XVIII. THE BAKERIAN LECTURE.—*On the Continuity of the Gaseous and Liquid States of Matter.*

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Received June 14,—Read June 17, 1869.

IN 1822 M. CAGNIARD DE LA TOUR observed that certain liquids, such as ether, alcohol, and water, when heated in hermetically sealed glass tubes, became apparently reduced to vapour in a space from twice to four times the original volume of the liquid. He also made a few numerical determinations of the pressures exerted in these experiments[*]. In the following year FARADAY succeeded in liquefying, by the aid of pressure alone, chlorine and several other bodies known before only in the gaseous form[†]. A few years later THILORIER obtained solid carbonic acid, and observed that the coefficient of expansion of the liquid for heat is greater than that of any aëriform body[‡]. A second memoir by FARADAY, published in 1826, greatly extended our knowledge of the effects of cold and pressure on gases[§]. REGNAULT has examined with care the absolute change of volume in a few gases when exposed to a pressure of twenty atmospheres, and POUILLET has made some observations on the same subject. The experiments of NATTERER have carried this inquiry to the enormous pressure of 2790 atmospheres; and although his method is not altogether free from objection, the results he obtained are valuable and deserve more attention than they have hitherto received[||].

In 1861 a brief notice appeared of some of my early experiments in this direction. Oxygen, hydrogen, nitrogen, carbonic oxide, and nitric oxide were submitted to greater pressures than had previously been attained in glass tubes, and while under these pressures they were exposed to the cold of the carbonic acid and ether-bath. None of the gases exhibited any appearance of liquefaction, although reduced to less than $\frac{1}{500}$ of their ordinary volume by the combined action of cold and pressure[¶]. In the third edition of MILLER's 'Chemical Physics,' published in 1863, a short account, derived from a private letter addressed by me to Dr. MILLER, appeared of some new results I had obtained, under certain fixed conditions of pressure and temperature, with carbonic acid. As these results constitute the foundation of the present investigation and have never been published in a separate form, I may perhaps be permitted to make the following extract from my original communication to Dr. MILLER. "On partially liquefying carbonic acid by pressure alone, and gradually raising at the same time the temperature to

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[*] Annales de Chimie, 2ème série, xxi. pp. 127 and 178; also xxii. p. 410.

[†] Philosophical Transactions for 1823, pp. 160–189.

[‡] Annales de Chimie, 2ème série, lx. pp. 427, 432.

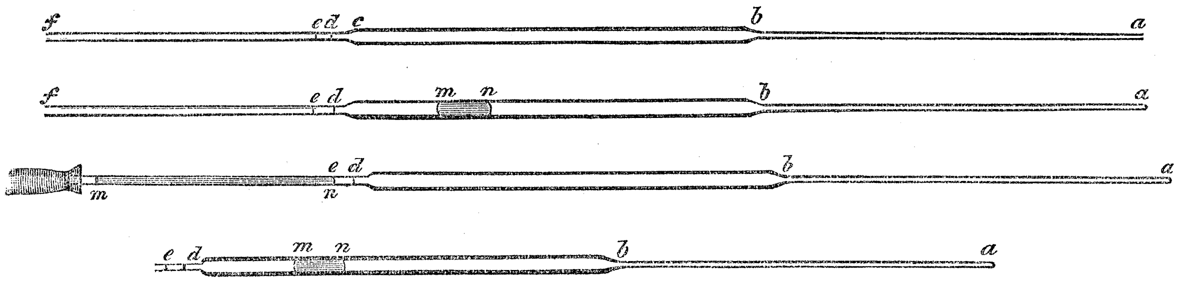
[§] Philosophical Transactions for 1845, p. 155.

[||] POGGENDORFF's 'Annalen,' xciv. p. 436.

[¶] Report of the British Association for 1861. Transactions of Sections, p. 76.

88° Fahr., the surface of demarcation between the liquid and gas became fainter, lost its curvature, and at last disappeared. The space was then occupied by a homogeneous fluid, which exhibited, when the pressure was suddenly diminished or the temperature slightly lowered, a peculiar appearance of moving or flickering striæ throughout its entire mass. At temperatures above 88° no apparent liquefaction of carbonic acid, or separation into two distinct forms of matter, could be effected, even when a pressure of 300 or 400 atmospheres was applied. Nitrous oxide gave analogous results"*.

The apparatus employed in this investigation is represented in Plate LXIII. It is shown in the simple form in which one gas only is exposed to pressure in figures 1 & 2. In figure 3 a section of the apparatus is given, and in figure 4 another section, with the arrangement for exposing the compressed gas to low degrees of cold *in vacuo*. In figures 5 and 6 a compound form of the same apparatus is represented, by means of which two gases may be simultaneously exposed to the same pressure. The gas to be compressed is introduced into a tube (*f a*) having a capillary bore from *a* to *b*, a diameter of about 2·5 millimetres from *b* to *c*, and of 1·25 millimetre from *c* to *f*. The gas carefully dried is passed for several hours through the tube open at both ends, as represented below.



The presence of a column of water of two metres in height was necessary to maintain a moderate stream of gas through the fine capillary tube. In the case of carbonic acid, the gas, after passing through the apparatus, was made to bubble by means of a connecting-tube through mercury, and a portion was collected from time to time, in order to ascertain its purity. The current was continued till the residual air, after the action of caustic potash, was reduced to a constant minimum. In repeated trials I found that in the complicated arrangements I had to adopt, the residual air could not be reduced to less than from $\frac{1}{500}$ to $\frac{1}{1000}$ of the entire volume of the carbonic acid. Even after continuing the current for twenty-four hours this residue appeared; and in discussing some of the results obtained by exposing the gas to high pressures, the presence of this small quantity of air must be carefully taken into account. The capillary end at *a* was then sealed, and the other end was also closed, and afterwards introduced under a surface of pure mercury contained in a glass capsule. The lower end, while under the surface of the mercury, was opened, and heat applied so as to expel a little of the gas. On cooling contraction occurred, and a short column of mercury entered. The capsule and lower end of the tube were then placed under the receiver of an air-pump, and a partial

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* MILLER's 'Chemical Physics,' 3rd edition, p. 328.

vacuum was formed till about one-fourth of the gas was removed. On restoring the pressure, a column of mercury entered and occupied the place of the expelled gas. By withdrawing the end of the tube from below the surface of the mercury in the capsule, and again exhausting cautiously, the column of mercury could be reduced to any required length. The tube, when thus filled, had the form shown (figure, p. 576).

