

XVII. THE BAKERIAN LECTURE.—*On the Gaseous State of Matter.*

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§ 1.

SINCE the investigation “On the Continuity of the Gaseous and Liquid States of Matter,” which formed the subject of the Bakerian Lecture for 1869, was communicated to the Society, I have continued to pursue the inquiry in a more extended form, with the view of discovering the general laws which determine the physical conditions of matter in the gaseous and liquid states. The subject in its whole extent and under all its aspects is so vast in itself, and its investigation in many cases has been surrounded by experimental difficulties of so high an order, that I must crave the indulgence of the Society if the amount of work actually accomplished appear small for the time devoted to it. I will give in the first place a few details regarding the method of mounting the apparatus, which will aid greatly any one who may hereafter desire to pursue the inquiry.

The apparatus employed is, in all the essential parts, the same as that which I formerly described. The packing of the steel screw, by which the pressure is produced, is an important part of the operation. It is effected by means of a number of circular disks of leather, pierced centrally with a fine hole, and rendered impervious to water by being saturated *in vacuo* with melted lard. These disks are introduced, one by one, into a cylindrical cavity above the female screw in the lower end-piece, care being taken to press down each disk separately by a few gentle blows of a wooden mallet. After the introduction of the leather packing, the brass end-piece is placed with the face downwards on a small wooden block, and the whole is firmly clamped to a steady bench or table. The steel screw is then inserted, and screwed through the leather packing till it enters into the wooden block. The connexion between the metal and glass tube in the upper end-piece is established by forming a protuberance on the glass tube accurately corresponding to a conical surface in the passage through the end-piece. The conical surface of the glass tube and the adjoining cylindrical surface for an inch and a half below the cone were covered with several layers of fine thread coated with ordinary shoemaker's wax. The brass end-piece was gently heated before the introduction of the glass tube, and the latter was firmly fixed in its place by steady pressure. So perfectly have these arrangements fulfilled their purpose, that the apparatus, when successfully mounted, will remain in perfect order and without a trace of leakage for an indefinite period of time. The greatest pressure to which I have exposed the apparatus is 500 atmospheres, but it

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would be easy with very fine glass tubes to make accurate observations even at much higher pressures.

As the metallic tubes, whether made of cold-drawn copper or of forged iron, which form the body of the apparatus are, as at present constructed, $\frac{5}{8}$ of an inch in internal diameter, I have been able to make an important improvement in the arrangements. The glass tubes containing the gases now dip into small mercurial reservoirs formed of thin test-tubes, which rest on ledges within the metal tubes. This arrangement has prevented many failures in screwing up the apparatus, and has given greater precision to the measurements.

In the following experiments the glass tube was filled with the gas in a pure and dry state by passing a stream for a long time through it while in an upright position; and when the air was entirely expelled, the upper end was hermetically sealed. The stream of gas being still maintained across the lower end of the tube, which was enclosed in a test-tube partly filled with mercury, the whole apparatus was left for half an hour in an apartment at a steady temperature, after which the gas was imprisoned at a known temperature and pressure, by bringing the lower or open end of the tube into contact with the surface of the mercury in the test-tube. By this process the original volumes of air in the manometer, and of carbonic acid in the carbonic acid tube, could be fixed with great accuracy.

The capacities of the entire tubes and of their capillary parts were ascertained by a set of careful determinations of the weight of mercury which filled them at a known temperature. Before the introduction of the mercury, the interior of each tube was carefully cleansed by boiling nitric acid in it, and afterwards washing it with distilled water and absolute alcohol. No attempt was made to remove by boiling the thin film of air which, even in the most carefully cleansed tube, is always interposed between the surface of the glass and the mercury drawn into the tube. Under the conditions of these experiments this correction must be very small; and its estimation would be a matter of extreme difficulty, as in screwing up the apparatus air of different densities would be imprisoned between the glass and mercury. On a future occasion I hope to lay before the Society the results of a special investigation of this subject. The average capacity of the capillary part of the tube of the air-manometer used in the greater number of the following experiments was for 1 millimetre 0.00018121 cubic centimetre, and this tube bore a pressure of upwards of 200 atmospheres without bursting. I have completed a series of experiments at higher pressures, which I hope soon to communicate to the Society, with a hydrogen manometer, whose capacity for each millimetre was only 0.000016861 cubic centimetre, or $\frac{1}{11}$ of the preceding. Such a tube would bear a pressure many times greater than the former, and no serious difficulty would arise in operating with even finer tubes. There is therefore scarcely any limit to the pressures which may be measured in glass tubes. The glass of which these tubes were made was of excellent quality, and was specially prepared for me by J. POWELL and Sons.

No pains were spared in calibrating the capillary portions of the tubes. For this

purpose a dividing and calibrating engine was employed, which was devised some years ago by myself. It was provided with a short steel screw of remarkable accuracy, specially constructed for this dividing engine by TROUGHTON and SIMMS. The results of the calibration were [plotted on a large scale, and the small errors arising from the abrupt passage between the calibrated lengths of the tube were estimated by a simple method, for which I am indebted to my friend Professor JAMES THOMSON. The thermometers employed were the same to which I formerly referred. They were all calibrated and divided by myself, and their agreement throughout the whole range between 0° and 100° was almost perfect. The shifting of the zero-points has not been considerable, but it was carefully observed from time to time.

The capacity c_0 of the glass tube at 0° C. in cubic centimetres was calculated by the following equation, in which w is the weight of the mercury, t the temperature at which the observation was made, and f (0.000158) the apparent dilatation for 1° C. of mercury in glass:—

$$c_0 = w \cdot \frac{1+ft}{13.596} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

The value of c_0 , as given by this expression, may be used without notable error for temperatures differing only by a few degrees from 0° C., but at high temperatures a correction is required for the expansion of the glass vessel. If the readings had been made by means of fine divisions etched on the tube, this correction would correspond to the cubic expansion of the glass; but when, as in my method of working, cathetometric readings are made from the extreme end of the internal cone above to the bounding surface of the mercury below, the correction will be the difference between the cubic and linear expansion of glass, or for small differences of this order it will be two thirds of the cubic expansion. If c_t be the capacity at the temperature t , k the cubic dilatation of glass for 1° C. (0.0000272), we shall have, under the conditions stated above,

$$c_t = c_0 \left(1 + \frac{2}{3} kt\right) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Combining equations (1) and (2), we obtain a general expression for c_t ,

$$c_t = w \cdot \frac{1+ft}{13.596} \left(1 + \frac{2}{3} kt\right) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

The original volume of gas at 0° and 760 millimetres was calculated by the usual formula,

$$v_0 = v_t \cdot \frac{1}{1+\alpha t} \cdot \frac{p}{760} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

where v_t is the capacity of the tube in cubic centimetres, α the coefficient of expansion at the ordinary pressure of the atmosphere (0.00367 for air and 0.00371 for carbonic acid), t the temperature of the observation, and p the height of the barometer reduced to 0° C. and the latitude of 45° .

The pressure in atmospheres, as indicated by the air-manometer, on the gas in the carbonic acid tube was given by the equation

$$p = \frac{V_0(1 + \alpha t)}{V_1} \mp \frac{q}{760}, \quad (5)$$

in which V_0 is the volume of the air at 0° and 760 millimetres, V_1 the observed volume at the temperature t , and q the difference of level (corrected when necessary for difference of capillary depression) of the surface of the mercury in the manometer and carbonic acid tubes, the negative sign applying to the case in which the mercury stands higher in the carbonic acid tube than in the manometer.

