

# On the Properties of Matter in the Gaseous and Liquid States under Various Conditions of Temperature and Pressure

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II. On the Properties of Matter in the Gaseous and Liquid States under various Conditions of Temperature and Pressure.\*

> By the late Thomas Andrews, M.D., LL.D., F.R.S. Communicated by Professor Stokes, D.C.L., P.R.S.

> > Received February 7,—Read March 18, 1886.

According to Dalton, the particles of one gas possess no repulsive or attractive power with regard to the particles of another gas; and accordingly, if m measures of a gas A be mixed with n measures of another gas B, each will occupy m+n measures of The density of A in such a mixture will be  $\frac{m}{m+n}$ , and of B,  $\frac{n}{m+n}$ , the pressure upon any one particle of such a gaseous mixture arising solely from particles of its "It is scarcely necessary," Dalton remarks, "to insist upon the application of this hypothesis to the solution of all our difficulties respecting the constitution of mixed gases where no chemical union ensues. The moment we admit it every difficulty vanishes. The atmosphere, or, to speak more properly, the compound of atmospheres, may exist together in the most intimate mixture without any regard to their specific gravities, and without any pressure upon one another. Oxygen gas, azotic gas, hydrogenous gas, carbonic acid gas, aqueous vapour, and probably several other elastic fluids, may exist in company under any pressure, and at any temperature, without any regard to their specific gravities, and without any pressure upon one another, while each of them, however paradoxical it may appear, occupies the whole space allotted to them all."

In conformity with this law, GAY LUSSAC found that the vapours of alcohol and water mix like two gases which have no action upon one another. The density of the

† 'Manchester, Phil. Soc. Mem.,' vol. 5, 1802, p. 543.

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<sup>\*</sup> The manuscript of this memoir was found among the author's papers, and was sent to me by Professor Tair, who thought that, as the former papers on the same subject were published in the 'Philosophical Transactions,' the manuscript ought to be submitted to the Royal Society. It has every appearance of being complete, though probably intended to be, in part at least, fair-copied before presentation. It was without title, but the title has been supplied from an earlier draft. This title shows that the paper must have been written a great many years ago, while Dr. Andrews was still connected with Queen's College, Belfast. For many years before his death the state of Dr. Andrews' health prevented him from continuing his scientific labours, even to the extent of preparing for publication an account of the results at which he had arrived in an investigation which was doubtless carried on with that conscientious accuracy which characterised all his work.—G. G. S.

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mixed vapours agreed closely with the density calculated according to Dalton's law.\* In 1836 Magnus published an important memoir on the same subject. He found that, if two liquids which do not mix with one another are introduced into a barometer tube, the tension of the mixed vapours at any temperature is equal to the sum of the tensions of the vapours of the two liquids. But when the liquids have the property of mixing with one another the behaviour of their vapours he found to be altogether different. The tension of the mixed vapours was no longer equal to the sum of the tensions of each vapour separately. This statement appears at first view to contradict the experiments of Gay Lussac, but, as Magnus himself has pointed out, the conditions under which the observations of the two eminent physicists were made were essentially different. In the experiments of Gay Lussac the mixed liquids were wholly converted into vapour, and therefore the mixed vapours formed were not in contact with any liquid, while in those of Magnus an excess of the mixed liquids was always present, and in contact with the vapour.†

The same subject was afterwards investigated with great care by Regnault in his elaborate work on the elastic force of vapours. His experiments were made by a similar method to that adopted by Magnus, but they embrace a larger number of bodies, and the results are given in fuller detail. The conclusions at which Regnault arrived are the same as those previously stated by Magnus, viz., that two volatile liquids, which are not capable of dissolving each other, give a vapour tension equal to the sum of the tensions which the same liquids give separately, but that two volatile liquids, which are capable of dissolving each other, give a complex vapour whose tension is always less than the sum of the tensions of the vapours of the two liquids, and often less than the tension of the vapour of the more volatile liquid alone.

The case of the elastic force or tension of a mixture of gas and vapour has also been investigated by Regnault. In his earlier researches on this subject he found the elastic force of aqueous vapour, at the point of saturation, in presence of air or nitrogen, to be always a little feebler than its elastic force in vacuo. The difference was, however, small, rarely exceeding one-fiftieth of the whole tension, and Regnault in his earlier investigations was inclined to attribute it to some constant error in his method. In his later researches he returned to the same subject, and in order to aid in the solution of the question he made a number of direct determinations of the density of the vapour of water within the limits of temperature at which he had formerly worked. He also extended his experiments to mixtures of air with vapours of other liquids more volatile than water. The results he obtained were in accordance with Dalton's law, provided the mixed gas and vapour were compressed so as to

<sup>\* &#</sup>x27;Annales de Chimie,' vol. 95, 1815, p. 314; Biot, 'Traité de Physique,' vol. 1, p. 298, where GAY LUSSAC'S experiments are first described.