Two file-marks had been made, one at *d*, the other at *e*, in the narrow part of the tube, about 10 millims. distant from each other, and the capacity of the tube from a mark near *a* to *d*, and also from the same mark to *e*, had been determined by filling it with mercury at a known temperature and weighing the mercury. The tube was now placed accurately in a horizontal position and connected by an air-tight junction with one limb of a long U-tube filled with mercury. Each limb of the U-tube was 600 millims. long, and 11 millims. in diameter. By removing mercury from the outer limb of the U-tube, a partial vacuum was obtained, and the column of mercury (*m n*) was drawn into the narrow tube (*d f*). From the difference of capacity of this part of the tube, the column of mercury was now about four times longer than before. It was easy with a little care so to adjust the pressure that the inner end of the mercurial column coincided with the mark *e*. When this was accomplished, the difference of level of the mercury in the two limbs of the U-tube was accurately read by means of a cathetometer, and the height of the barometer as well as the temperature were carefully noted. Similar observations were made with the gas expanded to the mark *d*. Two independent sets of data were thus obtained for calculating the volume of the gas at 0° C. and 760 millims., and the results usually agreed to less than $\frac{1}{1000}$ part. The tube, after being disconnected with the U-tube, was cut across a little beyond *e*, as shown (figure, p. 576), and was now ready to be introduced into the pressure apparatus.

The capillary tubes were calibrated with great care, and their mean capacity was determined by weighing a column of mercury whose length and position in the tube were accurately observed. One millim. of the air-tube used in these experiments had an average capacity of 0·00002477 cub. centim., and 1 millim. of the carbonic-acid-tube of 0·00003376 cub. centim. A table was constructed showing the corrected capacity of each capillary tube from the sealed end for every millimetre of its length. An allowance of 0·5 millim. was made for the cone formed in sealing the tube.

For the sake of clearness I have described these operations as if they were performed in the detached tube. In actual practice, the tube was in the brass end-piece before it was filled with gas (Plate LXIII. fig. 7).

The construction of the apparatus employed in these experiments will be readily understood from figures 3 and 4, Plate LXIII., which exhibit a section of the simple form. Two massive brass flanges are firmly attached round the ends of a cold-drawn copper tube of great strength, and by means of these flanges two brass end-pieces can be securely bolted to the ends of the copper tube, and the connexions made air-tight by the insertion of leather washers. The lower end-piece (fig. 7) carries a steel screw, 180 millims. long, 4 millims. in diameter, and with an interval of 0·5 millim. between each thread. The screw is packed with care, and readily holds a pressure of 400 atmospheres or more. A similar end-piece attached to the upper flange carries the glass tube containing the gas to be compressed (fig. 7). The apparatus, before being screwed up, is filled with water, and the pressure is obtained by screwing the steel screw into the water*.

In the compound apparatus (figs. 5 & 6) the internal arrangements are the same as in the simple form. A communication is established between the two sides of the apparatus through *a b*. It is indifferent which of the steel screws below is turned, as the pressure is immediately diffused through the interior of both copper tubes, and is applied through the moveable columns of mercury to the two gases to be compressed. Two screws are employed for the purpose of giving a greater command of pressure. In fig. 5 the apparatus is represented without any accessories. In fig. 6 the same apparatus is shown with the arrangements for maintaining the capillary tubes and the body of the apparatus itself at fixed temperatures. A rectangular brass case, closed before and behind with plate glass, surrounds each capillary tube, and allows it to be maintained at any required temperature by the flow of a stream of water. In the figure, the arrangement for obtaining a current of heated water in the case of the carbonic-acid tube is shown. The body of the apparatus itself, as is shown in the figure, is enclosed in an external vessel of copper, which is filled with water at the temperature of the apartment. This latter arrrangement is essential when accurate observations are made.

The temperature of the water surrounding the air-tube was made to coincide, as closely as possible, with that of the apartment, while the temperature of the water surrounding the carbonic-acid tube varied in different experiments from 13° C. to 48° C. In the experiments to be described in this communication, the mercury did not come into view in the capillary part of the air-tube till the pressure amounted to about forty atmospheres. The volumes of the air and of the carbonic acid were carefully read by a cathetometer, and the results could be relied on with certainty to less than 0·05 millim. The temperature of the water around the carbonic-acid tube was ascertained by a thermometer carefully graduated by myself according to an arbitrary scale. This thermometer was one of a set of four, which I constructed some years ago, and which all agreed so closely in their indications, that the differences were found to be altogether insignificant when their readings were reduced to degrees.

I have not attempted to deduce the actual pressure from the observed changes in the volume of the air in the air-tube. For this purpose it would be necessary to know with precision the deviations from the law of MARIOTTE exhibited by atmospheric air within the range of pressure employed in these experiments, and also the change of capacity in the capillary tube from internal pressure. In a future communication I hope to have an opportunity of considering this problem, which must be resolved rather by indirect than direct experiments. As regards the deviation of air from MARIOTTE's law,

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[*] The first apparatus was constructed for me by Mr. J. CUMINE, of Belfast, to whose rare mechanical skill and valuable suggestions I have been greatly indebted in the whole course of this difficult investigation.

it corresponds, according to the experiments of REGNAULT, to an apparent error of a little more than one-fourth of an atmosphere at a pressure of twenty atmospheres, and according to those of NATTERER, to an approximate error of one atmosphere when the pressure attains 107 atmospheres. These data are manifestly insufficient, and I have therefore not attempted to deduce the true pressure from the observed change of volume in the air-tube. It will be easy to apply hereafter the corrections for true pressure when they are ascertained, and for the purposes of this paper they are not required. The general form of the curves representing the changes of volume in carbonic acid will hardly undergo any sensible change from the irregularities in the air-tube; nor will any of the general conclusions at which I have arrived be affected by them. It must, however, always be understood that, when the pressures are occasionally spoken of, as indicated by the apparent contraction of the air in the air-gauge, the approximate pressures only are meant.