The value of ε , which is the ratio of the volume of the carbonic acid at the pressure p (as indicated by the air-manometer) and temperature t' to its volume at the same temperature t' under one atmosphere, is given by the equation

$$\varepsilon = \frac{V_1}{V_0(1 + \alpha t')}. \quad (6)$$

If we represent by θ the volume to which one volume of carbonic acid measured at 0° and 760 millimetres is reduced at the pressure p and temperature t' , we shall have

$$\theta = \frac{V_1}{V_0}. \quad (7)$$

It was manifestly impossible, at the great pressures employed, to surround the manometer and carbonic acid tubes with outer tubes of glass subjected internally to the same pressure, so as to equalize the pressure on both sides of the glass. Nor would any useful purpose have been attained if such an arrangement had been possible, as the thickness of the glass walls of the capillary tubes was never less than eight times the diameter of the bore, and any change in the capacity would be too small to affect sensibly the results. From a long series of experiments undertaken for the purpose of making a new determination of the compressibility of mercury, but not yet completed, I will give only the following result, as being sufficient for our present purpose:—A column of mercury 445 millimetres in length was exposed in a tube with a fine capillary bore to a pressure ranging from 5 to 110 atmospheres, at the temperature of $17^\circ.60$, the temperature scarcely varying $0^\circ.01$ during the experiments. The apparent change of volume for one atmosphere was found to be

$$0.0000070.$$

In a repetition of the same experiment at $18^\circ.55$, the result was

$$0.0000072.$$

From a series of experiments between 3.3 and 9.5 atmospheres of pressure, REGNAULT has calculated the absolute compressibility of mercury by the aid of a set of equations which were furnished to him by M. LAMÉ, and found it to be

$$0.0000035.$$

Although this latter result can only be regarded as an approximation to the truth, from the limited range of pressure employed, as well as from the uncertainty of some of the principles upon which the mathematical expressions depend, it may be taken to be sufficiently accurate for our present purpose. Combining it with the mean of the two foregoing numbers, we obtain for the change of internal capacity of the glass tube for one atmosphere of pressure

$$K=0.0000036.$$

From other experiments it would appear that the value of K diminishes as the pressure increases, a result which might be expected from the change of volume being chiefly due to the yielding of the inner layers of the glass of which the tube was composed. For 100 atmospheres the entire correction would, according to these experiments, amount only to $\frac{1}{3000}$ part. I have not thought it necessary to apply this correction, as it falls in most cases within the limits of the errors of observation; but the data I have given are sufficient to allow this omission to be readily supplied.

I have deemed it important to attempt the solution of a problem of the highest interest in itself and of the greatest importance to the accuracy of many fundamental determinations in physics and chemistry, but which, so far as I know, has never been made the subject of direct investigation. It is to ascertain whether mercury has to any extent the property of absorbing gases in the same manner as water and alcohol. The fact that gases like ammonia, which are largely absorbed by water, may be readily collected and preserved over mercury, and the absence of any diminution of volume in gaseous mixtures standing for long periods of time over mercury, rendered it highly improbable that any such absorption would take place. It was, however, important to ascertain whether under great pressures any indications of absorption could be found. The following is the way in which I have attempted to resolve this question.

Having reduced the pressure to 10 atmospheres in the apparatus, mounted with an air-manometer and carbonic acid tube, I allowed it to remain undisturbed at this low pressure for ten days. At the end of this time, on a sunless day, which favoured accurate observations, water was made to circulate from a large cistern, at a steady temperature of $8^{\circ}39$, through the rectangular vessels which enclosed the tubes; and the pressure was then quickly raised from 10 atmospheres till half a millimetre of liquid was formed in the carbonic acid tube. The air-manometer was then read, and the apparatus left at the new pressure for five days. It was again adjusted carefully, so that half a millimetre of liquid carbonic acid was formed as before. The temperature at this reading was $8^{\circ}45$. The calculated pressures, from the indications of the air-gauge, were on the first occasion 43.94 and on the last 44.00 atmospheres. A difference of pressure of 0.06 atmosphere corresponded therefore to a difference of temperature of $0^{\circ}06$. From experiments to be described in a future communication, it will appear that at this pressure a change of 0.06 atmosphere corresponds to $0^{\circ}055$. The agreement is complete, and the air in the manometer had therefore undergone no diminution of volume or absorption, after an interval of five days, from a change of pressure from 10 to 44 atmospheres.

Having thus shown that air is not absorbed by mercury, it remained to extend the inquiry to the case of carbonic acid gas. For this purpose the apparatus was again left at a pressure of 10 atmospheres for some days, and the pressure was then quickly raised at $4^{\circ}99$ to $35\cdot89$ atmospheres, at which pressure the carbonic acid was still wholly in the gaseous state. After reading the volumes of air and carbonic acid gas in the two tubes, the apparatus was left at the new pressure for two days, when the observation was repeated at the same temperature, the pressure having been adjusted as at the first observation. The readings of the two tubes were precisely the same as before. Now as the former experiments had proved that the air in the manometer under increased pressure undergoes no absorption, the last experiment evidently extends this conclusion to carbonic acid gas. In confirmation of this result, I may mention that after allowing the apparatus to stand for many hours at a pressure of above 100 atmospheres, and then suddenly reducing the pressure to 10 atmospheres, not the slightest evidence of the escape of gas from the surface of the mercury could be detected even with the aid of a strong magnifier. In filling a barometer-tube the air which is expelled by ebullition has not been dissolved in the mercury, but comes from the thin shell of air interposed between the mercury and the surface of the glass.

Two questions still remain to be considered. 1. Do the glass tubes undergo a permanent increase of capacity when exposed for a long time to these high pressures? 2. Is there any absorption of oxygen in the air-manometer from its slow combination with the mercury? To both questions I am able to give a satisfactory answer. The apparatus was mounted on October 30, and three days after the pressure at which carbonic acid liquefies when the temperature is $8^{\circ}41$ was found in two experiments to be $43\cdot90$ and $43\cdot94$ atmospheres, the mean being $43\cdot92$ atmospheres. During the following two months the apparatus was in daily use for a long course of experiments, in which the pressures varied from 12 to 120 atmospheres, and the latter pressure was often maintained for the space of 24 hours. On the 1st of January the pressure required for liquefaction was again determined at the same temperature of $8^{\circ}41$. In three experiments it was found to be $43\cdot96$, $43\cdot96$, and $43\cdot94$ atmospheres—the mean, or $43\cdot95$ atmospheres, differing only by $0\cdot03$ atmosphere from the former result. This is quite within the limits of error of observation, as it corresponded to a difference of less than $0\cdot1$ millimetre in the actual readings. It follows therefore that there has been no appreciable enlargement of the internal capacity of the tube, or reduction of the volume of the air from chemical combination or absorption, during a period of two months of active work. That no oxidation of the mercury had occurred was further shown by the bright metallic surface of the fine mercurial column, and the absence of any tendency to drag when the mercury rose or fell from change of pressure*.

It is with regret that I am still unable to give the true pressures which correspond

* While writing the above I have carefully examined the apparatus, and find it to be now in as perfect order as when it was mounted five months ago, the mercury in the air-manometer moving through its extreme range as readily and with as much precision as in a thermometer of the best construction.—[March 22.]

to the indications of the air-manometer. Since my former communication in 1869, I have given the most careful consideration to this subject, and I hope soon to submit to the Society a detailed statement of the only method by which, as far as I can discover, this highly important question can be resolved for high pressures. Even for pressures under 30 atmospheres the discordant results at which such distinguished physicists as OERSTED and SWENDSEN, ARAGO and DULONG, and REGNAULT have arrived, afford ample proof of the extraordinary difficulties of the investigation*. I shall have occasion presently to recur to this subject, and to refer to the attempts which have since been made by other methods to ascertain the compressibility of air and of the permanent gases at high pressures. In the absence of precise data, I have not attempted in this paper to correct the indications of the air-manometer so as to reduce them to true pressures. We shall see hereafter that up to 250 atmospheres there is good reason for believing that the deviations of the air-manometer from true pressures are not considerable, or such as to interfere with any general conclusions.

In the present investigation on the properties of the gaseous state of matter I have, as in my former researches, selected carbonic acid gas (CO_2) for experiment, partly from the facility with which it can be prepared in a state of purity, but chiefly from its critical temperature being only 31° above the freezing-point of water. It may fairly be taken as a typical representative of the gaseous state, and, as we shall see, it is in a condition peculiarly favourable for the discovery of the laws which govern the action of the internal or molecular forces in that state. The experiments of OERSTED and SWENDSEN, of DESPRETZ and of POUILLET, have shown that when exposed to increasing pressure it deviates sensibly from the law of BOYLE; and REGNAULT has measured with precision its compressibility at 3° for pressures reaching to 27 atmospheres, and has likewise confirmed the observation of VON WREDE, that even at pressures below one atmosphere it deviates sensibly from BOYLE's law.

The carbonic acid gas was prepared by the action of pure and dilute sulphuric acid, deprived of its air by boiling, upon marble. It was carefully desiccated by passing through a U-tube filled with fragments of pumice freed from chlorides, and moistened with pure sulphuric acid. In Tables I., II., and III. will be found the results of a large number of experiments on the compressibility of carbonic acid at temperatures differing little respectively from $6^\circ.5$, 64° , and 100° . For the lower temperature a stream of cold water from a large cistern was made to flow at a uniform rate around the carbonic acid tube. The manometer-tube was kept at a steady temperature by a similar arrangement. The temperature of 64° was obtained by passing the vapour of

* ARAGO and DULONG inferred from their experiments, extending from 1 to 27 atmospheres, that the law of BOYLE is strictly true in the case of air; and the same conclusion was also drawn by OERSTED and SWENDSEN from their own experiments. From a careful analysis of their results, as given in the original memoir of ARAGO and DULONG (*Mémoires de l'Académie des Sciences*, x. p. 207), it appears to me that their experiments rather indicate a deviation from the law of BOYLE, but to not more than one third of the amount given by the subsequent researches of REGNAULT (*Mém. de l'Acad. des Sciences*, xxi. p. 421).

pure and anhydrous methyl-alcohol through the apparatus*. About two thirds of a litre of the alcohol was distilled over in each observation, the temperature being observed by one of the thermometers before referred to. The temperature obtained in this way, after every precaution has been taken, is far from being so steady as that given by the vapour of water; but with a little care very accurate determinations can be made. A deduction of $0^{\circ}\cdot 14$ was made from the direct reading as a correction for the error of the thermometer due to irregular expansion of the mercury.

