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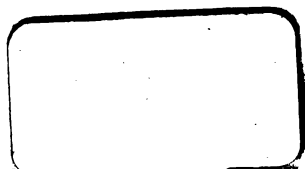
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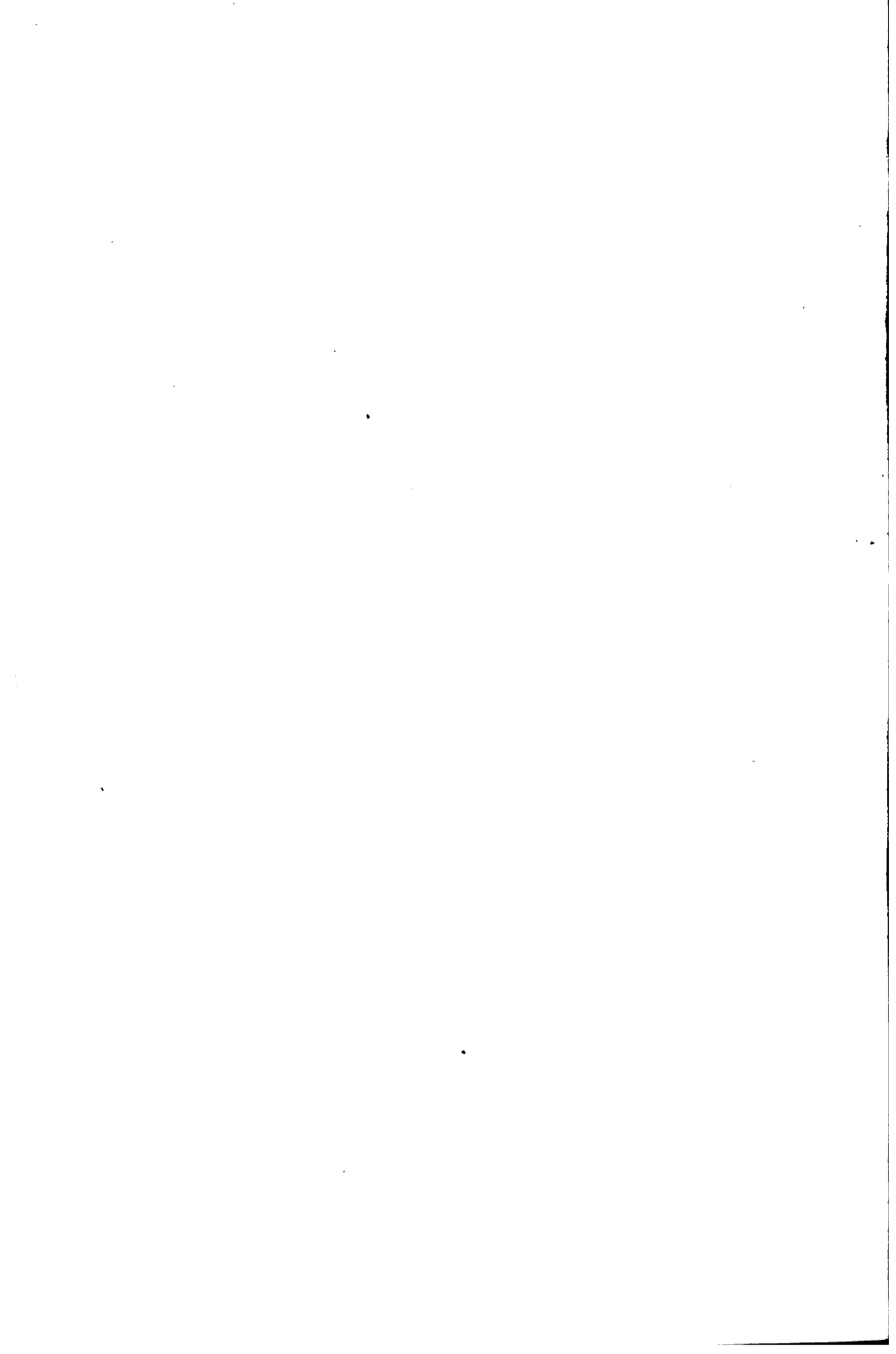
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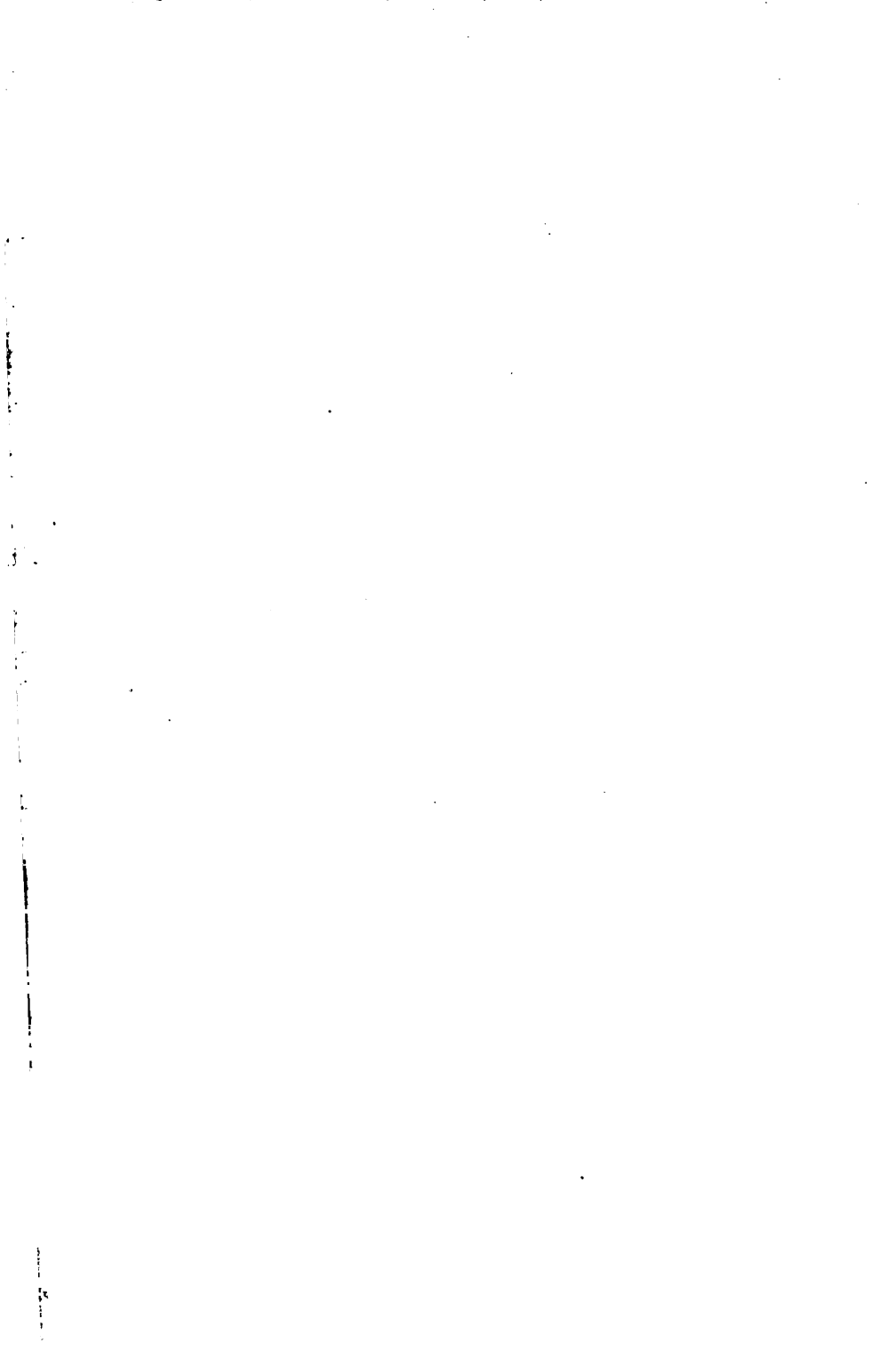
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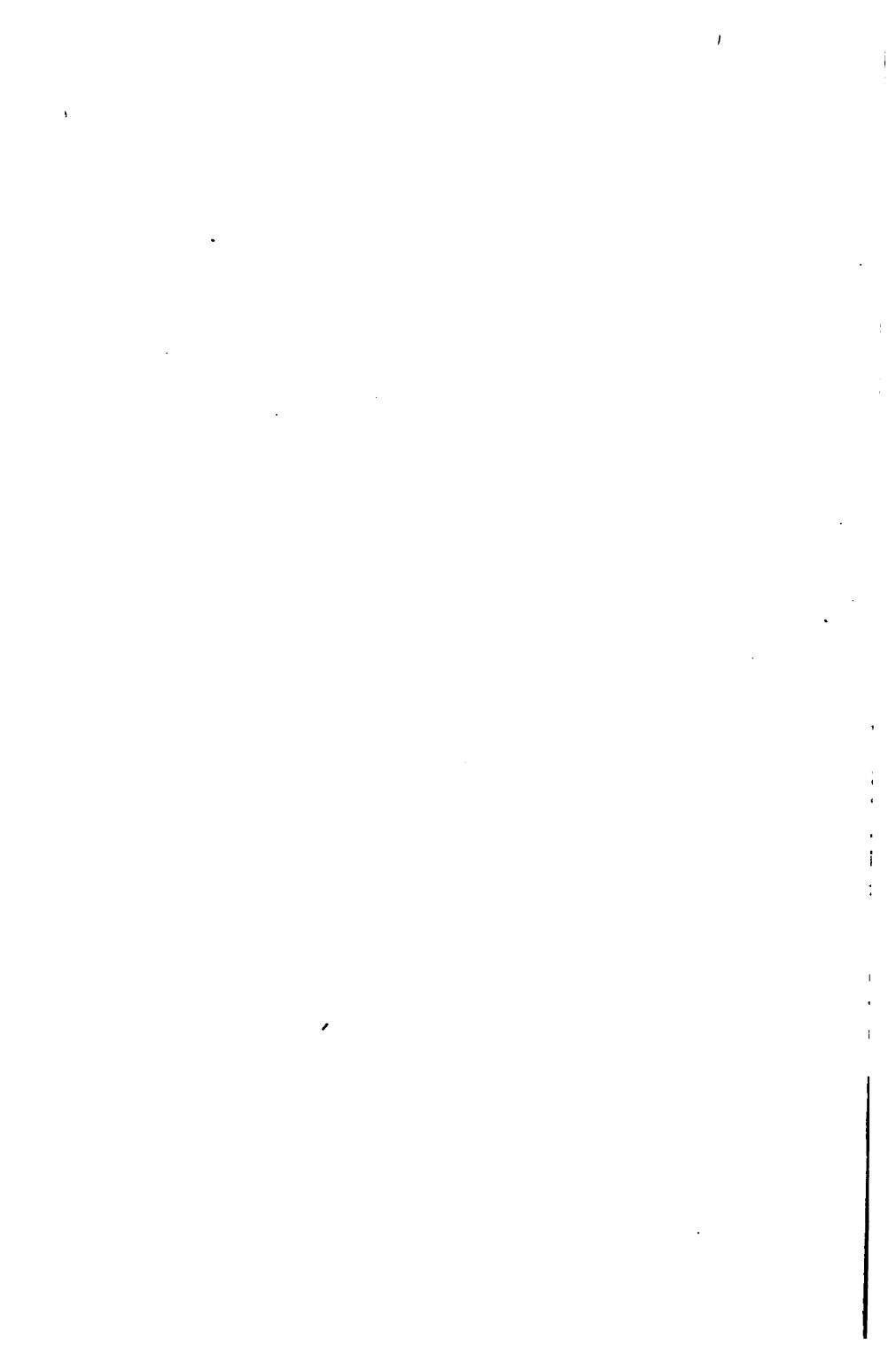


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SCIENTIFIC MEMOIRS

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XIV

THE EXPANSION OF GASES BY HEAT

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THE EXPANSION OF GASES BY HEAT

MEMOIRS BY DALTON, GAY-LUSSAC, REGNAULT
AND CHAPPUIS

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PREFATORY NOTE.

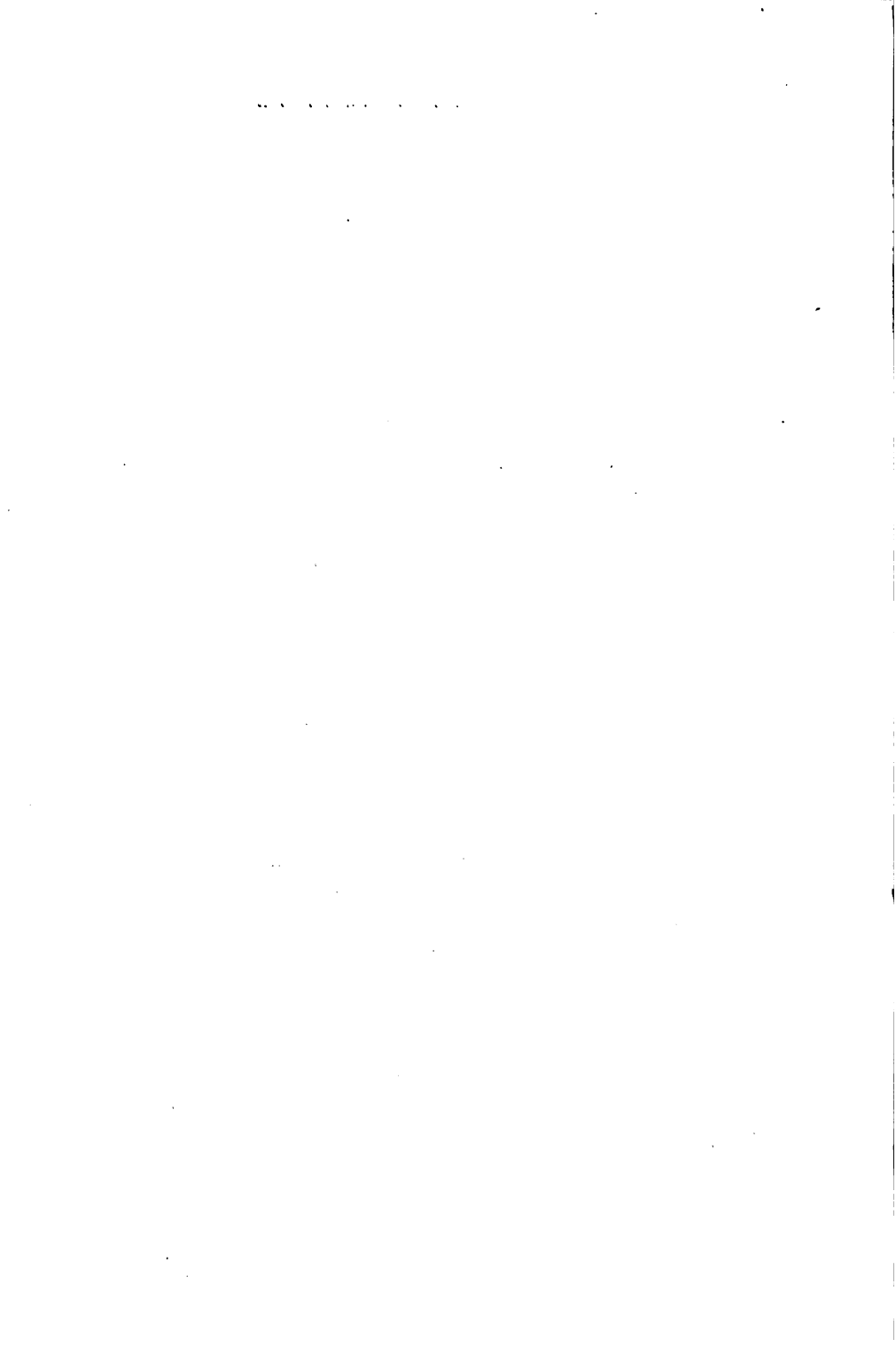
IN preparing a volume to contain the classical memoirs which treat of the law of the expansion of gases by heat, a choice which will be satisfactory from all points of view can scarcely be expected. The memoirs of Dalton, Gay-Lussac and Regnault are of course given in full; were it not for the very comprehensive abstract given in Regnault's first paper, the memoirs of Rudberg would certainly have been included. It has seemed best to the editor not to print in full any other than the memoirs mentioned; all others of sufficient importance are referred to in the historical Introduction. An exception has been made, however, in the case of Chappuis's research, for the proper comprehension of which a fuller abstract was needed than could readily be included in the Introduction. This abstract is therefore given separately.

The Bibliography contains, along with a few others closely connected, a list of the memoirs printed in full or discussed in the Introduction.

DOBBS FERRY, NEW YORK.

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INTRODUCTION.

THE Law of the Expansion of Gases by Heat, variously called the Law of Charles, Dalton, and Gay-Lussac, seems to have been for the first time definitely made known to the scientific world by the English chemist. As Roscoe says, "This law of equal expansion of all gases for equal increments of temperature has been generally known on the Continent as 'Gay-Lussac's' or 'Charles's law,' but ought to be called 'Dalton's law of expansion,' as he first announced it and gave experimental evidence of its truth, and the claims of the Manchester philosopher are generally now allowed." (*John Dalton, and the Rise of Modern Chemistry*, page 96.)

The experimental basis upon which Dalton founded his generalization was, however, meagre and, from a modern standpoint, quite inaccurate—as was the case also with the evidence upon the strength of which he put forth his Law of Multiple Proportions and the original Atomic Hypothesis. The work done upon this subject by Dalton and Gay-Lussac—and especially by the latter,—the results of which were published in 1802, forms an epoch in the history of the careful study of the properties of gases, if for no other reason than because of the recognition of the necessity for the thorough removal of water vapor from the gas examined, before concurrent results could be expected.

Of the investigations carried out prior to the beginning of the Nineteenth Century, Gay-Lussac gives a sufficient account in his first memoir. During the year 1801 Dalton read a series of papers before the Manchester Society, one of which treated of the rate of expansion of air and other gases and records, as its author states, experiments undertaken to test the results of the research of Guyton de Morveau and Duvernois. On account of its bearing upon certain theories which he held upon the nature of heat, Dalton's attention was especially drawn to the increase in the rate of expansion with rise of

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temperature, and he does not seem to have calculated an average coefficient of expansion on the basis of the volume of the gas at the melting-point of ice, from the results of these experiments. After the publication of Gay-Lussac's research, however, he apparently repeated his experiments with greater care, using 32°F. as one limit of the temperature-range, and calculated from the results thus obtained the coefficient which in his "New System" he states was the same as that announced by Gay-Lussac. This matter is discussed in a footnote on page 72. Dalton's first paper was published before that of the French savant, but in all probability not until the latter's experimental work had been completed.

It is singular that Gay-Lussac's later and, apparently in his opinion, more accurate investigation,—an account of which is given in the form of an extract from Biot's *Traité de Physique*—should have been made known to the world only through this means.

The results of the profound researches of Dulong and Petit upon the absolute expansion of mercury and the relation between the mercury and gas scales of temperature, were to a certain extent vitiated through their apparent acceptance of the Gay-Lussac coefficient 0.00375 for the expansion of air. One at least of their own experiments pointed to a figure much nearer that now accepted as correct, but such evidence as now exists indicates the use of the higher value in their computations. Their method involved the use of an open air-thermometer whose tip was sealed after it had been heated to some definite temperature; after the apparatus had been allowed to cool again to 0° , the tip of the thermometer tube was again opened under mercury and from the amount of mercury drawn in the expansion of the air at the previous high temperature was calculated. Practically the same method was afterwards employed by Rudberg and by Regnault in their researches upon the rate of expansion of gases. Assuming the coefficient 0.00375 for air and calculating on this basis the true temperatures registered by their air thermometers, Dulong and Petit naturally found greater deviation from the air standard on the part of mercury than the more accurate work of Regnault and others has since proved to exist. Since the coefficient of ex-

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pansion of mercury found by them has been shown by more recent investigations to be very nearly exact, it remains but to substitute the correct value for the coefficient of expansion of air to determine, with only slight error, the actual deviation of the mercury scale from the air scale of temperature.

In Gehler's *Physikalisches Wörterbuch* (1825) an account is given of two researches upon the rate of expansion of air by H. Flaugergues, published in the *Journal de Pharmacie*. Using a glass flask similar to that employed by Gay-Lussac in his earlier experiments, he found 0.371168 for the amount of the expansion of unit volume of air between 0° and 80° R. If allowance must be made for the expansion of the flask, this fraction becomes 0.375671—nearly the same as Gay-Lussac's. It is not clear from the context that Flaugergues took the expansion of the flask into account; nevertheless it is likely, and the coefficient first given, 0.00371, is probably his corrected result. The fact of the expansion of the containing vessel was at that time well known and generally allowed for; besides, in the experiments described in the second paper the author made use of a method intended to eliminate this factor: the gas was contained in a cylindrical glass vessel in which was a smaller leaden cylinder; the greater rate of expansion of the lead was to bring about a decrease of the vessel's capacity for gas exactly compensating for the increase in the size of the glass envelope. These experiments led to the figure 0.37174 for the amount of the expansion between 0° and 80° R.—practically identical with the former result. An experiment with moist air yielded as a result 0.411.

The determinations of Flaugergues seem to have attracted little attention, and, although they had pointed out the possibility of error in Gay-Lussac's coefficient, it was not until the publication of the very noteworthy memoirs of Rudberg that the matter received due consideration.

In the course of an investigation which had for its object the accurate determination of the melting points of the metals lead, tin and antimony on the scale of the air thermometer, Rudberg had found that, assuming Gay-Lussac's coefficient 0.00375 to be correct, he was led to conclude that the coefficient of expansion of glass was far greater at high temperatures than

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its behavior at ordinary temperatures would appear to promise. He accordingly undertook the re-determination of the air coefficient, employing, first, a method in which both volume and pressure varied, and, second, one in which the volume remained constant. The original memoirs are not given in the form of translation in this volume, as a sufficient abstract of them is given by Regnault in his first paper.

It will be well, in passing, to call attention to the fact that the first method of experiment employed by Rudberg was that which had been used previously by Dulong and Petit, but that the second seems to have been original with him; except for comparatively slight modifications intended to secure greater accuracy, the constant-volume air thermometer of to-day is the invention of Rudberg.

Both methods of determination led to the same result: Gay-Lussac's coefficient is too high by about one part in thirty-seven; the figure adopted by Rudberg as the probable coefficient of expansion of air is "between 0.00364 and 0.00365." It had been his intention to investigate other gases as well, but his death occurred shortly after the publication of the results obtained for air.

The great importance of the question involved was generally recognized and, consequently, within about four years the results of two careful, quite independent, investigations, one by Magnus in Berlin, the other by Regnault in Paris, made their appearance. While neither of them was led to a figure for the air coefficient quite so low as that adopted by Rudberg, both were able to support the latter's contention that the coefficient found by Gay-Lussac was far too high. It is interesting to note, however, that just as the more accurate work of Magnus and Regnault showed that Rudberg's coefficient was too low, exactly the same fate has befallen the coefficient adopted by Magnus and Regnault, through the investigations carried out since 1860.

Magnus—as did also Regnault—endeavored to repeat the later experiments of Gay-Lussac with air at constant pressure, but found it impossible to secure uniform results, evidently because the short mercury piston failed to close completely the bore of the thermometer tube: air leaked in or out according

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to the direction of movement of the mercury index and the relative tension within and without the tube. Turning to Rudberg's second method: that by which the increase of pressure within a gas reservoir of constant volume was measured instead of the increase in the volume of a gas kept at constant pressure: Magnus obtained eight values for α ranging from 0.00365032 to 0.00367899 with a mean of 0.00366508—at a barometric pressure of 28 inches; at 760 mm. pressure this mean value becomes 0.0036678. At 28 inches pressure the mean coefficient found for hydrogen was 0.00365659; for carbon dioxide, 0.00369087; for sulphur dioxide, 0.00385618. While the mean value for air found by Magnus, after recalculation for a pressure of 760 mm., is nearer than is the mean value found by Regnault by his four different methods, to the coefficient for constant volume now accepted, this fact cannot be interpreted as a proof of greater accuracy of experimental work on the part of the German physicist. Regnault's lowest result was 0.0036549, and highest 0.0036747—a range of 0.0000198 in fifty determinations carried out by four distinct methods; for any one method the range amounted to but two thirds of this amount, at the most. On the other hand, Magnus's results, all by one method and only eight in number, ranged 0.00002867. For hydrogen the range from highest to lowest was 0.0000029 in four determinations; for carbon dioxide, 0.00002228 in four; for sulphur dioxide, 0.00006552 in three determinations.

Magnus suggests as a possible explanation of the difference between the results of Gay-Lussac and those of Rudberg and himself, among other things, the fact that the former's gas reservoir was actually in the boiling water of the bath instead of in its vapor.

Regnault's two memoirs on the expansion of gases are given in full in the form of a translation. It is to be noted that he employed with success five different forms of apparatus to determine this expansion between 0° and 100° : in the first of these both volume and pressure varied to a considerable degree; in the second the volume remained more nearly constant; in the third and fourth the volume changed only to the extent of the expansion of the glass envelope; while in the fifth the increase

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of volume was directly determined under constant pressure. The last mentioned method established the fact that for most gases the coefficient of expansion at constant pressure is slightly greater than that at constant volume, because such gases do not exactly conform to Boyle's Law, but contract more rapidly in proportion than the pressure upon them increases. Thus the mean value found for air at constant volume is stated by Regnault to be 0.003665, and that for constant pressure, 0.0036706,—at about atmospheric pressure. The latter coefficient increases as the pressure is increased : at about $3\frac{1}{2}$ atmospheres it is between 0.00369 and 0.00370.

Both Magnus and Regnault then proceeded independently to re-determine the variation between the mercury scale and the air scale of temperature. Since the data showing the dimensions of the apparatus of Dulong and Petit were unknown, it was impossible with certainty to re-calculate their results with the aid of a more nearly correct coefficient of expansion for air. Gay-Lussac had declared that air and mercury expand proportionally even at comparatively high temperatures ; Dulong and Petit found in their research that soon after passing 100° mercury began to expand more rapidly, and that at about 300° the temperature by the mercury scale was over 7° higher than that calculated from the readings of their air thermometer.

Here, again, the superiority of the experimental work of Regnault cannot be questioned. It established the fact that the air thermometers and the mercury thermometers agree up to about 250° ; above this point mercury expands more rapidly in proportion than air, and at 350° (by the air thermometer) the mercury thermometer stands about 3° higher.

Magnus's work, on the other hand, led to the practical confirmation of the results of Dulong and Petit. As Magnus had used the coefficient 0.003665 (at 28 inches ; 0.0036678 at 760 mm.) in calculating his air thermometer temperatures, he was led to believe that Dulong and Petit had not after all made use of Gay-Lussac's coefficient, but that, having in a single independent determination—as was known—found the coefficient 0.00365, they had employed the latter instead. This supposition Regnault, in criticizing Magnus's results, considered extremely unlikely, on the ground that a study of Dulong and

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Petit's results does not seem at all to confirm it, and that the latter would hardly have depended upon a single determination of so important a factor, especially when so at variance with the generally accepted figure of Gay-Lussac. Into the criticisms passed upon one-another's apparatus there is no need here to go.

An investigation of the behavior of gas thermometers at about -88° led Regnault to the conclusion that the coefficients of expansion for air and hydrogen preserve closely the ratio shown at higher temperatures.

In his comparison of the various gas thermometers in the *Memoires* of the Academy of Sciences, Regnault speaks of using a coefficient for hydrogen smaller than he records in any of his experiments. Lord Kelvin has called attention to the fact that this statement is probably in error (See *Encyclopædia Britannica*, article "Heat").

Mention may be made here, finally, of the study by Regnault of the coefficient of expansion of gases under high pressures, the results of which are contained in a later volume of the *Memoires*.

The accuracy of the results of Regnault for air at constant volume was put to the test by Recknagel and, still more rigorously, by Balfour Stewart; the results of the former confirmed those of Magnus, so far as the value of the coefficient is concerned, Recknagel's mean value being 0.0036681. Stewart, like Recknagel, used the method employed successfully by Rudberg, Magnus and Regnault to find the coefficient of expansion from the rise of tension in a gas kept at constant volume while its temperature rises, but, using even greater care than did any of his predecessors to secure pure dry air for his apparatus, and employing every known refinement in the measurement of the pressure changes, he obtained the figure 0.0036728 as the average of four results, the highest of which was 0.0036739 and the lowest, 0.0036716.

The results recorded in the memoir of v. Jolly, although scarcely to be compared as regards accuracy with those of Stewart, are interesting because of the author's success in simplifying the constant-volume gas thermometer. The differences between his highest and lowest results were, how-

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ever, not so great as those between the corresponding figures in the several series of Regnault's determinations. He was also successful in determining the coefficient of expansion of oxygen, which Regnault had failed to do. For air, v. Jolly found in 20 experiments: highest, 0.0036724; lowest, 0.003665; mean, 0.00366957. For oxygen (18 experiments) the highest was 0.003680; lowest, 0.0036683; mean, 0.0036743. For hydrogen, the highest of 4 results was 0.0036600; lowest, 0.0036530; mean, 0.0036562. For nitrogen, the highest of 4 results was 0.0036717; lowest, 0.0036655; mean, 0.0036677. For carbon dioxide, the highest of 17 results was 0.0037144; lowest, 0.0036962; mean, 0.0037060.