To obtain the capacity in cubic centimetres from the weight in grammes of the mercury which filled any part of a glass tube, the following formula was used,

$$C=W\,.\,\frac{1+0{\cdot}000154\,.\,t}{13{\cdot}596}\,.\,1{\cdot}00012,$$

where C is the capacity in cubic centims., W the weight of the mercury which filled the tube at the temperature t, 0·000154 the coefficient of apparent expansion of mercury in glass, 13·596 the density of mercury at 0°, and 1·00012 the density of water at 4°.

The volume of the gas V, at 0° and 760 millims. of pressure, was deduced from the double observations, as follows,

$$V=C\,.\,\frac{1}{1+\alpha t}\,.\,\frac{h-d}{760},$$

where C is the capacity of the tube (figure, page 576) from a to d, or from a to e, t the temperature, α the coefficient of expansion of the gas for heat (0·00366 in the case of air, 0·0037 in that of carbonic acid), h the height of the barometer reduced to 0° and to the latitude of 45°, d the difference of the mercurial columns in the U-tube similarly reduced.

Having thus ascertained the volumes of the air and of the carbonic acid before compression, at 0° and 760 millims., it was easy to calculate their volumes, under the same pressure of 760 millims., at the temperatures at which the measurements were made when the gases were compressed, and thence to deduce the values of the fractions representing the diminution of volume. But the fractions thus obtained would not give results directly comparable for air and carbonic acid. Although the capillary glass tubes in the apparatus (fig. 6) communicated with the same reservoir, the pressure on the contained gases was not quite equal, in consequence of the mercurial columns, which confined the air and carbonic acid, being of different heights. The column always stood higher in the carbonic-acid-tube than in the air-tube, so that the pressure in the latter was a little greater than in the former. The difference in the lengths of the mercurial columns rarely exceeded 200 millims., or about one-fourth of an atmosphere. This correction was always applied, as was also a trifling correction of 7 millims. for a difference of capillary depression in the two tubes.

In order to show more clearly the methods of reduction, I will give the details of one experiment.

Volume of air at 0° and 760 millims. calculated from the observations when the air was expanded to *a e*, 0·3124 cub. centim.

Volume of same air calculated from the observations when the air was expanded to *a d*, 0·3122 cub. centim.

Mean volume of air at 0° and 760 millims., 0·3123 cub. centim.

The volumes of the carbonic acid, deduced in like manner from two independent observations, were 0·3096 cub. centim. and 0·3094 cub. centim. Mean 0·3095 cub. centim.

The length of the column of air after compression, at 10°·76, in the capillary air-tube was 272·9 millims., corresponding to 0·006757 cub. centim. Hence we have

$$\delta'=\frac{0{\cdot}006757}{0{\cdot}3123\times 1{\cdot}0394}=\frac{1}{48{\cdot}04}.$$

But as the difference in the heights of the mercurial columns in the air-tube and carbonic-acid-tube, after allowing for the difference of capillary depression, was 178 millims., this result requires a further correction ($\frac{178}{760}$ of an atmosphere), in order to render it comparable with the compression in the carbonic-acid-tube. The final value for δ, the fraction representing the ratio of the volume of the compressed air at the temperature of the experiment to its volume at the same temperature and under the pressure of one atmosphere, will be

$$\delta=\frac{1}{47{\cdot}81}.$$

The corresponding length of the carbonic acid at 13°·22, in its capillary tube, was 124·6 millims., equivalent to 0·004211 cub. centim., from which we deduce for the corresponding fraction for the carbonic acid

$$\varepsilon=\frac{0{\cdot}004211}{0{\cdot}3095\times 1{\cdot}0489}=\frac{1}{77{\cdot}09}.$$

Hence it follows that the same pressure, which reduced a given volume of air at 10°·76 to $\frac{1}{47{\cdot}81}$ of its volume at the same temperature under one atmosphere, reduced carbonic acid at 13°·22 to $\frac{1}{77{\cdot}09}$ of its volume at the temperature of 13°·22, and under a pressure of one atmosphere. Or assuming the compression of the air to be approximately a measure of the pressure, we may state that under a pressure of about 47·8 atmospheres carbonic acid at 13°·22 contracts to $\frac{1}{77{\cdot}09}$ of its volume under one atmosphere.

In the following Tables, δ is the fraction representing the ratio of the volumes of the air after and before compression to one another, ε the corresponding fraction for the carbonic acid, t and t' the temperatures of the air and carbonic acid respectively, l the number of volumes which 17,000 volumes of carbonic acid, measured at 0° and 760 millims., would occupy at the temperature at which the observation was made under the pressure indicated by the air in the air-tube. The values of l are the ordinates of the curve lines shown in the figure, page 583*.

TABLE I.—Carbonic Acid at 13°·1.

δ.	t.	ε.	t'.	l.
$\frac{1}{47\cdot50}$	10°·75	$\frac{1}{76\cdot16}$	13°·18	234·1 *
$\frac{1}{48\cdot76}$	10·86	$\frac{1}{80\cdot43}$	13·18	221·7
$\frac{1}{48\cdot89}$	10·86	$\frac{1}{80\cdot90}$	13·09	220·3
$\frac{1}{49\cdot00}$	10·86	$\frac{1}{105\cdot9}$	13·09	168·2
$\frac{1}{49\cdot08}$	10·86	$\frac{1}{142\cdot0}$	13·09	125·5
$\frac{1}{49\cdot15}$	10·86	$\frac{1}{192\cdot3}$	13·09	92·7
$\frac{1}{49\cdot28}$	10·86	$\frac{1}{268\cdot8}$	13·09	66·3
$\frac{1}{49\cdot45}$	10·86	$\frac{1}{342\cdot8}$	13·09	52·0
$\frac{1}{49\cdot63}$	10·86	$\frac{1}{384\cdot9}$	13·09	46·3
$\frac{1}{50\cdot15}$	10·86	$\frac{1}{462\cdot9}$	13·09	38·5
$\frac{1}{50\cdot38}$	10·86	$\frac{1}{471\cdot5}$	13·09	37·8
$\frac{1}{54\cdot56}$	10·86	$\frac{1}{480\cdot4}$	13·09	37·1
$\frac{1}{75\cdot61}$	10·86	$\frac{1}{500\cdot7}$	13·09	35·6
$\frac{1}{90\cdot43}$	10·86	$\frac{1}{510\cdot7}$	13·09	34·9