<sup>† &#</sup>x27;Poggendorff, Annalen,' vol. 38, 1836, p. 488.

i 'Mémoires de l'Académie des Sciences,' vol. 26, 1862, pp. 722 and 729.

<sup>§ &#</sup>x27;Annales de Chimie,' vol. 15, 1845, p. 137.

cause an abundant deposition of liquid, and the observations were made immediately after the application of the pressure. The slight deviations from that law under other conditions of the experiment he attributed to the hygroscopic affinity of the sides of the containing vessel, which condense a portion of the vapour and lower its tension

below that due to saturation. As the result of all his observations, Regnault concludes that the law of Dalton may be considered to be theoretically true in the case of mixtures of gases and vapours, and that it would probably be in all cases verified rigorously by experiment if the mixed gas and vapour could be enclosed in a vessel

whose sides were formed of the volatile liquid itself.\*

The only experiments, so far as I know, on the effects of pressure upon mixtures of the ordinary gases are a few recorded by Regnault on mixtures of atmospheric air and carbonic acid, and of hydrogen and sulphurous acid. The observations were made within limits of pressure extending from two-thirds of an atmosphere to two atmospheres, and the results indicated that within these limits the compressibility is intermediate between that which each gas, if isolated, would exhibit for the same variations of pressure. †

The result of these experimental investigations is to confirm, with one exception, the law of Dalton for all cases of mixtures of gases or of vapours, or of gases and vapours which have no chemical action upon one another. The exception referred to is that of a mixture of vapours derived from liquids capable of dissolving one another, and in presence of the compound liquid. To such a case the law of Dalton, as originally enunciated, is clearly inapplicable, since chemical affinities come into play which disturb the result. The diminution of volume and disengagement of heat which occur when water and alcohol in the liquid state are mixed prove, as GAY LUSSAC long ago pointed out, that there is a well-marked affinity between those liquids, resulting in the formation of a chemical compound, and that it is the tension of the vapour of this compound which is actually observed.

It would, however, be a hasty inference to conclude that the law of Dalton has been fully established by experiment, the more so as in none of the investigations to which I have referred was the pressure carried beyond two atmospheres. As the apparatus described in my former communications was well adapted to this inquiry, I

- \* 'Mémoires de l'Académie des Sciences,' vol. 26, 1862, pp. 680-696.
- † Ibid., p. 258.
- ‡ The following foot-note occurs in the earlier draft:—

<sup>&</sup>quot;I wish here to supply an omission in my former paper, and to explain, for the information of future experimenters, the mode of packing the screws and of connecting the glass tubes with the metallic flanges. In fig. 3 of the plate accompanying this paper a section of the steel screw is shown, from which it will be seen that the screw enters a female screw in the flange (fig. 7) for about half an inch, and afterwards a leather packing of more than one inch in length. This packing is formed of a number of circular disks of leather punched through in the centre and saturated in vacuo with melted lard After each disk is introduced it is pressed firmly into its place in the flange by hammering lightly with a wooden mallet upon an iron bolt, which fitted loosely the cylindrical cavity. The flange, when

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have examined with care the behaviour of a mixture of nitrogen and carbonic acid gases under varied conditions of pressure and temperature. According to the definition I ventured formerly to give of a vapour, viz., that it is a gas at any temperature below its critical point, that is to say, at any temperature at which it can be changed by the application of external pressure to the liquid state, carbonic acid is a vapour at temperatures below 31° C., and a gas proper at higher temperatures. Accordingly the properties of the mixture of nitrogen and carbonic acid have been examined at temperatures both above and below the critical point of pure carbonic acid.

The gaseous mixture, carefully dried, after flowing through the tube in which it was to be compressed, was collected over mercury and analysed. After all reductions were made its composition was found to be

3 vol.  $CO_2$  and 4.05 vol. N.