Of the extensive and important researches of Amagat one memoir and part of another have appeared in the form of a translation in an earlier volume of this series—"The Laws of Gases: Memoirs by Boyle and Amagat." Earlier than either of these is a study (1873) of the variation of the coefficient of expansion of gases with rise of temperature; a constant-volume method based upon that of Rudberg was employed. Assuming that for air the mean value of $\alpha = 0.00367$ between 0° and 100° , he finds the mean values of α for sulphur dioxide and carbon dioxide steadily decrease as the temperature rises. Thus, for the former gas it is 0.003904 between 10° and 60° , but 0.003798 between 10° and 250° ; between 0° and 10° it is 0.00413, at 25° 0.00394, at 100° 0.003757, at 250° 0.003685. For carbon dioxide the mean value of α between 0° and 50° , is 0.003714; between 0° and 250° , 0.0037028; at 0° it is 0.003724; at 50° , 0.003704; at 100° , 0.003695; at 250° , 0.003682.

From the memoir of 1881, the following may be quoted with regard to the behavior of gases under high pressures:

"1. The coefficient of expansion of gases (referred to unit volume) increases with the pressure up to a maximum value, beyond which it decreases indefinitely.

"2. The maximum occurs at a pressure for which the product $p\nu$ is a minimum; consequently at this point the gas *accidentally* obeys Mariotte's law.

"3. For continually rising temperatures this maximum becomes less and less distinct and, finally, disappears."

Hydrogen even at very low pressures seems already to have

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passed the point where pv is a minimum; hence its coefficient constantly decreases as pressure rises and as temperature rises. The pressures employed in these experiments ranged from 40 to 320 metres of mercury.

In a later memoir (1893) are recorded results obtained through a still greater range of pressures. Amagat says, "An inspection of Table 21 shows that at the outset the coefficient of expansion increases with the pressure, as Regnault had already found for pressures of a few atmospheres; it then passes through a maximum which occurs at a pressure rising regularly with the temperature. During my first researches on this subject these maxima seemed to coincide with those pressures for which the product pv is a minimum; but the more extended data of the present memoir show this law to be only approximate." With rise of pressure from 1000 to 3000 atmospheres, the coefficient of expansion of oxygen between 0° and 16° steadily decreased from 0.00236 to 0.00134, that of hydrogen from 0.00200 to 0.00128, that of nitrogen from 0.00193 to 0.00098, and that of air from 0.00206 to 0.00110. Another series of experiments showed that with rise of pressure from 200 to 1000 atmospheres a similar fall in the value of the coefficient was to be noted. The coefficient in the case of carbon dioxide rises to a maximum and decreases; this maximum occurs at higher and higher pressures as the temperature rises: thus, at 137° — 198° , α is 0.00369 (of the volume at 137° considered as unity) when the pressure is 75 atmospheres; 0.00798 (maximum value) at 200 atmospheres, 0.00386 at 500, and 0.00223 at 900 atmospheres. The coefficient of carbon dioxide for constant pressure rises at first with the temperature, passes a maximum, and then decreases as temperature rises; as the pressure is higher, the maximum occurs at higher and higher temperatures.

The elaborate investigations of Mendeléeff upon the properties of gases are to a large extent a *terra ignota* for those who cannot read Russian; only a few papers, usually meagre abstracts, contained in journals published in Western Europe, are available as sources of information. In papers published in conjunction with Kajander, he discussed the disadvantages of Regnault's constant-pressure method, among others that only

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about two thirds of the gas contained in the apparatus was at the temperature of the water vapor. In fact, in his *Principles of Chemistry* (2nd Edition, Volume 1, page 133, note), he goes so far as to state "Regnault, however, did not directly determine the change of volume between 0° and 100° , but measured the variation of tension with the change of temperature; but since gases do not entirely follow Mariotte's law, the change of volume cannot be directly judged by the variation of tension." Nine results obtained with an apparatus in which the entire volume of gas was surrounded with water vapor, and various devices were employed to increase the accuracy of the readings, ranged from 0.0036814 to 0.0036876, with a mean of 0.0036843. This is the coefficient of expansion of air at a constant pressure of about 760 mm.; the probable error of the mean value is estimated by Mendeléeff to be 0.0000005.

In his *Principles of Chemistry* Mendeléeff gives the results obtained at constant volume: for air, 0.00368; for hydrogen, 0.00367; for carbon dioxide, 0.00373; for hydrobromic acid gas, 0.00386. At $3\frac{1}{2}$ atmospheres pressure α becomes 0.00371 in the case of air. The coefficient of expansion of carbon dioxide rises with pressure as follows: at 1 atmosphere, 0.00373; at 3, 0.00389; at 8 atmospheres, 0.00413. In the case of hydrogen which is, on the other hand, less compressible than Boyle's Law would lead one to expect, the rise of the coefficient with increase of pressure is slower: at one atmosphere it is 0.00367; at eight atmospheres, 0.00369.

In one paper Mendeléeff recalculates the results of Magnus, Regnault and v. Jolly for air at constant volume, reducing the barometric readings to 45° latitude. He gives the following table:

Determinations		As given by author	Corrected value.
Magnus	8	0.0036651	0.0036700
Regnault	15	0.003665	0.0036694
v. Jolly	20	0.0036696	0.0036702
			Mean, 0.003670

The coefficient for constant pressure, as found by himself with Kajander, is recalculated in the same way and given as 0.003681.

The investigations of Andrews upon the critical state,

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among other points, led to a study of the coefficient of expansion of carbon dioxide at higher pressures. He gives the following figures for α (constant pressure) at 0° — 7.5° :

Pressures in { atmospheres }	12	16.25	20.01	24.8	27.7	31.1	34.5
Coefficient	0.00482	0.00520	0.00607	0.00700	0.00782	0.00895	0.01097.

The value of α (64° — 100°) increases with increasing pressure up to 0.01822 at 145.5 atmospheres; then decreases: at 223 atmospheres, $\alpha = 0.0084$.

The coefficient for constant volume rises from 0.003526 at 21–24 atmospheres to 0.007018 at 94–118 atmospheres.

Several researches conducted during the past fifteen years have shown extraordinary improvement in the accuracy of measurement of pressure changes in gas thermometers. The researches of Callendar upon the platinum thermometer and its standardization by means of the gas thermometer, have led to the improvement of the latter as an instrument for exact determinations. The work of Chappuis is so striking an example of the kind of accuracy referred to, that a much more detailed abstract of his memoir is given in the body of the book (page 153). The coefficients for hydrogen as found by him are: constant volume, 0.0036624; constant pressure, 0.0036600. If these are reduced to their limitary values which refer to zero pressure, they become 0.0036624 and 0.0036625 respectively, giving as “absolute zero” on the centigrade scale -273.04° . The mean coefficient of expansion found by him for nitrogen, at constant volume, between 0° and 100° is 0.00367466. The figure found for air by Callendar and Griffiths is almost identical, 0.0036749. The latter was, however, the result of but a single determination. Wiebe and Böttcher found an average value of 0.0036706 for air, in a series of figures ranging from 0.0036694 to 0.0036713. Finally, Harker and Chappuis, in a recent memoir, find as the coefficient of expansion of nitrogen at constant volume (in glass) the figure 0.00367180 for an initial pressure of 793.5 mm. of mercury, and 0.0036683 for an initial pressure of 530.8 mm. of mercury. In the limit, then, at zero pressure, it would be 0.0036613. The limiting value for the coefficient at constant pressure is 0.0036612. These results indicate the limit of accuracy attained up to this time.

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In 1895 Kuenen and Randall examined the rate of expansion of argon and helium through a considerable range of temperature; the fact that the coefficient remained almost constant showed the absence of dissociation in the gases examined and was taken as proof of their simple molecular condition.

Before closing, reference should be made to work done in the study of the behavior of gases at very low pressures. The results of the research of Melander are summarized in the following table, where p = initial pressure, p' = final pressure, α = coefficient of expansion at the pressure p' ; the probable error as calculated by Melander, is given for the first and last values of α only, these being the limiting values.

I—AIR.

p	p'	α	Error
752	1027.7	0.0036660	0.0000005
376	513.7	6624	
260	355.2	6606	
170	232.2	6594	
100	136.6	6630	
78	106.6	6657	
51.8	70.8	6717	
29.1	38.8	6853	0.0000021
13.2	18.1	7172	
6.6	9.1	7627	

II—AIR.

749	1023.4	0.0036642	0.0000004
254	346.9	6580	
101	138.0	6634	
75	102.5	6645	
18.6	25.5	6895	
5.8	7.98	7666	0.0000021

III—CARBON DIOXIDE.

749	1028.1	0.0037264	0.0000005
347	474.9	6856	
267	365.2	6803	
169.5	231.7	6701	
101.5	138.7	6657	
55.8	76.2	6641	
18.1	24.7	6753	0.0000015

IV—HYDROGEN.

764.5	1043.6	0.0036504	0.0000002
351.7	480.1	6518	
191.0	260.8	6547	
111.7	152.5	6548	
48.4	66.2	6595	
20.1	27.4	6721	
9.3	12.8	7002	0.0000022

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It will be noted that with decrease of pressure the value of α falls until a minimum is reached and then rises again ; with hydrogen, on the one hand, the minimum seems to have been reached at about atmospheric pressure ; with air the minimum occurs at about 300 mm. pressure, and with carbon dioxide at about 100 mm.

The accuracy of the results obtained by other experimenters at very low pressures, has been challenged by Baly and Ramsay, who point out the difficulty of the removal of all gas from a glass vessel and the likelihood of the presence in the gas examined of carbon dioxide and water vapor given off from the walls of the vessel after the pressure has been lowered. The shrinkage of the vessel under atmospheric pressure after the removal of most of the gas contained in it, is another source of serious error. Of course these difficulties become important only at very low pressures. The following table contains the figures found for the coefficients of expansion of hydrogen, oxygen and nitrogen at pressures below 5.5 mm. :

I—Hydrogen.

Pressure in mm.	4.7	3.47	0.25	0.096	0.077
Coefficient	$\left\{ \begin{array}{l} 273.5 \\ 0.003656 \end{array} \right.$	$\left\{ \begin{array}{l} 273.74 \\ 0.003653 \end{array} \right.$	$\left\{ \begin{array}{l} 278 \\ 0.003623 \end{array} \right.$	$\left\{ \begin{array}{l} 287 \\ 0.003366 \end{array} \right.$	$\left\{ \begin{array}{l} 286.5 \\ 0.003327 \end{array} \right.$

II—Oxygen.

Pressure in mm.	5.1	5.3	4.0	2.5	1.4	0.083	0.07
Coefficient	$\left\{ \begin{array}{l} 281 \\ 0.003831 \end{array} \right.$	$\left\{ \begin{array}{l} 280 \\ 0.003846 \end{array} \right.$	$\left\{ \begin{array}{l} 282 \\ 0.003817 \end{array} \right.$	$\left\{ \begin{array}{l} 281 \quad 280.1 \\ 0.003984 \quad 0.003998 \end{array} \right.$	$\left\{ \begin{array}{l} 283 \\ 0.004292 \end{array} \right.$	$\left\{ \begin{array}{l} 284 \\ 0.004098 \end{array} \right.$	$\left\{ \begin{array}{l} 286.3 \\ 0.004161 \end{array} \right.$

III—Nitrogen.

Pressure in mm.	5.3	4.97	3.0	1.1	0.8
Coefficient	$\left\{ \begin{array}{l} 304 \\ 0.003290 \end{array} \right.$	$\left\{ \begin{array}{l} 308.8 \\ 0.003238 \end{array} \right.$	$\left\{ \begin{array}{l} 301.8 \\ 0.003315 \end{array} \right.$	$\left\{ \begin{array}{l} 304 \\ 0.003290 \end{array} \right.$	$\left\{ \begin{array}{l} 311 \\ 0.003021 \end{array} \right.$

Pressure in mm.	0.6	0.6	0.6	0.6
Coefficient	$\left\{ \begin{array}{l} 335 \quad 343.5 \\ 0.002817 \quad 0.002911 \end{array} \right.$	$\left\{ \begin{array}{l} 377 \quad 323 \\ 0.002653 \quad 0.003096 \end{array} \right.$	$\left\{ \begin{array}{l} 301 \quad 327 \\ 0.003322 \quad 0.003058 \end{array} \right.$	$\left\{ \begin{array}{l} 371 \quad 343 \\ 0.002695 \quad 0.002915 \end{array} \right.$

Mean of eight results at 0.6 mm. = 342.38 [= 0.002919].

Baly and Ramsay give their results in common fractions ; the corresponding decimal fractions have been introduced for the

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sake of comparison with the results of others. The authors sum up their results as follows:

"1. The coefficient of expansion of hydrogen with temperature decreases as pressure is lowered. It is normal down to a pressure of 0.1 mm.

"2. The coefficient of expansion of oxygen is greater than the normal one, being $\frac{1}{273}$ instead of $\frac{1}{273}$; it increases with decrease of pressure to $\frac{1}{273}$ at 1.4 mm.; at 0.7 mm. of pressure it is erratic; but at lower pressures it again becomes more constant, still showing, however, a tendency to increase as the pressure is decreased.

"3. With nitrogen the coefficient of expansion is lower than the normal ($\frac{1}{273}$) at pressures between 5 and 1 mm.; at lower pressures, like that of hydrogen, its coefficient of expansion decreases; that is, the gas becomes more elastic.

"4. So far as it was possible to experiment with carbon dioxide, its behavior appears to resemble that of hydrogen and nitrogen, but owing to the tendency which it has to condense and cling to the gauge, trustworthy measurements were impossible to attain. These results confirm those of Mendeléeff¹ and Siljeström,² although they are deduced from thermal expansion, while theirs were deduced from the compressibility of the gas. And Bohr's results³ as regards the abnormality of oxygen were also confirmed, although likewise by a different method."

¹ *Annales de Chimie et de Physique*, [5] **9**, 111-116 (1876).

² *Bihang till K. Svenska Vet. Akad. Handlingar.*, **2**, 1 (1873); Pogendorff's *Annalen*, **151**, 462-482, 573-603 (1874).

³ *Wiedemann's Annalen*, **27**, 459-479 (1886).

EXPERIMENTAL ESSAYS

On the Constitution of Mixed Gases; On the Force of Steam or Vapor from Water and other liquids in different temperatures, both in a Torricellian Vacuum and in Air; On Evaporation; and on the Expansion of Gases by Heat

BY JOHN DALTON

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ON THE EXPANSION OF GASES BY HEAT.

BY JOHN DALTON.

THE principal occasion of this essay is another on the same subject by Messrs. de Morveau and du Vernois in the first volume of the *Annales de Chimie*. It appearing to them that the results of the experiments of De Luc, Col. Roi, de Saussure, Priestley, Vandermonde, Berthollet and Monge did not sufficiently accord with one another; and that it would be of importance to determine not only the whole expansion of each gas from two distant points, such as the freezing and boiling, but likewise whether that expansion be uniform in every part of the scale, they instituted a series of experiments expressly for those purposes. The result of which was that betwixt the temperatures of 32° and 212° , the whole expansion of one gas differs much from that of another, it being in one case about $\frac{1}{10}$ of the original, and in others more than 12 times that expansion; and that the expansion is much more for a given number of degrees in the higher than in the lower part of the scale. These conclusions were so extremely discordant with and even contradictory to those of others, that I could not but suspect some great fallacy in them, and found it in reality to be the fact: I have no doubt it arose from the want of due care to keep the apparatus and materials free from moisture.

My method of experimenting on this subject is simple, and therefore less liable to error. A straight manometer tube, such as has been mentioned, is duly divided into equal portions of capacity; it is then dried by a wire and thread, and the open end inserted through a cork into a phial containing sulphuric acid, in order that the aqueous vapour may be drawn out of the tube; this is essential if we operate in temperatures lower than that of the atmosphere, otherwise not. For want of this attention, Col. Roi, in his valuable paper in the *Phil. Trans.* vol. 67, has been led into some erroneous conclusions. —A small column of dry mercury is then let down to a proper

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point in the manometer, and it is ready for experiment with common air.

It requires some address to fill the manometer with any other gas.—I succeeded best as follows: filled the tube with dry mercury; then pushed down a wire and thread, so that when the wire was got to the end of the tube, a thick covering of thread just entered the open end, and held the mercury like a cork, so that the tube could be inverted without losing the contents; then having a glass funnel with a perforated cork over the water apparatus, containing the gas, I slipped the manometer through the hole in the cork, and putting my hand into the water under the funnel, drew the wire out of the manometer, and with it the mercury; upon which the gas entered the manometer. For carbonic acid gas, I opened the sealed end of the manometer, drew it out to a capillary bore, and forced a stream of the gas through the tube; then putting my finger on the other end, sealed it again by a blowpipe, and let down a small column of mercury to the proper point.

When the manometer was to be exposed to a heat of 212° , I used a Florence flask with a long glass tube corked into it, in such sort that as much of the manometer as was necessary to be exposed to the temperature might be in the tube; then water at the bottom of the flask was made to boil violently, so that a constant stream of vapour issued out of the top of the glass tube, which was found to raise the thermometer to 212° . Small specks of white paint were put upon the divisions of the manometer together with numbers which were discernible through the containing tube. For lower temperatures a deep tin vessel containing hot water was used in which the manometer was immersed, the water being well agitated previously to each observation.

From a great many experiments made in this way on common air, and likewise upon hydrogenous gas, oxygenous and nitrous gases, and carbonic acid gas, I can assert that the conclusions of DeLuc, Roi, Saussure, Berthollet, etc., are nearly accurate throughout, and that those of de Morveau and du Vernois are extremely inaccurate in the higher temperatures.

I have repeatedly found that 1000 parts of common air of the temperature 55° and common pressure, expand to 1321

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parts in the manometer; to which adding 4 parts for the corresponding expansion of glass, we have 325 parts increase upon 1000 from 55° to 212° ; or for 157° of the thermometric scale. As for the expansion in the intermediate degrees, which Col. Roi's experiments show to be a *slowly diminishing* one above the temperature of 57° , but which de Morveau's on the contrary show to be a *rapidly increasing* one in the higher part of the scale; I am obliged to allow that Col. Roi is right, though it makes in some degree against an hypothesis I have formed relative to the subject; he has certainly however made the diminution too great from 72° downwards, owing to his not perceiving that he actually *destroyed* a portion of the elastic fluid he was operating upon (aqueous vapour) in reducing its temperature so low; if his air had been previously dried by sulphuric acid, etc., he would not have found so remarkable diminution below 72° . My experiments give for $77\frac{1}{2}^{\circ}$ above 55° , 167 parts; for the next $77\frac{1}{2}^{\circ}$ only 158 parts: and the expansion in every part of the scale seems to be a gradually diminishing one in ascending.

The results of several experiments made upon hydrogenous gas, oxygenous gas, carbonic acid gas and nitrous gas, which were all the kinds I tried, agreed with those on common air not only in total expansion, but in the gradual diminution of it in ascending: the small differences observed never exceeded 6 or 8 parts on the whole 325; and differences to this amount will take place in common air when not freed from aqueous vapour which was the situation of all my factitious gases.

Upon the whole therefore I see no sufficient reason why we may not conclude, that *all elastic fluids under the same pressure expand equally by heat*—and that *for any given expansion of mercury, the corresponding expansion of air is proportionally something less, the higher the temperature*.

This remarkable fact that all elastic fluids expand the same quantity in the same circumstances, plainly shows that the expansion in solid and liquid bodies seems to depend upon an adjustment of the two opposite forces of heat and chemical affinity, the one a *constant* force in the same temperature, the other a *variable* one, according to the nature of the body; hence the unequal expansion of such bodies. It seems there-

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fore that general laws respecting the absolute quantity and the nature of heat, are more likely to be derived from elastic fluids than from other substances.¹

Dalton, in his *New System of Chemical Philosophy* (London: 1808), page 19, in discussing a proposed new method of denoting temperature, says in reference to the expansion of gases: "The volume at 32° is taken 1000, and at 212°, 1376 according to Gay-Lussac's and my own experiments. As for the expansion at intermediate degrees, Gen. Roy makes the temperature at midway of total expansion, 116½ old scale; from the results of my former experiments (*Manch. Mem.* Vol. 5, Part 2, page 599), the temperature may be estimated at 119½; but I had not then an opportunity of having air at 32°. By my more recent experiments I am convinced that dry air at 32° will expand the same quantity from that to 117° or 118° of common scale, as from the last term to 212°. According to the theory in the above Table it appears, that air of 117° will be 1188, or have acquired one half its total expansion. Now if the theory accord so well with experiment in the middle of the interval, we cannot expect it to do otherwise in the intermediate points."

BIOGRAPHICAL SKETCH.

John Dalton was born in Cumberland, England, in the year 1766. He was to a large extent self-taught and, when grown, was able to support himself by teaching school while, through the kindness of a friend, who helped him by lending him books on scientific subjects, he studied hard to acquire a knowledge of natural philosophy. His papers on meteorological subjects drew attention to him and in 1793 he was appointed to the professorship of mathematics and natural philosophy in the Manchester New College. Simultaneous observations made in Cum-

¹ Note by Translator: The paper concludes with an exposition of Dalton's theory that the absolute temperature increased at the same rate as the cube root of the volume in the case of gases, by which he finds the temperature of absolute cold to be 1515° below 0° F.

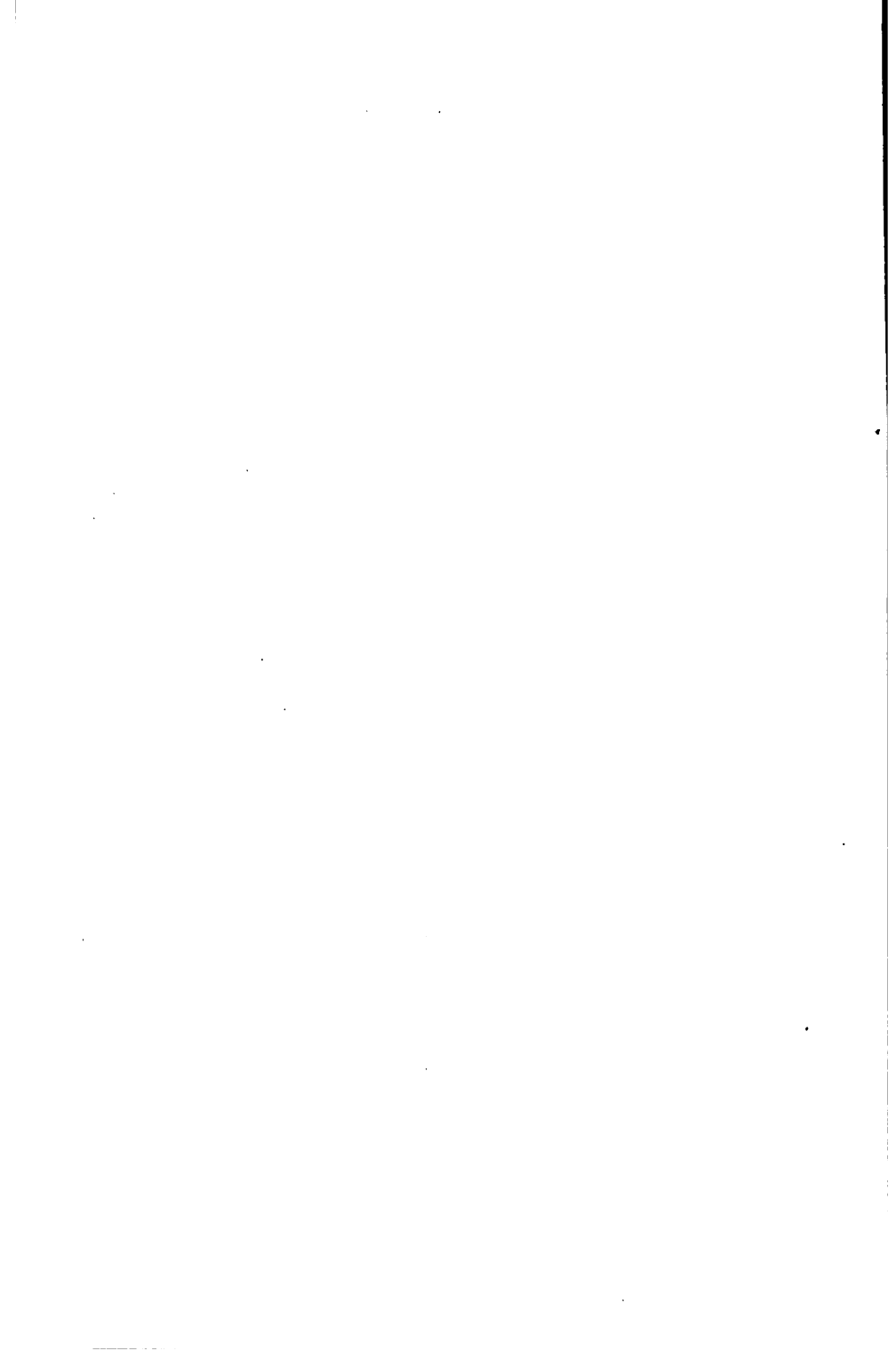
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berland and at Manchester enabled him to calculate the height of the aurora from the earth's surface. The fact that water vapor exists *mixed*, and not combined, in the air was announced by him at this time. In 1794 he called attention to the existence of color blindness or "Daltonism," as it was sometimes called, having discovered that it was a feature of his own vision. Continuing his meteorological studies, he was led to giving a definition of the "dew-point." In 1800 he noted the rise of temperature which takes place in gases when compressed. Of the four important papers read before the Manchester Society in 1801, the fourth is the one quoted in full. In the first he brings out "Dalton's law of mixed gases," assuming that gas particles are elastic only towards particles of the same kind. In the second paper, "On the force of steam," he describes the dew-point hygrometer and predicts the liquifaction of gases by cold and pressure. In the third paper he shows that evaporation is proportional to the temperature, whether in air or *in vacuo*. That four such contributions to science should have been presented at one time is striking proof of the extraordinary powers of their author.

The data upon which the Law of Multiple Proportions is based were next brought forward and, soon after, in 1803-5, the Atomic Hypothesis and the announcement of the atomic weights of some of the elements. Following the promulgation of his views in Thomson's *System of Chemistry* (1807), Dalton published in 1808 his *New System of Chemistry*. In this he anticipated in a way Dulong and Petit's Law, for he seemed to assume for the atoms of all elements equal capacity for heat.

In 1825, on the establishment of the Royal Society Prize, it was first bestowed upon Dalton in recognition of his contributions to the advancement of chemistry.

Dalton lived until 1844, but his classical memoirs practically all belong to the period before 1815.



RESEARCHES UPON THE RATE OF EXPAN- SION OF GASES AND VAPORS.

BY L. J. GAY-LUSSAC.

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RESEARCHES UPON THE RATE OF EXPANSION OF GASES AND VAPORS.

BY L. J. GAY-LUSSAC.

PART I.

Object of this Memoir.

FOR a long time physicists have busied themselves with [the problem of] the expansion of gases; but their researches present such great discrepancies in the results that, instead of establishing their views, they call, on the contrary, for a more rigorous investigation.

The expansion of vapors has attracted the attention of physicists to a less extent. Although for a long time the extraordinary properties of steam have been recognized and the most beneficent applications of them have been brought about, Ziegler and Bettancourt are the only ones, to my knowledge, who have endeavored accurately to determine them. Their experiments cannot however lead to a knowledge of the actual expansion of this vapor; since, having always some water in their apparatus, there was, for each new degree of heat, an expansion of the vapor produced by former increments of heat and an increase of volume due to the formation of new vapor—two causes which combined evidently to push up the mercury in their manometer.¹

¹ The apparatus of Bettancourt consists of a boiler of copper with a cover of the same metal, through which three tubes pass. The first serves to introduce water into the boiler; through the second is inserted the stem of a thermometer intended to show the temperature of the vapor, and to the third is attached a suitably shaped barometer tube to measure the tension of this same vapor. A vacuum is produced in the boiler with the aid of a pneumatic pump, which is connected by means of a tube provided with a stop cock. The apparatus of Ziegler differs but little from that of Bettancourt; but Ziegler not having produced, as Bettancourt did, a vacuum in his boiler, there results a great difference in their experimental data. (*Architecture hydraulique de Prony, Tome II*).

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The thermometer, as it exists to-day, cannot serve to show with accuracy relative amounts of heat, because we do not yet know what relation exists between the degrees of the thermometer and the quantities of heat which they can indicate. We believe, it is true, in general, equal divisions of its scale correspond to equal increments of caloric; but this view is supported by no very positive fact.