It will be observed that at the pressure of 48·89 atmospheres, as measured by the contraction of the air in the air-tube, liquefaction began. This point could not be fixed by direct observation, inasmuch as the smallest visible quantity of liquid represented a column of gas at least 2 or 3 millims. in length. It was, however, determined indirectly by observing the volume of the gas 0°·2 or 0°·3 above the point of liquefaction, and calculating the contraction the gas would sustain in cooling down to the temperature at which liquefaction began. A slight increase of pressure, it will be seen, was required even in the early stages to carry on the process. Thus the air-guage, after all reductions

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* As l is the entire volume to which the carbonic acid is reduced, it does not always refer to homogeneous matter, but sometimes to a mixture of gas and liquid. Its value in the example given in the text is obtained as follows:—

$$l=17000\,.\,\frac{0\cdot004211}{0\cdot3095}=231\cdot3.$$

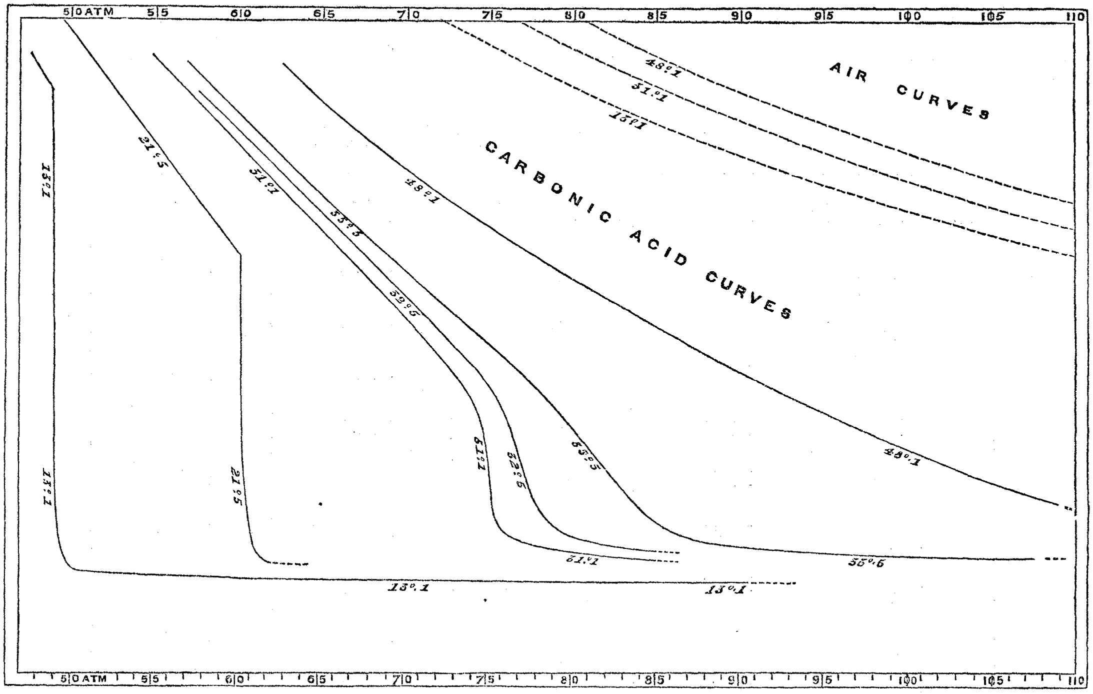
When l is homogeneous, $\frac{1}{\varepsilon}$ represents the density of the carbonic acid referred to carbonic acid gas, at the temperature t', and under a pressure of one atmosphere.

were made, indicated an increase of pressure of about one-fourth of an atmosphere (from 48·89 to 49·15 atmospheres) during the condensation of the first and second thirds of the carbonic acid. According to theory no change of volume ought to have occurred. This apparent anomaly is explained by the presence of the trace of air (about $\frac{1}{500}$ part) in the carbonic acid to which I before referred. It is easy to see that the increase of pressure shown in these experiments is explained by the presence of this small quantity of air. If a given volume of carbonic acid contain $\frac{1}{500}$ of air, that air will be diffused through a space 500 times greater than if the same quantity of air were in a separate state. Compress the mixture till 50 atmospheres of pressure have been applied, and the air will now occupy, or be diffused through, ten times the space it would occupy if alone and under the pressure of one atmosphere; or it will be diffused through the space it would occupy, if alone and under the pressure of $\frac{1}{10}$ of an atmosphere. While the carbonic acid is liquefying, pressure must be applied in order to condense this air; and to reduce it to one-half its volume, an increase of $\frac{1}{10}$ of an atmosphere is required. The actual results obtained by experiment approximate to this calculation. From similar considerations, it follows that if a mixture of air and carbonic acid be taken, for example in equal volumes, the pressure, after liquefaction has begun, must be augmented by several atmospheres, in order to liquefy the whole of the carbonic acid. Direct experiments have shown this conclusion to be true.

The small quantity of air in the carbonic acid disturbed the liquefaction in a marked manner, when nearly the whole of the carbonic acid was liquefied, and when its volume relatively to that of the uncondensed carbonic acid was considerable. It resisted for some time absorption by the liquid, but on raising the pressure to 50·4 atmospheres it was entirely absorbed. If the carbonic acid had been absolutely pure, the part of the curve for 13°·1 (figure, page 583) representing the fall from the gaseous to the liquid state, would doubtless have been straight throughout its entire course, and parallel to the lines of equal pressure.

TABLE II.—Carbonic Acid at 21°·5.