For temperatures about 100° , vapour of water from a boiler in an adjoining apartment was passed around the carbonic acid tube and conveyed away by an exit-pipe through an outer wall of the apartment. Its pressure when in the vessel around the carbonic acid tube was usually about 50 millimetres of water above that of the atmosphere, as ascertained by a U-shaped water-gauge connected with the apparatus. By adding the pressure indicated by the water-gauge to the height of the barometer, the elastic force of the steam, and consequently its temperature, was known.

In the following tables I have recorded the results of direct experiments, all made by myself, and reduced by the equations already given. In every case two experiments at least, and often more than two, were made, the apparatus being thrown out of adjustment and readjusted between each observation. The mean numbers given in the tables scarcely differed by an appreciable amount from the results of the individual experiments.

In Tables I., II., and III., p is the pressure in the carbonic acid tube calculated from the indications of the air-manometer, t the temperature of the manometer, ϵ the ratio of the observed volume of the carbonic acid at the pressure p and temperature t' to its volume at the same temperature t' under a pressure of one atmosphere, t' the temperature of the carbonic acid, and θ the volume to which one volume of carbonic acid, measured at 0° and under one atmosphere, is reduced at the pressure p and temperature t' . By one atmosphere of pressure is meant the pressure of a column of mercury 760 millimetres in length measured at 0° and under the latitude of 45° .

* Both the air-tube and carbonic acid tube were enclosed in rectangular brass vessels, having plate-glass sides inserted before and behind, by which means accurate readings, not attainable in ordinary glass cylinders, were secured. Through these rectangular vessels the water or vapour circulated, by means of which the tubes were maintained at fixed temperatures. A detailed description, with a figure of the apparatus, will be found in my former communication, *Philosophical Transactions* for 1869, p. 578.

TABLE I.—Compressibility of Carbonic Acid Gas.—6°·0–6°·9.

p .	t .	ϵ .	t' .	θ .
12·01	6°·91	$\frac{1}{12\cdot95}$	6°·89	0·07921
13·22	6·90	$\frac{1}{14\cdot36}$	6·90	0·07143
14·68	6·90	$\frac{1}{16\cdot12}$	6·90	0·06364
17·09	6·45	$\frac{1}{19\cdot12}$	6·44	0·05371
20·10	6·79	$\frac{1}{23\cdot01}$	6·79	0·04456
22·26	6·07	$\frac{1}{25\cdot99}$	6·05	0·03934
24·81	6·72	$\frac{1}{29\cdot60}$	6·73	0·03462
27·69	6·07	$\frac{1}{34\cdot09}$	6·05	0·02999
31·06	6·65	$\frac{1}{39\cdot57}$	6·62	0·02589
34·49	6·03	$\frac{1}{45\cdot96}$	6·02	0·02224

TABLE II.—Compressibility of Carbonic Acid Gas.—63°·6–64°·0.

p .	t .	ϵ .	t' .	θ .
17·60	9°·30	$\frac{1}{18\cdot57}$	63°·86	0·06671
20·36	9·19	$\frac{1}{21\cdot66}$	63·76	0·05710
22·56	8·82	$\frac{1}{24\cdot19}$	63·79	0·05113
25·06	8·82	$\frac{1}{27\cdot09}$	63·77	0·04564
28·07	8·85	$\frac{1}{30\cdot65}$	63·85	0·04035
31·39	8·85	$\frac{1}{34\cdot68}$	63·83	0·03560
34·92	8·85	$\frac{1}{39\cdot10}$	63·65	0·03162
40·54	8·75	$\frac{1}{46\cdot37}$	63·64	0·02665
46·56	8·97	$\frac{1}{54\cdot61}$	63·68	0·02264
54·33	8·99	$\frac{1}{66\cdot05}$	63·57	0·01871
64·96	9·05	$\frac{1}{83\cdot53}$	63·74	0·01480
81·11	9·13	$\frac{1}{114\cdot2}$	63·75	0·01083
106·88	9·20	$\frac{1}{186\cdot0}$	63·75	0·00665
145·54	9·25	$\frac{1}{327\cdot6}$	63·70	0·00377
222·92	9·22	$\frac{1}{447\cdot0}$	63·82	0·00277

TABLE III.—Compressibility of Carbonic Acid Gas.—99°·5–100°·7.

p .	t .	ϵ .	t' .	θ .
17·42	5·83	$\frac{1}{18\cdot01}$	100·39	0·07628
20·17	6·04	$\frac{1}{20\cdot97}$	100·37	0·06543
22·37	6·01	$\frac{1}{23\cdot34}$	100·41	0·05880
24·85	6·00	$\frac{1}{26\cdot07}$	100·72	0·05269
27·76	5·83	$\frac{1}{29\cdot30}$	100·65	0·04687
31·06	5·88	$\frac{1}{33\cdot03}$	100·64	0·04158
34·57	5·92	$\frac{1}{37\cdot06}$	100·62	0·03705
40·09	5·94	$\frac{1}{43\cdot50}$	100·60	0·03156
45·99	6·31	$\frac{1}{50\cdot60}$	100·37	0·02712
53·81	6·34	$\frac{1}{60\cdot26}$	100·33	0·02277
64·27	6·34	$\frac{1}{73\cdot89}$	100·37	0·01857
80·25	6·35	$\frac{1}{96\cdot52}$	100·37	0·01422
105·69	6·36	$\frac{1}{137\cdot3}$	100·37	0·01000
145·44	8·73	$\frac{1}{219\cdot0}$	99·46	0·00625
223·57	8·72	$\frac{1}{380\cdot3}$	99·44	0·00359

Before discussing these results on the compressibility of carbonic acid, it will be convenient to have accurate data for reducing the experiments in each table to the same temperature. These data will be supplied when the coefficients of expansion of carbonic acid under varied pressures and at different parts of the thermometric scale are known. The determination of these coefficients will form the subject of the next section.

§ II.

In the limiting case of the so-called perfect gas, which is closely approximated to but probably never actually realized in nature, the change of volume under a constant pressure would for the same range of temperature correspond exactly to the change of elastic force under a constant volume*. In the case of carbonic acid, REGNAULT has shown that, even at low pressures, there is a marked difference in the value of α as given by the two methods; and from the experiments I am about to describe, it will appear that at high pressures the results diverge so widely that they must not in any way be

* According to RUDBERG the coefficient of expansion of air between 0° and 100°, deduced from the two methods, is precisely the same; according to REGNAULT there is an actual difference of $\frac{1}{733}$ part of the whole coefficient (POGGENDORFF's 'Annalen,' vol. xlv. p. 122; Mém. de l'Acad. des Sciences, vol. xxi. p. 119).

confounded with one another. For the sake of precision, I propose to designate by α the coefficient of expansion for change of temperature under a constant pressure, and by α' the coefficient of elastic force for change of temperature under a constant volume. We shall confine our attention in this section to the determination of the values of α under varied pressures and at different parts of the thermal scale.

In the next table the results are given of a set of experiments I have made to determine the *average* coefficient of expansion for heat of carbonic acid from 0° to about $7^\circ\cdot5$ under pressures varying from 12 to $34\cdot5$ atmospheres. For this range of temperature the pressures could not be carried higher, on account of the liquefaction of the gas. In this table p is the pressure as indicated by the air-manometer, t the temperature of the manometer, and v' the volume in cubic centimetres of the carbonic acid at the pressure p and temperature t' .