At the conclusion of the long series of experiments now to be described, which occupied several months, during which this mixture was exposed from day to day to

filled with its packing, was strongly clamped upon the edge of a table, the flat surface resting on the table, and the steel screw afterwards turned till it passed through the packing and entered the table for a short way. On removing the flange from the table, the leather was always found to project beyond the surface of the brass; it was cut away till it formed a thin cylinder round the screw, which cylinder was afterwards strengthened by tying it with a silk thread. I have been thus minute in describing this operation, as a screw successfully packed in this way will resist for many months a pressure of several hundred atmospheres. The upper flange which carried the glass tube was traversed by a cylindrical cavity terminating in a hollow cone, and the glass was fashioned into a form which, when covered with its packing, fitted into this cavity. The packing was effected by rolling round the glass cone and cylinder several strands of a fine hempen thread covered with shoemaker's wax, which was applied slightly heated. The flange was then warmed, and the glass tube very firmly pressed down into its place, and the whole allowed to cool. A junction of this kind will also bear a pressure of several hundred atmospheres without yielding."

The following is given in the text of the same draft:-

"So perfectly did the apparatus work that in a long investigation, extending over several months, during which the apparatus was never dismounted, I was able without any difficulty to make a continuous series of experiments at pressures varying from 50 to 300 atmospheres, and to read the changes of volume of the gases of these pressures in glass tubes with almost as great ease as an ordinary barometer. One precaution only requires to be mentioned. If the pressure is either largely augmented or diminished in the course of an experiment, the readings should not be made for some time after, as the apparatus, without the slightest leakage, takes time to adjust itself to the new condition. I presume it is the slow change of volume in the leather packings to which this is due. Indeed, the effect is equally marked on taking off the pressure suddenly as on augmenting it. The mercury in the manometer will rise, in the former case, visibly to the eye for some time. When working at very high pressures, I was formerly in the habit of making the observations as quickly as possible after each augmentation of pressure, but since I discovered the true action of the apparatus I have always given time for all the parts to adjust themselves to the new condition, when the readings can be made with great ease and accuracy."

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pressures varying from 40 to 300 atmospheres, it was again analysed as it existed in the tube, and found to consist of

3 vol. CO<sub>2</sub> and 4.02 vol. N.

In the following Tables p is the pressure as indicated by a hydrogen-manometer, t the temperature of the manometer,  $\epsilon$  a fraction representing the ratio of the volume of the mixture after compression to its volume at the temperature t' under one atmosphere, t' the temperature of the mixed gases, and  $\theta$  the volume which 1 volume of the mixture measured at 0° and 760 millimetres would occupy, at the temperature at which the observation was made, and under the pressure indicated by the hydrogenmanometer.

Table I.—Compressibility of 3 v. CO<sub>2</sub>+4 v. N at 2°·2.

p	t	ε	t'	θ	
42.05	7:30	1 47'18	° 2·32	0.02138	
48.68	7:30	1 55°90	2:34	0.01805	
51.64	7.22	1 5 9 9 7	2.08	0.01681	
54.73	7.26	1 64.05	2.38	0.01575	
58.43	7.21	1 69'28	2.06	0.01455	
62.63	7.21	1 7 5 * 4 3	2.10	0.01338	
67:20	7.20	1 82.04	2.16	0.01229	
79:47	7.18	1101'0	2.21	0.00998	
87.73	7.17	1 114.4	2.21	0.00881	
97.21	7.17	1 1 3 0 7	2.17	0.00772	
108.60	7.17	1 1 5 1 0	2.21	0.00668	
123.40	7.17	1776	2.25	0.00568	

In the following Table the denominator of  $\epsilon$  in the second line is given in both manuscripts as 49.06, which must have been an error of copying. 46.09 corresponds with  $\theta$ .—G. G. S.]

# DR. T. ANDREWS ON THE PROPERTIES OF MATTER IN THE Table II.—Compressibility of 3 v. $CO_2$ and 4 v. N at 7° 5.

	· I	The second of th		1
p	t	ε	t'	θ
39.68	7.47	1 4 3 7 4	7·50	0.02350
41.56	7.48	1 46.09	7:50	0.02231
43.66	7.42	1 48.75	7:50	0.02109
46.00	7.46	1 51'67	7.53	0.01987
51.48	7.48	1 58'95	7.51	0.01744
54.75	7.42	1 6 3 2 4	7.59	0.01625
58.24	7.54	1 68.00	7.50	0.01512
$62 \cdot 46$	7.50	1 73'90	7.50	0.01391
67.07	7.48	1 80'69	7.50	0.01274
73.00	7.59	1 89'47	7.50	0.01149
79.22	7.65	1 99'18	7.51	0.01054
87.20	7.55	11110	7.50	0.00926
96.50	7.80	1 2 6 9	7.08	0.00808
108.70	7.54	1 2 6 9	7.48	0.00691
144.00	7.58	1488 1 207'5	7.54	0.00495
166.40	7.79	1 2 4 3 5	7.50	0.00422
173.40	7.63	1 2 5 4 · 7	7.49	0.00404
215.70	7.67	1 309'9	7.50	0.00332
283.90	7.58	1	7.49	0.00272
283.90	7.58	377'9	7.49	0.00272