It must therefore be admitted that we are far from having exact knowledge of the expansion of gases and vapors and of the movements of the thermometer; and in the meantime there is every day a call, in physics and in chemistry, to reduce a given volume of gas at one temperature to another; to measure the heat given off or absorbed in the change of constitution of substances, that given off or absorbed by the same body in passing from one temperature to another; in the arts, in calculating the efficiency of steam engines, in ascertaining the rate of expansion of many substances; in meteorology, in determining the quantity of water held in solution in the air—a quantity which varies with its temperature and its density and follows a law as yet unknown. Finally, in the preparation of tables of refraction by astronomers and in the application of the barometer to the measurement of altitudes, it becomes indispensable to know with accuracy the temperature of the air and the law of its expansion.

Although these facts have made it very desirable to engage in a work of such general application, the difficulty of the investigations which it demands would have prevented my devoting myself to it, had I not been on the other hand strongly urged by Citizen Berthollet, whose pupil I have the honor to be. To him I owe the means necessary for the prosecution of this research, during which I have often been assisted by his advice and by that of Citizen Laplace: men whose reputation will add to the confidence my work would inspire.

The researches I have undertaken upon the law of the expansion of gases and vapors, and upon the movements of the thermometer, not being yet complete, I have for my object in this memoir only to investigate the expansion of gases and vapors for one definite rise of temperature and to make it clear that this is the same for all these fluids; but before giving an

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account of my experiments, I think I ought to give an historical survey of what has been done upon this subject. And as I add at the same time some comments upon the means which have been employed, I intend to preface them with a discussion of one of the chief causes for uncertainty which can enter into this class of investigations. Although it is very important and although it seems to have been unknown to the majority of the physicists who have studied the expansion of gases, it will be enough for me merely to state it to make its influence felt. What I say of atmospheric air will apply to other gases.

This cause of uncertainty is due to the presence of water in the apparatus. As a matter of fact if a few drops of this fluid are left in a vessel filled with air whose temperature is then raised to that of boiling water, this water, on passing into the form of a vapor, will occupy about 1800 times as great a volume as at first, and by this means will drive out a very large part of the air originally enclosed in the vessel. It necessarily follows that when this vapor is condensed—and therefore occupies a space 1800 times as small—we should ascribe to the air remaining in the vessel an expansion far too great; for it would be assumed that it was this air which at the temperature of boiling water filled all the space in the vessel. If we do not carry the temperature up to this point, the same source of inaccuracy will nevertheless exist, and its extent will be proportional to the temperature at which we stop: for in this case the water will not all evaporate, but the air will dissolve more and more as the temperature rises and will consequently assume a greater and greater volume over and above that which it owes to the heat; so that when we pass to a lower temperature the volume of air which fills all the space in the vessel will decrease from two causes: (1) through the loss of its caloric, (2) through that of the water which it holds in solution. Too great an expansion would thus be assumed for the air.

Speaking generally, whenever there is enclosed with gases any liquid, or even any solid which like sal ammoniac, for example, can be dissolved or become vaporized at the temperature to which it is to be raised, errors must of necessity result in the determination of the expansion of these gases.

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PART II.

Historical Sketch of what has been done upon the Expansion of Gases.

The expansion of atmospheric air by heat was well known before the time of Amontons, but this physicist is apparently the first to seek to determine its amount for a given rise of temperature. To attain this result he enclosed some air with the aid of mercury in a flask connected with one of the arms of a reversed siphon, and placed this apparatus in a bath of hot water.¹ The air expanded by the heat presses upon the mercury and forces it into the other branch of the siphon; so that he judged, by the height of the mercury compared with its level in the flask, the tension the air had reached.

From various experiments made upon different volumes of air, he concludes (*Mem. de l'acad.*, 1699, 1702): (1) "That the heat of boiling water has limits which it does not pass; (2) that various volumes of air increase their tensions at the same rate for equal degrees of heat, and *vice versâ*; (3) that the heat of boiling water increases the tension only until it is capable of sustaining about the weight of a column of mercury of ten inches' height."

It appears then that, however compressed a volume of air may be, the heat of boiling water always increases its tension one third; that is to say, a volume of air compressed, for example, under a column of 60 inches of mercury, including the weight of the atmosphere, will support, at the temperature of boiling water, a column of mercury of about 80 inches. He therefore concludes "that the same degree of heat, small as it may be, will always increase the tension of the air more and more as this air is supporting a greater and greater weight."

If Amontons had started from a degree of heat more clearly defined than what he calls an *average*,—which would have been at that time scarcely possible—it would have been possible to calculate from his experiments with sufficient approximation

¹The air enclosed in the flask, not being able to escape when the mercury is poured in, is a little more compressed than it would be naturally; but if no other pressure than that of the atmosphere is desired, it would be very easy to avoid this slight inconvenience.

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the expansion of atmospheric air; yet, since he conducted his comparisons with volumes of gas of very unequal density, one may conclude from them that, *however dense a volume of air may be, the increase of elasticity which this air acquires for the same degree of heat always bears the same relation to that which it had prior to the experiment.*

Nuguet, in seeking to verify the results of Amontons, obtained others entirely unlike them. In one of his experiments, the volume of the air expanded by the heat of boiling water and the original volume were to one another as 2 to 1, and in two other experiments as 16 to 1. His apparatus consisted of a flask inverted and sunk in a water bath whose temperature he raised to that of boiling water. It is evident that this apparatus was extremely defective, since the air in it was always in contact with water; and Nuguet had in addition let some water into his flask. It is not surprising, therefore, that he obtained results so discordant and, so to speak, so extraordinary. (*Mem. de l'acad.*, 1708. *Lahire.*)

This great difference between the results of Amontons and those of Nuguet upon the rate of expansion of atmospheric air, and the realization that it had been subjected to experiment under conditions which were not usual, led Lahire to apply himself to the same problem. The apparatus of which he made use was identical with that of Amontons, except that the bulb carried a small tube which he sealed after having introduced the mercury. By this means, the mercury being at the same level in the bulb and in the syphon, the air which he subjected to experiment was no more compressed than the surrounding air. With this apparatus Lahire found, first, in one experiment that the air expanded from an average temperature up to that of boiling water, could not sustain a column of mercury of one third of the weight of the atmosphere; later, he found in another, the thermometer being lower and the barometer higher than in the former experiment, that the air, expanded by the heat of boiling water, could not support a column of mercury so high as the former one. These two results are evidently contradictory; but Lahire suspected no error and drew the conclusion from them that we are bound to admit that we do not yet know the nature of the air.

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In order to explain the great difference which existed between his results and those of Nuguet, a difference far too great not to be due to some outside influence, Lahire noticed that Nuguet had let a little water into his apparatus; and from this fact he concluded that it might be this water which, on being converted into vapor and expelling a large part of the air enclosed in the flask, had produced so great an expansion. He was thoroughly confirmed in his opinion by the result of an experiment carried out after Nuguet's method, in which he let a little water into the flask; for he found that the volume of the air expanded from the average temperature up to that of boiling water, and the original volumes were to one another as $35\frac{1}{2}$ is to 1. (*Mem. de l'acad.*, 1708.)

At the same time M. Stancari of Bologna showed that water increases to a considerable degree the volume of air at a temperature but slightly raised. We therefore owe to these two physicists the important discovery of the influence of water upon the expansion of atmospheric air; yet although they have by their experiments given the matter prominence, it has since been generally overlooked. To the slight attention paid to this influence must be ascribed the great divergencies found in the results of physicists upon the expansibility of gases.

It is known that the altitudes to which one ascends in the atmosphere are given by the logarithms of the corresponding heights of the barometric column. If the density of the air were always the same, it would be easy thus to calculate the altitude of one place above another stated place, by observing the barometer there. It would therefore be important to distinguish the causes that affect the density of the air, in order to make the necessary corrections in the heights given by the barometer.

Deluc, who has inaugurated a new era in this department of physics, recognized in heat one of these causes. In order clearly to identify its effect, he began by endeavoring to fix the temperature at which the logarithms indicate directly the correct altitudes, and found, on comparing numerous observations made at places whose altitudes he had determined with accuracy, that this was the case at the temperature of $16\frac{3}{4}^{\circ}$ of the thermometer graduated in 80 divisions, and this he calls *tem-*

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pérature fixe. Therefore to make correction for the effects of heat above and below this fixed point, he again compared the altitudes found from the logarithms with those he had measured, attributing to heat the variations of the first from the second, and drew the conclusion that "in the neighborhood of the fixed temperature, the correction for one degree of the thermometer would be to the altitude of the place as 1 is to 215." (*Recher, sur les modif. de l'at., IV Part, Ch. III.*)

Colonel Roy has found a far greater rate of expansion for air. According to him, in the neighborhood of 15° on a thermometer graduated in 80 divisions, air expands $\frac{1}{77}$ of its volume for each degree. He also found that moist air expands much more than dry air; but Saussure noted that in carrying out his experiments, Col. Roy had admitted into his manometer either water in a liquid state or water vapor and had confused two things which should be distinguished, namely, the conversion of water into an elastic fluid, and the expansibility of air mixed with this vapor. (*Philos. transact., 1777, p. 704.*)

Saussure determined the rate of expansion of air in the neighborhood of 6° to be $\frac{1}{77}$ of its volume for each degree. His experiments were performed with a large flask in which were enclosed a thermometer and a barometer to indicate the variations of the temperature of the air and the corresponding tension acquired. In order to study the effect of water upon the expansion of air, he enclosed in his flask air of varying degrees of dryness, avoiding the formation anew of vapor, and, far from finding this air more expansive than very dry air, he thought he had discovered, on the contrary, that very dry air was even a little more expansive than air which was very moist, but was holding its moisture all the time entirely uncondensed. (*Essai sur l'hygrometrie, page 108.*)

Up to this time physicists had limited themselves to the expansion of atmospheric air, and the first to occupy himself with that of other gases is the celebrated Priestley. He proceeded as follows:

After having filled a flask, over mercury, with the gas he wished to test, he fitted to it a bent tube, one of whose arms was nearly horizontal, and left a little mercury in the neck of the flask so that the expansion of the gas could push it into the

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tube. This done, he put his apparatus in a small wooden box, introduced a thermometer, and carried it into rooms at different temperatures: the expanded air caused the mercury to move a greater or less distance along the tube, and it was by this distance measured in inches that Priestley determined the expansibility of different gases. As all the experiments were made with the same flask and the same tube, which he probably inclined always in the same way, they give a ratio among the expansibilities of different gases, but not the actual expansion; for it would be necessary to know for that purpose the volume of that part of the tube traversed by the mercury in comparison with that of the flask, and to know, in addition, the exact inclination of the tube, of which Priestley makes no mention. I shall not pause longer to discuss these experiments; all the more as Priestley himself did not put much confidence in them and wished to repeat them under better conditions. Assuming the volumes of the different gases equal, the expansion measured in inches along the tube, for 4.44° of the thermometer graduated in 80 divisions,¹ would be:

Ordinary air	1.82 inches
Hydrogen gas	2.05 "
Nitrous gas	2.02 "
Carbonic acid gas	2.20 "
Muriatic acid gas	1.33 "
Oxygen gas	2.21 "
Nitrogen gas	1.65 "
Sulphurous acid gas	2.37 "
Fluoric acid gas	2.83 "
Ammoniacal gas	4.75 "

(Experiments and Observations, etc., Book VII, Section VI.)

In a memoir printed among those of the Academy for the year 1786, Citizens Monge, Berthollet and Vandermonde have concluded from an experiment that, for one degree atmospheric air expands $\frac{1}{181.55}$ of its volume, and hydrogen gas $\frac{1}{181.55}$.

Lastly, Citizen Guyton, realizing how little accord there was on [the subject of] the rate of expansion of atmospheric air,

¹ Note by Translator: On an 80-degree thermometer scale (e. g. Reaumur's) 4.44° is the equivalent to 10° Fahrenheit. The latter was evidently the temperature interval employed by Priestley.

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and that there were still no direct experiments on record which determined the expansion of gases for slightly elevated degrees of heat and for successive degrees near together, undertook, with Citizen Duvernois, to throw some light upon this matter. As their work is the most recent, I shall pause a moment to endeavor to show what the causes are which were able to affect their result.

Their apparatus consisted of a flask fitted with a bent tube by means of which the air expelled from the flask by heat was caught in a receiver in the mercury trough. The flask, full of the gas they wished to subject to experiment, was immersed in a bath at the temperature of melting ice and was held there by an iron cover. They heated the bath to 20° , 40° , 60° , 80° , successively, and caught in different receivers the gas forced out by expansion through each of these intervals; they finally determined the volumes of air escaping from the flask by measuring them in their respective receivers after having reduced them to the temperature of melting ice, and thus found the volume of that remaining in the flask.¹ But apart from the fact that their apparatus made it necessary for them to determine many constants—which must interfere with the accuracy of their results—I note that, after the sinking of the bent tube in the mercury, not having introduced some more air into the flask to replace the mercury which was pushed into the tube as a result of the pressure of the mercury of the bath, several degrees of heat would be needed before a single bubble of air escaped from the flask; so that, if they had made use of lesser intervals, as, [for example] of 5° each, they would have found that, starting from zero, the first degrees of heat would have shown no expansion in the different gases. Indeed they have observed an expansion for the first 20 degrees which, for the majority of the gases, is far too small.

This source of error, although serious, would not have carried the results of Citizens Guyton and Duvernois so wide of the truth, had there not been others still more serious. Thus I suspect that their flask had not been properly dried and that a little water may have got in during the introduction of the

¹ *Annales de Chimie*, Vol. I.

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gases. Had a decigram of water remained, it would have served to affect their results in a marked way, especially towards the higher degrees, where, in changing into an elastic fluid, it would have forced a large part of the air out of the flask.

In this way can be explained the noticeably increasing progression which they have determined for all the gases, whereas they ought to have found a decreasing one, on lowering to the temperature of melting ice the amount forced out by each expansion. I note in connection with this point, that Citizen Guyton expresses himself as regards the expansion of hydrogen gas as follows:¹ "The four [volumes] resulting from the expansion were caught this time in a receiver which had been surrounded with vessels filled with ice. In spite of this, the mercury of the little trough showed upon the thermometer [a temperature] 2, 3, 4, 6 degrees above zero, while the water of the bath was at the same moment at 20, 40, 60, and 80 degrees—a thing which could produce some inaccuracy in the determination of each of these quantities, but which cannot be of much consequence, the expansion being very slight through these first degrees."

From this one may conclude that these physicists gave no more care to reducing the volumes of the other gases to zero; and, if this be the case, there results another source of uncertainty in their experiments.

In comparing the volumes of gas left in the flask with those that had been driven out by heat, Citizens Guyton and Duvernois have found that the gases oxygen, hydrogen, carbonic acid and atmospheric air had shown a contraction and have given as its cause combinations which had taken place during the time of the experiments. Employing mercury which was very pure and free from oxide, I have been unable to detect any noticeable action between the metal and these gases from the temperature of melting ice up to that of boiling water.

Below is a table of the results of Citizens Guyton and Duvernois; they have enclosed between parentheses those in which they have little confidence.

¹*Annales de Chimie, T. I, page 284.*

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	From 0° to 20°	From 20° to 40°	From 40° to 60°	From 60° to 80°	From 0 to 80°
Ordinary air expands	1.57	2.81	3.45	(3.57)	1.687
Vital air	2.12	4.52	1.53	(3 + 1.73)	4 + 2.52
Nitrogen gas	2.41	2.41	1.52	5 + 2.72	5 + 1.682
Hydrogen gas	1.51	2.52	(2.52)	(2.52)	2.52
Nitrous gas	1.33	2.52	3.72	(2.52)	1.52
Carbonic acid gas	2.42	2.52	2.31	(2.52)	1 + 1.63
Ammoniacal gas	2.52	1.72	1 + 1.32	(3 + 2.52)	5 + 1.322

Before going further, I ought to say that, although I had noted a great many times that the gases oxygen, nitrogen, hydrogen, carbonic acid and atmospheric air expand to the same extent from 0° to 80°, Citizen Charles had, fifteen years before, discovered the same property in those gases ; but, never having published his results, it was by the greatest chance that I learned of them. He had also endeavored to determine the rate of expansion of gases soluble in water and had found for each a characteristic rate of expansion different from that of the other gases. In respect to this my conclusions differ much from his.

Citizen Charles employed as his apparatus a barometer the chamber of which was of a large size. The gas which he wished to submit to experiment was enclosed in the reservoir of the barometer at the temperature 0° and under a pressure of 28 inches of mercury. When this barometer was submerged in boiling water, the mercury rose in the tube and the excess of the entire column over that of 28 inches indicates the tension the gas had acquired ; but Citizen Charles having been kind enough to show me the apparatus, I saw that the tube of the barometer was very large in proportion to the capacity of the reservoir ; so that the rise of the mercury above 28 inches did not show all the tension the gas had acquired, since for that it would be necessary that its volume in the reservoir had remained constant. It therefore seems to me that the true

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rate of expansion of gases cannot be deduced from these experiments.

PART III.

Description of Apparatus.

A flask *B* (*Fig. 1*) is provided with an iron tap to which a bent tube *ID* (See *Fig. 2*) can be fitted. The key of the tap carries a lever *LL* pierced at its two ends to receive two cords by which one can open and close the tap under water.

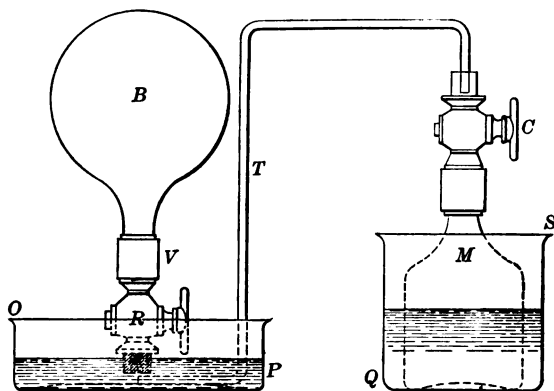


FIG. 1

To introduce gases into the flask, I made use of a glass bell jar *M* (*Fig. 1*), to which are fitted a tap and a bent tube *T*, and sunk in a vessel *QS*. On pouring water into the vessel and opening the tap, the gas compressed in the bell jar escaped by the tube and filled the flask *B* placed mouth-downward in the mercury bath *PO*. When the flask is full, I close the tap, adjust the tube *ID* (*Fig. 2*) and fix it in a cylindrical iron cage *EFGH*, which I then place in a copper vessel *AD*, full of water. In order that there might be no communication between the outside air and the gas enclosed in the flask when the tap is opened, I lowered the end of the tube *ID* one or two millimeters into the small mercury bath *KX*. This done, I heat the bath and at intervals of 10° , let us say, open the tap and immediately close it again. The gas, tending to expand

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on account of the heat, escapes rapidly from the flask and has soon driven out the atmospheric air which filled the tube ; from 40° on the tap can with safety be left open until the end of the operation : I prefer however alternately to open it and close it, as I find that [under these circumstances] the gas in the flask comes more rapidly to the temperature of the bath. After 15 or 20 minutes of boiling—a sufficient time for every-

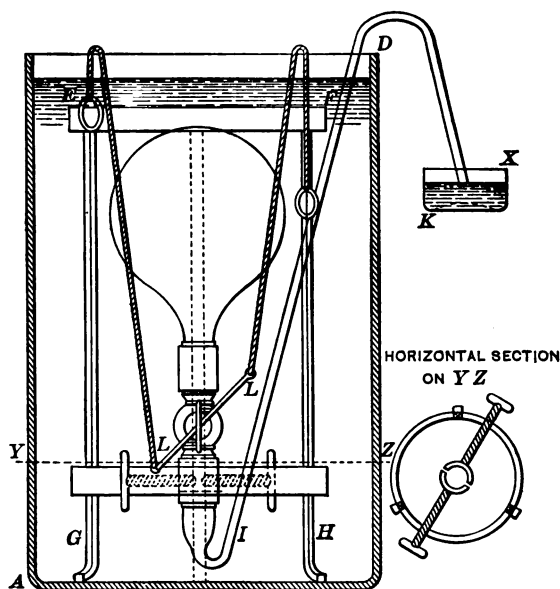


FIG. 2.

thing to come to the same temperature—I remove the end of the tube *ID* from the mercury, in order to secure equilibrium between the outside air and the gas in the flask, and then close the tap. After having cooled the bath with ice or water, I remove the apparatus, disconnect the flask from which I remove the tube *ID* and also the lever *LL* and submerge it completely in a bath of known temperature where I leave it long enough for it to come perfectly to that temperature.

Now, on opening the tap, there enters the flask a volume of water which is exactly equal, when equilibrium is restored, to that of the gas which has been driven out by the heat. The tap

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being closed, I remove the flask, carefully dry its surface and weigh it in this condition; afterwards I weigh it full of water and empty, recording the results of each weighing. These being known, I find the volume of the flask by subtracting the weight of the empty flask from that of the flask filled with water, and the volume of the water which represents the volume of air driven out of the flask by the heat, by subtracting, again, the weight of the empty flask from that of the flask when it contained this water. It will thus be very easy to determine the relationship between the original volume and the volume when expanded.

This method has the advantage of possessing great accuracy; for, as the volumes are found from the weights, the error which can be made in this determination must be very small, even when use is made of balances of no great sensibility.

The apparatus I have described is simple enough in itself,

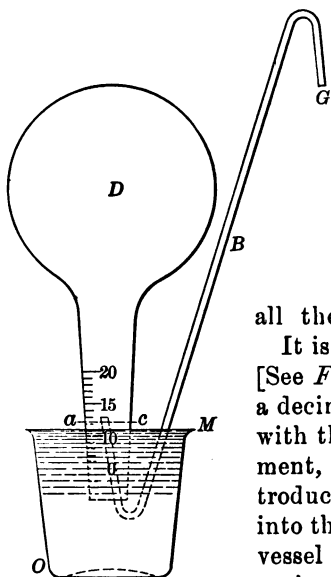


FIG. 3.

yet, as it calls for the use of cements and of a tap which must be of iron by reason of the mercury, its manipulation is somewhat difficult. It will not therefore be out of place to describe another apparatus also which I have used and which, along with great simplicity and easy manipulation, possesses at least nearly all the advantages of the former one.

It is a simple flask *D* (*Fig. I*, *Plate II*) [See *Fig. 3*] whose neck must be at least a decimeter long. After having filled it with the gas I wish to subject to experiment, in the way already described, I introduce its neck about two centimeters into the mercury contained in an ordinary vessel *OM*, and fasten it in an iron frame as in the case of the former apparatus.

If I immerse it in this condition in a bath of hot water, the gas expanded by the heat, in order to escape, will have to overcome, not only the pressure of the mercury in the vessel, but that of

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the water of the bath as well. To do away with this inconvenience, I introduce into the neck of the flask the end of a very narrow bent tube *B*, taking care to keep the end *G* closed until it has been lowered into some mercury. To support the tube, I fasten to the middle of it a cord on the end of which I hang a weight and pass it over a support, in such a way that the weight by its action tends to lift the tube. The apparatus being thus arranged, I place it in a glass tank where there is a depth of water equal to that which should be in the bath, I open for a moment the end of the tube in order to establish equilibrium with the pressure of the outside air, and close it again at once. As there is a scale whose divisions are very small upon the neck of the flask, I read the exact level of the mercury *ac* inside the neck of the flask and record it, since it is to this level that the volume of the flask extends. The end of the tube *B* must be raised above the level *ac*, for otherwise the mercury will enter the tube and offer a resistance to the escape of the gas expanded by the heat. After all these manipulations—which take longer to describe than to carry out—I place the apparatus in a bath of hot water and open the end of the tube *G* after having put it in a small mercury bath, as in the former apparatus. When the flask has come to the temperature of the boiling water, I remove the tube *B* (whose end must have been previously withdrawn from the mercury), and cool the bath. The mercury then rises in the flask; but it will be easy to put water in its place, when everything is at a lower temperature. The volume of the flask and the volume of the water which has taken the place of that part of the gas driven out by the heat, are found in the way I have already described; only it is necessary in this calculation to add to the weight of the empty flask that of the cylinder of water extending from the level *ac* on the one hand to the end of the neck of the flask on the other.

I should be able to give still further details, but I withhold them in order not to be too diffuse: those a little practiced in manipulation will readily supply them. However, as it is a matter of importance, after what I have said about the effects of moisture, to remove it entirely from the apparatus, I will describe how I have been successful in doing so.

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If the flask is evidently wet, I begin by drying it with filter paper ; then I heat it so as to evaporate a part of the moisture which it still may contain, and, with the aid of a bellows to which I have attached a glass tube, I carry into its interior a current of air to drive out the vapor. These last operations being repeated many times with the flask and the tube, both become perfectly dry. With regard to the mercury which I have used in my experiments, I have invariably used what was very dry and pure.

In all the experiments the results of which I am about to give, I have always brought back to the temperature of melting ice the gases whose rate of expansion I have been able to determine with the apparatus I have described ; and for this purpose I had a bath where I kept the ice and in which the flask was completely covered after having been taken from the bath in which it had been subjected to experiment, and here I left it for about half an hour, during which time I constantly stirred the bath. The other fixed temperature which I resolved upon for the same gases, is that of boiling water.

I have made some experiments at other temperatures ; but they will have to be repeated, and moreover they will become part of a treatise which I have begun upon the law of the expansibility of gases and vapors ; I shall confine myself therefore, as I have said, to a consideration of the rate of expansion of gases for a definite rise of temperature—which will be that comprised between the degree for melting ice and that for boiling water. With respect to vapors, I shall compare their rate of expansion with that of gases.

PART IV.

Experiments and Results.

MAKING use of the two [forms of] apparatus I have described—but more often the second than the first—and avoiding all the sources of inaccuracy which I could foresee, I have found from six experiments upon atmospheric air, the six following results :¹

¹ My flask held about 350 grams of water.

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Starting from the temperature of melting ice, at that of boiling water equal volumes of atmospheric air represented by 100 had become, respectively :—

137.40 ; 137.61 ; 137.44 ; 137.55 ; 137.48 ; 137.57 ;
the mean of which is nearly 137.50.¹

If the total increase of volume be divided by the number of degrees which produced it, or by 80, we find, making the volume at 0° temperature equal to unity, that the increase of volume for each degree is $\frac{1}{80}$, or on the other hand, $\frac{1}{80}$ for each degree of the centigrade thermometer.

Deluc having found $\frac{1}{80}$ for the coefficient, it would appear at first sight that our results are the same ; but if it be noted that he starts from a temperature of 16 $\frac{1}{2}$ °, while I start from a temperature of 0°, it will be seen that our results are quite different.² I shall later consider this difference and show that the coefficients of expansion vary with the temperature from which we set out.

Hydrogen gas produced from iron by weak sulphuric acid was submitted to two experiments : in one, through an elevation of temperature from that of melting ice to that of boiling water, 100 parts [by volume] became 137.49 ; and in the other, through the same rise of temperature 100 parts became 137.56. The average of these two results is 137.52—which differs only slightly from the average result found for the expansion of atmospheric air.

Oxygen gas given off from the oxygenated muriate of potash [*i. e.*, potassium chlorate] was tested three times and gave the following results : 100 parts became

¹ Although the differences among the results are not very considerable, I believe I could have made them very small had I been able to note the state of the barometer during the boiling of the water. However, I have always taken care to note its temperature at the moment of boiling and I confess I have never noticed any marked variations. As a matter of fact it requires a change of an inch in the barometer to produce one of a degree in the boiling point of water,—which must occur but rarely. However that may be, the mean result, 137.50, must be very close.

² Note by Translator:—In the memoir the second temperature stated is “0 $\frac{3}{4}$ ° ;” it seems evident that this is a typographical error.

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137.47 ; 137.54 ; 137.45 ;

the mean of which is 137.48.

Nitrogen gas obtained through the decomposition of ammonia by oxygenated muriatic acid [*i. e.* chlorine] gave the following five results : 100 parts became

137.42 ; 137.56 ; 137.50 ; 137.46 ; 137.55 ;

the mean of which is 137.49.

On bringing together the preceding results and comparing the expansion of the gases oxygen, hydrogen and nitrogen with that of atmospheric air, there results a table like this—

Between the temperature of melting ice and that of boiling water, 100 parts of	Suffer an increase of	Differences
Atmospheric air	37.50 parts	
Hydrogen gas	37.52	+ 0.02
Oxygen gas	37.48	— 0.02
Nitrogen gas	37.49	— 0.01

The slight differences observable in the above results may arise from the fact that it is impossible to make the conditions rigorously identical in every experiment, and as they amount to only two ten-thousandths of the original volume, we may safely conclude that atmospheric air and the gases oxygen, hydrogen and nitrogen expand to the same extent between the temperature of melting ice and that of boiling water.

In order to determine the rate of expansion of gases soluble in water, I made a change in the apparatus. I used two tubes *TT* (*Fig. 2, Plate II*) [See *Fig. 4*] calibrated at the same time over the same mercury bath *AC*, by means of a very small measure.

Each time that I made use of this apparatus, I took care that the quantity of mercury should be the same as when the tubes were calibrated. I ought to say that, if the basin which held the mercury suffered any injury, it was necessary to recalibrate the tubes for another bath ; indeed it would be well to cut them from the same cylinder of glass and to give them the same height, in order to have all the conditions as much the same as possible.