δ.	t.	ε.	t'.	l.
$\frac{1}{46·70}$	8°·63	$\frac{1}{67·26}$	21°·46	272·9
$\frac{1}{60·05}$	8·70	$\frac{1}{114·7}$	21·46	160·0
$\frac{1}{60·29}$	8·70	$\frac{1}{174·8}$	21·46	105·0
$\frac{1}{60·55}$	8·70	$\frac{1}{240·5}$	21·46	76·3
$\frac{1}{61·00}$	8·70	$\frac{1}{367·7}$	21·46	49·9
$\frac{1}{62·21}$	8·70	$\frac{1}{440·0}$	21·46	41·7
$\frac{1}{62·50}$	8·70	$\frac{1}{443·3}$	21·46	41·4



The curve representing the results at 21°·5 agrees in general form with that for 13°·1, as shown in the above figure. At 13°·1, under a pressure of about 49 atmospheres, the volume of carbonic acid is little more than three-fifths of that which a perfect gas would occupy under the same conditions. After liquefaction carbonic acid yields to pressure much more than ordinary liquids; and the compressibility appears to diminish as the pressure increases. The high rate of expansion by heat of liquid carbonic acid, first noticed by THILORIER, is fully confirmed by this investigation.

The next series of experiments was made at the temperature of 31°·1, or 0°·2 above the point at which, by compression alone, carbonic acid is capable of assuming visibly the liquid form. Since I first announced this fact in 1863, I have made careful experiments to fix precisely the temperature of this critical point in the case of carbonic acid. It was found in three trials to be 30°·92 C., or 87°·7 FAHR. Although for a few degrees above this temperature a rapid fall takes place from increase of pressure, when the gas is reduced to the volume at which it might be expected to liquefy, no separation of the carbonic acid into two distinct conditions of matter occurs, so far as any indication of such a separation is afforded by the action of light. By varying the pressure or temperature, but always keeping the latter above 30°·92, the great changes of density which occur about this point produce the flickering movements I formerly described, resembling in an exaggerated form the appearances exhibited during the mixture of liquids of different densities, or when columns of heated air ascend through colder strata. It is easy so to adjust the pressure that one-half of the tube shall be filled with uncondensed gas and one-half with the condensed liquid. Below the critical temperature this distinction is easily seen to have taken place, from the visible surface of demarcation between the liquid and gas, and from the shifting at the same surface of the image of any perpendicular line placed behind the tube. But above 30°·92 no such appearances are seen, and the most careful examination fails to discover any heterogeneity in the carbonic acid, as it exists in the tube.

TABLE III.—Carbonic Acid at 31°·1.

δ.	*t*.	ϵ.	*t'*.	*l*.
$\frac{1}{54\cdot79}$	$1\overset{\circ}{1}\cdot59$	$\frac{1}{80\cdot55}$	$3\overset{\circ}{1}\cdot17$	235·4
$\frac{1}{55\cdot96}$	11·59	$\frac{1}{83\cdot39}$	31·22	227·4
$\frac{1}{57\cdot18}$	11·58	$\frac{1}{86\cdot58}$	31·15	219·0
$\frac{1}{58\cdot46}$	11·55	$\frac{1}{90\cdot04}$	31·19	210·6
$\frac{1}{59\cdot77}$	11·41	$\frac{1}{93\cdot86}$	31·18	202·0
$\frac{1}{61\cdot18}$	11·40	$\frac{1}{98\cdot07}$	31·20	193·3
$\frac{1}{62\cdot67}$	11·44	$\frac{1}{103\cdot1}$	31·19	183·9
$\frac{1}{64\cdot27}$	11·76	$\frac{1}{109\cdot6}$	31·13	173·0
$\frac{1}{65\cdot90}$	11·73	$\frac{1}{116\cdot2}$	31·19	163·2
$\frac{1}{67\cdot60}$	11·63	$\frac{1}{124\cdot4}$	31·15	152·4
$\frac{1}{69\cdot39}$	11·55	$\frac{1}{134\cdot5}$	31·03	140·9
$\frac{1}{71\cdot25}$	11·40	$\frac{1}{147\cdot8}$	31·06	128·2
$\frac{1}{73\cdot26}$	11·45	$\frac{1}{169\cdot0}$	31·09	112·2
$\frac{1}{73\cdot83}$	13·00	$\frac{1}{174\cdot4}$	31·08	108·7
$\frac{1}{75\cdot40}$	11·62	$\frac{1}{311\cdot1}$	31·06	60·9
$\frac{1}{77\cdot64}$	11·65	$\frac{1}{369\cdot1}$	31·06	51·3
$\frac{1}{79\cdot92}$	11·16	$\frac{1}{383\cdot0}$	31·10	49·4
$\frac{1}{82\cdot44}$	11·23	$\frac{1}{395\cdot7}$	31·07	47·9
$\frac{1}{85\cdot19}$	11·45	$\frac{1}{405\cdot5}$	31·05	46·7

The graphical representation of these experiments, as shown in the preceding page, exhibits some marked differences from the curves for lower temperatures. The dotted lines in the figure represent a portion of the curves of a perfect gas (assumed to have the same volume at 0° and under one atmosphere as the carbonic acid) for the temperatures of 13°·1, 31°·1, and 48°·1. The volume of the carbonic acid at 31°·1, it will be observed, diminishes with tolerable regularity, but much faster than according to the law of MARIOTTE, till a pressure of about 73 atmospheres is attained. The diminution of volume then goes on very rapidly, a reduction to nearly one-half taking place, when the pressure is increased from 73 to 75 atmospheres, or only by $\frac{1}{37}$ of the whole pressure. The fall is not, however, abrupt as in the case of the formation of the liquid at lower temperatures, but a steady increase of pressure is required to carry it through. During this fall, as has already been stated, there is no indication at any stage of the process of two conditions of matter being present in the tube. Beyond 77 atmospheres carbonic acid at 31°·1 yielded much less than before to pressure, its volume having become reduced nearly to that which it ought to occupy as a liquid at the temperature at which the observations were made.

TABLE IV.—Carbonic Acid at 32°·5.