TABLE IV.—Values of α from 0° to $7^\circ\cdot5$.—Constant Pressure.

p .	t .	v' .	t' .	α .
12·02	$7^\circ\cdot53$	0·07298	$7^\circ\cdot54$	0·00462
12·00	$6^\circ\cdot73$	0·07065	0·00	
16·22	$7^\circ\cdot65$	0·05243	$7^\circ\cdot64$	0·00520
16·25	$6^\circ\cdot65$	0·05031	0·00	
20·10	$7^\circ\cdot61$	0·04108	$7^\circ\cdot63$	0·00607
20·09	$6^\circ\cdot64$	0·03928	0·00	
24·81	$7^\circ\cdot63$	0·03192	$7^\circ\cdot64$	0·00700
24·80	$6^\circ\cdot64$	0·03031	0·00	
27·70	$7^\circ\cdot44$	0·02775	$7^\circ\cdot45$	0·00782
27·66	$6^\circ\cdot47$	0·02627	0·00	
31·07	$7^\circ\cdot65$	0·02386	$7^\circ\cdot65$	0·00895
31·06	$6^\circ\cdot64$	0·02234	0·00	
34·49	$7^\circ\cdot45$	0·02058	$7^\circ\cdot46$	0·01097
34·48	$6^\circ\cdot64$	0·01903	0·00	

In calculating the values of α in the foregoing table, the observed volume (v') of the carbonic acid at the higher temperature ($7^\circ\cdot54$ &c.) was in each case corrected for the small differences of pressure which occurred in the observations at that temperature and at 0° . In many cases it would have been sufficient to make this correction by BOYLE'S law; but the exact data for the purpose being supplied by Tables I., II., and III., I have in these and other similar cases always employed the direct results given by experiment of the compressibility of carbonic acid at the pressures and temperatures indicated.

In the two following tables the values of α are calculated from the results in Tables I., II., and III., the value of θ in Table I. having been first reduced to 0° by means of the coefficients at the respective pressures given in Table IV.

TABLE V.—Values of α from 0° to 64° .—Constant Pressure.

p .	t' .	θ .	α .
17.09	0.00	0.05190	0.005136
	63.86	0.06892	
20.10	0.00	0.04280	0.005533
	63.76	0.05790	
22.26	0.00	0.03785	0.005811
	63.79	0.05188	
24.81	0.00	0.03306	0.006204
	63.77	0.04614	
27.69	0.00	0.02864	0.006737
	63.85	0.04096	
31.06	0.00	0.02444	0.007429
	63.83	0.03603	
34.49	0.00	0.02086	0.008450
	63.65	0.03208	

TABLE VI.—Values of α from 0° to 100° .—Constant Pressure.

p .	t' .	θ .	α .
17.09	0.00	0.05190	0.004994
	100.39	0.07792	
20.10	0.00	0.04280	0.005324
	100.37	0.06567	
22.26	0.00	0.03785	0.005597
	100.11	0.05906	
24.81	0.00	0.03306	0.005922
	100.72	0.05278	
27.69	0.00	0.02864	0.006369
	100.65	0.04700	
31.06	0.00	0.02444	0.006968
	100.64	0.04158	
34.49	0.00	0.02086	0.007762*
	100.62	0.03715	

* By an entirely different method REGNAULT has examined the expansion by heat of carbonic acid gas between 0° and 100° for pressures varying from 1 to 15.6 atmospheres. As his results form a consecutive series with those of Table VI. I subjoin them. It must be remembered that p represents here true pressures in atmospheres.

p .	α .
1.00	0.003710
3.32	0.003845
5.64	0.004006
9.17	0.004227
11.27	0.004408
15.61	0.004858

(Mém. de l'Acad. des Sciences, vol. xxi. p. 117, and vol. xxvi. p. 575.)

From Tables V. and VI. it is easy to calculate the values of α from 64° to 100° referred to the unit volume at 0° . These values will be found in the fourth column of the next table, and for comparison the values of α at the corresponding pressures from 0° to $7^{\circ}5$, and from 0° to 64° , have been taken directly from the same tables.

TABLE VII.—Values of α at different temperatures.—Constant Pressure.

p .	α .		
	0° – $7^{\circ}5$.	0° – 64° .	64° – 100° .
17.09	0.005136	0.004747
20.10	0.00607	0.005533	0.004958
22.26	0.005811	0.005223
24.81	0.00700	0.006204	0.005435
27.69	0.00782	0.006737	0.005730
31.06	0.00895	0.007429	0.006169
34.49	0.01097	0.008450	0.006574

It has hitherto been assumed, but without direct experimental proof, that matter in the gaseous state will expand for every degree through which it is heated by the same fraction of its volume at 0° , provided the pressure remains constant. This important law, which is due to GAY-LUSSAC, is unquestionably true in the case of the perfect (ideal) gas; and in the case of air and other gases which have not been liquefied, it may be employed for all practical purposes without sensible error. But, as far as I have been able to discover, no experiments have hitherto been published to determine under what limitations it applies to the gaseous state as that state is presented to us in nature*. It will be evident from a cursory inspection of Table VII. that this law does not hold good in the case of carbonic acid gas even at moderate pressures, and that the divergence from the law becomes greater as the pressure is increased. Thus under a pressure of 20.1 atmospheres the coefficients of expansion, referred to the same unit, between 0° and $7^{\circ}5$, 0° and 64° , and 64° and 100° respectively, are in the ratio of the numbers

$$1.000, \quad 0.911, \quad 0.817;$$

and under a pressure of 34.49 atmospheres the corresponding ratios for the same ranges of temperature are

$$1.000, \quad 0.770, \quad 0.599.$$

It is scarcely necessary to add that if the law of GAY-LUSSAC held good, the coefficients

* BIOT states, indeed, somewhat vaguely, that GAY-LUSSAC verified this law experimentally for air and other gases and found it to be strictly true; but the experiments themselves have never been published, and the methods of investigation employed by GAY-LUSSAC are now known to have been imperfect, so that they failed even to show the differences in the dilatation by heat of different gases (BIOT, 'Traité de Physique,' vol. i. p. 188). The experiments of REGNAULT on the comparative march of the air and carbonic acid thermometer, to which I shall have occasion hereafter to refer, were made by observing the change of elastic force under a constant volume. REGNAULT states expressly that he made no corresponding experiments under constant pressure (Mém. de l'Acad. des Sciences, vol. xxi. pp. 168–171).

in all these cases would have been the same, and their ratios expressed by 1·000. I have not made any comparative experiments at pressures lower than 17 atmospheres; but there can be no doubt that, even at the ordinary pressure of the atmosphere, carbonic acid gas will diverge sensibly from GAY-LUSSAC'S law, and that its coefficient of expansion under constant pressure will change with the temperature, being less at high than at low temperatures.

It follows from these observations that the coefficients of expansion in the foregoing tables are the average coefficients for the ranges of temperature to which they apply. It would not be difficult from the experimental results to obtain an empirical formula which would give approximately the coefficient or rate of expansion, at any temperature and under any pressure, within the range of the experiments, so as to construct tables showing the expansion by heat of carbonic acid under different pressures. But I have refrained from doing so, as such a table would seldom be required in practice; and for scientific purposes, as I have had occasion in the course of this inquiry more than once to observe, the results of empirical formulæ are apt to mislead the investigator and rarely aid research.

For the same temperature, the coefficient of expansion increases as the pressure augments, and more rapidly at low than at high temperatures. In the preceding tables, the pressures, being always referred to the unit volume at 0°, could not be carried beyond 34·5 atmospheres. In the next table the coefficient of expansion for heat of carbonic acid gas, referred to the unit volume at 64°, is given at pressures ranging from 17 to 223 atmospheres.

TABLE VIII.—Values of α from 64° to 100°.—Constant Pressure. Volume at 64°=1.

p .	t .	θ .	α .
17·09	63·86	0·06892	0·003572
	100·39	0·07792	
20·10	63·76	0·05790	0·003657
	100·37	0·06567	
22·26	63·79	0·05188	0·003808
	100·11	0·05906	
24·81	63·77	0·04614	0·003892
	100·72	0·05278	
27·69	63·85	0·04096	0·004008
	100·65	0·04700	
31·06	63·83	0·03603	0·004187
	100·64	0·04158	
34·49	63·65	0·03208	0·004266
	100·62	0·03715	
40·54	63·64	0·02665	0·004596
	100·60	0·03118	
46·54	63·68	0·02264	0·004946
	100·37	0·02676	

TABLE VIII. (continued).

$p.$	$t.$	$\theta.$	$\alpha.$
54.33	63.57	0.01871	0.005535
	100.33	0.02252	
64.96	63.74	0.01480	0.006512
	100.37	0.01833	
81.11	63.75	0.01083	0.008033
	100.37	0.01402	
106.9	63.75	0.00665	0.013150
	100.37	0.00986	
145.5	63.70	0.00377	0.018222
	99.62	0.00625	
223.0	63.82	0.00277	0.008402
	99.44	0.00360	

The coefficient of expansion, it will be observed, steadily increases with the pressure, till at 145.5 atmospheres it has reached the large value of 0.01822. But as the pressure is further augmented, the coefficient, instead of continuing to increase, begins to diminish; and at 223 atmospheres it has actually fallen to 0.008402, or to less than one half its value at 145 atmospheres. This change of direction in the value of the coefficient is easily explained, if we observe that carbonic acid at 64° has entered, under these high pressures, into those intermediate conditions which form the link between the gaseous and liquid states of matter. It has, in short, at 223 atmospheres, approached the liquid volume without liquefying, and its coefficient begins to change to that which belongs to the liquid state. We shall find in the course of this inquiry abundant proofs of the accuracy of this statement.