Into one of these tubes I admitted atmospheric air down to

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the 100th division, for example, and into the other the gas whose rate of expansion I wished to determine, also as far as the 100th division. I thus subject to test 100 equal measures of each of two gases. I then place the apparatus in a heater whose temperature I can control and watch the progress of the expansion of the gases. However great the care I have taken to observe closely, I have never perceived any difference and have always noticed that the same divisions were passed at the same time in the two tubes.

The gases I have thus examined have never been introduced directly into the tubes; I have kept them for some time before in an intermediate vessel in which I put some drying-agent,—for example, muriate of lime, [*i. e.* calcium chloride]—and made them pass thence into the tubes by compressing them with the aid of mercury which I introduced by means of a safety tube fitted to the intermediate

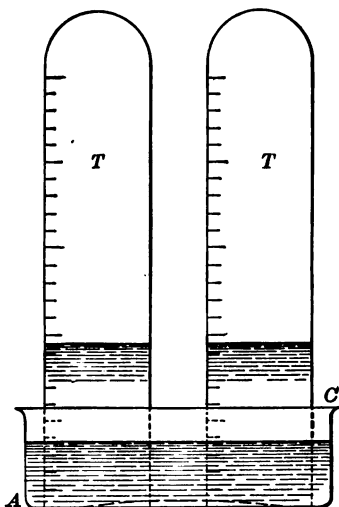


FIG. 4.

flask. If these precautions are neglected, there will almost always result far too great an expansion; we must therefore avoid the contamination of unabsorbed moisture or of any other substance capable readily of assuming the gaseous state.

100 measures of carbonic acid gas obtained from marble with the aid of sulphuric acid were compared with 100 measures of atmospheric air. From the fifth degree up to the 90th degree the expansions were the same in the two tubes.

100 measures of muriatic acid gas produced with the aid of concentrated sulphuric acid from muriate of soda [*i. e.* common salt] thoroughly dried by heat, having been compared with 100 measures of atmospheric air from the 3d degree up to the 86th, the expansions of the two gases were absolutely the same. This experiment, as well as the preceding one, was repeated many times, and always gave the same result.

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Sulphurous acid gas and nitrous gas, again, showed under the influence of heat the same expansion as atmospheric air.

Dr. Priestley and Citizens Guyton and Duvernois have found very great expansibility in the case of ammonia gas. With the idea of discovering the cause which was capable of vitiating the results of their experiments, I introduced directly into one of the tubes some ammonia gas produced by the decomposition of muriate of ammonia by means of ordinary lime, and into the other a suitable volume of atmospheric air. As the temperature rose, the ammonia gas expanded proportionally more than the atmospheric air, in fact to such a degree as soon to become twice as great; yet on examining the mercury surface and the walls of the tube, after lowering the temperature, I noticed a trace of liquid and some crystalline needles which could be only muriate or carbonate of ammonia, and the whole disappeared on raising the temperature to a sufficient degree. However that may be, I began the experiment again by allowing the ammonia gas to stand some time in an intermediate flask where there was some caustic potash, and then, from 0° up to 95° , its expansion followed exactly that of atmospheric air. I again examined the surface of the mercury and the walls of the tube, when the temperature had returned to 0° , but this time I noticed neither liquid nor crystalline needles. This experiment, repeated many times, always met with the same success.

It is thus evident, from what I have said, that not only a liquid, but any other substance capable of assuming the gaseous state can easily lead to error; it is necessary therefore to avoid such things with the most scrupulous care.

The experiments of which I have given an account and all of which were made with great care, prove without a doubt that atmospheric air and the gases oxygen, hydrogen, nitrogen, nitrous gas, ammonia, muriatic acid, sulphurous acid and carbonic acid gases expand to the same extent for the same degrees of heat; and that consequently their greater or less density under the same pressure and at the same temperature, their greater or less solubility in water, and their individual character, have no influence upon their expansibility.

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In consideration of this fact I conclude that all gases, speaking generally, expand to the same extent through equal ranges of heat; provided all are subject to the same conditions.

These researches upon the rate of expansion of gases naturally led me to investigate that of vapors; but expecting, from the result of the above determinations, that they would expand like gases, I decided to experiment upon only one vapor, and chose that of sulphuric ether as being very easy to work with.

In order then to determine the rate of expansion of ether vapor I made use of the two tubes of which I have already spoken, atmospheric air serving throughout as a means of comparison. This apparatus having been kept for some time in a heater whose temperature was about 60° , I admitted ether vapor into one of the tubes and atmospheric air into the other, in such a way that each was filled to the same point. I then raised the temperature of the heater from 60° to 100° , and had the satisfaction of seeing that, whether rising or falling, the ether vapor and the atmospheric air always stood at the same division at the same moment. This experiment, which Citizen Berthollet has witnessed, was repeated many times and I have never been able to note any difference in its rate of expansion as compared with that of atmospheric air. I would however emphasize the fact that a few degrees above the boiling point of ether, its contraction was a little more rapid than that of atmospheric air. This phenomenon goes with one which many substances exhibit in passing from the liquid to the solid state, but which is no longer noticeable a few degrees above that at which the change is made.

This experiment, by showing that ether vapor and gases expand at the same rate, makes it evident that this property is in no way dependent upon the peculiar nature of the gases and the vapors but solely upon their elastic character, and consequently leads us to the conclusion that all gases and all vapors expand to the same extent for the same degrees of heat.

Since all gases are expanded to the same extent by heat and are equally compressible, and since these two properties are mutually dependent, as I shall show elsewhere, vapors—which are expansible to the same degree as gases—must also be equally compressible; yet I emphasize the fact that this latter

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conclusion can be true only so long as the compressed vapor remains completely in its elastic state, and this demands that its temperature shall be high enough to overcome the pressure which would tend to make it assume the liquid state.

I have quoted Saussure—and my experiments confirm his view—to the effect that very dry air and air holding in solution more or less moisture expand at the same rate; I am therefore in a position to draw from all I have said the following conclusions:—

I. All gases, whatever their density or the quantity of water which they hold in solution, and all vapors expand to the same extent for the same degree of heat.

II. In the case of the permanent gases, the increase of volume which each of them suffers between the degree of melting ice and that of boiling water, amounts to $\frac{1}{213.33}$ of the original volume, for a thermometer divided in 80 parts, or $\frac{1}{268.88}$ of the same volume, for a centigrade thermometer.

In order to complete this research, it remains for me to determine the law of the expansion of gases and vapors, with the object of finding with its aid the coefficient of expansion for any given degree of heat, and of establishing the true movement of the thermometer. I am at work upon this new research and, as soon as it is concluded, I shall have the honor of laying an account of it before the Institute.

BIOGRAPHICAL SKETCH.

LOUIS JOSEPH GAY-LUSSAC was born in 1778. He received his scientific education at the École Polytechnique and the École des Ponts et Chaussées, and in 1800 became assistant to Berthollet. The research upon the expansion of gases by heat was one of his first. Like his contemporary, Dalton, he was much interested in the study of the atmosphere and in 1804 made analyses of the air, securing specimens from various places—one, at a height of over 6,000 meters, in a balloon ascent. The analysis of water was also made at this time. In 1807 he published papers upon terrestrial magnetism and the

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results of his classic investigation of the volume-relations of gases undergoing chemical change. Along with Thenard, he studied the properties of the metals of the alkalies and of chlorine, advocating, with Davy, their elementary character. In 1809 he became Professor of Physics in the Faculté des Sciences and Professor of Chemistry in the École Polytechnique; in the same year, working with Thenard, he was able to isolate boron and, later, iodine. The latter is considered one of his most brilliant investigations. During the next few years he published important memoirs upon the relationships existing between ethylene, alcohol and ether. In 1815 he discovered cyanogen and prepared pure hydrocyanic acid. In 1815 he devised the syphon barometer.

Gay-Lussac's ingenuity frequently made itself evident in the construction of new forms of apparatus: in addition to the syphon barometer, we owe to him a large number of useful instruments constantly employed in the laboratory. His death occurred in 1850.

THE DETERMINATION OF THE RATE OF
EXPANSION OF GASES BY HEAT.

By J. B. BIOT.

*Translated from Volume I, Chapter IX, of the Author's "Traité
de Physique."*

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EXTRACT FROM BIOT'S TREATISE ON PHYSICS:

BEING CHAPTER IX OF VOLUME I.

The Determination of the Rate of Expansion of Gases by Heat.

THE experiments of MM. Lavoisier and Laplace upon the expansion of solid substances have shown us that between the limits of [the temperature of] melting ice and [that of] boiling water, the expansion of solid metals is practically proportional to that of mercury. The same relation, between these limits, exists as well between the expansion of mercury and that of dry gases. This important deduction has been completely established by the experiments which M. Gay-Lussac has made with this object in view, upon the rate of expansion of gases. This skilful physicist having been willing to make known to me the details of his experiments, and to permit me to sketch the apparatus which he has devised for the purpose, I shall proceed to describe here the course which he followed in his investigations and the results to which he was led.

In order to measure with accuracy the rate of expansion of gaseous substances, it is necessary, first of all, to introduce them, in known quantity, into tubes accurately graduated into divisions of equal volume, and terminating in a bulb whose volume should be considerable as compared with that of the tube. It is necessary, further, that they should be kept there under a known pressure, exposed to different temperatures and the amounts by which they expand or contract under the different conditions observed; in a word, it is necessary to make a veritable gas thermometer. Yet although the statement of this operation may be very simple, it demands, in order to be accurate, many essential precautions which we shall now discuss.

The first is, that the tubes in which the gases are contained must be perfectly dry; for we have already stated that glass

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tubes lying open and exposed to the atmosphere, become covered inside with a slight, imperceptible layer of water which heat sets free by converting it into vapor. If one did not begin by removing this thin layer of water, the vapor which it gives off at different temperatures would mix with the gas introduced into the tube and would increase its volume; and, since the amount of the vapor thus produced would increase with the temperature until the slight layer of water had become completely removed, it is evident that this outside cause will constantly increase the expansion proper of the gas, in proportion as the temperature rises: such is the error into which many physicists have fallen.

The only way to avoid this difficulty is to drive out this slight film of moisture by heating the tube until it is changed to vapor; but in order that the air may not enter again, it is necessary to fill the tube with mercury, which is made to boil



FIG. 1.

there, as in a thermometer; and—which is important to notice—whether this boiling removes or not the whole of the film adhering to the glass, at least it can no more give off vapor when the tube is kept at any temperature less than that at which mercury boils. This is the first precaution M. Gay-Lussac has taken.

Next, in order to introduce only air or dry gases into the tube, he connects to its open end another, larger tube *TT*, *Fig. 66* [*Fig. 1*], which may be regarded as a kind of receiver intended to hold the gas. This tube is partly filled with bits of muriate of lime [*i. e.*, calcium chloride] or of any other salts capable of absorbing moisture. It is even possible to produce a vacuum in it in order to introduce the gas without admixture of air. Then in order to let a definite quantity enter the tube, M. Gay-Lussac makes use of a very fine iron wire previously introduced into the bore. He inclines the tube or turns it upside down, and thus removes a large part of the mercury which it contains, whose place is taken by a definite volume of gas represented by *GG*, *Fig. 67*, [*Fig. 2*]. With care, it can be arranged to have only a short column of mercury *M* which acts

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as a piston, and all the space GG , from this point to the bulb of the tube is filled with the dry gas which has been introduced. If he is employing atmospheric air, there is no need of producing a vacuum in the receiver TT ; the air should be allowed to remain some time in contact with the salts, after which it is introduced into the tube GT , as we have described.

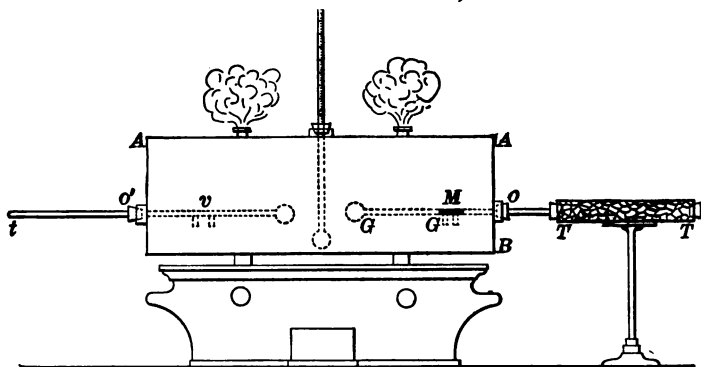


FIG. 2.

The gas having been introduced, it remains only to try the effect of various known temperatures successively upon it; for this M. Gay-Lussac made use of a metal vessel AB , *Fig. 67* [*Fig. 2*] rectangular in shape, the bottom of which fits upon a furnace of the same size. Water is put in this vessel and is heated to different temperatures. A thermometer V , placed vertically in this water and whose stem projects above the cover of the vessel, serves to indicate its temperature approximately and to show if it is necessary to increase or diminish the heat.

The tube TG , however, which contains the gas, must not be put in the water in this position; for we have already shown by experiment that the different horizontal layers of a liquid, which is being heated from the bottom, are not at the same degree of temperature. Thus, in order to know exactly that [temperature] which is producing an effect upon the gas, the tube which contains it must be fixed in a horizontal position, as *Fig. 67* [*Fig. 2*] shows it; then its temperature may be accurately determined by an excellent thermometer tt placed opposite it in the same layer and likewise fixed in a horizontal position.

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But we have stated that the vessel was of metal; how then observe through its walls the divisions of the thermometer tt and the movable point G of the graduated tube to which at any moment the gas-volume extends? The point G and the stem t of the thermometer cannot be kept continually outside the hot-water bath, for then these parts respectively, being no longer at the temperature of the bath, would introduce an error into the determination. Yet one can, without inconvenience, draw out the tubes from time to time, during the short interval required to observe them: this M. Gay-Lussac accomplished in a very simple way. The openings oo' through which the tubes pass into the vessel are closed with corks pierced along their axes with a hole through which the tube in either case can slip with some friction. Is it desired to observe the condition of the gas GG' ? The tube TG is drawn out until the end M of the short column of mercury comes into sight at the opening O . It can then be seen at what division of the tube it stands, and the volume of the gas at this moment is known. Is it desired to note the temperature at the same time? The stem is similarly drawn out until the end t of the mercury column appears at the opening O' , and then the division of the thermometer to which this corresponds indicates the temperature at the time of the horizontal layer in which the gas has been placed.

Thus at each moment the temperature of the gas is known in the most exact way. Putting water at 0° at first, therefore, in the vessel, then raising the temperature by successive steps to that of boiling; or, *vice versa*, returning from boiling to the melting point of ice; the movement of the gas and that of the thermometer can be compared with accuracy—that is to say, at any time, by the divisions marked upon the tube, the apparent volume of the mercury and the apparent volume of the gas may be known; but to have the real volumes, it is still necessary to take into account the expansion of the glass of which the tubes are made.

To study this effect properly, let us start from some definite temperature—for example, that of melting ice. Let us designate by V the number of divisions which the gas then occupies in the glass vessel that encloses it, and let us make use of

EXPANSION OF GASES

this number to express its volume. On the temperature rising t degrees, the volume of the gas will increase and become $V(1+\delta)$, designating by δ its cubical expansion from 0° to t degrees, and this is the unknown quantity we are looking for. Let V' be the number of divisions it now occupies in the tube. As the latter expands each of its divisions has in reality a different value from that which it had at the initial temperature, and if the cubical expansion of the material of the tube, for one degree of the thermometer, is represented by K , V' divisions at the temperature t will be equal to $V'(1+Kt)$ of the original divisions. This will therefore be the actual expression of the new volume of the gas stated in terms of the original divisions—that is to say, we shall have

$$V(1+\delta) = V'(1+Kt),$$

from which we obtain

$$\delta = \frac{V'-V}{V} + \frac{V'Kt}{V}$$

The first term, $\frac{V'-V}{V}$, is the cubical expansion for a volume equal to unity, assuming the vessel did not expand; and the second term, $\frac{V'Kt}{V}$, is the correction which must be made in the first result on account of the expansion of the vessel.

V is determined at the beginning of the experiment; it is the number of divisions occupied by the gas at the initial temperature; subsequently, at other temperatures, the reading gives V' , the number of divisions the gas occupies at any given moment. Moreover K is found from the expansion of solids; thus the whole second number of our equation is known and, consequently, on substituting their values for V , V' , K , t , the expansion δ is found just as it would have been determined in a vessel upon which [a change of] temperature produced no effect.

It only remains to take account of the pressure to which the gas is subjected, for we have seen that the volumes which a given gas will occupy, at a given temperature, are inversely proportional to the pressures to which it is subjected. Here, during the experiments, the receiver, *TT*, *Fig. 67* [*Fig. 2*] remains always open; the pressure of the atmosphere thus acts freely upon the short column of mercury, *M*, close to the gas *GG*.

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If the tube TG were vertical or inclined to the horizon, the weight of this short column M would also act upon the gas; but the tube being horizontal, this weight is entirely carried by the glass tube. The short column M opposes no pressure, no resistance to the motion of the gas—unless, perhaps, that resulting from its friction against the inner walls of the glass tube; and this force is so small, when the column is short, that it may be neglected. The weight, then, of the atmosphere is the only force which weighs upon the gas GG , and it is determined by observing the height of the barometer at the time of taking the readings. If this pressure remains constant throughout the experiment, the corresponding volumes of gas and of mercury may be directly compared with one another; but, if it varies, all the readings must be reduced to one pressure—which is easy, making use of Mariotte's Law.

Thus, let p be the atmospheric pressure observed at the beginning of the experiment and at the initial temperature, when the gas in the vessel occupies a number V of divisions. Let us suppose that it is desired to reduce this volume to what it would have been under the constant pressure of 0.76 m., to which we refer all observations. Then, according to Mariotte's Law, the volume V must be reduced inversely as the pressures; that is to say, in place of V we have $\frac{Vp}{0.76}$.

In the same way, if we assume the pressure of the atmosphere to be p' , when the gas is at the temperature t , and that it occupies in the vessel a number of divisions represented by V' , this number, under a pressure of 0.76 m., but at a temperature t , will become $\frac{V'p'}{0.76}$.

Therefore to arrive at the expansions which would have resulted if the pressure had remained constant and equal to 0.76, we must substitute for V and V' in our formula, $\frac{Vp}{0.76}$ and $\frac{V'p'}{0.76}$; then the value of δ becomes

$$\delta = \frac{p' V' - p V}{p V} + \frac{p' V' K t}{p V}.$$

Use must be made of this formula in order to take account of all the attending conditions. When the pressure is con-

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stant throughout the experiment, we have $p = p'$, and we fall back upon the formula which we had found at first.

When δ shall have been thus determined for an interval of t degrees, the experiment is begun again or is continued for an interval $2t, 3t, \dots$; and by comparison of the values of δ with one another, it may be known whether the rate of expansion is uniform or variable. For, if it is uniform, the successive expansions, $\delta, 2\delta, 3\delta, \dots$, will be proportional to the differences in temperature; but if the rate of expansion is increasing or decreasing, this proportionality will not obtain. Performing the experiment in this way, with all the precautions we have described, repeating it a great number of times, as well with atmospheric air as with the different gases, M. Gay-Lussac arrived at the following results:

All the permanent gases, subjected to equal [changes of] temperature, under the same pressure, expand by exactly the same amount.

The amount of their common expansion, from the temperature of melting ice up to that of 100 degrees of the centigrade thermometer, is equal to 0.375 of their original volume at 0° , assuming pressure to be constant.

Between these two limits the expansion of a gas is exactly proportional to the expansion of mercury; whence it follows that, for every degree of the centigrade thermometer, and under a given pressure, all gases expand by an amount equal to 0.00375 of the volume which they occupy at the temperature of melting ice.

These results had been obtained almost simultaneously by Mr. Dalton, the brilliant physicist of Manchester; but the work of M. Gay-Lussac was completed in France before that of the English physicist could have been known. Mr. Dalton finds the actual expansion slightly different from that [found] by M. Gay-Lussac. He makes it equal to 0.372, and finds that, for a given expansion of mercury, that of atmospheric air is a little less in proportion and that this difference increases as the temperature rises. Yet however great the skill of this philosopher in experimental research, we believe that the result of M. Gay-Lussac may be considered as still more accurate, as much by reason of the endless precautions he has taken to

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obtain it, as because it agrees very well with all the other physical determinations in which there is need to use the figure for the absolute rate of expansion of gases.

It would not be out of the way to note on the other hand that the ratio 0.00375 is exactly the one that has been found for atmospheric air by the distinguished astronomer Tobie Mayer, who appears to have been as skilful in the art of physical experiment as in that of making and coördinating astronomical observations. M. Gay-Lussac has stated in his memoir that our renowned physicist, M. Charles, had long before discovered the equal rate of expansion of gases and had made it apparent by an apparatus constructed for his splendid museum; but he had made no attempt to measure accurately the absolute rate of their expansion. Doubtless we have reason to regret the many other results of observation and experiment which M. Charles had intended for use only in his public lectures and which have never been published.

M. Gay-Lussac is in the same way convinced that the gaseous substances produced by the evaporation of liquids expand at the same rate as gases, so long as they do not become condensed to liquid form. To prove this, he removed the drying-salts from the receiver *TT*, introduced into the tube *TG* gases which had not been dried and consequently were charged with moisture which could there take the form of vapor: moisture which the drying-salts would take up with increase of weight. By this means the space *GG* becomes filled with a mixture of gas and aqueous vapor; and this mixture, raised to different higher temperatures in succession, expands exactly as would an equal volume of dry gas. But one must not look for the same law on lowering the temperature below the point at which the gas was introduced; for we shall prove later on, that a definite volume of gas at a given temperature can hold only a certain limited amount of water in the form of vapor, whence it follows that if it is thus saturated with aqueous vapor at a given degree of the thermometer and the temperature is lowered, a portion of this vapor will be condensed to the liquid state. That part which becomes liquid, occupying a far smaller volume, will decrease the total volume of gas, will diminish its tension and,

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as a result of this double effect, will cause an apparent variation in the laws of expansion.

M. Gay-Lussac has in the same way studied the rate of expansion of ether vapor ; he finds it the same as that of gases, —which leads to the belief that the conclusion holds good for all kinds of vapors, so long as they remain in the gaseous state.

With the aid of the results we have just described, we can answer with accuracy all physical questions which might be asked concerning the volume of a given quantity of gas subjected in turn to various pressures and to various temperatures.

RESEARCHES UPON THE RATE OF EXPANSION OF GASES.

BY HENRI VICTOR REGNAULT.

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RESEARCHES UPON THE RATE OF EXPANSION OF GASES.

BY VICTOR REGNAULT.

PART I.

Upon the Rate of Expansion of Atmospheric Air.

THERE is no numerical quantity in physics which has been submitted to a greater number of experimental determinations than the coefficient of expansion of air, and yet we cannot say that up to the present time this coefficient is known with sufficient accuracy.

The experiments of the older physicists gave such diverse numbers that it was impossible to draw a satisfactory conclusion; most of the conditions which affect the phenomenon [of gas expansion] were entirely unknown.

The brilliant experiments of M. Gay-Lussac upon the rate of expansion of gases seemed bound to put an end forever to the uncertainty of physicists. M. Gay-Lussac showed by a great many experiments that the coefficient of expansion between 0° and 100° was the same for all gases, and for vapors so long as they are kept a little above their points of condensation, and that its value was 0.375. This coefficient was adopted by all physicists and used in computations, until within the last few years a Swedish physicist, M. Rudberg, threw doubt upon its accuracy. By a series of carefully conducted experiments Rudberg sought to show that the coefficient of M. Gay-Lussac was too high and that its true value must be between 364 and 365.

As Rudberg's work has never appeared in France, it would seem as well to give an abstract of it here.

Rudberg has published two memoirs upon the coefficient of expansion of air. In the earlier (Poggendorff's *Annalen*, Volume XLI) he uses for its determination a species of air-thermometer formed of a bulb of glass [capable of] enclosing from 120 to 150 grams of mercury and fused to a capillary tube. A beginning is made by filling this apparatus with dry air.

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For this purpose the open [end of the] capillary is inserted in a tube filled with bits of calcium chloride. The bulb is thoroughly heated with an alcohol lamp, then is allowed to cool. After repeating this operation fifty or sixty times there is nothing but dry air in the bulb.

At other times he placed the chloride-tube in communication with an air-pump and produced a vacuum in it fifty or sixty times in succession, allowing the air to return each time. These two methods of drying were employed indifferently; they never gave [results] that differed noticeably.

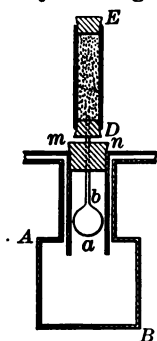


FIG. 1.

The bulb, full of dry air and always fitted with its calcium-chloride tube, was placed in a vessel *AB* in which water was boiling (Fig. 1), of such size that the bulb and capillary tube were completely surrounded by the vapor. After the water had boiled for three quarters of an hour or an hour, the calcium-chloride tube was removed and, ten minutes later, the drawn-out point of the tube was sealed with a flame, and at the same time the height of the barometer was read.

The bulb was weighed upon a very delicate balance; it was then fixed in the apparatus [shown in] Fig. 2. The capillary tube passes through a hole in a metal capsule *abc* fastened to the upright *AB*. The arm *CD* is lowered until the point of the capillary tube dips deep enough in the small mercury-bath *EFGH*. The point of the tube is broken off and the mercury rises into the bulb. The latter is surrounded with crushed ice placed in the capsule *abc*; the water formed by the melting of the ice flows off through the little tube *f*. The bulb is thus kept at 0° for at least two hours, the ice being renewed as fast as it melts. The end of the capillary tube is then stopped by means of a little soft wax held in a small iron spoon, and at the same time the height of the barometer is recorded.

The snow is then removed and a measurement made of the height of the raised [column of] mercury. Rudberg used for this purpose the apparatus *KML* consisting of a vertical standard supported by a tripod with levelling-screws. Up and down this stem travels an arm *lmo* carrying a cylindrical ring *gn*

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whose lower edge is exactly horizontal. This ring is lowered until its lower edge coincides with the level of the mercury in the bulb. At the same time the screw-rod KS is lowered until its point reaches the level surface of the mercury in the bath. The apparatus KML is then removed and the distance from the ring to the point is measured with the aid of a graduated rule.

The bulb is weighed with the mercury which it contains, after the little piece of wax has been removed.

The thermometer tube is bent by means of a lamp in such a way that its open end can dip in a small dish full of mercury. The whole apparatus is filled with mercury which is carefully

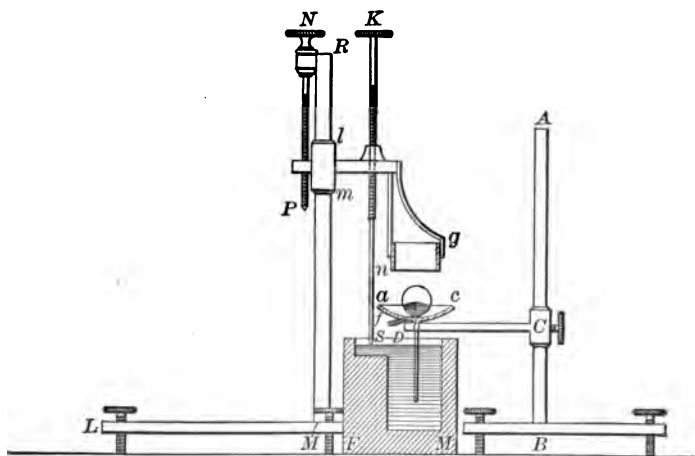


FIG. 2.

heated until it boils. After it has cooled down again, the bulb and tube are covered with crushed ice so that they may become completely filled with mercury at 0° . The bulb is then removed, care being taken to catch in a small capsule the mercury which escapes on account of expansion, and placed in the boiler, the mercury which flows out being caught in the same little capsule. This mercury is carefully weighed, as is also that which has remained in the bulb. We thus have the total weight of mercury which filled the apparatus at 0° , and

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all the data necessary for calculating the coefficient of expansion of the glass.¹

The glass used for Rudberg's apparatus was a Swedish potash glass of Reymira make. Its coefficient of expansion between 0° and 100° was found to be 0.002285 as a mean of twenty-four experiments, the extreme figures of which are 0.002256 and 0.002321.

The first three experiments to determine the coefficient of expansion of air were made without bringing the air to 0° ; the bulb was merely placed in a cylinder full of water whose temperature was taken with a thermometer. The three experiments gave the following numbers:

0.3633
0.3617
0.3623

Mean = 0.3624

Rudberg does not consider these experiments very accurate, (1) because the temperature of the water surrounding the bulb was never perfectly stationary, but varied to a noticeable extent during the experiment; (2) because the difference of temperature was not 100° but only 90° . The experiments made with cooling of the air to 0° , gave:

0.3643
0.3654
0.3644
0.3650
0.3653
0.3636
0.3651
0.3643
0.3645

Mean = 0.3646

These experiments were made under very diverse barometric pressures; in fact, the height of the barometer varied from 742.77 to 779.85. Consequently, the temperature to which the air was heated varied from 99.89° to 100.73° . The height of

[¹ Note by Translator.—Rudberg's method and apparatus are similar, in all essential points, to those of Dulong and Petit in their comparison of the air thermometer and the mercury thermometer. See page 3.]

