proceed to describe the actual manipulation of the apparatus. The generating flask A is charged with about half its volume of the carbonate, and then with water sufficient to produce a thin paste. It is then connected with the long-stemmed dropping funnel C containing concentrated sulphuric acid—freshly boiled and cooled—and with the condenser D, and is immersed in the boiling water of the bath B. A rather copious evolution of carbon dioxide ensues, as the heat of the bath penetrates the charge and partially decomposes the acid carbonate. This is usually found to continue about half an hour. During this time the driers remain closed and the gas escapes through the mercury seal E. At the end of the period, when the spontaneous evolution of gas begins to slacken, acid is admitted in a very slow stream from the funnel. The driers are opened so as to permit the passage of about 1/4 of a liter of gas per minute, and the flow of acid is regulated so as to furnish slightly more than this. The surplus escapes slowly but continuously through the mercury in E.

Having passed the driers F G, the gas is tested from time to time until it reaches a maximum degree of purity. The tests are made by passing the gas through the tube H which delivers directly into the funnel K, and so to the burettes. At the rate of flow already mentioned, about 15 minutes are required to accumulate sufficient impurity over the potassium hydroxide to admit of accurate measurement. The course of the test is as follows: The gas is first led into the water burette O during some convenient aliquot part of a minute, and the volume is noted. By means of the 3-way cock M the stream is then directed for the space of 2 or 3 minutes into the other burette P containing potassium hydroxide, and the exact interval is noted. Then follows another speed test with the water burette and a second absorption in the potassium hydroxide. These readings continue alternately until a sufficient quantity of unabsorbed gas has been accumulated.

For the better reading of the volume of the impurity, the gas is transferred into a narrow burette having a cross section of about 1 sq. mm. A small pipette whose tip is bent upwards like the lower part of the letter J, and is provided with a rubber stopper of such size as to fit the lower end of P, is partially filled with potassium hydroxide solution and then connected with the base of P. By blowing into the upper end of the pipette the unabsorbed gas is forced into the reading burette through R. The reading burette is then transferred to a cylinder of water, as usual. The volume of the impurity divided by the total volume of gas delivered to the absorber, which may be easily calculated from the readings taken at the water burette, gives the relative impurity of the gas.

The time usually required to reach the maximum of purity, reckoned from the opening of the driers, is about one hour. In the meantime the receiver has been carefully filled with mercury and inverted over the mercury bath. It is then supplied with the feeding tube, and connection is made with the end of the tube N leading from the driers. By opening S the mercury in the receiver is at once displaced by carbon dioxide which then bubbles up from the mouth of the receiver into the funnel and is delivered to the testing burettes. In the course of another hour the gas is usually found to have reached its maximum purity again.

It is of course understood that this method does not at once dislodge all of the air which adheres to the inner wall of the receiver. This result might be secured by heating the latter while it is being filled. Unfortunately it was impossible to do this in the case described. For our purpose the receiver had to be mounted in the steel cap T before filling. Sufficient heat to dislodge the air effectively would have ruined the wax joint in the cap. To avoid the difficulty, the receiver was allowed to stand 24 hours or more after the first filling, in order to permit the air layer to evaporate, so to speak, into the carbon dioxide. At the end of such a period the tube was again swept with purest carbon dioxide as before, and it was then assumed that the analytical tests fairly represent the purity of the gas within the receiver.

The Results.—The table below contains a summary of five sample runs which were made with this apparatus. Each of these should be thought of as having been made with a tube already filled, at least 24 hours previously, with pure gas. In each case moreover the tube had been cleaned and dried in advance of the preliminary filling. For each run, whether preliminary or final, the generator was recharged. The final runs given in the table are therefore entirely independent of one another.

Period of absorption. Min.	Gas delivered. cc.	Impurity. cc.	Ratio, $\frac{\text{Gas}}{\text{Imp.}}$
15	2916	0.090	32,400
15	4343	0.120	36,190
15	3831	0.106	36,140
15	3495	0.095	36,800
15.5	4261	0.107	39,950

Thus the impurity varies from 1 part by volume in 30,000 to 1 in 40,000.

By contrast with these results two others may be given. These were obtained under exactly the same conditions, so far as known, except that in the first of the two the apparatus included three *unjacketed* rubber joints, and in the second, two of these. The extremities of the rubber connections however, as always, had been carefully smoothed within with vaseline and wired securely to the ends of the glass tubing. The ends of the glass tubes met each other within the connection.

I. Three unjacketed red rubber connections.

Period of absorption	6 minutes.
Volume of gas delivered	669 cc.
Volume of impurity	0.05 cc.
Ratio, Gas/Imp	13,400

II. Two unjacketed red rubber connections.

Period of absorption	6 minutes.
Volume of gas delivered	744 cc.
Volume of impurity	0.045 cc.
Ratio, Gas/Imp	16,500

It is well known that rubber is permeable to carbon dioxide. We might have been prepared therefore for some loss of gas through the rubber connections, but we were certainly not prepared to expect such a penetration of atmospheric gases from without inward, especially against a pressure of 50 mm. of mercury. If the difference in results is due to some other cause than this, we are unable to form a conjecture as to what it may have been.

Summary.

A method is described for producing carbon dioxide whose impurity, unabsorbable in potassium hydroxide solution, varies from 1 in 30,000 to 1 in 40,000.

An apparent permeability of rubber tubing to air against pressure is noted.

Wesleyan University, Middletown, Conn.,
March 24, 1908.