δ.	*t*.	ϵ.	*t'*.	*l*.
$\frac{1}{57\cdot38}$	12°·10	$\frac{1}{85\cdot90}$	32°·50	221·7
$\frac{1}{71\cdot52}$	12·15	$\frac{1}{140\cdot3}$	32·34	135·6
$\frac{1}{73\cdot60}$	12·30	$\frac{1}{156\cdot0}$	32·45	122·0
$\frac{1}{74\cdot02}$	12·30	$\frac{1}{159\cdot9}$	32·46	119·1
$\frac{1}{76\cdot25}$	12·40	$\frac{1}{191\cdot7}$	32·38	99·3
$\frac{1}{78\cdot52}$	12·50	$\frac{1}{311\cdot8}$	32·48	61·1
$\frac{1}{79\cdot77}$	12·35	$\frac{1}{351\cdot3}$	32·54	54·2
$\frac{1}{84\cdot90}$	12·35	$\frac{1}{387\cdot8}$	32·75	49·1

TABLE V.—Carbonic Acid at 35°·5.

δ.	*t*.	ϵ.	*t'*.	*l*.
$\frac{1}{56\cdot80}$	15°·68	$\frac{1}{82\cdot72}$	35°·49	232·5
$\frac{1}{59\cdot34}$	15·70	$\frac{1}{88\cdot94}$	35·54	216·2
$\frac{1}{62\cdot15}$	15·66	$\frac{1}{96\cdot41}$	35·52	199·5
$\frac{1}{65\cdot23}$	15·66	$\frac{1}{106\cdot0}$	35·51	181·4
$\frac{1}{68\cdot66}$	15·75	$\frac{1}{118\cdot4}$	35·47	162·4
$\frac{1}{72\cdot45}$	15·79	$\frac{1}{135\cdot1}$	35·48	142·3
$\frac{1}{76\cdot58}$	15·52	$\frac{1}{161\cdot2}$	35·55	119·3
$\frac{1}{81\cdot28}$	15·61	$\frac{1}{228\cdot0}$	35·55	84·4
$\frac{1}{86\cdot60}$	15·67	$\frac{1}{351\cdot9}$	35·48	54·6
$\frac{1}{89\cdot52}$	15·67	$\frac{1}{373\cdot7}$	35·50	51·5
$\frac{1}{92\cdot64}$	15·64	$\frac{1}{387\cdot9}$	35·61	49·6
$\frac{1}{99\cdot57}$	15·61	$\frac{1}{411\cdot0}$	35·55	46·8
$\frac{1}{107\cdot6}$	15·47	$\frac{1}{430\cdot2}$	35·53	44·7

TABLE VI.—Carbonic Acid at 48°·1.

δ.	t.	ε.	t'.	l.
$\frac{1}{62\cdot60}$	15°·67	$\frac{1}{86\cdot45}$	47°·95	231·5
$\frac{1}{68\cdot46}$	15·79	$\frac{1}{99\cdot39}$	48·05	201·4
$\frac{1}{75\cdot58}$	15·87	$\frac{1}{117\cdot8}$	48·12	170·0
$\frac{1}{84\cdot35}$	15·91	$\frac{1}{146\cdot8}$	48·25	136·5
$\frac{1}{95\cdot19}$	15·83	$\frac{1}{198\cdot5}$	48·13	100·8
$\frac{1}{109\cdot4}$	16·23	$\frac{1}{298\cdot4}$	48·25	67·2

The curve for 32°·5 (page 583) resembles closely that for 31°·1. The fall is, however, less abrupt than at the latter temperature. The range of pressure in the experiments at 35°·5 extends from 57 to above 107 atmospheres. The fall is here greatly diminished, and it has nearly lost its abrupt character. It is most considerable from 76 to 87 atmospheres, where an increase of one-seventh in the pressure produces a reduction of volume to one-half. At 107 atmospheres the volume of the carbonic acid has come almost into conformity with that which it should occupy, if it were derived directly from liquid carbonic acid, according to the law of the expansion of that body for heat.

The curve for 48°·1 is very interesting. The fall shown in the curves for lower temperatures has almost, if not altogether, disappeared, and the curve itself approximates to that which would represent the change of volume in a perfect gas. At the same time the contraction is much greater than it would have been if the law of MARIOTTE had held good at this temperature. Under a pressure of 109 atmospheres, the carbonic acid is rapidly approaching to the volume it would occupy if derived from the expansion of the liquid; and if the experiment had not been interrupted by the bursting of one of the tubes, it would doubtless have fallen into position at a pressure of 120 or 130 atmospheres.

I have not made any measurements at higher temperatures than 48°·1; but it is clear that, as the temperature rises, the curve would continue to approach to that representing the change of volume of a perfect gas.

I have frequently exposed carbonic acid, without making precise measurements, to much higher pressures than any marked in the Tables, and have made it pass, without break or interruption from what is regarded by every one as the gaseous state, to what is, in like manner, universally regarded as the liquid state. Take, for example, a given volume of carbonic acid gas at 50° C., or at a higher temperature, and expose it to increasing pressure till 150 atmospheres have been reached. In this process its volume will steadily diminish as the pressure augments, and no sudden diminution of volume, without the application of external pressure, will occur at any stage of it. When the full pressure has been applied, let the temperature be allowed to fall till the carbonic acid has reached the ordinary temperature of the atmosphere. During the whole of this operation no breach of continuity has occurred. It begins with a gas, and by a series of gradual changes, presenting nowhere any abrupt alteration of volume or sudden evolution of heat, it ends with a liquid. The closest observation fails to discover anywhere indications of a change of condition in the carbonic acid, or evidence, at any period of the process, of part of it being in one physical state and part in another. That the gas has actually changed into a liquid would, indeed, never have been suspected, had it not shown itself to be so changed by entering into ebullition on the removal of the pressure. For convenience this process has been divided into two stages, the compression of the carbonic acid and its subsequent cooling; but these operations might have been performed simultaneously, if care were taken so to arrange the application of the pressure and the rate of cooling, that the pressure should not be less than 76 atmospheres when the carbonic acid had cooled to 31°.