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the mercury column drawn up into the apparatus varied from 35 mm. to 166.5 mm.

Rudberg then discusses the causes which could introduce constant errors in his results. He states that capillarity could not produce a noticeable effect in his apparatus because it was acting in a surface of mercury of about two-thirds of an inch diameter. The friction of the mercury against the walls of the capillary tube produced no effect: otherwise differences would have been noticed among the experiments where the height [of the column] of the mercury drawn up varied from 35 mm. to 166 mm.

Rudberg made, further, two experiments with large glass tubes of $\frac{3}{4}$ -inch diameter and 8 inches length. These experiments he did not consider as accurate as the earlier ones, since he could not boil the mercury in this form of apparatus. They gave the two figures

0.3646

0.3662

Mean = 0.3654

Two experiments made with air which had not been dried gave 0.3840 and 0.3902, which gives an idea of the influence of moisture upon the coefficient of expansion. The same apparatus, having been dried again with care and filled with dry gas, gave 0.3652.

In his second memoir (Poggendorff's *Annalen*, Volume XLIV), Rudberg gives a series of experiments made by means of a special apparatus having for its object the determination of the tension which a given quantity of dry air exhibits at 0° and at 100° ; this quantity always occupying the same volume, allowance being made each time for the expansion of the glass.

This apparatus is represented in Fig. 3. It consists of a cylinder *AB* filled with dry air and communicating with a second tube *dC* by means of a capillary tube *Bbd*. The tube *dC* is cemented into the cover of a box containing a leather pouch filled with mercury, the volume of which can be reduced, as in the case of barometers, by means of the screw *M*. A barometer-tube about 50 centimeters high is cemented into

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the same cover. By means of the screw the mercury is made to rise in the tubes. Upon the vertical part of the tube *bd* a very fine scratch is made at *a*. The mercury is forced up to this mark by means of the screw, (1) when the reservoir *AB* is cooled to 0° by the aid of ice ; (2) when it is heated to 100° .

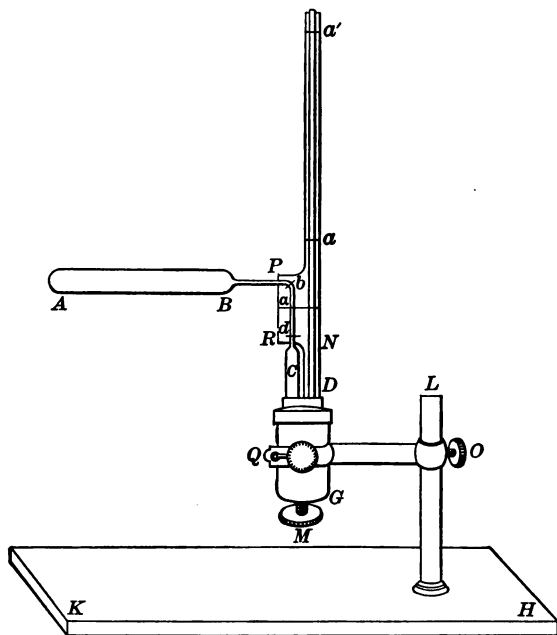


FIG. 3.

The volume of the air thus remains the same at the two temperatures, if the expansion of the glass be left out of account. In order to measure the heights of the mercury in the two tubes, there is placed directly behind these tubes a brass rule *EPRND*, graduated in millimeters, the divisions of which on the lower portion, from *a* to *b*, have been extended enough to pass behind both of the tubes at one time. The difference in height between *a* and the meniscus of the mercury in *ED* can thus be easily determined.

The reservoir *AB* was thoroughly dried before cementing the tubes into the box. To this end, the lower portion of the

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tube dC was drawn out to a point and connected with a very large tube filled with calcium chloride, which in turn was connected with a pump. The air having been exhausted about fifty times and replaced by dry air, the drawn-out tip is closed by means of a lamp. The tube dC was fitted into the box filled with dry mercury, and when this tube was firmly cemented in place, its point was broken off below the surface of the mercury.

The capillary depression at a was determined by a direct experiment before the narrow tube Bbd had been fused to the reservoir AB . This depression had been found to be 18.5 mm.

The calculation of the experiment is extremely simple. When the air is cooled to 0° , let

H' = the barometric pressure,

h' = the difference of level aa ,

e = the capillary depression at a ;

we then have for the tension of the air, $H' + h' - e$.

When the air is heated to the temperature T by means of [the vapor of] boiling water, we have for its tension, $H'' + h'' - e$. Hence

$$1 + \alpha T = \frac{H'' + h'' - e}{H' + h' - e} (1 + \delta T).$$

Twelve experiments made according to this method gave the following figures :

0.3640	0.3643
0.3648	0.3648
0.3641	0.3653
0.3648	0.3640
0.3640	0.3664
0.3656	0.3645

Mean = 0.36457.

This mean is the same as that found by the former method ; Rudberg concludes that the expansion of air from 0° to 100° must be between 0.364 and 0.365.

Rudberg closes his second memoir with an important statement which had already been made by Gilbert in 1803 (Gilbert's *Annalen*, Volume XIV, page 267), but which has since been completely forgotten, namely, that the experiments of Mr. Dalton and M. Gay-Lussac which have been looked upon as

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having given almost identical results, on the contrary differ a good deal. In fact, in Dalton's memoir¹ taken from the Memoirs of the Manchester Society (Gilbert's *Annalen*, Volume XII, page 313), it is stated, "I found from many determinations that 1000 parts of atmospheric air, under the ordinary pressure of the atmosphere, expand between 55° F. and 212° F., so as to form a volume of 1321; which gives, after adding 4 parts for the expansion of the glass, an expansion of 325 parts for a difference of temperature of 157° of the Fahrenheit scale."

It is evident that the volume of air which is here regarded as unity is that which the air had at 55° F. or 12.78° C. If on the other hand we consider as unity the volume of the air at 0°, and if we denote by 100α the expansion between 0° and 100°, the results of Dalton give :

$$1 + 12.78\alpha : 1 + 100\alpha :: 1000 : 1325 ; \text{hence} \\ 100\alpha = 0.392.$$

This is therefore the real result of Dalton's experiments.² Dalton does not, however, seem to have been aware of the error which had crept into his calculations, for he says in his "New System of Chemical Philosophy"³ : "The volume of the air, according to the experiments of M. Gay-Lussac and my own, being 1000 at 32° F., becomes 1376 at 212° F."⁴

¹ See pages 20-21.

² Note by Translator:—The figure 0.3912, as given by Rudberg and by Magnus, is more nearly correct than 0.392.

³ See page 22.

⁴ Note by Translator:—If Dalton made use of the data given in his memoir of 1801 (See p. 20-21) as a basis for the statement quoted by Regnault above—as the latter evidently assumes—he was clearly in error. It happens that the coefficient in accordance with which a volume of 1000 would become 1325 through a rise of temperature of 157° F., or 87.22° C.—that is, for the number of degrees lying between the lowest temperature he employed, 55° F., or 12.78° C., and the boiling-point of water—is 0.00207 for each Fahrenheit, and 0.00373 for each Centigrade degree. This coincides quite closely with that found by Gay-Lussac in the case of gases when the volume at 0° C. is compared with that at 100° C. Yet it is clear that Dalton's 0.00373 represents the fraction of its volume at 12.78° C. by which the volume of a gas increases for each degree between 12.78° and 100° C.; while Gay-Lussac's 0.00375 represents

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Thus, according to the experiments of Rudberg, the coefficient of expansion of air accepted for a long time by physicists is much too high. Should the figure 0.3646, which is the mean result of his experiments, be adopted now in physical computations?

It seemed to me that new experiments were called for to remove all doubts in this direction, and I have not hesitated to devote myself to the work, feeling that the determinations would be of service to science, even if they merely confirmed the results obtained by the skillful Swedish physicist.

I have carried out my experiments by four different methods.

the fraction of its *volume* at 0° C. by which the volume of a gas increases for each degree between 0° and 100° C. The two coefficients are not "sensibly the same," because they do not represent the same thing. The words in quotation-marks are from Preston's *Theory of Heat* (p. 190, footnote) where the author, following Regnault, assumes that Dalton calculated his coefficient from the data of his memoir of 1801, but somehow misunderstands Regnault's method of calculating the coefficient, and claims (incorrectly) that the French *savant* had overlooked the fact that Dalton's lowest temperature was 12.78° C. and not 0° . Yet if we use the coefficient 0.00373 in the way Gay-Lussac used his 0.00375, Dalton's 1000 volumes at 12.78° would have been reduced to 954.5 at 0° , and would have expanded to 1312.4 at 100° , instead of the 1325 which he records. If, on the other hand, we make use of the coefficient 0.00392 calculated by Regnault, Dalton's 1000 volumes at 12.78° would have been reduced to 952.3 at 0° , and would have expanded to 325.6 at 100° ,—which is what actually was found.

It would appear, however, that neither Rudberg, Regnault nor Preston has carefully read Dalton's statement in his "New System," for in it he says, "The volume at 32° is taken 1000, and at 212° , 1376, according to Gay-Lussac's and my own experiments. As for the expansion at intermediate degrees, Gen. Roy makes the temperature at midway of total expansion, $116\frac{1}{2}$ old scale; from the results of my former experiments (*Manch. Mem.* Vol. 5, Part 2, page 599) the temperature may be estimated at $119\frac{1}{2}$; but I had not then an opportunity of having air at 32° . By my more recent experiments, I am convinced that dry air at 32° will expand the same quantity from that to 117° or 118° of common scale, as from the last term to 212° ," etc.

A study of this passage apparently shows that, after the publication of Gay-Lussac's memoir, Dalton repeated his experiments with greater care, using the freezing point of water as his lowest temperature, and

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FIRST SERIES OF EXPERIMENTS.

The determination was made by a method similar to that used by Rudberg in his earlier research, and which is in other respects that by the aid of which Dulong and Petit made the comparison of the mercury thermometer with the air thermometer. I replaced Rudberg's small bulb, however, which held but 150 to 200 grams of mercury, by cylindrical reservoirs of 25 to 30 mm. diameter and of about 110 mm. length, capable of holding 800 to 1000 grams of mercury. I preferred the cylindrical to the spherical form, because the former does not produce the refraction effects of the latter, which are likely to introduce considerable errors when the heights of the mercury [columns] drawn up are read from a distance with the aid of a glass. It also seemed advisable to me to increase the capacity of the air reservoir.

The cylindrical reservoir *AB* (*Fig. 4*) ended in a capillary tube *ACD* the bore of which varied in different cases between $\frac{1}{2}$ mm. and 2 mm. The capillary tube was drawn out to a point and its end was bent at a right angle.

This apparatus was fixed by means of a cork *E* in the cover

obtaining results confirming closely those of his French contemporary. These later figures are thus the ones referred to in the first part of the passage quoted above. The fact that "more recent experiments" with "dry air at 32°" were made by Dalton seems to have been entirely overlooked by the authors referred to above.

Moreover, nowhere in his 1801 memoir does Dalton calculate the coefficient of expansion between 0° and 100° of the gases with which he experimented. He does not appear to have considered the question of their volume at 32° F. at all; his whole attention was directed to their behavior above 55° F. Yet Biot, in his *Treatise on Physics*, praises Dalton's skill as an experimenter and states that the latter found the expansion of gases between 0° and 100° to be 0.372. (See page 59.) Biot must himself have calculated the figure 0.372 from Dalton's data of 1801—for Dalton does not give it in either of the extracts quoted above,—or else it is based upon later and more accurate determinations made by the English philosopher after the publication of the work of Gay-Lussac.

It seems much more reasonable to suppose that Dalton actually obtained results—after 1801—justifying the claim he makes in his *New System* and explaining the statement of Biot, than to suppose that both Dalton and Biot were guilty of the same arithmetical blunder.

EXPANSION OF GASES

KK' of a tin-plate vessel *V* in which water is boiled. The vapor which is formed in the lower part of the vessel is obliged to pass out by way of the annular space *LL'* which is for the purpose of preventing its cooling by reason of the contact of the outside air, before escaping by the lateral pipe *M*. At *N* there is a small tubulure and, in the inner wall and directly opposite, a small round hole *O*. In the neck is fitted by means of a cork a bent glass tube *F* which acts as a manometer, and one of the open ends of which passes through the hole *O* and is thus in direct communication with the interior of the vessel *V*. The other end is open to the air. The water column contained

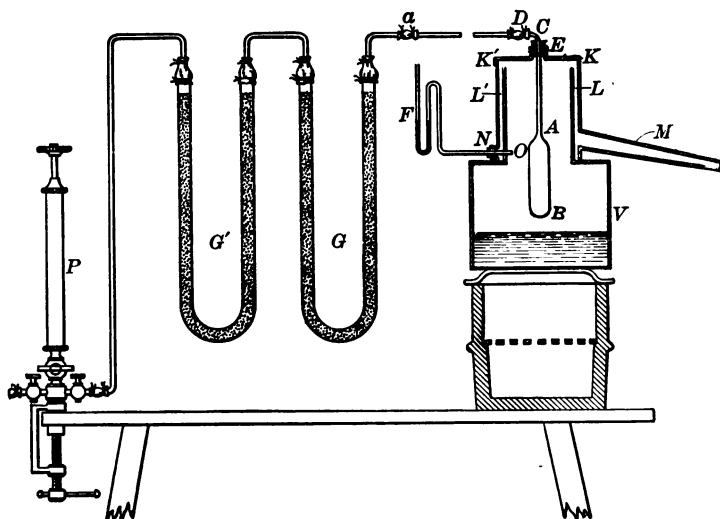


FIG. 4.

in the two vertical arms shows, by the difference of level, whether the pressure is the same inside and out. The reservoir *AB* and the capillary tube attached to it are thus completely surrounded by the vapor of boiling water.

When the water is boiling vigorously, the tip of the capillary tube is connected by means of a rubber tube with a drying apparatus. This consists of U-shaped tubes *G*, *G'*, each about

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a meter long and 20 mm. in diameter. These tubes are filled with broken pumice stone moistened with concentrated sulphuric acid ; they are connected with one another by rubber tubes, and with a small hand pump *P*. By means of this pump a vacuum is produced twenty-five or thirty times in the apparatus, and, each time, the air is allowed to enter again very slowly by opening the taps in the proper way. The taps are left wide open the last time so that the air in the reservoir is in direct communication with the atmosphere.

The apparatus is left in this condition for from a half-hour to an hour ; the drying apparatus is then disconnected. As it

is conceivable that the pumice stone might by chance become packed somewhere in the tubes *GG'* and the enclosed acid produce a continual obstruction to the entrance of the air, and as in consequence an excess of pressure would be needed to force it into the reservoir, I have always taken care to disconnect first the rubber tube *a* ; it is evident that in this way, even if the air of the reservoir is under a slightly lower pressure than that of the atmosphere, it will still be dried air, that contained between *a* and *D*, which will enter the reservoir and produce equilibrium. In my experiments this precaution was unneces-

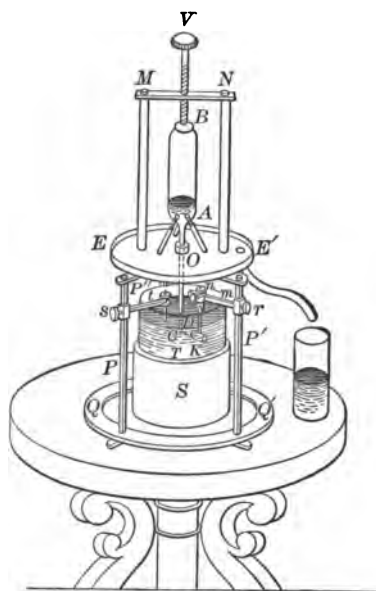


FIG. 5.

sary, as the pumice stone was only soaked in sulphuric acid. The rubber tube *D* is then removed and the apparatus allowed to stand several minutes in direct communication with the atmosphere ; finally the drawn-out tip of the capillary tube is

EXPANSION OF GASES

closed by means of a blowpipe, and at the same time the height of the barometer is recorded. We thus have the reservoir AB filled with dry air at the temperature of the [water-] vapor and under the pressure of the atmosphere.

The reservoir after being removed from the heater was fastened in the support shown in perspective in *Fig. 5*. This support consists of a circular plate EE' in the centre of which is a short tube O , and supported upon three vertical legs P , P' , P'' , joined for greater steadiness at their lower ends by a circle of metal QQ' . Three inclined metal rods are arranged symmetrically about the short tube O ; they terminate above in small balls with screw adjustment. The air reservoir AB rests upon these balls and the capillary stem is held by a cork fitted into the short tube. Greater steadiness is given it by means of the screw V working in the movable cross-bar MN .

Upon one of the vertical legs P' is mounted a cross-bar mn which carries a movable piece shown on a larger scale in *Fig. 6*. It consists of a little iron spoon K attached to an iron stem fg which can be raised or lowered at will in the piece $abcd$. This piece can be slid along the horizontal arm mn , which in turn can be fastened at any height to the leg P' by means of the set screw v .

Upon another leg P is arranged a horizontal arm st which is capable of adjustment and can be held by a set screw; it carries a screw rod ending at top and bottom in a rounded point.

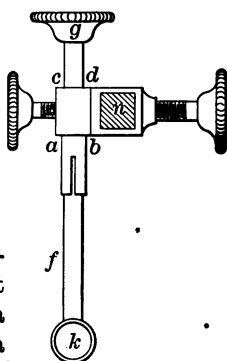


FIG. 6.

The reservoir is fixed in the apparatus in such a way that the bent portion CD of the capillary tube is pointed directly towards the leg P' , and a mark is made upon the leg P' at the height at which the adjustable piece mn must be fastened in order that the centre of the little spoon K shall be exactly at the height and in the direction of the bent portion of CD .

This being arranged, the apparatus is placed above a small bath of mercury, in such a way that the capillary tube dips in the mercury at least 5-6 centimeters. A very fine file mark has been previously made across the stem CD at the point

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where it is desired to break it off. The tip is then broken off with a small pair of pincers; the mercury enters the capillary tube and rises to a certain height in the reservoir; this is then surrounded with snow or finely crushed ice, and the apparatus is allowed to stand undisturbed for at least an hour or an hour and a half, in order to let it come exactly to the temperature of melting ice. Meantime the spoon has been carefully lowered to the proper depth in the mercury. From time to time the apparatus is gently jarred to overcome the resistance—should there be any—which the mercury might meet with in its ascent within the capillary tube.

The little spoon is then pushed forward along its arm until the opening of the capillary tube is buried in the wax, and at the same time the exact height of the barometer is recorded. The arm *st* is lowered along the leg *P*, and the point of the screw is accurately adjusted to the level of the mercury surface in the bath. The ice which enveloped the tube is completely removed, and the drawn-up column of mercury is allowed to come to the temperature of the surrounding air.

It now remains to measure the height of the drawn-up mercury; for this, I made use of a cathetometer of M. Gambey's design, which gives directly, with its vernier, a reading within a fiftieth of a millimeter. One sights with the horizontal telescope at the level of the mercury¹ in the tube *AB*, then the glass is lowered and is sighted at the upper point of the screw; adding to the difference of level thus found the distance between the two points of the screw—which has been previously measured with the same instrument—one has the total height of the drawn-up mercury. More commonly we sight directly at the lower point of the screw, after having lowered the bath *T*—which is easily done by removing the support *S*.

The reservoir *AB* with the mercury drawn up is then removed. It is weighed, then completely filled with mercury

¹ Care must be taken, when one sights with the glass at the upper line of the meniscus, not to be led into error through reflection-phenomena at the curved surface of the mercury. The procedure which seems to me surest, consists in placing a candle in the line of the meniscus and behind it, in such a way that the shape of the meniscus is outlined in black against the flame of the candle.

EXPANSION OF GASES

which is thoroughly boiled to drive out air and moisture entirely; finally it is buried in ice while the open end dips in a dish full of mercury. After an hour and a half or two hours, when one is certain that the mercury is perfectly stationary at the opening in the tip, the ice is removed and the mercury which flows out of the apparatus through expansion is caught in a small capsule. The reservoir is next hung in the same boiler which was used to expand the air; the mercury which escapes is caught in the little capsule. The barometer is read while the boiling is in progress. The mercury caught in the capsule is weighed, as well as the reservoir with the mercury it still contains. The weight of the mercury at 0° which exactly fills the reservoir at 0° is consequently known, and one has given all that is necessary for calculating (1) the expansion of the containing vessel; (2) the expansion of the air contained.

Let H be the barometric pressure at the time when the drawn-out tip of the tube was sealed with the blowpipe;

T the boiling point of water under this pressure;

H' the barometric pressure when the tip was closed with the wax under the mercury;

h the height of the drawn-up mercury;

P the weight of the mercury drawn up;

P' the weight of the mercury at 0° which fills the apparatus at 0° ;

p the weight of the mercury forced out by expansion between the temperature of melting ice and that (T_1) of water boiling under a barometric pressure H_1 ;

100 δ the amount, finally, by which a volume 1 of glass expands between 0° and 100° ;

And 100 α the amount by which a volume 1 of dry air expands between the same limits.

The heights H , H' , h , are supposed, for greater simplicity, to have been reduced to 0° by calculation. We shall have for determining δ the equation:

$$(P' - p) \left(1 + \frac{T_1}{5550} \right) = P' (1 + \delta T_1).$$

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whence

$$\delta = \frac{(P' - p) \left[1 + \frac{T_1}{5550} \right] - P'}{P' T_1} ;$$

and for calculating a ,

$$(P' - P) (1 + a T) \frac{H' - h}{H} = P' (1 + \delta T),$$

whence

$$1 + a T = \frac{P' (1 + \delta T) H}{(P' - P) (H' - h)}.$$

In making my experiments in the way that has been described I have not been slow to see a very serious source of error. In breaking off the point of the capillary tube under the mercury, I noticed that even when the stem dipped almost a decimeter into the mercury, there was always a minute quantity of air drawn in which added itself to the air in the reservoir. The mercury does not wet the glass, and there is a little space, probably filled with air, between the glass tube and the mercury. It is by way of this sheath that the outside air is drawn in, by a process similar to that of a bugle, during the ascending movement of the mercury. This phenomenon of aspiration is sometimes noticed by the fact that whole bubbles of air rise in the capillary tube after the manner of a piston.

I had much difficulty at first in preventing this result. By placing upon the part of the tube under the mercury many small discs of a substance wetted by mercury, like well cleaned brass, I succeeded in preventing the entrance of the outside air. In order to be completely out of reach of this source of error, I combined this method with another which consists in pouring upon the mercury, before breaking off the point and after having taken hold of the tip with the pincers, a layer of concentrated sulphuric acid. This layer of acid is removed when the reservoir has been lowered to 0° by the ice ; the surface of the bath of mercury is cleaned and then the arm Kn is lowered.

It is also important that the iron pincers with which the point of the capillary tube is broken off, should always be at some distance from the scratch of the file upon the stem by which the break is brought about. Otherwise, if the opening of the capillary tube touches the pincers, one may see rise in

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the tube a little bubble of air which has its source in that which remains adhering to the surface of the pincers.

I bring together in the following table the results obtained in the fourteen experiments I made by this method.

Number of Experi- ment	H	H'	h	P	P'	T	H ₁	T ₁	p	100 δ	1+100 α
	mm.	mm.	mm.	gr.	gr.	°	mm.	°	gr.		
1	760.08	760.57	111.02	856.145	119.915	100.00	760.60	100.02	12.870	0.002714	1.36556
2	759.67	755.72	98.67	770.465	116.780	99.99	753.75	99.77	11.665	0.002576	1.36626
3	750.40	749.81	99.82	805.75	122.60	99.64	"	"	"	0.002650	1.36659
4	744.61	744.78	100.60	800.27	120.19	99.43	744.80	99.43	12.050	0.002601	1.36579
5	747.99	748.79	106.35	790.69	114.81	99.55	748.20	99.56	11.981	0.002592	1.36625
6	751.48	752.68	102.32	913.48	137.74	99.68	"	"	"	0.002680	1.36549
7	763.27	763.27	97.45	855.24	136.318	100.13	763.30	100.13	13.015	0.002544	1.36673
8	765.34	765.00	102.50	854.86	130.60	100.20	765.30	100.20	13.025	0.002537	1.36634
9	764.14	763.92	102.87	805.14	122.79	100.16	764.10	100.16	12.225	0.002588	1.36689
10	763.34	763.62	102.17	854.79	131.10	100.13	763.51	100.14	13.005	0.002548	1.36610
11	754.55	752.34	105.80	790.49	113.364	99.80	754.50	99.80	11.942	0.002607	1.36671
12	750.29	750.57	68.48	853.82	163.794	99.64	"	"	"	0.002570	1.36591
13	751.94	751.72	74.91	760.452	141.710	99.70	750.86	99.66	11.633	0.002576	1.36641
14	764.62	764.50	122.31	853.447	108.417	100.18	768.63	100.32	13.008	0.002551	1.36673

$$\text{Mean} = \frac{19.12776}{14} = 1.36623$$

$$\text{Extremes} \dots \dots \dots \begin{cases} 1.36689 \\ 1.36549 \end{cases}$$

$$\text{Greatest difference} \dots \dots 0.00140$$

The mean for the fourteen experiments is 1.36623. The difference between the two extreme figures..... 1.36689 and..... 1.36549 is.....0.00140

that is, what amounts to, at most, $\frac{1}{1000}$ of the quantity to be measured.

The figures given by the fourteen experiments are all much higher than the mean 1.3646 which Rudberg obtained in the experiments made by a quite similar method. I believe that this difference can be ascribed to the fact of the sucking in, in Rudberg's experiments, of the outside air; it seems unlikely that, working by his method, this source of error could have been avoided: on the other hand it is clear that it escaped his notice, if only because he does not mention it.

The errors introduced through this sucking-in are so much the more noticeable as one works with a smaller volume of air.

I did not at first succeed in preventing this sucking-in; I am

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convinced that in my earlier experiments it still had a noticeable effect and rendered some of my figures too low. What confirms me in this view is that, starting from the time when the sucking-in was made impossible, I obtained no figure lower than 1.3658.

SECOND SERIES OF EXPERIMENTS.

The experiments of this second series were made by a method slightly different from that followed in the former series ; but the apparatus was arranged so that the volume of air subjected to experiment remained practically the same at the temperature of melting ice and at that of boiling water, so that the whole effect of the expansion by heat is changed to a variation of tension.

A glass bulb of 350 to 400 cubic centimeters' capacity is sealed to a capillary tube about 38 centimeters long ; on this capillary tube, at a distance of 11 centimeters from the bulb, is put a piece of very regular tubing about 50 mm. long and of sufficiently great diameter to show only a very slight capillary effect. The capillary tube at its end is drawn out to a point and bent at a right angle.

The first thing to be done consists in calibrating this apparatus accurately and determining its coefficient of expansion. For this it must be completely filled with mercury at the temperature of 0° . This is a delicate operation, as all physicists will agree, for it is nothing else than constructing a thermometer whose reservoir shall contain about 5 kilograms of mercury.

To introduce the mercury, the bulb is connected, by means of a rubber tube *D*, *Fig. 7*, with a bent tube *DE* fastened to a support ; mercury is poured into this tube *DE*. If the bore of the capillary tube is not very small, the bulb is easily filled three-quarters full without any necessity for exhausting through the tube *E* ; but to succeed in filling it, one may have to exhaust several times by means of the tube *E*. The best way is to connect this tube with the small pump of *Fig. 4*, page 75. The bulb may thus be filled in a very short time.

It is then necessary to bring the mercury to boiling : to this

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end the bulb *A* is placed upon a hollow grating *GG* over a small furnace *F*, *Fig. 8*, the capillary tube having an inclination of about 45° and its bent end *CD* being below the surface in a dish full of very pure mercury. Some coals are then put in the furnace, below the grating, then they are successively placed upon the grating itself and upon the bulb, and finally

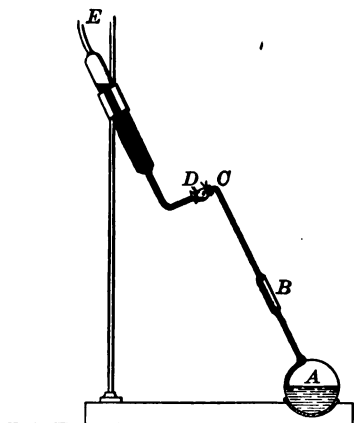


FIG. 7.