§ III.

We now proceed to consider the change in the elastic force of a gas when, the volume being maintained constant, the temperature is altered. As in the expansion of a gas under constant pressure, we have here two distinct questions to consider, both of which are highly important in reference to the laws of molecular action. The first question is the effect of increase of pressure on the value of the coefficient; the second, the change, if any, of the coefficient for different parts of the thermal scale. The apparatus required no modification whatever for these experiments; but in making the adjustments for constant volume, the change of volume of the glass tube must be carefully allowed for, as the same reading by the cathetometer will not correspond to the same volume at different temperatures. The correction was always made by the equation given before,

$$c_v = c_0(1 + \frac{2}{3}kt').$$

As I have already mentioned, the coefficient of elastic force under constant volume will be designated by α' , to distinguish it from α the coefficient of expansion under constant pressure. In the following tables the letters p , t , and t' have the same signi-

fication as before, but instead of θ , the actual volumes, in fractions of a cubic centimetre, of the carbonic acid are given in the column designated CO_2 . In calculating the coefficients, a slight correction had to be applied to the observed pressures when the volume of the carbonic acid was not precisely the same at the corresponding observations.

TABLE IX.—Values of α' from 0° to $6^\circ.5$.—Constant Volume.

p .	t .	CO_2 .	t' .	α' .
21.48	$7^\circ.27$	0.03623	$0^\circ.00$	0.00537
22.18	6.08	0.03623	6.07	
25.87	7.17	0.02867	0.00	0.00588
26.86	6.51	0.02867	6.51	
33.53	7.27	0.01983	0.00	0.00734
35.13	6.51	0.01983	6.50	

TABLE X.—Values of α' from 0° to 64° .—Constant Volume.

p .	t .	CO_2 .	t' .	α' .
16.42	$7^\circ.29$	0.04969	$0^\circ.00$	0.004754
21.42	3.68	0.04968	64.00	
21.48	7.27	0.03623	0.00	0.005237
28.65	3.69	0.03624	63.80	
25.87	7.17	0.02867	0.00	0.005728
35.29	3.70	0.02869	63.74	
30.37	6.75	0.02304	0.00	0.006357
42.74	3.27	0.02303	63.98	
33.53	7.27	0.01983	0.00	0.006973
48.40	3.36	0.01986	63.94	

TABLE XI.—Values of α' from 0° to 100° .—Constant Volume.

p .	t .	CO_2 .	t' .	α' .
16.42	$7^\circ.29$	0.04969	$0^\circ.00$	0.004700
24.19	3.70	0.04969	100.67	
21.48	7.27	0.03623	0.00	0.005138
32.60	3.70	0.03622	100.67	
25.87	7.17	0.02867	0.00	0.005610
40.44	3.73	0.02870	100.67	
30.37	6.75	0.02304	0.00	0.006177
49.25	3.65	0.02303	100.54	
33.53	7.27	0.01983	0.00	0.006741
56.16	3.64	0.01986	100.48	

From Tables X. and XI. the values of α' from 64° to 100° referred to the unit pressure at 0° are easily calculated. In the next table the values of α' at the different parts of the thermal scale are given, p being the initial pressure in each case.

TABLE XII.—Values of α' at different temperatures.—Constant Volume.

p .	α' .		
	0°–6°·5.	0°–64°.	64°–100°.
16·42	0·004754	0·004607
21·48	0·00537	0·005237	0·004966
25·87	0·00588	0·005728	0·005406
30·37	0·006357	0·005861
33·53	0·00734	0·006973	0·006334

It follows from this investigation that the value of α' is greater at high than at low pressures; it changes also with the temperature, the pressure remaining constant, being less at high than at low temperatures. The values are, for this reason, average values for each range of temperature. The law of GAY-LUSSAC, therefore, fails both in the case of α and of α' ; that is to say, *the dilatation by heat of a body in the ordinary gaseous state, whether measured by its expansion under constant pressure or by the increase of elastic force under constant volume, is not a simple function of the initial volume or initial elastic force, but a complex function changing with the temperature**.

In the next Table will be found the change in the value of α' between 64° and 100° under a large range of pressure and referred to the pressure at 64° as unit.

TABLE XIII.—Values of α' from 64° to 100°.—Constant Volume. Pressure at 64°=1.

p .	t' .	CO ₂ .	α' .
21·42	64°·00	0·04968	0·003526
24·19	100·67	0·04969	
28·65	63·80	0·03624	0·003718
32·60	100·67	0·03622	
35·29	63·74	0·02869	0·003956
40·44	100·67	0·02870	
42·74	63·98	0·02303	0·004166
49·25	100·54	0·02303	
48·40	63·94	0·01986	0·004387
56·16	100·48	0·01986	
67·65	63·80	0·01288	0·005392
80·99	100·50	0·01289	
94·27	63·78	0·00778	0·007018
118·60	100·50	0·00778	

* The statement of REGNAULT that the air and carbonic acid thermometers march sensibly together appears to be at variance with this conclusion. But REGNAULT's own experiments, which were made at pressures differing little from that of the atmosphere, indicate an unequivocal although small difference, and in the right direction, between the two thermometers. With a sulphurous acid thermometer the difference was considerable, and in conformity with the result stated in the text (Mém. de l'Acad. des Sciences, vol. xxi. pp. 187–88).

§ IV.

We are now prepared for the discussion of the general results of this investigation. For this purpose it will be convenient to reduce the values of ε as given in Tables I., II., and III. to the exact temperatures of $6^{\circ}5$, 64° , and 100° respectively. The differences between the temperatures (t') at which the observations were made and these numbers are so small that the reductions presented no difficulty with the data furnished in § II. In the last column of the three following tables will be found the values of ρ as given by the equation

$$\rho = \varepsilon p.$$

TABLE XIV.—Values of ρ at $6^{\circ}5$.

p .	t' .	ε .	ρ .
12.01	$6^{\circ}5$	$\frac{1}{12.95}$	0.9274
13.22	$6^{\circ}5$	$\frac{1}{14.37}$	0.9200
14.68	$6^{\circ}5$	$\frac{1}{16.13}$	0.9101
17.09	$6^{\circ}5$	$\frac{1}{19.12}$	0.8938
20.10	$6^{\circ}5$	$\frac{1}{23.03}$	0.8728
22.26	$6^{\circ}5$	$\frac{1}{25.96}$	0.8575
24.81	$6^{\circ}5$	$\frac{1}{29.62}$	0.8376
27.69	$6^{\circ}5$	$\frac{1}{34.03}$	0.8137
31.06	$6^{\circ}5$	$\frac{1}{39.59}$	0.7845
34.49	$6^{\circ}5$	$\frac{1}{45.80}$	0.7530

TABLE XV.—Values of ρ at 64° .

p .	t .	ε .	ρ .
17.60	64°	$\frac{1}{18.57}$	0.9478
20.36	64	$\frac{1}{21.65}$	0.9404
22.56	64	$\frac{1}{24.18}$	0.9330
25.06	64	$\frac{1}{27.08}$	0.9254
28.07	64	$\frac{1}{30.64}$	0.9161
31.39	64	$\frac{1}{34.67}$	0.9054
34.92	64	$\frac{1}{39.08}$	0.8935
40.54	64	$\frac{1}{46.34}$	0.8748
46.56	64	$\frac{1}{54.57}$	0.8532
54.33	64	$\frac{1}{65.97}$	0.8235
64.96	64	$\frac{1}{83.44}$	0.7785
81.11	64	$\frac{1}{114.0}$	0.7115
106.88	64	$\frac{1}{185.5}$	0.5762
145.54	64	$\frac{1}{325.9}$	0.4466
222.92	64	$\frac{1}{446.4}$	0.4994

TABLE XVI.—Values of ρ at 100° .