Table III.—Compressibility of 3 v.  $CO_2$  and 4 v. N at  $31^{\circ}$ .

p	t	ε	t'	θ		
42.26	° 11.61	1 45.60	° 31·35	0.02445		
49.43	11.94	1 54 30	31.31	0.02055		
55.82	11.86	1 62'13	31.21	0.01795		
63.87	12:38	1 7 2 3 5	31.40	0.01542		
72.34	12:38	1 83'40	31.14	0.01337		
89.26	12:38	1 1066	31.06	0.01045		
110.00	11.96	1 3 6 7	31.36	0.00816		
145.60	11.63	1 90'2	31:35	0.00586		
221.70	11:70	1 295°9	31:30	0.00377		

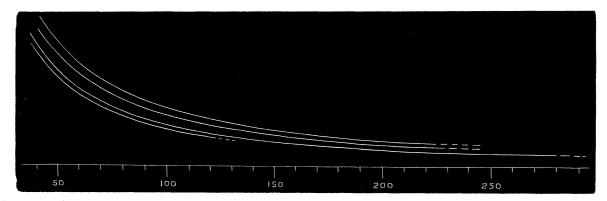
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Table IV.—Compressibility of 3 v. CO<sub>2</sub> and 4 v. N. at 48°·4.

p	t	ε	ť′	θ	
41.90	8:39	1 4 4 6 6	。 48·22	0.02635	
48.80	8.42	1 52'59	48.11	0.02239	
55.86	12.06	1 61'10	48.48	0.01929	
64.18	12.08	7092	48.43	0.01662	
72.54	12.18	1 81'56	48.66	0.01448	
110.50	12:36	1 1 3 1 4	48:38	0.00896	
147.10	12:36	1 182'3	48.49	0.00646	
223.60	12:40	1 276'5	48.47	0.00430	

No liquid carbonic acid was formed in any of these experiments, although the experiments in the first series were made at a temperature 29° below the critical point of pure carbonic acid. The results of the foregoing experiments are represented graphically in the following figure, in which the curves for the different temperatures present a remarkable similarity of form, giving no clear indications of a difference of character for temperatures above and below 31°.

Fig. 1.

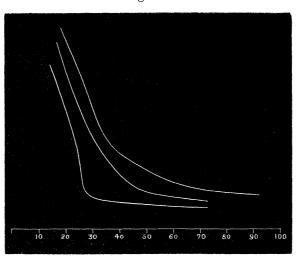


If we assume Dalton's law to be true, and Boyle's law to be true in the case of nitrogen for the pressures employed, the following curves will represent the changes of volume of the carbonic acid in the mixture at the indicated pressures and [See fig. 2, which is taken from a provisional figure in the MS.] temperatures.

I have endeavoured to ascertain approximately the form of the carbonic acid curve in this mixture, assuming as sufficiently accurate for my purpose that nitrogen in contracting obeys the law of Boyle; but the curves so obtained, although they give indications of a fall to the liquid volume at the two lower temperatures, are wholly

different from those for the unmixed gas. It is manifest, therefore, that the law of Dalton does not hold under the conditions of these experiments. Like the other laws of the gaseous condition of matter, it appears to be strictly true only in the (ideal) perfect state. The small differences in the elastic force of aqueous vapour when alone and when mixed with air, as given in the original experiments of REGNAULT, are, it is highly probable, due, not to accidental or extraneous causes, but to the law of Dalton being only approximately true in the case of such a mixture of gas and vapour.

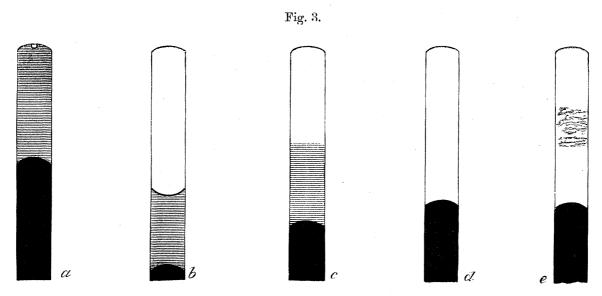
Fig. 2.