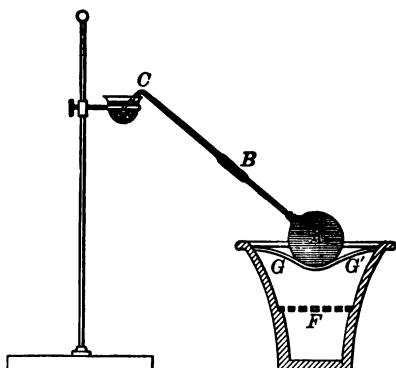


FIG. 8.

the latter is entirely covered with hot coals. When the mercury in the bulb approaches the boiling temperature, the mercury in the dish *D* is heated with an alcohol lamp, and with a second alcohol lamp the capillary tube is cautiously heated throughout its length. As soon as the mercury begins to boil in the bulb, the operation must be watched with the greatest care ; for if this boiling becomes too vigorous, if it drives out of the bulb too large a volume of liquid mercury displaced by mercury vapor, it is almost impossible to prevent the apparatus being broken at the instant when, the boiling having stopped, the mercury rushes back into the bulb ; this results in very violent hammering and return-shocks which ordinarily extend as far as the bent part *CD* of the capillary tube.

Therefore as one sees the mercury boiling in the vessel, a part of the coals must quickly be removed and the operation be made as smooth as possible. The coals are taken away entirely as soon as the moisture seems to have been completely

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driven out, or even when the volume of mercury vapor has become considerable. The mercury then returns into the apparatus and, as it has been previously heated in the dish, it does not break the capillary tube, as it would certainly do without this. When the bulb is once more full, one looks to see if a trace of moisture remains; in case some still remains, the boiling must be begun again. Speaking generally, it serves better to bring it to the boiling point again and again, rather than to continue the boiling for too long a time; in this way the breaking of the apparatus is more easily avoided.

When the vessel is completely full of mercury, it is allowed to cool to the temperature of the air, then is surrounded with a thick envelope of crushed ice. It requires many hours for the mass of mercury to arrive absolutely at the temperature of 0° . When it is certain that this point has been reached, the dish full of mercury is removed and is replaced by a small empty capsule. The ice having been got out of the way, the bulb is warmed with the aid of hot coals placed at some distance from it, so as to raise it to a temperature some degrees higher than the surrounding one; then it is hung in a small bag in the boiling apparatus of *Fig. 4* [page 75], to which an extension has been fitted, so that the whole capillary tube is surrounded by the steam, and the mercury is caught in the same capsule. By weighing the mercury forced out and that remaining in the apparatus, it is evident we have the necessary data for calculating the volume of the apparatus at 0° and the extent to which it expands between 0 and 100° .

To find the expansion of air, the bulb is hung in the boiler after the mercury has been so completely removed that not the smallest globule remains upon the walls or in the tube. The bulb is connected with the drying apparatus, *Fig. 4*. In a word, one goes to work exactly as has been described in the account of the former series.

When the end of the capillary tube has been sealed with a lamp, the apparatus is adjusted to a support shown in *Fig. 9*. The expanded part *B* of the tube comes below the plate *EE'*. By means of a cork on the stem at *M*, a tin-plate tray is put in place, in which crushed ice must be piled up, to keep the volume *B* at 0° . The capillary tube dips in a small bath of mer-

EXPANSION OF GASES

cury *T*. The tip of the bent part *CD* is broken off, all the precautions being exactly followed which have been pointed out in the first account, to prevent the entrance of air; finally the vessel *A* is surrounded with ice after having put over it from above a cylinder of tin-plate which is entirely filled with crushed ice. In the same way the volume *B* and the part of the capillary stem which is above the tray *M* are surrounded with ice.

Upon one of the legs of the support *P'* is arranged a movable arm *mn* carrying the small adjustable spoon of *Fig. 6*; this is lowered into the mercury. A mark has previously been

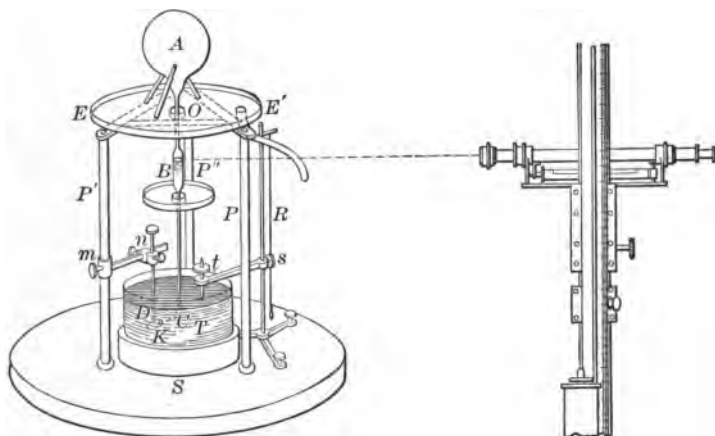


FIG. 9.

made upon the leg *P'* at the point where *mn* should be clamped in order that the spoon *K* may be at the level and in a line with the tube *CD*.

The apparatus having been left in the ice for about an hour, the tip *D* is sealed by pushing forward the spoon *K*, and at the same time the barometer is read; finally, the point of the screw *t*, which is arranged upon a small special apparatus *R*, is made to coincide with the surface of the mercury in the bath.

The ice which is in the tray *M* is then removed. At the end of three-quarters of an hour or an hour, when it is certain that the column of mercury drawn up is in temperature-equi-

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librium with the surrounding air, the height of this column is measured with the cathetometer. The dimensions of the tube and the level at which the mercury bath is placed, are such that the mercury comes to rest in the space B and fills it about half full.

The apparatus is detached and the mercury which has made its way in is weighed.

The tubing of which the space B is made was chosen in successive cases of different diameters; these dimensions were never great enough for the capillarity to become *nil*, but the capillary depression is determined each time, by direct experiment, in that part of the tube where the surface of the mercury comes to rest. For this purpose this tube is held vertical with both ends open, and dipping in a bath of mercury. On the slide which supports the glass of the cathetometer a horizontal metallic rod is fastened, to the end of which is fixed a vertical pointer whose tip is adjusted for contact, successively with the top of the meniscus in the tube and with the mercury surface in the bath. The distance traversed by the zero of the vernier of the instrument is the capillary depression.

We then have all the data necessary for calculating the expansion of the air. Using the same letters to designate similar things, as in the former method and, in addition, representing by c the capillary depression in the space B , clearly we have the equation

$$(1 + \delta T) H = \left(1 - \frac{P}{P'}\right) [H' - (h + c)] (1 + \alpha T);$$

whence

$$1 + \alpha T = \frac{(1 + \delta T) H}{[H' - (h + c)] \left(1 - \frac{P}{P'}\right)}$$

Let us assume in all cases that the columns of mercury have been reduced to 0° by calculation.

Three different vessels, A, B, C, were used in these experiments; to these were successively joined capillary tubes of different bores.

I shall distinguish as many series of experiments as different forms of apparatus.

EXPANSION OF GASES

I. The results with this apparatus are as follows:

$$P = 4330.0 \text{ gr.}$$

$$c = 1.10 \text{ mm.}$$

The coefficient of expansion of the glass could not be determined as the apparatus was broken during the boiling of the mercury. For this one experiment made with vessel A the assumption is made that $100\delta = 0.002306$, as was found by experiment with the vessel B.

The experiment upon the expansion of air gave

	H mm.	H' mm.	$h + c$ mm.	P' gr.	T	$1 + 100 \alpha$
1	739.61	739.86	194.38	14,233	99.23°	1.36629

II. This apparatus was made with the vessel B; we have:

$$P = 4274.34 \text{ gr.,}$$

$$p = 65.708,$$

$$c = 1.10 \text{ mm.,}$$

$$H = 749.37, \quad \text{whence } T_1 = 99.60^\circ.$$

We deduce from this

$$100\delta = 0.002306.$$

	H mm.	H' mm.	$h + c$ mm.	P' gr.	T	$1 + 100 \alpha$
2	739.24	739.21	193.58	17,735	99.22°	1.36645
3	758.64	758.53	199.51	17,335	99.95	1.36593

III. Apparatus made with the vessel B, but using for the space *B* on the capillary tube, a tubing of much greater diameter.

For this apparatus it was found

$$P = 4306.86 \text{ gr.,}$$

$$p = 66.68,$$

$$c = 0.22 \text{ mm.,}$$

$$H_1 = 769.04, \text{ hence } T_1 = 100.34 ;$$

from which we find

$$100\delta = 0.002302.$$

With this apparatus I obtained the following figures :

	H mm.	H' mm.	$h + c$ mm.	P' gr.	T	$1 + 100 \alpha$
4	764.70	764.31	198.78	36.095	100.18°	1.36610
5	767.24	767.19	199.98	34.825	100.27	1.36585
6	768.10	767.40	199.62	34.845	100.30	1.36590
7	770.57	770.70	200.86	34.490	100.40	1.36615
8	771.07	770.26	199.53	41.780	100.41	1.36691

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IV. Apparatus made with the vessel C.

$$P = 4878.60 \text{ gr.},$$

$$p = 74.795,$$

$$c = 0.54 \text{ mm.},$$

$$H_1 = 749.32, \text{ hence } T_1 = 99.60^\circ.$$

From this we deduce $100 \delta = 0.002349.$

	H mm.	H' mm.	$h + c$ mm.	P' gr.	T	$1 + 100 a$
9	748.13	745.89	193.04	32.42	99.56°	1.36708
10	754.10	751.51	194.73	30.64	99.78	1.36695
11	740.14	744.53	196.86	32.305	99.26	1.36633
12	746.91	748.13	196.23	31.355	99.51	1.36708
13	747.54	747.28	194.69	31.486	99.53	1.36650

V. Apparatus made with the bulb C, but using for the space *B* a tubing of a greater diameter and for capillary tubing one of finer bore.

For this apparatus we have :

$$P = 4923.60 \text{ gr.},$$

$$c = 0.22 \text{ mm.};$$

we have assumed $100 \delta = 0.002349.$

	H mm.	H' mm.	$h + c$ mm.	P' gr.	T	$1 + 100 a$
14	746.69	747.16	191.98	58.551	99.50°	1.36615
15	751.97	750.18	191.50	56.69	99.70	1.36594
16	746.49	746.19	191.76	54.865	99.50	1.36660
17	752.50	751.45	192.17	61.30	99.72	1.36666

VI. Apparatus constructed with the same bulb, substituting for the finer capillary tube another of a larger bore.

The data for this apparatus are the following :

$$P = 4926.4 \text{ gr.},$$

$$c = 0.22 \text{ mm.};$$

we have assumed $100 \delta = 0.002349.$

This apparatus was used for but one experiment upon atmospheric air; it was intended for some experiments upon other gases.

	H mm.	H' mm.	$h + c$ mm.	P gr.	T	$1 + 100 a$
18	758.24	758.78	195.68	58.31	99.93°	1.36614

Then bringing together all the figures obtained in this series of experiments—

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1.36629	1.36695
1.36645	1.36633
1.36593	1.36708
1.36610	1.36650
1.36585	1.36615
1.36590	1.36594
1.36615	1.36660
1.36591	1.36666
1.36708	1.36614

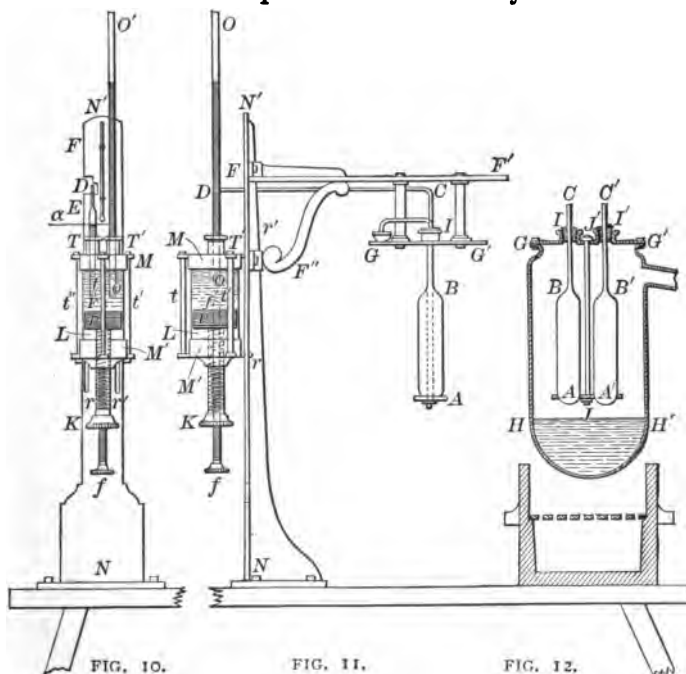
The mean of all these experiments is

1.36633.

It does not practically differ from that obtained in the former series.

THIRD SERIES OF EXPERIMENTS.

This third series of experiments was made by means of an ap-



paratus copied from that described by Rudberg in his second memoir and which is represented in *Fig. 3* [page 70]. The apparatus which I constructed is shown in *Figs. 10, 11, 12.*

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A cylindrical glass reservoir AB , 35 millimeters in diameter and 170 mm. long, is sealed to a capillary tube $BCDE$, twice bent at right angles. This tube terminates in a piece of tubing EE of much larger size, which dips in a small mercury bath MM' .

This bath consists of a cylinder of heavy glass whose two edges are tightly pressed against the two cast mountings M , M' , by means of the screw rods t, t', t'' . The upper casting has two tubulures T, T' , provided with screw threads on the outside. These tubulures are closed by two copper screw caps bored through the centre with holes to allow tubes to enter. The lower casting carries a screw thread in which works a large screw rod KL supporting a cast piston P inside the glass cylinder. This piston has a covering of linen greased with tallow: at its centre is a small packing-box filled with oakum, through which moves an iron rod ff' , 8 millimeters in diameter, which screws up and down inside the large rod KL , and ends outside with the knob f .

The small bath is fixed by means of set screws to a cast vertical support NN' , but in such a way that it can be made to move along the slots rr' ,—which is convenient for adjusting the tubes. This bath is otherwise completely filled with thoroughly dry mercury.

We begin by determining by a preliminary experiment the capacity of the cylindrical reservoir AB and its coefficient of expansion. We determine in the same way the volume of the capillary tube from C to E , as well as that of the small portion of the larger tube Ea down to a very fine mark scratched upon this tube at a . We then dry the reservoir completely and fill it with dry air: for this the drawn-out end of the tube is connected with the drying apparatus, *Fig. 4*, page 75, and the whole length of the reservoir and tube are warmed with hot coals. A vacuum is produced a great many times and each time the air is allowed to enter again. The hot coals are then removed, there being free communication with the atmospheric air. When the reservoir has cooled, it is placed in very cold water or even in some ice; finally, after some time, the tip of the tube is closed by means of the blowpipe.

The cast upright NN' carries a cast bracket-arm $FF'F''$

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fastened with screw bolts in the slots cut in the upright NN' ; it can thus be adjusted at various heights. To this bracket-arm is fastened permanently the copper cover GG' of a vessel of the same metal $HHH'G'$. The cover is provided with two tubulures I, I' : in one the reservoir of air AB is fixed by means of a cork; in the other is placed a mercury weight-thermometer $A'B'$, of exactly the same shape and dimensions as the air reservoir. The two tubes rest upon a small cross piece AA' fastened to the rod JJ' .

The tube EF is introduced into the tubulure T and, in order to fasten it hermetically, is wrapped with a strip of linen greased with tallow, which is then forced by means of the screw cap E into the annular space formed in the tubulure. We thus obtain an air-tight connection which will resist very great pressure. The point of the tube EF is then broken off by means of an iron rod introduced through the second tubulure T' , and in this second tubulure is fastened, in exactly the same way, a piece of barometer tubing OO' , perfectly cylindrical throughout its length and of exactly the same diameter as the end tubing EF possesses below where it is drawn out. Besides it was shown by direct experiment that there was no difference between the capillary depressions in the two tubes.

To conduct the experiment, the two reservoirs $AB, A'B'$ are surrounded with melting ice which is put in a small bag and hung from the copper cover GG' . By turning the rod KL the piston is forced up until the mercury comes to rest at a in the tube EF ; the fine adjustment is made with the aid of the thin rod ff' . A determination of the difference of level is then made with the cathetometer, and at the same time the barometric pressure is recorded.

The ice and the bag which contains it are then removed, the vessel $HHH'G'$ is fastened by means of screws to its cover GG' , and the water which it contains is then raised to boiling. By pushing up the piston the mercury is maintained at the level a in the tube EF . When it is certain that the air has come to the temperature of the vapor, the mercury level is adjusted exactly at a by means of the rods KL and ff' , and the difference of level of the two columns of mercury is read with the cathetometer, as well as the height of the barometer.

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I made some experiments at first, taking, as Rudberg did, the point a upon the capillary stem; but I found that it was very difficult by this method to get accurate results. Thus, although in one experiment the tube was of more than 1 mm. diameter, the movement of the mercury in the tube was very irregular, by reason of the variation in the capillary action. Sometimes the column in OO' would rise more than 1 mm., without the mercury at a being displaced to a visible extent; in the same way, on lowering the piston, the column had often fallen several millimeters in the tube OO' , while the meniscus at a had only become flattened; this sluggishness was not entirely overcome by even quite sharp taps given the apparatus.

It became necessary to take the point a upon the larger tubing EF . As this tubing was of exactly the same diameter as the barometer tubing there was no correction to introduce for capillarity; but it was necessary to take account of the small volume of air which was not heated.

Let P be the weight of mercury at 0° filling the reservoir AB up to C when it is at 0° ;

p the weight of mercury which flows out at the temperature of water boiling under the pressure H' , or at the temperature T^1 ;

p' the weight of mercury which fills the capillary tube CDE and the part Ea of the larger tubing EF ;

H the barometric pressure at the time when the reading is made, the reservoirs being kept at 0° by melting ice;

h the difference of level of the two columns of mercury;

t the temperature of the surrounding air.

In the same way let us represent by

H' the barometric pressure when the reservoirs are heated by boiling water;

T' the corresponding temperature of the vapor;

h' the difference of level of the two columns;

t' the temperature of the air.

Evidently we shall have the equation

$$\left[P + p' \frac{1}{1 + \alpha t} \right] (H + h) = \left\{ P (1 + \delta T) \frac{1}{1 + \alpha T} + p' \frac{1}{1 + \alpha t'} \right\} (H' + h'),$$

hence

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$$1 + \alpha T = \frac{(1 + \delta T) (H' + h')}{(H + h) - \frac{p'}{P} \frac{1}{1 + \alpha t} [H' + h' - H - h]};$$

for, by reason of the small value of $\frac{p'}{P}$, we can always assume that $t = t$.

I shall again here distinguish as many series of experiments as special pieces of apparatus.

I. An experiment made to determine the volume of the air reservoir and its coefficient of expansion, gave

$$P = 1975.862 \text{ gr.},$$

$$p = 29.852,$$

$$H_1 = 745.51 \text{ mm.},$$

$$T_1 = 99.46^\circ,$$

$$\text{whence } 100 \delta = 0.002555.$$

By measurement, there was found for the weight of mercury filling the capillary tube and the small piece of larger tubing as far as the mark,

$$p = 9.740 \text{ gr.},$$

$$\text{whence } \frac{p}{P} = 0.00493.$$

The tube being heated by the vapor of boiling water, two readings made with a half-hour interval gave

$$H' \dots\dots\dots 751.01 \qquad 751.01$$

$$h' \dots\dots\dots 296.70 \qquad 296.70$$

$$t' \dots\dots\dots 8.6^\circ \qquad 8.8^\circ$$

$$T' \dots\dots\dots 99.66^\circ \qquad 99.66^\circ$$

$$\text{whence } H' + h' = 1047.71 \qquad 1047.71$$

The reservoir being in melting ice, we have

$$H \dots\dots\dots 749.98 \qquad 749.88 \qquad 749.78$$

$$h \dots\dots\dots 20.53 \qquad 20.59 \qquad 20.63$$

$$t \dots\dots\dots 8.5^\circ \qquad 8.5^\circ \qquad 8.5^\circ$$

$$H + h \dots\dots\dots 770.51 \qquad 770.47 \qquad 770.41$$

We shall take as an average

$$H + h = 770.47.$$

Comparing this mean with the two determinations at the boiling point of water, we have [the ratios]

$$1.36688, \qquad 1.36688.$$

A second series of experiments made with this apparatus gave:

The tubes being in melting ice,

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H	746.16	746.26	746.39	746.61	746.66
h	24.53	24.41	24.21	24.11	24.09
t	8.3°	8.3°	8.3°	8.3°	8.3°
$H + h$	770.69	770.67	770.60	770.72	770.75

Mean of $H + h = 770.69$.

In boiling water we have:

H'	740.79	741.01	741.14	743.20	743.26
h'	305.58	305.62	305.36	303.72	303.64
t'	9.00°	9.00°	9.00°	9.00°	9.00°
T'	99.28°	99.29°	99.29°	99.37°	99.37°
$H' + h'$	1146.37	1046.63	1046.50	1046.92	1046.90

On comparing each of the values of $H' + h$ with the mean 770.69 of the determinations in melting ice, we have [the ratios]:

$$\begin{array}{r} 1.36612 \\ 1.36643 \\ 1.36626 \\ 1.36651 \\ 1.36649 \\ \hline \text{Mean} = \frac{6.83181}{5} = 1.36636. \end{array}$$

II. With a second apparatus made with a reservoir cut from the same piece of tubing as the former, we have

$$\begin{array}{rcl} \text{assuming} & P = & 1817.50 \text{ gr.;} \\ & 100 \delta = & 0.002555, \\ & p' = & 8.50 \text{ gr.}, \\ & \frac{p'}{P} = & 0.00468. \end{array}$$

In melting ice we have:

H	752.60	752.60	752.65	752.57	752.40	752.25
h	19.58	19.58	19.76	19.66	19.74	20.24
t	11.0°	11.0°	11.0°	11.0°	11.0°	11.0°
$H + h$	772.18	772.18	772.41	772.23	772.14	772.49

Mean of $H + h = 772.29$.

In boiling water we have:

H'	751.15	751.13	751.13	751.08	751.05
h'	299.16	299.66	299.66	299.76	299.86
t'	13.7°				
$H' + h'$	1050.31	1050.79	1050.79	1050.84	1050.91
T	99.67°				

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The five values of $H' + h'$, compared with the mean of $H + h$, give [the ratios]:

$$\begin{array}{r} 1.36672 \\ 1.36714 \\ 1.36714 \\ 1.36730 \\ 1.36747 \\ \hline \text{Mean} = \frac{6.83577}{5} = 1.36715. \end{array}$$

Thus the three series of experiments made by this method gave the following mean values:

$$\begin{array}{r} 1.36688 \\ 1.36636 \\ 1.36715 \\ \hline \text{General mean} = \frac{4.10039}{3} = 1.36679. \end{array}$$

This average differs little from that found in the two former series.

I do not think this method leads to the same accuracy as the others which I have used. The tubes in which the columns of mercury are measured, are not of large enough diameter to make the capillary effect negligible; the capillary depression amounts in these tubes to about 1 mm. This capillary depression, theoretically, does not enter into the calculation of the constant, and, if it remains always the same, it exerts no influence. Yet it is easy to show that this effect must vary between rather wide limits, by measuring from time to time the heights of the tops of the menisci; we may thus realize that these sometimes vary in the same experiment from a certain amount to double that amount. As a matter of fact, here is a series of measurements of the corresponding heights of the two menisci:

Tube EF	Tube 00'
1.08 mm.	1.14 mm.
0.72	1.64
1.00	1.64
1.10	1.32
1.38	1.36
0.96	1.20
0.80	1.18

It is not possible that such marked variations in the heights of the menisci do not involve very considerable changes in the capillary depressions.

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Rudberg with his apparatus has found lower figures than mine. It is difficult with any certainty to determine the causes of these differences. I have already stated above that I had never obtained good results when I fixed the mark *a* on the capillary part *ED* of the tube; but I believe that still another reason could be given which has led Rudberg to results that are too low. This physicist has always in his calculations neglected the little volume of air, not heated, which is contained in the portion *Ba* of his capillary tube. This volume is very small, nevertheless it is hardly probable that it can be entirely neglected. Unfortunately, Rudberg has not given in his memoir the dimensions of the different parts of his apparatus; hence it is impossible to calculate now the correction this fact would involve in his results.

FOURTH SERIES OF EXPERIMENTS.

This series of experiments was made with an apparatus

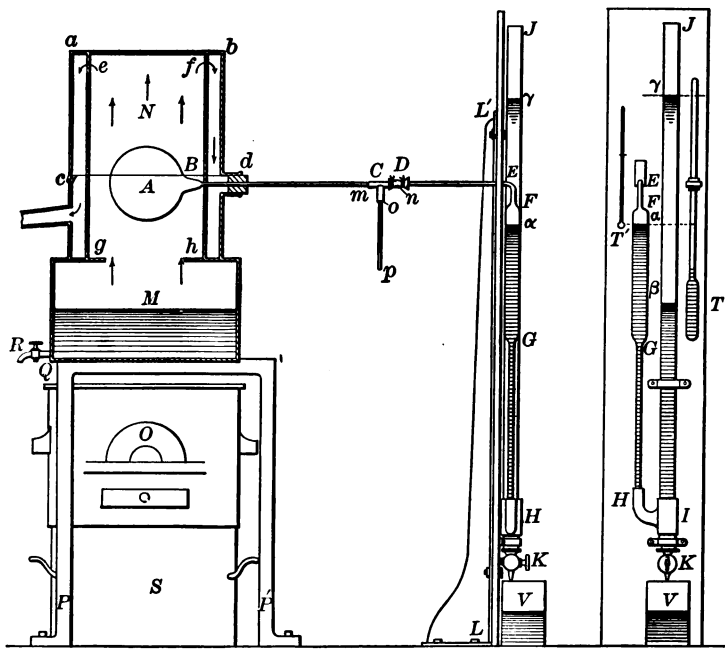


FIG. 13.

FIG. 14.

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which served the same end as that of the preceding series, without possessing the same disadvantages. It consists of a large bulb *A* (*Figs. 13 and 14*) of 800 to 1000 cubic centimeters' capacity, to which is sealed a capillary tube about 20 centimeters in length. This bulb serves as the air-reservoir and must be brought successively to 0° and to 100° ; it is put in communication with a syphon tube full of mercury, which serves to measure the tension of the air.

A tube *JI* of 16 to 17 mm. internal diameter, perfectly cylindrical, is fastened by means of gum-mastic in an iron casting *IH* provided with a tap *K*. This carries a side tubulure *H* in which is cemented a second tube *HGFE* of the same diameter as the first throughout the length *FG*. This tube ends at the top in a bent capillary tube *FED*, cut from the same capillary tubing as the tube *BC* sealed to the bulb. The tube *BC* fits close in a small copper three-way tube *mno* in which it is firmly fastened with mastic. In the second arm *o* is cemented a short piece of capillary tubing *op* which has been drawn out at its end *p*.

The system of the two tubes *IJ* and *EH* is fastened to a plank which is itself firmly secured, and in a perfectly vertical position, to a cast-iron upright *LL*.

The bulb *A* is fastened once for all in a vessel of tin plate *MN*, in which water can be boiled, or the bulb surrounded with ice. This vessel rests upon an iron tripod *PQQ'P'*. A furnace *O* upon a support *S* can be put below the vessel *MN* and withdrawn at will.

This is now the way an experiment is made. The open end of the tube *op* is connected with the drying apparatus (*Fig. 4*) [page 75]; and in order to close the arm *n* of the copper tube, a bit of tubing completely closed is attached to it with a piece of rubber tubing. The water in the vessel *MN* is brought to boiling, and a vacuum is produced a great many times within the bulb, each time allowing the air to enter again very slowly.

The tube *HGFED* had been dried at a high temperature in the same way before being cemented in the tubulure *H*, and very dry mercury is immediately poured into the tube *JI*, so as to fill completely the tube *HGF* up to the open end *D*. In

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this way moisture is kept out of this tube. With the same idea care is taken to keep the end of the tube *D* covered with a cap of rubber.

The bulb *A* being filled with very dry air, the bit of stopped-up tubing, which during the drying was over the tubulure *n*, is removed, and the capillary tube *DE* is connected with this tubulure by means of rubber; this tube fits closely in the copper tubulure and comes butt-to-butt against the tube *BC*, so that within the little copper three-way tube *mno* the only space there is is the bore of the capillary tubes which meet there. At other times the tube *DE* is fastened in the tubulure by means of mastic.

The tap *K* is opened; the mercury which flows out is replaced in the tube *EFG* by air which has passed through the drying apparatus. The mercury is run out until the level stands in the tube *FG* at a mark *a* scratched on the glass. The mercury stands at the same level in the two tubes, since on both sides it is freely open to the air.

The drying apparatus is now disconnected and the tip *p* of the tube *op* is closed by means of a lamp. At the same time the height *H* of the barometer is recorded.

The furnace which keeps the water boiling in the sheet-iron vessel is removed. In order that the bulb *A* may become cool more rapidly, the hot water is drawn off by opening the tap *R*; the cover *abcdefgh* is taken off and cold water is poured several times into the vessel to cool the walls. Finally the bulb *A* is completely covered with crushed ice, which is kept in place by a cloth fastened to the edge *cd* of the vessel.

The air contracts on cooling, the mercury rises in the tube *GF*; but it is maintained at the same level *a* by running out some of the mercury through the tap *K*.