p .	t .	ε .	ρ .
20.17	100°	$\frac{1}{20.98}$	0.9614
22.37	100	$\frac{1}{23.35}$	0.9580
24.85	100	$\frac{1}{26.09}$	0.9525
27.76	100	$\frac{1}{29.32}$	0.9468
31.06	100	$\frac{1}{33.05}$	0.9398
34.57	100	$\frac{1}{37.09}$	0.9320
40.09	100	$\frac{1}{43.54}$	0.9208
45.99	100	$\frac{1}{50.63}$	0.9083
53.81	100	$\frac{1}{60.30}$	0.8924
64.27	100	$\frac{1}{73.97}$	0.8689
80.25	100	$\frac{1}{96.65}$	0.8303
105.69	100	$\frac{1}{137.6}$	0.7681
145.44	100	$\frac{1}{218.0}$	0.6671
223.57	100	$\frac{1}{379.3}$	0.5894

From the results given in the last three tables, it is manifest that the values of ρ , which in the case of a perfect (ideal) gas would always be unit, steadily diminish for the same temperature as the pressure increases. An important exception to this remark occurs in the last recorded result in Table XV., from which it appears that at the temperature of 64° the value of ρ , which had diminished from 0.9478 to 0.4466 as the pressure was raised from 17.6 to 145.5 atmospheres, instead of continuing to diminish with a further increase of pressure, actually changes its direction, and at 223 atmospheres has increased to 0.4994. No change of this kind occurs at 100° , although the experiments were carried to 224 atmospheres. The explanation of this change in the value of ρ , after a certain pressure has been reached, I have already anticipated when referring to a similar change in the coefficient of expansion by heat at high pressures, as shown in Table VIII. At the temperature of 64° , and under a pressure of 223 atmospheres, carbonic acid has in fact approached the liquid volume, while passing through those intermediate conditions of matter which, in a former Bakerian Lecture, I have described as establishing an unbroken continuity between the ordinary gaseous and ordinary liquid states. At 100° carbonic acid under the same external pressure has not reached this stage of the process; but if the experiment had been carried to higher pressures, a like change in the value of ρ would no doubt have occurred. These remarks will be fully confirmed when I give the values of ρ for the gaseous and liquid states at the same temperature, as calculated from my former experiments*. The true import of the values of ρ at a constant temperature will be considered hereafter.

From Tables XIV., XV., and XVI. it further appears that the values of ρ approach more nearly to unit the higher the temperature, in accordance with the principle I deduced from my former experiments, that as the temperature becomes higher the curves representing the change of volume of carbonic acid at different pressures approach more nearly to the curve of a perfect gas. But to find the actual relation which exists between these curves it will be necessary to make a preliminary calculation.

In the curves representing the changes of volume of a gas by pressure at different temperatures, I propose to designate those points where the values of ρ are equal, homologues, or homologous points, and the lines passing through corresponding homologues, homologous lines. Let μ be the ratio between the external pressures p and p' at homologous points on the curves of any two temperatures, or

$$\mu = \frac{p}{p'}.$$

In Tables XVII. and XVIII. the values of μ are calculated for the respective temperatures of $6^\circ.5$ and 64° , and of 64° and 100° , from the values of ρ in the preceding tables. The necessary reductions to obtain the homologous points at each temperature were carefully made.

* Philosophical Transactions for 1869, p. 581.

TABLE XVII.—Values of μ for $6^{\circ}5$ and 64° .

ρ .	p ($6^{\circ}5$).	p' (64°).	μ .
0.9254	12.31	25.06	0.491
0.9161	13.79	28.07	0.491
0.9054	15.39	31.39	0.490
0.8935	17.13	34.92	0.491
0.8748	19.81	40.54	0.489
0.8532	22.83	46.56	0.490
0.8235	26.51	54.33	0.488
0.7785	31.73	64.96	0.489

From the foregoing table it appears that the values of μ within the limits of pressure employed are always equal—that is to say, *the ratio of the external pressures is always the same for homologous points of the curves of $6^{\circ}5$ and 64° .* The experiments could not be carried to higher pressures on account of the liquefaction of the gas at $6^{\circ}5$. In the next table the values of μ for the homologues of 64° and 100° are given.

TABLE XVIII.—Values of μ for 64° and 100° .

ρ .	p (64°).	p' (100°).	μ .
0.9404	20.36	30.79	0.661
0.9330	22.56	34.10	0.662
0.9254	25.06	37.88	0.662
0.9161	28.07	42.37	0.662
0.9054	31.39	47.39	0.662
0.8935	34.92	53.29	0.655
0.8748	40.54	61.76	0.656
0.8532	46.56	70.95	0.656
0.8235	54.33	83.04	0.654
0.7785	64.96	101.53	0.640
0.7115	81.11	127.96	0.634
0.5762	106.80	236.84	0.451

The values of μ are again equal till very high pressures are reached. Thus from 20.4 to 31.4 atmospheres, and from 30.8 to 47.4 atmospheres, the agreement is absolute; after which a slight diminution in the value of μ occurs, but only to the amount of $\frac{1}{90}$ of the whole, till the respective pressures of 54.3 and 83.0 atmospheres are attained. Even at 81.1 and 128.0 atmospheres the value of μ has only fallen from 0.661 to 0.634. But at still higher pressures we reach a new phase, and at the respective pressures of 107 and 237 atmospheres the value of μ has fallen to 0.451.

I have calculated the values of ρ and μ from the experiments at lower temperatures in my former communication*. As these experiments were chiefly made at temperatures not much above the critical point of carbonic acid, when the intermediate conditions of matter corresponding to the fall from the gaseous to the liquid state, and those corresponding to the liquid state itself, are easily recognized, they form a valuable complement to the foregoing.

* Philosophical Transactions for 1869, pp. 584–86.

TABLE XIX.—Values of ρ at $31^{\circ}\cdot 1$, $35^{\circ}\cdot 5$, and $48^{\circ}\cdot 1$.

$31^{\circ}\cdot 1$.		$35^{\circ}\cdot 5$.		$48^{\circ}\cdot 1$.	
p .	ρ .	p .	ρ .	p .	ρ .
54·79	0·6802	56·80	0·6866	62·60	0·7241
55·96	0·6710	59·34	0·6672	68·46	0·6888
57·18	0·6604	62·15	0·6446	75·58	0·6416
58·46	0·6493	65·23	0·6154	84·35	0·5746
59·77	0·6368	68·66	0·5799	95·19	0·4795
61·18	0·6238	72·45	0·5363	109·40	0·3666
62·67	0·6078	76·58	0·4751		
64·27	0·5864	81·28	0·3565		
65·90	0·5671	86·60	0·2461		
67·60	0·5434	89·52	0·2395		
69·39	0·5159	92·64	0·2388		
71·25	0·4821	99·57	0·2423		
73·26	0·4335	107·60	0·2501		
73·83	0·4233				
75·40	0·2424				
77·64	0·2103				
79·92	0·2087				
82·44	0·2083				
85·19	0·2101				

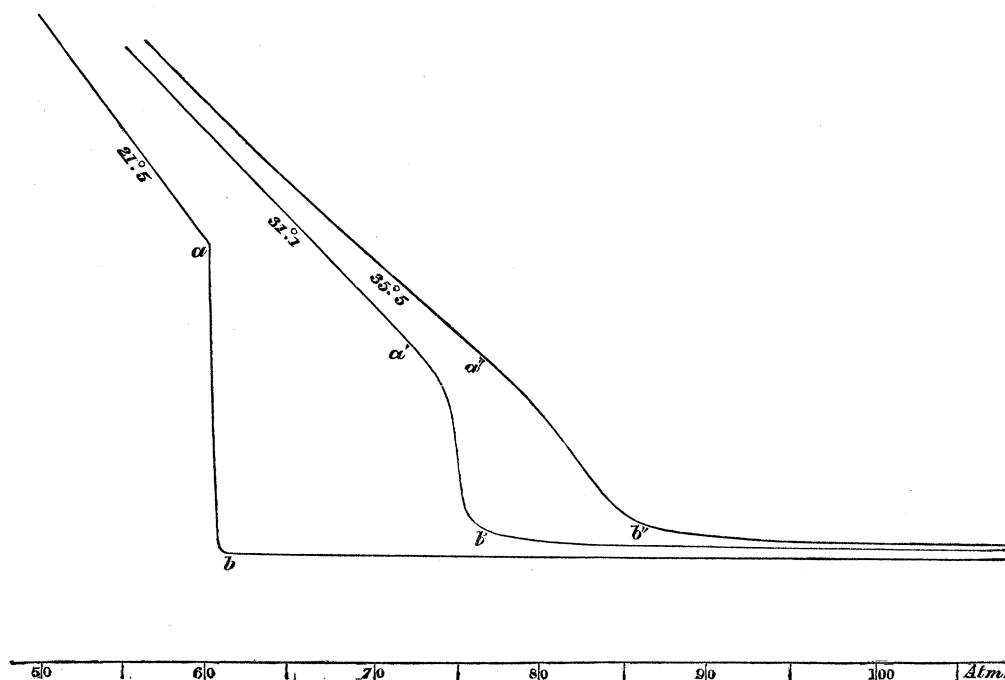
TABLE XX.—Values of μ for $31^{\circ}\cdot 1$ and $48^{\circ}\cdot 1$.