We are now prepared for the consideration of the following important question. What is the condition of carbonic acid when it passes, at temperatures above 31°, 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°, or at a higher temperature, when all indications of a fall had disappeared, the probable answer which 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 pressure, 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°, 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.

The answer to the foregoing question, according to what appears to me to be the true interpretation of the experiments already described, is to be found in the close and intimate relations which subsist between the gaseous and liquid states of matter. The ordinary gaseous and ordinary liquid states are, in short, only widely separated forms of the same condition of matter, and may be made to pass into one another by a series of gradations so gentle that the passage shall nowhere present any interruption or breach of continuity. From carbonic acid as a perfect gas to carbonic acid as a perfect liquid, the transition we have seen may be accomplished by a continuous process, and the gas and liquid are only distant stages of a long series of continuous physical changes. Under certain conditions of temperature and pressure, carbonic acid finds itself, it is true, in what may be described as a state of instability, and suddenly passes, with the evolution of heat, and without the application of additional pressure or change of temperature, to the volume, which by the continuous process can only be reached through a long and circuitous route. In the abrupt change which here occurs, a marked difference is exhibited, while the process is going on, in the optical and other physical properties of the carbonic acid which has collapsed into the smaller volume, and of the carbonic acid not yet altered. There is no difficulty here, therefore, in distinguishing between the liquid and the gas. But in other cases the distinction cannot be made; and under many of the conditions I have described it would be vain to attempt to assign carbonic acid to the liquid rather than the gaseous state. Carbonic acid, at the temperature of 35°·5, and under a pressure of 108 atmospheres, is reduced to $\frac{1}{430}$ of the volume it occupied under a pressure of one atmosphere; but if any one ask whether it is now in the gaseous or liquid state, the question does not, I believe, admit of a positive reply. Carbonic acid at 35°·5, and under 108 atmospheres of pressure, 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. The same observation would apply with even greater force to the state in which carbonic acid exists at higher temperatures and under greater pressures than those just mentioned. In the original experiment of CAGNIARD DE LA TOUR, that distinguished physicist inferred that the liquid had disappeared, and had changed into a gas. A slight modification of the conditions of his experiment would have led him to the opposite conclusion, that what had been before a gas was changed into a liquid. These conditions are, in short, the intermediate states which matter assumes in passing, without sudden change of volume, or abrupt evolution of heat, from the ordinary liquid to the ordinary gaseous state.

In the foregoing observations I have avoided all reference to the molecular forces brought into play in these experiments. The resistance of liquids and gases to external pressure tending to produce a diminution of volume, proves the existence of an internal force of an expansive or resisting character. On the other hand, the sudden diminution of volume, without the application of additional pressure externally, which occurs when a gas is compressed, at any temperature below the critical point, to the volume at which liquefaction begins, can scarcely be explained without assuming that a molecular force of great attractive power comes here into operation, and overcomes the resistance to diminution of volume, which commonly requires the application of external force. When the passage from the gaseous to the liquid state is effected by the continuous process described in the foregoing pages, these molecular forces are so modified as to be unable at any stage of the process to overcome alone the resistance of the fluid to change of volume.

The properties described in this communication, as exhibited by carbonic acid, are not peculiar to it, but are generally true of all bodies which can be obtained as gases and liquids. Nitrous oxide, hydrochloric acid, ammonia, sulphuric ether, and sulphuret of carbon, all exhibited, at fixed pressures and temperatures, critical points, and rapid changes of volume with flickering movements when the temperature or pressure was changed in the neighbourhood of those points. The critical points of some of these bodies were above 100°; and in order to make the observations, it was necessary to bend the capillary tube before the commencement of the experiment, and to heat it in a bath of paraffin or oil of vitriol.

The distinction between a gas and vapour has hitherto been founded on principles which are altogether arbitrary. Ether in the state of gas is called a vapour, while sulphurous acid in the same state is called a gas; yet they are both vapours, the one derived from a liquid boiling at 35°, the other from a liquid boiling at −10°. The distinction is thus determined by the trivial condition of the boiling-point of the liquid, under the ordinary pressure of the atmosphere, being higher or lower than the ordinary temperature of the atmosphere. Such a distinction may have some advantages for practical reference, but it has no scientific value. The critical point of temperature affords a criterion for distinguishing a vapour from a gas, if it be considered important to maintain the distinction at all. Many of the properties of vapours depend on the gas and liquid being present in contact with one another; and this, we have seen, can only occur at temperatures below the critical point. We may accordingly define a vapour to be a gas at any temperature under its critical point. According to this definition, a vapour may, by pressure alone, be changed into a liquid, and may therefore exist in presence of its own liquid; while a gas cannot be liquefied by pressure—that is, so changed by pressure as to become a visible liquid distinguished by a surface of demarcation from the gas. If this definition be accepted, carbonic acid will be a vapour below 31°, a gas above that temperature; ether a vapour below 200°, a gas above that temperature.

We have seen that the gaseous and liquid states are only distant stages of the same condition of matter, and are capable of passing into one another by a process of continuous change. A problem of far greater difficulty yet remains to be solved, the possible continuity of the liquid and solid states of matter. The fine discovery made some years ago by James Thomson, of the influence of pressure on the temperature at which liquefaction occurs, and verified experimentally by Sir W. Thomson, points, as it appears to me, to the direction this inquiry must take; and in the case at least of those bodies which expand in liquefying, and whose melting-points are raised by pressure, the transition may possibly be effected. But this must be a subject for future investigation; and for the present I will not venture to go beyond the conclusion I have already drawn from direct experiment, that the gaseous and liquid forms of matter may be transformed into one another by a series of continuous and unbroken changes.

APPENDIX.

The following experiments, made at temperatures differing from any of the foregoing series, are added, as they may hereafter be useful for reference.