When it is certain that the air in the bulb *A* has come to the temperature of melting ice, the barometric height *H'* is recorded, and the difference of level $as = h'$ is measured by means of the cathetometer. We thus have already all the data necessary for determining the rate of expansion of air; but we can get a second determination in the following way:

The closed tip *p* is again connected with the drying appara-

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tus; this apparatus is exhausted several times in succession, to make sure that it is full of dry air; then the tip p is broken off. The mercury now falls in the tube FG , but it is brought back to a by pouring mercury into the tube JI .

After some time the tip p is again closed by means of a lamp and the height H'' of the barometer is recorded. The ice is then removed; the cover $abcd$ of the tin vessel is put back, and the water poured into the vessel is brought to boiling once more. By pouring mercury into the tube IJ the level is maintained at a in the tube FG . After the bulb has remained about an hour in [the vapor of] the boiling water, [the height of] the barometer H''' is noted, and the difference of level $ay = h'''$ of the mercury in the two columns is measured.

In the calculation of the experiment it is necessary to take account of the small volume of air that remains constantly at the temperature of the surrounding air. For this we must know the ratio of this volume to that of the bulb A . The latter volume V had been determined by measurement with distilled water, and the volume v of the air contained in the capillary tubes BC , DEF , op , as well as in the part Fa of the larger tube, had been found by measurement with mercury. We thus had:

$$\begin{array}{l} \text{Weight of mercury filling } V = 9889.9 \text{ gr.,} \\ \text{ditto.....ditto.....} v = 26.85; \end{array}$$

hence $\frac{v}{V} = 0.002715.$

I was not able directly to determine the coefficient of expansion of the bulb A ; it would have been necessary, for this, to have boiled a mass of 9 to 10 kilograms of mercury in a bulb of glass ending in a capillary tube, which seemed to me a practically impossible operation. I have assumed the figure 0.00233 for this coefficient, which is the mean of those found for the two bulbs used in my Second Series of determinations. These bulbs were the product of the same factory and were of the same kind of glass.

The temperatures t , t' , t'' , t''' , of the small volume of air v were indicated by the small thermometer T' ; that of the columns of mercury by the thermometer T whose cylindrical reservoir had the same diameter as the tubes IJ and FG .

MEMOIRS ON

The equation which serves for the first half of the experiment is the following:

$$1 + \alpha T = \frac{(1 + \delta T) H}{H' - h' - \frac{v}{V} \frac{1}{1 + \alpha t} [H - H' + h']};$$

that which applies to the second half is

$$1 + \alpha T'' = \frac{(1 + \delta T'') H''' + h'''}{H'' - \frac{v}{V} \frac{1}{1 + \alpha t''} [H''' + h''' - H'']};$$

We have assumed in these equations

$$t = t' \text{ and } t'' = t''.$$

We now have the figures obtained by this method:

First Half.							
	<i>H</i>	<i>T</i>	<i>t</i>	<i>H'</i>	<i>h'</i>	<i>t'</i>	$1 + 100 \alpha$
1	747.83	99.55°	14.0°	747.43	197.49	14.0°	1.36592
2	742.27	99.34°	13.9	744.25	198.56	13.5°	1.36710
3	747.97	99.55°	13.0	748.52	198.76	12.5°	1.36662
Mean.....							1.36655
Second Half.							
	<i>H''</i>	<i>t''</i>	<i>H'''</i>	<i>T'''</i>	<i>h'''</i>	<i>t'''</i>	$1 + 100 \alpha$
1	747.30	14.2°	746.45	99.50°	270.28	15.1°	1.36682
2	744.59	13.1°	745.27	99.45°	267.59	15.6°	1.36674
3	748.72	12.9°	749.19	99.59°	269.59	13.9°	1.36580
Mean.....							1.36645

Thus the mean of the six determinations is 1.3665.

In the Fourth Method the expansion of the air is measured under very different pressures: in fact, in the first half of each experiment the air was under a pressure of only about 0.550 m. when at 0°, and under the atmospheric pressure 0.760 m., when heated to 100°. In the second half, the air at 0° is under the atmospheric pressure 0.760 m., and the air heated to 100° is under a pressure of about 1.040 m. As the experiments show no difference in the numbers obtained in the two halves, it must be concluded that, within these pressure limits, dry air shows a practically constant coefficient of expansion.

It is very easy to arrange the apparatus so that it will serve for the study of the expansion of air under greater pressures; in fact, it will suffice for this to give the tube *EFGH* a considerable capacity from a certain point *s* to *H*, *Fig. 15*, sealing the tip *p* at the time when the bulb as well as the tube *EH* as far as *H* are full of dry air, then pouring mercury into the tube

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IJ until the mercury-level coincides with *a* in the tube *FaG*, the bulb being surrounded with melting ice; the mercury then rises in the tube *IJ* a certain distance *h*, so that the volume of gas is then at 0° under a pressure $H+h$. The bulb being raised to 100° , in order to keep the level of the mercury at *a* in the tube *FG*, it is necessary to pour a new lot of mercury into the tube *JI*, which gives a difference of level *h'* and, consequently, for the pressure upon the gas at 100° , $H+h'$. The heights *h* and *h'* will be more considerable as the volume of the tube δH is greater in proportion to the volume of the bulb. Some experiments made by the method thus modified will be discussed later.¹

¹ I have also made some experiments to determine the coefficient of expansion of air by the method of M. Gay-Lussac. This method consists, as is well known, in observing the expansion suffered by dry air enclosed in an actual thermometer, this air being separated from the outside air by a tiny index of mercury.

The capillary tube was measured, then graduated with the greatest care; it was of 2.7 mm. bore and was marked with 600 divisions in a length of 558 mm. The experiment was begun by filling this thermometer with mercury which was again and again brought to boiling in the bulb and in the tube, then was entirely surrounded with ice; the point where the mercury came to rest on the scale was noted. A portion of the mercury in the stem was made to flow out and was weighed, then the thermometer was once more put in the ice and the point noted where the column came to rest. This operation repeated three times in different parts of the scale, gave the following results:

Mercury at 0° between	375.8 and 602.0	= 226.2 div.;	6.629 gr.
	103.0	375.8 = 272.8	7.9945
	50.9	499.0 = 448.1	13.128

From this we deduce for the weight of mercury at 0° occupying one division:

in the first interval.....	0.029306 gr.
in the second	0.029305
in the third.....	0.029297

$$\text{Mean} = \frac{0.0293008}{3} = 0.0293003.$$

The close agreement to be noticed in these figures proves satisfactorily the accuracy of the graduation.

The mercury which at 0° filled the bulb and the stem as far as division 50.9, weighed 27.916 gr.

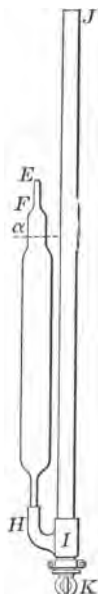


FIG. 15

MEMOIRS ON

The four series of experiments which I have described in detail have therefore given the following averages :

After the mercury has been completely removed from the apparatus, it is connected by means of rubber tubing with a U-shaped tube containing pumice stone moistened with sulphuric acid and is exhausted a great many times while being warmed by means of hot coals. This thermometer tube was fitted at the end with a bit of larger tubing in which had been left a tiny drop of mercury to form the index. The apparatus being filled with dry air, the bulb is raised to such a temperature that the globule of mercury, when drawn into the capillary tube, comes to rest at a convenient point when the thermometer is placed in melting ice.

The greatest pains were taken to place the stem of the thermometer in a perfectly horizontal position where the instrument was in ice or in [the vapor of] boiling water, and it was given light taps to assist the movement of the index.

I shall not describe in detail the numerous experiments made by this method ; suffice it to say I was unable to get constant figures. The way in which the thermometer tube was tapped, the points on the tube where it was struck, produce a very marked effect upon the position of the index. The movement of the index even seemed to depend upon the more or less rapid changes of the temperature, which seems to show that the mercury index does not close the tube perfectly, and that would not be surprising after what we have seen above [page 80]. What confirms me in this opinion is that, in many experiments, the index did not return to the same point, the thermometer being surrounded with ice, when, in the interval, the apparatus had been heated to the boiling point of water.

Thus, in one experiment, the index came to rest when the thermometer was in ice, at.....152.7 div.

In [the vapor of] boiling water at 534.5 div.; the apparatus being again surrounded with ice, the index came to rest at..154.5 div. and meantime the barometer had not changed to any noticeable extent.

In another experiment the index came to rest in melting ice at 66.5 div. before the instrument had been put in [the vapor of] boiling water, and at 66.0 div. after it had been heated. The barometer had changed in a very marked way during the interval, but this change should have produced a movement in the opposite direction.

However that may be, here are some of the figures I obtained by this method :

1.3641
1.3626
1.3635
1.3647
1.3552

It is remarkable that all these figures are smaller than those yielded by the other methods. This circumstance is probably the result of mere chance.

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First series.....1.36623 ;

Second series.....1.36633 ;

Third series.....1.36679 ;

Fourth series.....1.36650 ;

That is to say, about.....1.3665.

I therefore propose to adopt for the coefficient of expansion of dry air for each degree centigrade between the two fixed points of the thermometer, 0.003665.¹

We shall now proceed to take up in succession all the quantities which enter into the calculation of the experiments, in order to obtain an approximate value, at least, for the error each of them may introduce.

The equation

$$1 + \alpha T = \frac{P' (1 + \delta T) H}{(P' - P) (H' - h)},$$

which applies to the first two series, comprises the weights P and P' of mercury which can be determined with what may be called absolute precision. Thus the factor $\frac{P'}{P' - P}$ cannot introduce any noticeable error arising from its experimental determination.

The factor $1 + \delta T$ depends upon the expansion of the glass. We have seen that this expansion was determined for each apparatus by direct experiment and it must be admitted to be rigorously exact; besides, since it is very small, a noteworthy error in this coefficient would exert no appreciable effect upon the value of the coefficient of expansion of air.

The coefficient of expansion of glass was determined as being a function of the coefficient of expansion of mercury; I have assumed for the latter coefficient the value $\frac{1}{85.5} = 0.011802$, found by Dulong and Petit. Unfortunately, some uncertainty exists regarding the numerical value of this coefficient; in fact, Dulong and Petit gave in their memoir only the following values:

Expansion of mercury for each degree centigrade between

0° and 100°, $\frac{1}{85.5}$

ditto.....ditto.....0° and 200°, $\frac{1}{84.25}$

ditto.....ditto.....0° and 300°, $\frac{1}{83.5}$

¹ M. Babinet has called my attention to the fact that, adopting for the coefficient of expansion of air the figure 0.0036666... , this coefficient may be represented by the very simple fraction $\frac{1}{273}$, which is very easy to use in calculations.

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The temperatures are given here, as these distinguished physicists explicitly state, with reference to the air thermometer, assuming for the coefficient of expansion 0.375; but if this coefficient is inaccurate and if the figure 0.3665 must be used, then the intervals of temperature change appreciably and the temperature 100° of Dulong becomes 102.7°, so that the coefficient $\frac{1}{273.5}$ should be about $\frac{1}{270}$ greater.¹

It is possible, however, that the coefficient of absolute expansion of mercury between 0° and 100° given by Dulong and Petit may be that which they found directly in their experiments from [the temperature of] melting ice up to [that of] boiling water, without deducing it from their interpolation-formula. In this event it would not be affected by the same source of error as the values between 0° and 200° and between 0° and 300°. However that may be, new experiments alone can decide the point.

What interests us at this moment is to see what difference this could bring about in our coefficient of expansion of air. Assuming the coefficient of absolute expansion of mercury between 0° and 100° too great by $\frac{1}{270}$, the coefficient of expansion of glass would be too great by about $\frac{1}{170}$. Thus, instead of the figure 1.0026, we should have in the numerator the figure 1.0024, smaller than the former by $\frac{1}{10,000}$, which would reduce the figure 1.3665 by $\frac{1}{10,000}$, that is to say, would give 1.3662; consequently this change would affect only the fourth decimal: after all, it is a correction easily made in all my figures.

The factor $\frac{H}{H'-h}$ which depends upon the barometric measurements, is the one which is liable to the largest errors of observation. Physicists who have had occasion to make a large number of barometric observations, know how difficult these observations are when the attempt is made to reach the highest limit of accuracy. I do not believe I exaggerate when I take it for granted that a barometric reading cannot be made closer than $\frac{1}{10}$ of a millimeter, however improved the measuring apparatus may otherwise be. The difficulty lies in the fact that the atmospheric pressure is constantly changing, but this

¹ This point has already been made by M. Poggendorff, *Poggendorff's Annalen*, Vol. XLI, page 467.

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variation is at once shown by the barometer, yet as a rule, only the changes in the form of the meniscus, and the variations in height do not take place in any regular way, but rather by jerks. It is well, in order to avoid this trouble, to tap the barometer to make the mercury column move back and forth, before making a reading, yet it is clear that the source of error is not completely done away with by this means.

Each of the measurements H , H' , h , is liable to the same error ϵ . In order to determine the maximum deviation of individual experiments, we shall suppose the errors made in H , H' , h , to have such signs as will produce the greatest difference in the final result. Thus, we will assume that instead of the accurate factor $\frac{H}{H'-h}$, observation has given us the factor

$$\frac{H+\epsilon}{(H'-\epsilon)-(h+\epsilon)}$$

The error is then represented by

$$\frac{H+\epsilon}{H'-h-2\epsilon} - \frac{H}{H'-h},$$

or

$$\frac{\epsilon (2H + H' - h)}{(H' - h)(H' - h - 2\epsilon)},$$

or simply

$$\epsilon \frac{2H + H' - h}{(H' - h)^2},$$

by neglecting 2ϵ in the denominator in comparison with $H' - h$.

As a result, the value of $1 + \alpha T$ becomes

$$1 + \alpha T = \frac{P'(1 + \delta T)}{(P' - P)} \frac{1}{H' - h} \left[H + \epsilon \frac{2H + H' - h}{H' - h} \right].$$

Assuming $H = H' = 760$ mm., $h = 190$ mm.; we shall have for the last factor

$$\begin{aligned} \text{or} \quad & 760.00 \text{ mm.} + \epsilon \cdot \frac{2090}{570}, \\ & 760.00 \text{ mm.} + \epsilon \times 3.67. \end{aligned}$$

If $\epsilon = 0.1$ mm., then the total error resulting for 760.00 mm. will be 0.367 mm., that is to say $\frac{4}{10800}$.

This gives for the total possible range of error in the experiments, for this source of error alone, $\frac{8}{10800}$.

It may thus be seen that if we assume it impossible to attain

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an accuracy greater than $\frac{1}{10}$ of a millimeter in barometric observations, the determinations of the rate of expansion of air will be liable, from this source of error alone, to show a maximum variation of about $\frac{1}{1000}$. It will be noticed that this is close to the maximum variation to be observed in my results.

In order that the coefficient of expansion of air may be exact up to the third decimal, the experiment which determines it must not lead to an error of more than $\frac{1}{1400}$. The direct experiment does not tell us, as a matter of fact, that 1000 parts of air expand between 0° and 100° by 366 parts, which would be an accuracy of only $\frac{1}{388}$; but rather that 1000 parts of air become 1366 in passing from 0° to 100° , which gives an accuracy of $\frac{1}{1388}$.

The formulas which apply to the two later series of experiments are evidently open to the same sources of error. The possible error in the measurement of the heights of the columns of mercury is probably even greater in the apparatus of the Third Series, since the tubes are narrower and on this account show a greater variability in the capillary depression.

Yet there is in addition another source of uncertainty in these two methods which did not enter into the two earlier ones: it lies in the determination of the temperature of the volume of air which was not heated. The error resulting from this might be quite large if this volume formed an appreciable fraction of that which is brought to the fixed points: it is entirely negligible in my experiments, since I took pains to carry them out so that the volume of the air that was not heated should never be but an extremely small fraction of the total volume.

The temperature T of the vapor was calculated from the observed barometric heights at the time of the boiling. I have assumed in this calculation that a variation of 1° in the boiling-point of the water corresponded to a difference of pressure of 26.7 mm. This figure is that given in the tables of the tensions of water-vapor recently calculated by M. Biot. It seemed to me better to adopt this figure, than to take the numbers found by different physicists by determining with some one thermometer the boiling point of water under various barometric pressures. These experiments could not result in great accu-

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racy, for they were frequently carried out on days quite separated from one another, and because the instrument had probably already suffered some appreciable change in the interval through the movement of the fixed points.

In order that these experiments should yield results that could not be questioned, it must have been possible to take note of the boiling point of water under various pressures, at times close together, for example, in an apparatus where the pressure could be varied at will, as in the apparatus of M. Tabarié. A series of observations might even be made during the ascent of a mountain and while care was being taken to keep the thermometer constantly in [the vapor of] boiling water during the ascent, in order to avoid as far as possible movement of the fixed points.

However that may be, the figure I have assumed must be very near the true one, and the error which could be produced by it in the coefficient of expansion of air is entirely inappreciable.

My barometric observations were made with a barometer with a Fortin cistern, which had been carefully compared in a series of measurements, with that of the Paris Observatory, corrected for capillary depression, and all my observations were reduced by calculation to [those of] the Observatory barometer.

After all, a small constant difference in the absolute values of all the barometric heights would have had no appreciable effect upon the coefficient of expansion of air, since it would have had to do only with the determination of the temperature of the vapor, and its influence upon the other would be quite inappreciable.

PART II.

Upon the Rate of Expansion of certain other Gases.

The old coefficient adopted for the expansion of air being inaccurate to the extent of $\frac{1}{37}$, it is clear that it cannot be considered as proved that all gases have the same coefficient of

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expansion; new determinations are necessary to decide whether this law is strictly true or is only approximate.

I have made experiments upon nitrogen, hydrogen, oxide of carbon [carbon monoxide], carbonic acid, sulphurous acid, cyanogen, protoxide of nitrogen [nitrous oxide], hydrochloric acid and ammonia. Most of these determinations were made by Method II; some however were made by Method IV.

First, I shall describe in a few words how the experiment was managed when Method II was employed. The bulb being suspended in the steam vessel and connected with the drying-apparatus, it was exhausted many times and the air allowed to re-enter slowly, in such a way as to dry the bulb thoroughly; then to the second tubulure of the pump was attached the apparatus in which the gas was produced. The bulb being exhausted, as well as the gas-generating apparatus, the tap is gradually opened so as to allow the gas to enter as fast as it is formed: the progress of the operation is indicated by a safety tube placed somewhere in the generating apparatus. When the bulb was full of gas, it was exhausted, then allowed to become full of gas once more, and so four or five times in succession. In other respects the experiment was conducted as has been described [page 84].

In these determinations Bulb VI [page 88] was used, and two new bulbs, VII and VIII, for which the following data were obtained:

	Bulb VII.	Bulb VIII.
$P =$	4358.15 gr.	4250.70 gr.
$p =$	67.17	65.10
$H_1 =$	753.62 mm.	752.68 mm.
$T_1 =$	99.76°	99.73°
Whence $100 \delta =$	0.002291	0.002385
$c =$	0.10 mm.	0.10 mm.

I have brought together in a single table the results obtained by this method with different gases.

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	BULB	H	H'	h + c	P'	P	T	1 + 100 α	MEAN
1. Nitrogen.....	VI	760.19	759.49	193.89	70.48	4926.4	100.00°	1.36675	—
	VI	761.87	760.56	194.16	67.93	"	100.07°	1.36686	—
	VIII	765.73	765.28	196.43	57.00	4250.0	100.22°	1.36685	1.36682
2. Oxygen.....	VIII	755.67	756.14	193.99	58.75	4250.0	99.84°	1.36692	—
3. Hydrogen.	VII	756.27	756.47	198.04	28.49	4357.0	99.86°	1.36682	—
	VIII	758.94	759.26	194.09	64.16	4250.0	99.97°	1.36677	—
	VII	759.21	761.24	199.81	95.44	4357.0	99.97°	1.36662	1.36678
4. Oxide of Carbon.....	VIII	767.91	767.76	197.29	56.65	4250.0	100.29°	1.36647	—
	VII	767.81	767.95	202.21	24.30	4357.0	100.29°	1.36686	1.36667
5. Carbonic Acid.....	VI	754.73	754.05	194.21	59.17	4926.4	99.80°	1.36844	—
	VI	749.47	746.28	191.11	54.84	"	99.61°	1.36981	—
	VI	745.18	744.60	189.95	73.55	"	99.44°	1.36913	—
	VI	749.52	748.77	191.05	72.07	"	99.61°	1.36848	1.36896
6. Cyanogen.....	VIII	758.62	758.86	194.22	65.22	4250.0	99.95°	1.36792	—
	VII	758.97	759.16	196.84	49.50	4357.0	99.96°	1.36850	1.36821
7. Protoxide of Nitrogen.....	VIII	759.62	765.10	198.40	75.07	4250.0	99.99°	1.36768	—
	VI	760.16	765.47	204.10	37.82	4926.4	100.00°	1.36780	—
	VII	765.46	765.11	197.80	50.05	4357.0	100.20°	1.36742	1.36763
8. Sulphurous Acid.....	VI	757.16	756.71	197.82	32.60	4926.4	99.89°	1.36738	—
	VIII	752.89	752.02	190.86	64.82	4250.0	99.73°	1.36667	—
	VII	752.49	751.82	195.41	31.60	4357.0	99.72°	1.36645	—
	VI	751.95	753.22	202.14	39.10	4926.4	99.70°	1.36734	1.36696
9. Hydrochloric Acid Gas.....	VIII	763.03	759.30	193.50	51.82	4250.0	100.11°	1.36800	—
	VII	762.94	759.04	195.45	37.65	4357.0	100.11°	1.36825	1.36812
10. Ammonia.....									

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I shall add a few words upon the way in which each gas was prepared.

1. *Nitrogen*.—This gas was obtained by removing the oxygen of the air by passing it through a glass tube filled with copper turnings¹ heated to redness. This tube was connected with the tubulure of the pump. The bulb having been exhausted, the tap is opened little by little; the air in passing over the hot copper loses its oxygen and, later, gives up its moisture in the drying tubes.

2. *Oxygen*.—I made many experiments upon oxygen gas, but they yielded figures so various that it was impossible to reach any decision from them. Mercury cannot be left in contact with oxygen gas, even for a very short time, without absorbing a small amount of the gas: its surface soon gives evidence of mercury oxide and leaves a trail on the glass tube.

The same thing is noticed with mercury which is left in contact with the air, but the change in this case is much slower, requiring a period of several weeks to become appreciable.

The oxygen was prepared by heating potassium chlorate.²

3. *Hydrogen*.—This gas was prepared by treating zinc with dilute sulphuric acid; before entering the pump and the drying apparatus, it was passed through two tubes, a meter long, filled with pumice stone moistened with a solution of caustic potash, and a third tube filled with pumice stone moistened with a solution of silver sulphate. The gas was entirely without odor. The introduction of the two tubes of pumice soaked in a solution of potash is chiefly to hold back the small quantity of odorous oily vapor which hydrogen gas always takes with it and which is sufficient to change appreciably the expansibility of the gas. In fact, in one experiment where the hydrogen gas passed merely through a wash bottle containing water, I found for its coefficient of expansion the figure 0.3686;

¹ The copper turnings were first oxidized by heating in the presence of air, then reduced by a current of hydrogen gas.

² Note by Translator: It seems likely that Regnault's oxygen was not pure—possibly contained chlorine, or oxides of chlorine; v. Jolly states that oxygen carefully prepared from potassium chlorate, or electrolytically, is entirely without action on mercury at the temperature of the experiment.

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a second determination in which the wash bottle contained potash-solution, gave the figure 0.3679.

4. *Oxide of Carbon*.—Prepared by decomposing oxalic acid in the presence of concentrated sulphuric acid: the gas was passed through a flask containing a solution of caustic potash to absorb the carbonic acid, then through a long tube filled with pumice stone moistened with potash solution; from this it passed into the drying apparatus.

5. *Carbonic Acid*.—Obtained by the decomposition of white marble with dilute hydrochloric acid. The gas passed through a wash bottle containing water and thence into the drying apparatus.

6. *Cyanogen*.—This gas was prepared through the decomposition by heat of cyanide of mercury contained in a small glass retort; it passed through a flask provided with a safety tube and filled with concentrated sulphuric acid, which serves to regulate the flow of the gas.

7. *Protoxide of Nitrogen*.—The protoxide of nitrogen was prepared by decomposing with the aid of heat ammonium nitrate contained in a retort. The gas, before entering the drying tubes, passed through a wash bottle containing a solution of protosulphate of iron [ferrous sulphate].

8. *Sulphurous Acid*.—This gas was prepared by heating mercury with concentrated sulphuric acid. The gas passed through a wash bottle containing concentrated sulphuric acid, then the usual drying apparatus.

9. *Hydrochloric Acid Gas*.—Obtained by treating sea salt with concentrated sulphuric acid; it was passed through a flask containing concentrated sulphuric acid, then through two tubes full of pumice stone soaked with sulphuric acid.

The experiments upon hydrochloric acid gas present nothing out of the way. The mercury retained its brilliant surface. I cannot have entire confidence, however, in the results obtained. In fact, mercury is apparently not attacked by hydrochloric acid gas by itself, but it is very quickly [attacked] as soon as the gas is mixed with oxygen. It is conceivable that a few thousandths of air, mixed with the hydrochloric acid gas in the bulb, would serve to bring about a very perceptible

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absorption of gas and in consequence to interfere with the expansion.

10. *Ammonia Gas*.—Prepared by gently heating a concentrated aqueous solution of the gas. It passed through a tube a meter long, filled with caustic potash broken in small pieces.

Ammonia gas yielded most various figures. The mercury seemed to be greatly changed at the surface: it left a trail: there had evidently been an absorption of gas; but it has been impossible for me to determine the chemical reaction which took place.

I found in succession the figures 0.370, 0.371, 0.373, according as the gas had remained a longer or shorter time in contact with the mercury.

It will be seen in the table above that nitrogen, hydrogen, oxide of carbon have practically the same coefficient of expansion as air, under the conditions when the determinations were made, that is to say, the gases being under atmospheric pressure when they are at the boiling point of water, and under a pressure of about 550 millimeters when they are at the melting point of ice.

Carbonic acid, protoxide of nitrogen and cyanogen, on the contrary, show under the same circumstances a greater coefficient of expansion.

Sulphurous acid gas gave figures a little higher than those obtained for the above gases; but the difference is so small that one does not know whether it may not be due to the inevitable errors of experiment.

I do not discuss hydrochloric acid gas, since I look upon the numbers obtained for this gas as doubtful.

My experiments therefore seem to show that gases do not have, under the same conditions, exactly the same coefficient of expansion. This coefficient varies for the gases I have examined, and with the conditions under which the determinations were made, from 0.3665 to 0.3685.

This variation cannot be attributed to the fact that, at the temperature of melting ice and under a pressure of 0.555 m., certain of these gases are close to their point of condensation; for sulphurous acid is, of all these gases, the easiest to liquefy

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and yet its coefficient of expansion is smaller than that of carbonic acid which at 0° is still removed by more than 90° from its condensation point.

This modification, which must be made in one of the most beautiful laws of physics, seemed to me too important for me not to endeavor to support it by other determinations.

I began by making several experiments with Method IV, using exactly the same apparatus as had been used for air.

For carbonic acid gas I obtained the following results:

First Half.

	<i>H</i>	<i>T</i>	<i>t</i>	<i>H'</i>	<i>h'</i>	<i>t'</i>	$1+100\alpha$
1	756.52	99.87°	13.4°	755.47	200.58	13.0°	1.36831
2	757.54	99.91°	12.9°	758.02	202.55	11.7°	1.36857
Mean =							1.36844

Second Half.

	<i>H''</i>	<i>t''</i>	<i>H'''</i>	<i>T'''</i>	<i>h'''</i>	<i>t'''</i>	$1\ 100\alpha$
1	758.47	11.8°	758.80	99.95°	275.67	14.8°	1.36846
2	758.47	11.8°	759.10	99.97°	275.51	14.1°	1.36866
Mean =							1.36856

These determinations give at least nearly the same figure as that found by Method II.

An experiment made with protoxide of nitrogen gave :

FIRST HALF.

SECOND HALF.

$$H = 747.03 \text{ mm.}$$

$$H'' = 747.72 \text{ mm.}$$

$$T = 99.52^\circ$$

$$t'' = 3.6^\circ$$

$$t = 4.2^\circ$$

$$H''' = 748.49 \text{ mm.}$$

$$H' = 748.08 \text{ mm.}$$

$$T''' = 99.57^\circ$$

$$h' = 198.39 \text{ mm}$$

$$h''' = 269.73 \text{ mm.}$$

$$t' = 3.6^\circ$$

$$t''' = 3.9^\circ$$

$$1+100\alpha = 1.36701$$

$$1+100\alpha = 1.36797$$

$$\text{Mean} = 1.36749$$

The mean given by the determinations described above and made by Method II, is 1.36763.

We have seen that Method II gave for the coefficient of expansion of sulphurous acid a figure practically identical with that found for air. I wished to find out whether this coefficient would not become larger when working under greater pressures.

An experiment made with sulphurous acid by Method IV, gave :

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FIRST HALF.