As no liquid was formed in any of these experiments, it follows that the admixture of carbonic acid with a permanent gas, such as nitrogen, has the effect of lowering the critical point or critical temperature. It will be remembered that for pure carbonic acid the critical temperature is 30.9°. In order to examine the phenomena with more precision, mixtures of carbonic acid and nitrogen were taken containing a smaller proportion of nitrogen than the foregoing.

With a mixture of 6.2 vol. carbonic acid and 1 vol. nitrogen, and which therefore contained 13.9 per cent. of nitrogen, liquid first appeared at the temperature of 3°.5, when the pressure was raised to 48.3 atmospheres. As the pressure was increased the volume of the liquid augmented, and after each increase of pressure the liquid continued for some time slowly to augment. Thus at 82 atmospheres the relative volumes of gas and liquid in the above mixture were at first 8.5 and 5.8, but on leaving the apparatus to itself there was a small increase in the volume of the liquid. When the pressure was raised to 102 atmospheres the volume of the gas, at first 1.7, gradually diminished till it became reduced to a minute globule, which also at last disappeared, the nitrogen dissolving in the liquid carbonic acid. These are the ordinary phenomena of the solution of a gas in a liquid, the gas retaining the form of a small globule, as is shown in figure 3a, till it finally disappeared. But on repeating the experiment at higher temperatures the phenomena exhibited were very different.

The temperature being kept steady, the liquid carbonic acid appeared at first with the usual concave surface, and on augmenting the pressure its volume for some time steadily increased without any marked change in its appearance (fig. 3, b). By further increase of pressure, the surface of separation became a faint line without curvature (fig. 3, c), and on continuing the pressure it finally disappeared, the whole mass assuming the homogeneous state (fig. 3, d).



The position of the surface of separation in the tube before it disappeared depended upon the temperature at which the observations were made. At 14° the liquid occupied about two-thirds of the entire space just before the surface was effaced.

It is difficult to fix with precision the exact pressure at which for a given temperature the last trace of the surface of separation disappears, but a definite point can be obtained if, after having completely effaced the surface by pressure, we diminish the pressure till a cloud appears, when the liquid surface in a faint form is immediately restored (fig. 3, e). The appearance of this cloud is remarkable. It occupies several millimetres of the tube, and as it subsides the plane surface of separation appears, not in the middle of the space occupied before by the cloud, but about one-third from the lower end.

For a mixture composed of 1 volume of nitrogen and 3.43 volumes carbonic acid, or containing 22.5 per cent. nitrogen, the critical point of temperature was found to be 14°0, and the corresponding pressure 98 atmospheres. This point was determined by gradually lowering the temperature till it was just possible to obtain a small trace of liquid by the application of pressure. With this mixture a number of experiments were made at lower temperatures than the critical point (14°), in order to fix the pressures at which, for the same temperature, the liquid first appeared, and was afterwards effaced. As it was difficult to fix the latter point directly with precision, I found it better in the first place completely to efface the liquid, and afterwards to

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remove the pressure till the cloud appeared. In this way precise and concordant results were obtained.

At the temperature of 6°.3, liquid first appeared when the pressure was raised to 68.7 atmospheres, and, after being effaced by pressure, it reappeared at 113.2 atmospheres.

At 9°9, liquid appeared at a pressure of 77.6 atmospheres, and, after being effaced by pressure, it reappeared at 107.8 atmospheres.

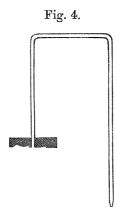
At 13°2, liquid appeared at 91.6 atmospheres, and, after being effaced by pressure, it reappeared at 103.2 atmospheres.

It is evident that, as we approach the critical point, the pressures at which the liquid first appears, and after being effaced reappears, will come almost exactly to This pressure, as already stated, for the mixture under examination was 98 atmospheres. If we take the mean of the pressures at which the liquid appears and reappears after being effaced for the above temperatures, we shall have the following results:—

0								Atmosphere			
6.3				•			٠			90.9	
9.9		•		•			•			92.7	
13.2			•							97.4	
14.0										98.0	

The last numbers are the temperature and pressure for the critical state of the mixture.

In making these experiments, it was found convenient to modify the form of the apparatus by bending the carbonic acid tube before introducing it into the apparatus, as shown in the annexed figure. On compressing the mixture below the critical



point, the liquid carbonic acid accumulated in the lower end of the tube, although a part of it was at first formed in contact with the mercury. But the latter portion soon fell down, and the whole of the liquid collected below.