δ.	t.	ϵ.	t'.
$\frac{1}{48\cdot15}$	12°·42	$\frac{1}{75\cdot00}$	15°·76
$\frac{1}{53\cdot04}$	11·13	$\frac{1}{92\cdot53}$	16·45
$\frac{1}{47\cdot45}$	11·50	$\frac{1}{64\cdot14}$	31·91
$\frac{1}{71\cdot75}$	13·10	$\frac{1}{148\cdot5}$	31·65
$\frac{1}{73\cdot88}$	13·20	$\frac{1}{170\cdot5}$	31·71
$\frac{1}{73\cdot92}$	13·20	$\frac{1}{157\cdot9}$	33·15
$\frac{1}{73\cdot77}$	12·74	$\frac{1}{152\cdot3}$	33·58
$\frac{1}{73\cdot89}$	13·14	$\frac{1}{144\cdot5}$	35·00
$\frac{1}{73\cdot89}$	13·21	$\frac{1}{140\cdot0}$	36·03
$\frac{1}{76\cdot05}$	13·27	$\frac{1}{153\cdot4}$	36·05
$\frac{1}{78\cdot35}$	13·38	$\frac{1}{171\cdot1}$	36·11
$\frac{1}{80\cdot74}$	13·40	$\frac{1}{197\cdot8}$	36·22
$\frac{1}{83\cdot31}$	13·45	$\frac{1}{251\cdot4}$	36·20
$\frac{1}{86\cdot01}$	13·50	$\frac{1}{323\cdot6}$	36·08
$\frac{1}{88\cdot92}$	13·53	$\frac{1}{358\cdot1}$	36·18
$\frac{}{92\cdot06}$	13·55	$\frac{1}{377\cdot8}$	36·22

Fig. 1.

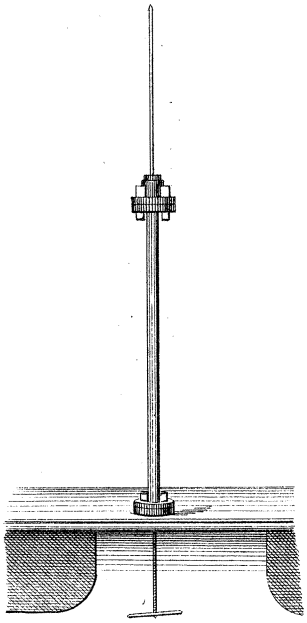


Fig. 2.

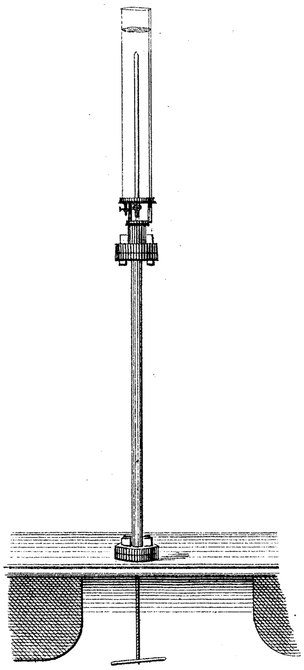


Fig. 3.

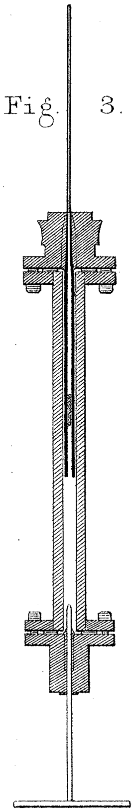
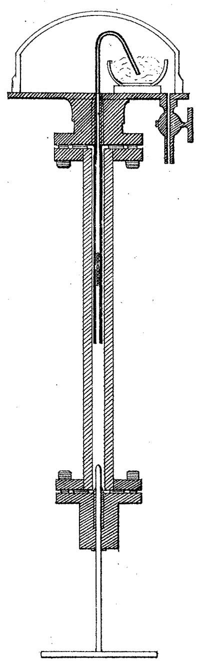


Fig. 4.



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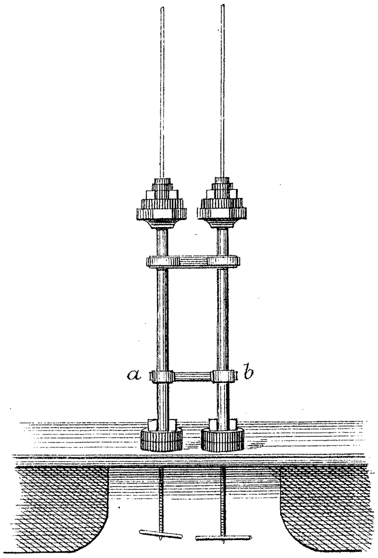


Fig. 6.

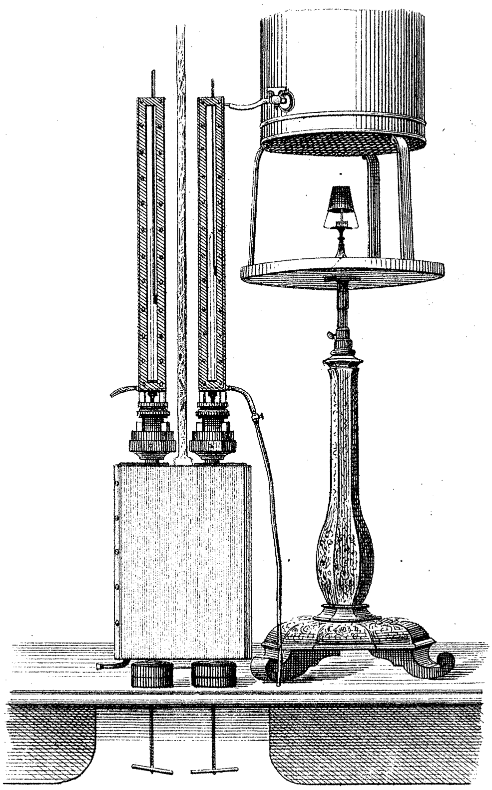
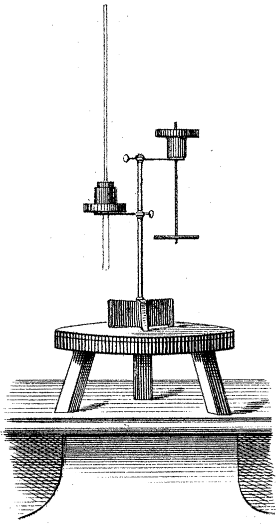


Fig. 7.



W.H.Wesley lith.

W. West imp.