ρ .	p ($31^{\circ}\cdot 1$).	p' ($48^{\circ}\cdot 1$).	μ .
0·6802	54·79	69·81	0·785
0·6710	55·96	71·26	0·785
0·6604	57·18	72·93	0·784
0·6493	58·46	74·51	0·785
0·6368	59·77	76·25	0·784
0·6238	61·18	78·06	0·784
0·6078	62·68	80·00	0·784
0·5864	64·27	82·81	0·777
0·5671	65·90	85·20	0·773
0·5434	67·60	87·91	0·769
0·5159	69·39	91·04	0·762
0·4821	71·25	94·90	0·751
0·4335	73·26	100·98	0·726
0·4233	73·83	102·26	0·722
0·2424	75·40	125·00	0·603

TABLE XXI.—Values of μ for $35^{\circ}\cdot 5$ and $48^{\circ}\cdot 1$.

ρ .	p ($35^{\circ}\cdot 5$).	p' ($48^{\circ}\cdot 1$).	μ .
0·6866	56·80	68·81	0·826
0·6672	59·34	71·86	0·826
0·6446	62·15	75·16	0·827
0·6154	65·23	79·22	0·824
0·5799	68·66	83·71	0·820
0·5363	72·45	88·98	0·814
0·4751	76·58	95·72	0·800

These results, calculated from experiments published seven years ago, are in complete accordance with the conclusions I have deduced from the present investigation. On comparing the pressures with the graphic representation given in the paper referred to, it will be seen that, so long as the values of μ are equal, the carbonic acid is in the gaseous state proper at the lower as well as at the higher temperature; but when they undergo a marked diminution, the carbonic acid has entered into the intermediate conditions corresponding at lower temperatures to the fall to the liquid state. Finally, when the liquid volume has been attained, the value of ρ itself changes its direction, as may be seen in the results of the final experiments at 64° , $31^\circ.1$, and $35^\circ.5$ (Tables XV. and XIX.). In the annexed sketch the portions of the curves above a , a' , a'' are in the gaseous state; from a to b we have in the curve for $21^\circ.5$ the fall from the gaseous to the liquid state; and from a' to b' and a'' to b'' , in the curves for $31^\circ.1$ and $35^\circ.5$, the



intermediate conditions between the gaseous state and liquid volume corresponding to the fall to the liquid state at lower temperatures. As in a gas below the critical temperature we have, (1) the gaseous state, (2) the fall to the liquid, and (3) the liquid state, so in a gas above the critical temperature we have, (1) the gaseous state, (2) the intermediate conditions corresponding to the fall, and (3) the conditions corresponding to the liquid volume. The first or gaseous state is characterized by the external pressures for homologous points at any two given temperatures being always in the same ratio to

one another; in the second state, or state of change corresponding to the fall to the liquid, this ratio changes rapidly; while in the third, or, as we may designate it, the liquid-volume state, new molecular conditions supervene, as shown by the increase in the value of ρ .

As the result of the foregoing investigation, the relations between pressure and volume in the *ordinary gaseous* state at different temperatures may be stated in the following terms:—

On any two isothermal curves which show the volume of carbonic acid gas under change of pressure at definite temperatures, the values of ρ at the homologous points being always equal, or

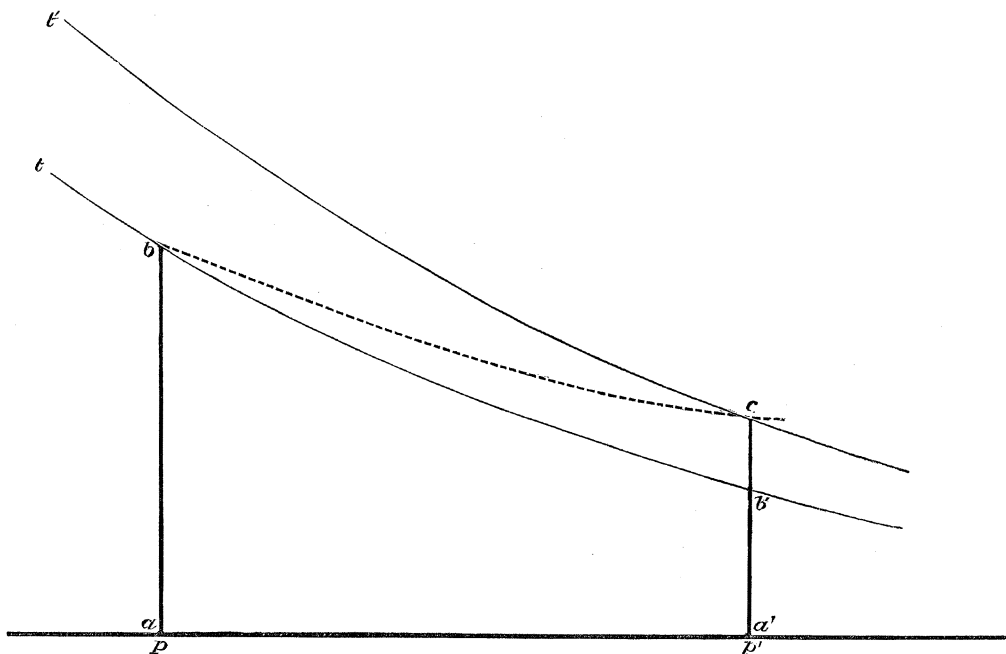
$$pv = p'v' (A)$$

(where, it must be carefully observed, v and v' are the volumes of the gas on different isothermals), it has been shown that for all such homologous points on any two isothermals

$$\frac{p}{p'} = \mu (B)$$

where μ is a constant.

The full import of homologous points will be further understood from the following considerations:—Let the line ab represent a volume of carbonic acid gas at the tempe-



rature t and pressure p , and let the pressure be increased to p' , the new volume $a'b'$ of the gas will be less than $ab \frac{p}{p'}$. Let the gas be now heated at the pressure p' till its

volume $a'c$ is equal to $ab\frac{p}{p'}$, and let the temperature be now t' ; the point c on the isothermal t' will be the homologue of the point b on the isothermal t . If the gas from p to p' had diminished in volume as a perfect gas, c would have been a point on the isothermal t . In short, the homologue c , of the point b on the isothermal t , is a point on the isothermal t' at which the action of the internal forces, in reducing the volume of the gas when the external pressure is increased from p to p' , is exactly counterbalanced by the action of the expansive forces in heating the gas from t to t' .

By means of equations (A) and (B), if we know the relations of pressure and volume for a gas at any one temperature, we can, by the observation of a homologue at any other temperature, calculate the volume corresponding to all pressures at the second temperature. Thus the whole relations of volume and pressure in the case of a gas can be discovered from a set of primary observations at one fixed temperature, and the determination of a single homologue at each of the other temperatures.

We have now to inquire into the relations between the pressure and volume in the case of a gas at a constant temperature; in other words, to discover, if possible, the character of the primary curve from which, as we have seen, by means of the homologues, the curves of other temperatures may be traced. For this purpose we must find the values of $1-\rho$ from Tables XIV., XV., and XVI., and thence calculate the values of $\varepsilon(1-\rho)$ as given in the fourth column of the following tables.