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I was long perplexed with anomalous results, the carbonic acid sometimes liquefying by the application of pressure at temperatures above 20°, at other times refusing to liquefy at temperatures several degrees below that point. After many trials these irregularities were at last traced to the gaseous mixture having separated into two portions, one rich and the other poor in carbonic acid, when the pressure was reduced after liquefaction so as to convert the whole mixture into the gaseous state. case the lower end of the tube, which had been before occupied by the liquid, contained a large excess of carbonic acid, particularly if the tube had been previously exposed to  $-10^{\circ}$  so as to liquefy nearly the whole of the carbonic acid in the mixture. On reducing the pressure so as to restore the carbonic acid to the gaseous state, and raising the temperature to 26°, I have succeeded in liquefying the carbonic acid by the application of pressure alone at this temperature, provided the experiment was performed without loss of time. But, on allowing the mixture to remain for some time in the gaseous state, diffusion gradually occurred, and the temperature at which liquefaction was possible underwent a corresponding reduction. The diffusion was not complete for several hours, after which no liquid was formed by the application of pressure till the temperature was reduced to 14°. The true critical point for this mixture was therefore just below 14°, and when liquid was formed by pressure at higher temperatures it arose from carbonic acid gas being present in excess in the lower end of the tube.

Advantage was taken of this mode of separating a mixture of nitrogen and carbonic acid to ascertain whether any or what change of volume occurs in the diffusion of these gases at high pressures. For this purpose the gases were left for about twenty hours under nearly the same pressure as that at which the observations were subsequently made. The volume of the mixture was then carefully read at a fixed temperature and pressure. The mixed gases were now exposed to high pressure at the temperature of  $-12^{\circ}$  so as to liquefy the carbonic acid. They were again restored to the original pressure and temperature, and the volume was read. It was always found to have increased, usually about one-sixtieth part. On allowing the whole to remain at rest, and preserving the temperature and pressure steadily the same, the original volume was gradually restored by the expansion which occurred as the gases slowly diffused into one another. In an hour and a half the mixture had recovered four-fifths of the first contraction. On the other hand, the application of strong pressure at temperatures at which no liquefaction occurred did not produce any change in the volume of the mixture when the original temperature and pressure were restored. The following are the details of three sets of observations:—

At  $8^{\circ}.5$ , and under a pressure of 46.4 atmospheres, the volume of the mixed gases, after complete diffusion for many hours, was found to be 162.2. After liquefying the carbonic acid by strong pressure at  $-12^{\circ}$ , and again restoring the temperature to  $8^{\circ}.5$  and the pressure to 46.4, the volume of the mixed gas was reduced to 159.5, a contraction of 2.7 volumes having taken place from the separation of the diffused gases.

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In an hour and a half diffusion had partially occurred and the volume had increased to 161.5.

At 16°0, and under a pressure of 47.9 atmospheres, the volume of the mixture was 164.6; after liquefaction of the carbonic acid and restoration of the original temperature and pressure the volume was 161.9, or a contraction of 2.7 volumes. hour and a half the volume had increased to 164.1.

Similar experiments at 20°, and under a pressure of 46.4 atmospheres, gave a reduction of volume from 175.8 to 173.5 after separation of the gases.

It hence appears that when carbonic acid and nitrogen diffuse into one another at high pressures an increase of volume takes place; and, on the other hand, when they are separated from one another there is a diminution of volume. A similar change of volume no doubt occurs at ordinary pressures, but its amount would be so small as to The result now described is the reverse of what render the observation difficult. commonly happens when liquids diffuse into one another, but it is in accordance with what might be expected in the case of the diffusion of two bodies such as carbonic acid and nitrogen of unequal compressibility, and which do not combine with one another.

The following are the general conclusions to which this inquiry has led:—

- 1. The law of gaseous mixtures, as enunciated by Dalton, is largely deviated from in the case of mixtures of nitrogen and carbonic acid at high pressures, and is probably only strictly true when applied to mixtures of gases in the so-called perfect state.
  - 2. The critical point of temperature is lowered by admixture with a permanent gas.
- 3. When carbonic acid gas and nitrogen diffuse into each other at high pressures the volume of the mixture is increased.
- 4. In a mixture of liquid carbonic acid and nitrogen at temperatures not greatly below the critical point, the liquid surface loses its curvature and is effaced by the application of pressure alone, while at lower temperatures the nitrogen is absorbed in the ordinary way, and the curvature of the liquid surface is preserved so long as any portion of the gas is visible.