TABLE XXII.—Values of $\varepsilon(1-\rho)$ at $6^{\circ}5$.

p .	ε .	t' .	$1-\rho$.	$\varepsilon(1-\rho)$.
12.01	$\frac{1}{12.95}$	6.5	0.0726	0.00561
13.22	$\frac{1}{14.37}$	6.5	0.0800	0.00557
14.68	$\frac{1}{16.13}$	6.5	0.0899	0.00557
17.09	$\frac{1}{19.12}$	6.5	0.1062	0.00555
20.10	$\frac{1}{23.03}$	6.5	0.1272	0.00552
22.26	$\frac{1}{25.96}$	6.5	0.1425	0.00549
24.81	$\frac{1}{29.62}$	6.5	0.1624	0.00549
27.69	$\frac{1}{34.03}$	6.5	0.1863	0.00547
31.06	$\frac{1}{39.59}$	6.5	0.2155	0.00544

TABLE XXIII.—Values of $\varepsilon(1-\rho)$ at 64° .

p .	ε .	t' .	$1-\rho$.	$\varepsilon(1-\rho)$.
17.60	$\frac{1}{18.57}$	64°	0.0522	0.00281
20.36	$\frac{1}{21.65}$	64	0.0596	0.00275
22.56	$\frac{1}{24.18}$	64	0.0670	0.00277
25.06	$\frac{1}{27.08}$	64	0.0746	0.00275
28.07	$\frac{1}{30.64}$	64	0.0839	0.00274
31.39	$\frac{1}{34.67}$	64	0.0946	0.00273
34.92	$\frac{1}{39.08}$	64	0.1065	0.00273
40.54	$\frac{1}{46.34}$	64	0.1252	0.00270
46.56	$\frac{1}{54.57}$	64	0.1468	0.00269
54.33	$\frac{1}{65.97}$	64	0.1765	0.00268
64.96	$\frac{1}{83.44}$	64	0.2215	0.00266
81.11	$\frac{1}{114.0}$	64	0.2885	0.00253
106.88	$\frac{1}{185.5}$	64	0.4238	0.00228
145.54	$\frac{1}{325.9}$	64	0.5534	0.00170
222.92	$\frac{1}{446.4}$	64	0.5006	0.00112

TABLE XXIV.—Values of $\varepsilon(1-\rho)$ at 100° .

p .	ε .	t' .	$1-\rho$.	$\varepsilon(1-\rho)$.
20.17	$\frac{1}{20.98}$	100°	0.0386	0.00184
22.37	$\frac{1}{23.35}$	100	0.0420	0.00180
24.88	$\frac{1}{26.09}$	100	0.0475	0.00182
27.76	$\frac{1}{29.32}$	100	0.0532	0.00181
31.06	$\frac{1}{33.05}$	100	0.0602	0.00182
34.57	$\frac{1}{37.09}$	100	0.0680	0.00183
40.09	$\frac{1}{43.54}$	100	0.0792	0.00182
45.99	$\frac{1}{50.63}$	100	0.0917	0.00181
53.81	$\frac{1}{60.30}$	100	0.1076	0.00178
64.27	$\frac{1}{73.97}$	100	0.1311	0.00177
80.25	$\frac{1}{96.65}$	100	0.1697	0.00176
105.69	$\frac{1}{137.6}$	100	0.2319	0.00169
145.44	$\frac{1}{218.0}$	100	0.3329	0.00152
223.57	$\frac{1}{379.3}$	100	0.4106	0.00108

From these tables it is evident that the value of $\varepsilon(1-\rho)$ is constant so long as the carbonic acid is in the gaseous state, but that it rapidly diminishes when the gas passes into the intermediate conditions, till at high pressures it falls nearly as low as if the liquid had actually been formed. This will at once appear from the following short table, calculated from my former experiments at $13^{\circ}.1$, showing the values of $\varepsilon(1-\rho)$ in the gaseous and liquid states:—

TABLE XXV.—Values of $\varepsilon(1-\rho)$ at $13^{\circ}.1$.

p .	ε .	t .	$1-\rho$.	$\varepsilon(1-\rho)$.
47.50	$\frac{1}{76.16}$	13.1	0.3763	0.00494
48.76	$\frac{1}{80.43}$	13.1	0.3938	0.00490
48.89	$\frac{1}{80.90}$	13.1	0.3957	0.00489
54.56	$\frac{1}{480.4}$	13.1	0.8864	0.00184
75.61	$\frac{1}{500.7}$	13.1	0.8490	0.00169
90.43	$\frac{1}{510.7}$	13.1	0.8229	0.00161

From this investigation it follows that the relations of pressure and volume at a constant temperature for a body in the gaseous state is given by the equation

$$v(1-pv)=c \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (C)$$

where p is the external pressure, v the volume of the gas, and c a constant.

From this equation the properties of homologous points already given in equations (A) and (B) follow as a direct consequence. For if

$$v(1-pv)=c$$

and

$$v'(1 - p'v') = c'$$

be the equations of any two isothermals; then, since at homologous points $pv=p'v'$, we shall have

$$\frac{v'}{v} = \frac{c'}{c}$$

and

$$\frac{p}{p'} = \frac{c'}{c} = \mu.$$

If the values of $\varepsilon(1-\rho)$ in Tables XXII., XXIII., XXIV. are carefully examined, it will be seen that they have a slight tendency to diminish, particularly at the lower temperatures; and a similar observation applies to the values of μ in former tables. It must be remembered that the pressures recorded in these tables are those of the airmanometer, and would require a small correction to reduce them to true pressures. The data for making this correction are so imperfect, and for the higher pressures so uncer-

tain, that I have not ventured to use them. According to REGNAULT, the indications of the air-manometer are $\frac{1}{83}$ too high at 20 atmospheres; according to CAILLETET, they are $\frac{1}{80}$ too high at 60 atmospheres, and only $\frac{1}{1000}$ in error at 200 atmospheres. The application of these corrections would nearly remove in many cases the slight differences in the values of μ and of $\varepsilon(1-\rho)$; but I have thought it better to give only the direct results of experiment till the true corrections to be applied are accurately known.

Another disturbing cause must be noticed, of little importance under the conditions of the foregoing experiments, but one which would seriously derange the results if the experiments had been carried down to pressures of 2 or 3 atmospheres. In all the tables I have given it has been assumed that, under a pressure of one atmosphere, one volume of the carbonic acid gas corresponds to one atmosphere of pressure. This assumption is not strictly legitimate, as it was shown long ago by VON WREDE that the density of carbonic acid compared with air is slightly less at one fourth of an atmosphere than at one atmosphere. In the absence again of complete data I have not attempted to correct for this disturbing cause, particularly as its influence would be very small at the pressures recorded in this paper. I hope to be able to supply hereafter both deficiencies; but in the mean time it is certain that none of the general laws I have given will be disturbed by the application of the corrections referred to.

I will now make a few observations on the properties of the gaseous state of matter.

1. In the ideal, or, as it is commonly called, the perfect gaseous state, matter would obey implicitly the external forces which act upon it, the volume being always inversely as the forces externally applied. In this state it would neither offer resistance to change of volume*, nor, from the action of internal attractive forces, would it undergo a greater diminution of volume than that due to the external pressure. The characteristic property of this state is

$$\alpha = \alpha',$$

where α is the coefficient of expansion at constant pressure, and α' the coefficient of elastic force at constant volume. It has not been ascertained with certainty whether this condition of matter actually exists in nature, although, in gases which are at temperatures greatly above their critical points and at ordinary pressures, the deviation from it can only be discovered by the most exact experiments. Whether at higher temperatures or lower pressures the ideal condition is absolutely realized, or only indefinitely approached, is a question which will perhaps scarcely admit of a direct experimental solution.

2. In the gaseous state, as we observe it, there are two distinct causes of internal disturbance whose results are directly opposed, and, according to the nature of the gas and the conditions of pressure and temperature, sometimes the one and sometimes the other predominates. One of these disturbances is due to the action of internal forces tending

* By resistance to change of volume is to be understood a resistance from internal causes whereby the gas undergoes a less diminution of volume under increased pressure than would occur in the case of an ideal gas obeying BOYLE'S law.

to produce a diminution of volume; the other is due to molecular conditions producing a resistance to diminution of volume other than that which occurs in a perfect gas. In the case of ordinary liquids the resistance to change of volume from increase of pressure is very great; in such liquids as liquid carbonic acid it is not so great, but it augments as the pressure is increased.

In the case of the permanent gases (or gases which have not hitherto been liquefied) the resistance to change of volume becomes predominant between 100 and 200 atmospheres, and at higher pressure it steadily increases. In hydrogen it appears under the lowest pressures at which that gas has been examined. It is probable, therefore, that this resistance to change of volume occurs in all gases even at low pressures, although, except in the case of hydrogen, it cannot be directly observed at low pressures, from the internal attractive forces producing a much greater change in the opposite direction. In the play of these opposing internal actions we have the explanation of the singular fact that the air-manometer indicates almost true pressures at 200 atmospheres, while at lower pressures its indications are above, and at higher pressures below the truth*. It is commonly assumed that in hydrogen gas the molecular forces producing internal attraction are absent; but this conclusion is doubtful, as the effects observed are probably here also differential. In carbonic acid, on the other hand, the internal attractive forces are very powerful, and mask the effects due to resistance to pressure till the gas is reduced to a small fraction of its volume under one atmosphere. In the experiments from which the laws of the ordinary gaseous state, as enunciated in equations (A), (B), and (C), were derived, I have always operated under the most favourable conditions for eliminating the influence of resistance to change of volume; and these laws are therefore to be regarded as characteristic of the gaseous state when the properties of the ideal gas are modified solely by the action of internal attractive forces.

* CAILLETET, 'Comptes Rendus,' vol. lxx. p. 1133.