$H = 742.08 \text{ mm.}$
 $T = 99.33^\circ$
 $t = 5.6^\circ$
 $H' = 742.31 \text{ mm.}$
 $h' = 196.64 \text{ mm.}$
 $t' = 4.5^\circ$

$1+100 a = 1.36689$

SECOND HALF.

$H'' = 742.49 \text{ mm.}$
 $t'' = 5.3^\circ$
 $H''' = 742.85 \text{ mm.}$
 $T''' = 99.36$
 $h''' = 267.64 \text{ mm.}$
 $t''' = 6.6^\circ$

$1+100 a = 1.36777$

The figure obtained in the first half of the determination is identical with that found in the experiments made by Method II, whereas that given by the second half, that is, under greater pressures, is notably greater.

A second trial was made by subjecting the sulphurous acid to a little more than atmospheric pressure when the gas was at 0° . The bulb was surrounded with ice and the side tube put in communication with the apparatus generating sulphurous acid gas, when the mercury was run out by opening the tap, so as to let the tube FH become entirely filled with sulphurous acid gas. The tube p was then sealed with a lamp. Mercury was poured into the tube G , so as to bring the level to a in the tube FH . A difference of level h is then noted between the two menisci. The ice was removed and the bulb raised to the boiling point of water, as in the ordinary determinations. We thus have :

$H \dots\dots\dots 743.59 \text{ mm.}$
 $t \dots\dots\dots 5.6^\circ$
 $h \dots\dots\dots 28.69 \text{ mm.}$
 $H' \dots\dots\dots 743.92 \text{ mm.}$
 $T' \dots\dots\dots 99.40^\circ$
 $h' \dots\dots\dots 308.22 \text{ mm.}$
 $t \dots\dots\dots 6.1^\circ$
 $1+100 a \dots\dots\dots 1.36907$

Finally, a third determination was made subjecting the gas to a much higher pressure still. For this the tube FH was replaced by another, the lower part of which had a much greater volume. This tube is shown in *Fig. 15* [page 101].

Working exactly as in the second determination, we find :

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$H = 764.77$ mm.	$H' = 764.64$ mm.
$t = 5.9^\circ$	$T' = 100.17$
$h = 136.29$ mm.	$h' = 469.71$ mm.
	$t' = 7.00^\circ$

$$\frac{v}{V} = .00336$$

whence

$$1 + 100\alpha = 1.37413.$$

Thus for sulphurous acid the results are :

The gas at 0° under a pressure of	At 100° under a pressure of	
545.67 mm.	742.08 mm.	1.36689
742.49	1010.49	1.36777
772.28	1052.14	1.36907
901.06	1234.35	1.37413

The coefficient of expansion of sulphurous acid therefore increases in a very marked way in proportion as the pressure to which the gas is subjected becomes greater. It is probable that the same thing takes place in all compound gases for which the law of volumes does not rigorously hold or which do not exactly follow Mariotte's Law.

A similar variation is to be noticed in carbonic acid gas, although in a much less decided way. We have seen that Method IV, applied to this gas, gave :

Pressure at 0°	At 100°	
554.89 mm.	756.52 mm.	1.36831
555.47	757.54	1.36857
758.47	1034.47	1.36846
759.10	1034.61	1.36866

The difference is not noteworthy. But an experiment made with the modified apparatus which I have described, gave :

$H = 766.32$ mm.	$H' = 766.14$ mm.
$t = 6.4^\circ$	$T' = 100.23^\circ$
$h = 134.77$ mm.	$t' = 6.4^\circ$
	$h' = 464.23$ mm.

$$\frac{v}{V} = 0.00336.$$

$$1 + 100\alpha = 1.36943.$$

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Thus, at 0° under a pressure of 901.09 mm. and at 100° under a pressure of 1230.37, the coefficient of expansion of carbonic acid gas is distinctly higher.

I have constructed an apparatus by means of which one may at once detect unequal expansion in gases and which may serve to measure this difference with accuracy. This apparatus, which is a kind of differential thermometer, consists of two bulbs of equal capacity, complete with capillary tubes and arranged exactly like the bulb of Method IV (Fig. 13), [page 96]. Each of these bulbs connects with a tube similar to the tube *FH* of Figs. 13 and 14, cemented into a three-way tube of iron provided with a tap, Fig. 16. The third branch, in the

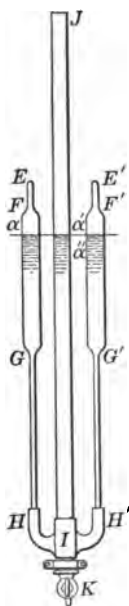


FIG. 16.

middle, holds a piece of barometer tubing. The two tubes *FGH* and *F'G'H'* were cut from the same accurately cylindrical piece of tubing and have exactly the same shape; they are fixed as alike as possible in the tubulures. One of the bulbs is filled with dry air and the other with the gas whose expansibility it is desired to compare with that of air. Moreover, the bulbs are fastened in the same tin vessel.

The bulbs being surrounded with melting ice, and the mercury having been adjusted to the level of a mark scratched on one of the tubes, the two side tubes *op* are closed with a lamp. The mercury is then of necessity at the same level in the two tubes *FGH* and *F'G'H'* and in the upright tube between them. The ice having been removed and water put in the tin vessel, the latter is brought to boiling while mercury is poured into the intermediate tube to keep the level at the same point in the tube *FGH*. If the two gases have the same coefficient of expansion, the two menisci in the tubes *FGH* and *F'G'H'* will be at the same level; there will be a difference of level, on the other hand, if the [rates of] expansion are unequal.

It would be very difficult to find two bulbs of exactly the same capacity when they are sealed to their capillary tubes,

EXPANSION OF GASES

and also so to arrange the tubes FGH and $F'G'H'$ that the volume of air contained in the upper part of these tubes should be exactly equal when the mercury is at the same level and adjusted to the mark made on one of them. Yet this is not necessary; it will, in fact, serve if the ratio $\frac{v}{V}$ is the same for the two pieces of apparatus. It will do, indeed, for this to take two bulbs of nearly the same volume and gauge them carefully by means of distilled water, after they have been attached to their capillary tubes. In the same way the tiny volume in the part F_a of the tube FGH as far as the mark a , is measured by means of mercury; on the other tube $F'G'H'$ are made two marks, a' and a'' , and the volume up to a' and that between the two marks a' and a'' , are calibrated by means of mercury.

This done, we know the ratio $\frac{v}{V}$ for the first bulb, and the volume V' of the second bulb; then v' must be equal to $\frac{v}{V} V'$. It is easy to find the point on the tube $G'H'$ which corresponds to this volume v' ; its distance d from the mark a' is then calculated.

The tube FGH being cemented in its tubulure and the apparatus fastened to its vertical support, the tube $F'G'H'$ is fixed in the place where it belongs. For this purpose, the level of the mark a upon the tube FGH is found with the cathetometer, and the glass is then turned towards the tube $F'G'H'$. If the latter tube is in the proper position, the crossing of the threads of the glass should be aiming at the point which corresponds to the volume v' ; consequently the mark a' should be at a distance d above or below; by means of the instrument we find whether this is in fact the case, that is, the glass is raised or lowered by an amount d , and the tube $F'G'H'$ is adjusted so that the mark a' is hidden by the horizontal thread of the glass in its new position; then the tube is fastened in place with mastic.

To make sure that the differential apparatus is properly adjusted, an experiment is made, filling both bulbs with dry air. The two side tubes op are closed when the bulbs are in melting ice and the mercury has been brought to the level of a

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in the tube FGH . The three columns of mercury are then at the same level. Water is then put in the boiler and the level of the mercury is kept at a ; the mercury must be at exactly the same height in $F'G'H'$ if the apparatus is properly put together.

The results reached by this method are rendered still more certain by performing a second experiment in which the gas whose expansibility we wish to determine, is introduced into the bulb which has hitherto held the air, while, on the other hand, atmospheric air is put in the bulb which in the former experiment contained the gas.

The equation which gives the expansibility of the gas in the case of this apparatus is clearly

$$1 + \alpha T = \frac{(H''' + h'')(1 + \delta T)}{H'' - \frac{v}{V} \left(\frac{1}{1 + \alpha t} \right) (H''' + h''' - H'')},$$

the symbols having the same meaning as on page 100.

If we differentiate with respect to α and h''' , bearing in mind that the factor $\frac{v}{V} \frac{1}{1 + \alpha t} (H''' + h''' - H'')$ is very small and may be supposed constant and equal to k , we have

$$\frac{d\alpha}{d h'''} = \frac{(1 + \delta T)}{H'' - k} \frac{d h'''}{d h''};$$

we can then write it simply

$$\Delta \alpha = \frac{\Delta h'''}{H''}$$

That is, the difference in the coefficients of expansion of the two gases is equal to the difference in the levels of the columns of mercury in the two tubes FGH and $F'G'H'$, divided by the barometric height at the time the two tubes were sealed when the bulbs were in melting ice.

This result is not however altogether accurate, since we have taken no account of the variation of the ratio $\frac{v}{V}$ — which is not the same at 100° as at 0° — for the gas which does not expand at the same rate as air. But when the difference in the ratio of expansion is very slight, the error introduced by this omission is practically inappreciable. On the other hand, it is easy to take it into account.

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A test determination made by this method with carbonic acid gas and atmospheric air, gave

$$\Delta h''' = 1.48 \text{ mm.}, H'' = 757.20;$$

hence

$$\Delta \alpha = \frac{1.48 \text{ mm.}}{757.20} = 0.002 \text{ (about);}$$

that is, the coefficient of expansion of carbonic acid gas is 0.002 higher than that of air—which gives 0.3685; and this, in fact, is the figure which we found above [page 113].

To prove the accuracy of the differential apparatus, I filled both bulbs with dry air; I then found

$$\Delta h''' = 0.08 \text{ mm.}$$

This difference is probably due to the fact that the tubes were not quite perfectly adjusted, but it is entirely inappreciable.

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BIOGRAPHICAL SKETCH.

Henri Victor Regnault was born at Aix la Chapelle in the year 1810, July 21. He was educated at the École Polytechnique and the École des Mines. He became Gay-Lussac's successor as Professor of Chemistry in the former institution in 1840, and, the next year, Professor of Physics in the Collège de France. Up to this time his researches were confined to organic chemistry: an important paper on the ethers appeared in 1835. From 1847 to 1854 he was Chief Engineer of Mines, and subsequently became director of the famous porcelain works at Sèvres. From 1841, for over twenty years, he published the results of research after research upon the physical constants of gases, of liquids and of solids. In this extraordinary series are to be found investigations of the compressibility of gases, liquids and solids; of their densities, and rates of expansion; of the tension of vapors; of calorimetric methods; of the latent heat of substances; of their specific heat, etc., etc. In addition, may be mentioned contributions to the mechanical theory of heat and study of the velocity of sound. All the records of his latest work were, to his great sorrow and to the loss of the scientific world, destroyed during the Franco-Prussian War. His scientific labors ended in 1872, but he lived until Jan. 19, 1878. Regnault's great reputation rests upon his extraordinary skill in devising and using apparatus. It may be said that in whatever direction his researches led him, he invariably succeeded in discovering sources of error in the work of his predecessors and in eliminating it, at least in large measure, from his own results.

RESEARCHES UPON THE EXPANSION
OF GASES.

BY HENRI VICTOR REGNAULT.

Second Memoir.

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RESEARCHES UPON THE EXPANSION OF GASES.

BY M. VICTOR REGNAULT.

Second Memoir.

IN a former treatise (*Annales de Chimie et de Physique*, 3d Series, volume IV, page 5), I discussed the determination of the coefficients of expansion of air and of some other gases between the fixed points of the thermometer and under pressures little removed from that of the atmosphere. The various methods of experimentation employed, speaking generally, show one point in common: the expansions were not measured directly, but were calculated from the changes in the tension. In this second memoir I propose:

I. To complete the earlier researches and to study the rate of expansion of gases between the same limits of temperature but under very diverse pressures, by the use of analogous methods, that is, those based upon the measurement of the variations of the tension which a given volume of gas shows when its temperature rises from 0° to 100° ;

II. To examine the same subject in a direct way by an entirely different method, in which we measure at once the increase of volume which a rise of temperature from 0° to 100° produces in a given quantity of gas subjected all the time to the same pressure.

FIRST PART.

On the Rate of Expansion of Gases under Various Pressures, Calculated from the Changes in the Tension.

Physicists generally assume that the rate of expansion of gases is constant between the limits of temperature mentioned, whatever the pressure to which the gases are subjected; consequently, that it is entirely independent of the original density of the gas. Yet it is difficult to cite any conclusive experiments upon which this law may be based. Many observers

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have obtained the same figure for the coefficient of expansion of air under various barometric pressures, and have from this fact concluded that the coefficient of expansion of gases remains constant under all pressures. Yet the barometric variations in any given place are within limits too narrow to permit of drawing so general a conclusion from such observations; they only prove that, for slight variations of pressure, the changes in the coefficient of expansion of air are inappreciable.

H. Davy is the only physicist who has studied the expansibility of gases under very varied pressures (*Philosophical Transactions*, 1823, volume II, page 204). He states that he found the expansion for air at the densities $\frac{1}{2}$, $\frac{1}{3}$, $\frac{1}{4}$, 1 and 2. Yet the determinations were not made by a method exact enough for us to consider their results as sufficiently accurate.

I have made experiments upon air under pressures much lower than that of the atmosphere and, again, others under pressures far greater.

Experiments under Pressures less than the ordinary Barometric Pressure.

These determinations were carried out by Method IV (*Annales de Chimie*, volume IV, page 38 [above, page 96]), and by means of the apparatus shown in *Figs. 13 and 14* [page 96]; greater length, however, is given the tube *FGH*—about 770 millimeters from the tubulure *H* up to the mark *a*. After placing the bulb in the vapor of boiling water and connecting it, on the one hand, with the drying apparatus by means of the side tube *op* and, on the other, with the tube *FGH* which is cemented with mastic into its copper tubulure *n*, it is exhausted a great many times, and the air allowed each time to enter again very slowly: the tubes *FH* and *IJ* contain enough mercury for a vacuum to be produced in the bulb without the mercury rising above *F* in the tube *FH*. When the apparatus is completely dried out, the amount of air we wish to experiment with is admitted; its density being determined by the difference of level of the two columns of mercury. The side tube *op* is then sealed with a lamp and the drying apparatus removed.

By pouring mercury into the tube *IJ*, the level in the tube *FH* is adjusted at the mark *a*, the bulb being all the time in

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the vapor of boiling water; by means of the cathetometer the difference of level of the two columns is read, and at the same time the barometric height is recorded.

The furnace *O* is then removed, the hot water in the vessel *M* is drawn off and, when the latter has become quite cold, the bulb *A* is surrounded with crushed ice. Mercury is drawn off by opening the tap *K* so as to maintain the mercury level at the point *a* in the tube *FH*. When temperature equilibrium has once more been established, the difference of level of the mercury columns is measured, as well as the barometric height.

Several determinations were thus made with the same specimen of air, having the bulb successively in the vapor of boiling water and in melting ice. They were performed in some cases after several days' interval; in this way it was easy to decide whether the apparatus was perfectly gas-tight.

I have brought together in a single table the determinations made of the rate of expansion of air under pressures lower than that of the atmosphere; those that were made upon the same specimen of air are comprised in a single series.

I used the same bulb as in my earlier experiments (volume IV, page 42 [page 88, above]), but the tube *FH* of the old apparatus was replaced in Experiments II, III, IV, and V, by another of greater height.

For Series I, we have

$$\frac{v}{V} = \frac{26.85}{9889.9} = 0.00272,$$

and for Series II, III, IV and V,

$$\frac{v}{V} = \frac{29.0}{9889.9} = 0.00293.$$

The formula which serves for the calculation of the experiment is the following:

Representing by *H'* the barometric height at the time when the experiment is carried out in [the vapor of] boiling water, *T* the temperature of the vapor,

h' the difference of level of the mercury columns,

t' the temperature of the minute air-volume *v*,

H, *h*, *t*, the corresponding quantities when the experiment is conducted in melting ice;

We then have:

$$1 + \alpha T = \frac{(H' - h')(1 + \delta T)}{(H - h) - \frac{v}{V} \frac{1}{1 + \alpha t} [H' - h' - H + h]}$$

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We have assumed that $t' = t$.

The heights H , h , H' , h' have been reduced to 0° by calculation.

In the calculation of the determinations the same figure for melting ice has been combined with several results for boiling water, made before and after, to eliminate the extreme values.

Table of Experiments made upon Air under Pressures lower than that of the Atmosphere.

Number of Series of Experiments.	H m.	t	h mm.	$H-h$ mm.	H' mm.	T'	t'	h' mm.	$H'-h'$	$1 + 100 a$	MEAN
I	763.68	9.4°	388.48	375.20	763.04	100.14°	18.5°	252.89	511.05	1.36605	
	763.68	11.4	388.36	375.27	763.54	100.13	12.5	252.65	510.89	1.36540	1.36572
II	764.79	11.9	390.12	374.67	764.89	100.18	12.8	254.53	510.36	1.36609	
	764.79	11.9	390.12	374.67	767.79	100.29	9.4	257.44	510.35	1.36566	1.36587
III	757.47	8.2	491.32	266.15	757.52	99.90	8.8	395.47	362.05	1.36525	
	756.88	9.3	490.91	265.97	756.53	99.87	10.7	394.66	361.87	1.36560	1.36542
IV	756.13	9.3	581.70	174.43	756.13	99.85	10.4	518.96	237.15	1.36469	
	756.13	9.3	581.70	174.43	756.04	99.85	10.0	518.86	237.18	1.36487	
V	760.56	6.6	586.35	174.21	760.91	100.04	7.8	523.74	237.17	1.36588	1.36513
	761.14	8.3	651.50	109.64	761.14	100.04	8.6	611.81	149.33	1.36639	
	761.19	7.6	651.49	109.70	760.92	100.03	9.5	611.71	149.21	1.36459	
	761.18	8.8	651.55	109.63	761.09	100.04	9.9	611.89	149.20	1.36535	
	761.24	8.6	651.61	109.63	761.14	100.04	9.9	611.92	149.21	1.36554	
	765.87	8.8	656.08	109.79	765.57	100.21	9.0	616.18	149.39	1.36448	
	765.82	9.2	656.07	109.75	765.64	100.21	9.6	616.33	149.31	1.36425	
	765.87	8.8	656.08	109.79	765.64	100.21	9.6	616.33	149.31	1.36376	
	765.82	9.2	656.07	109.75	765.57	100.21	9.0	616.18	149.39	1.36498	
	765.87	8.8	656.08	109.79	765.64	100.21	11.9	616.28	149.36	1.36421	
	765.82	9.2	656.07	109.75	765.64	100.21	11.9	616.28	149.36	1.36471	1.36482

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This table shows clearly that the coefficient of expansion of air continues to decrease with the pressure.

It is noteworthy that, in the several experiments made upon the same specimen of air, greater variations are recorded than in those made under atmospheric pressure. Thus, in Series V, which comprises determinations made under very low pressures, the extremes are 1.36376 and 1.36639; difference, 0.00263. The reason for this is simple; the same error made in the reading of one of the heights H , H' , h , or h' , of necessity produces much more considerable variations in the final result, the lower the pressures. It is only by a great many determinations arranged so as to eliminate extreme figures, and by taking into account all results that were obtained, that it has been possible to prove the existence of the law stated above.

Experiments under Pressures greater than the ordinary Barometric Pressure.

The apparatus [shown in] Volume IV, *Fig. 13 and 14* [page 96] serves very well for experiments under pressures higher than the atmospheric, when modified as follows:

The tube IJ is replaced by a much longer glass tube held fast to a wall by numerous supports throughout its length. Instead of the straight side tube op , there is cemented into the tubulure o a tube of the form shown in *Fig. 1* and consisting of a bent capillary tube abc of which the portion ab is horizontal, and of a larger tube cd sealed to the capillary tubing and vertical in position. The latter connects with a large tube LL' containing pumice stone moistened with concentrated sulphuric acid: for this purpose, the ends of the two tubes are brought together inside the little cover tube of copper which is then covered all over with gum mastic. The tube LL' can be connected by means of a rubber tube with a small air pump or cemented into the tubulure t of a condensing pump.

A number of pellets of gum mastic are put in the tube cd .

This being arranged and the bulb being in the vapor of boiling water, the apparatus is exhausted many times for the purpose of drying it completely, then the vacuum pump is replaced by the condensing pump; dry air is slowly forced into the bulb

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and, at the same time, mercury is poured into the tube *IJ*. Some minutes are allowed to elapse between consecutive strokes of the piston, in order to let the air remain some time in contact with the sulphuric acid in the pumice stone before it makes its way into the bulb.¹ When it is seen by the difference

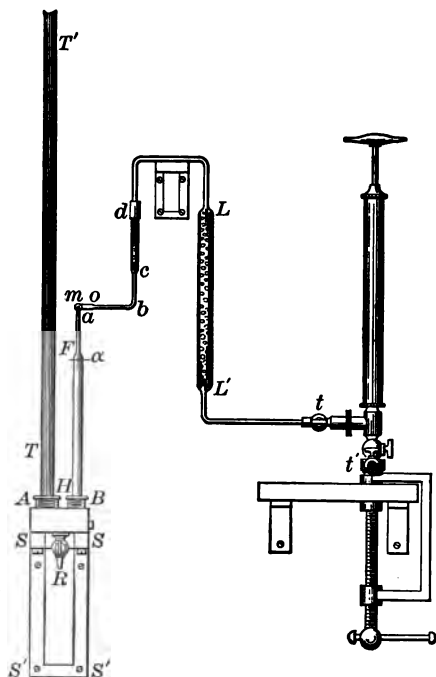


FIG. 1.

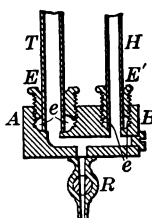


FIG. 2.

of height of the mercury columns, that the air in the bulb is at the desired density, the small pellets of gum mastic contained in the tube *cd* are melted with the aid of an alcohol lamp, and at the same time the tap *K* is opened a little; the

¹ It is even more necessary in the case of determinations made under high pressures than of those under low, that the air admitted to the bulb should be perfectly dry. To secure this result to a certainty, care is taken to fit a second tube of pumice stone and sulphuric acid to the tubulure *t'* of the condensing pump, so that the air introduced comes into the pump already well dried.

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mercury which runs out lowers the tension within enough to cause a short column of melted gum mastic to make its way into the capillary tube cb , where it solidifies. The same end is manifestly reached by forcing in more air by means of the condensing pump. The apparatus is now hermetically sealed at c , when the gum mastic becomes cold; the tube LL and the condensing pump can then be removed.

The determination proceeds as usual; only, since the columns to be measured are very long, they cannot be brought within the range of a single cathetometer. I have therefore used in these experiments two cathetometers at one time, each of 1 meter's range. One of these instruments served to determine the distance of the meniscus in the tube FH down from a mark r made upon the tube IJ at about 800 millimeters above the mark a . The other cathetometer, fixed upon a very steady base which the observer does not touch, serves to measure the distance from the meniscus in the tube IJ down to another mark r' made upon this same tube. When the distance rr' is greater than 1 meter, other marks are put upon the same tube in the interval, separated by about 900 millimeters. All these distances were each time determined with the greatest care by means of cathometers, before the experiment was begun and again after it was finished.

The meniscus, in the tube FH was adjusted in each experiment approximately to coincide with the mark a on the tube: since it is rather difficult to adjust such long columns of mercury, I did not attempt each time to make the coincidence perfect; I preferred to secure it only approximately and to take account of the variation in the minute volume v , from the position of the meniscus with respect to the mark a ,—which was made easy by a previous calibration of the tube.

The mercury column was protected from radiated heat by a wall of several planks on top of one another: the temperature was determined by means of three thermometers with very large bulbs, placed at different points along its length. The mean of the readings of these thermometers was taken as the temperature of the mercury column.

By means of the apparatus thus arranged I was able to

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make determinations up to a pressure of about four atmospheres. The bulb was no longer that which had served for the previous experiments; that was of too thin glass and probably would not have withstood so great a pressure. I chose a thicker glass bulb and one of somewhat smaller diameter; it held 6786.5 grams of mercury at 0° .

In order to make observations at yet higher pressures, I was compelled to resort to a new arrangement. I was unable to procure glass tubing in single pieces of more than three meters in length, and moreover I was afraid that a glass tube of greater dimensions would not withstand the pressure and would give way at the lower end. I had recourse to the following apparatus (*Fig. 1*) [page 128]:

An iron tube, about three meters in length, is fitted into the tubulure *A* of an iron vessel provided with a tap (*Fig. 1, 2*);¹ it is fastened in this tubulure by means of a packing of linen greased with tallow, which is forced into the annular space around the tube by means of the screw cap *E*.

In the second tubulure *B* is fixed in the same way the glass tube *FH*. The iron vessel *ABR* is firmly fastened by a support *SS'* fixed upon a vertical wall. The iron tube is arranged exactly vertical; its upper end is made wider and is provided with a screw-thread, and in this is fitted a glass tube about 2 meters in length with the aid of a packing of linen greased with tallow and a screw cap. The iron tube and the glass tubing which it carries have an interior diameter of 14 to 15 millimeters.

The bulb with the vessel that contains it is placed in a neighboring room, separated from the first by the wall upon which the vertical iron tube is fastened. This wall is pierced with a hole through which the capillary tube of the bulb is passed before it is cemented into the copper three-way tube *mno*. The side tube *mo* carries a small bent tube *abcd* containing pellets of gum-mastic, and is connected with the condens-

¹ *Fig. 2* shows a vertical section of the vessel *ABR* on a scale double that of *Fig. 1*. All the figures are $\frac{1}{10}$ actual size, except *Fig. 2* and 4 of this memoir [see page 138] which are $\frac{1}{2}$ actual size.

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ing pump by means of the tube *LL* full of pumice stone moistened with sulphuric acid.

The determination is in other respects carried out exactly as with the former apparatus: the two menisci are followed with two cathetometers. The instrument which follows the meniscus of the long column is placed on an upper floor, through the planking of which the iron tube passes.

The tubes bear marks at chosen distances which have been measured with the greatest care by means of one of the cathetometers placed for this purpose upon high supports made as firm as possible and upon which the observer does not rest. The very sensitive spirit level of the cathetometer, moreover, enables one easily to judge if the condition of steadiness is satisfactorily secured.

Mercury thermometers with large bulbs are arranged along the mercury column and indicate its temperature.

The bulb used in these determinations was one of thick glass which I had blown for me at the glass works of Choisy-le-Roi. The walls of the bulb were about 3 millimeters thick and were practically uniform throughout. The coefficient of expansion of this bulb was determined from another smaller one, blown at the same time, of the same material, and having almost the same thickness of glass; it was found to be 0.002130 between 0° and 100°. ¹

The bulb used in the experiments on the rate of expansion of gases held 5864.45 gr. of mercury at 0°, apart from the capillary stem.

Finally, there is a factor which we must know in order to be able to calculate the rate of expansion of air from the results of experiment: this is the increase in the capacity of the bulb through the variation in the pressure upon the gas at 0° and at 100°. This variation would be difficult to determine perfectly accurately, but it is easy to obtain an approximate figure.

To this end the bulb was filled with water to within a short distance from the end of the capillary stem, and this end was then

¹ The data of this determination are the following:

$P = 1265.647$ gr.

$H_1 = 763.50$ mm.

$p = 19.783$

$T_1 = 100.13^\circ$

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cemented into a bent glass tube, whose long vertical arm was open. If it was desired to determine the changes of volume for slight pressures, mercury was poured into the open end: the air compressed in the other arm exerts pressure upon the water surface in the capillary tube. The increase in the capacity of the bulb is gauged by the movement of the water meniscus in the capillary tube, and the pressure by the difference of level of the mercury columns. The bulb was immersed in a vessel of water at the ordinary temperature, to render inappreciable the volume-changes due to variations of temperature.

Below are some data obtained with the bulb which was used in the determinations of page 56 [page 126] and in those of the former memoir, page 42, volume IV [page 88]:

Under a pressure of	The capacity increased by
227.7 mm. of mercury	0.000054
436.5 “	0.000103
687.8 “	0.000160

Evidently the capacity increases with the pressure; yet this increase of volume is so slight that it may be completely neglected in experiments made upon the expansibility of gases under atmospheric pressure. The change in the capacity of the bulb is actually still less than is here indicated, for in the experiment described the apparent change was composed not only of the increase in the volume of the glass bulb, but also of the decrease in volume of the water; I have entirely neglected the latter and have ascribed the whole change observed to the variation in the bulb's capacity.

For studying the increase in the volume of the bulb under higher pressures, I sealed a capillary tube of rather large bore to a thick glass bulb similar to that of the experiments described on page 61 [page 131]. This bulb was completely filled with water and connected with a condensing pump and a small air-manometer; in this way I obtained the following results:

Under an increase of pressure of	The volume changed by	Under an increase of pressure of 1 meter [of mercury]
0.715 m.	0.0000740	0.0001035
1.814	0.0001940	0.0001069
3.035	0.0003288	0.0001083
4.178	0.0004538	0.0001086

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We shall assume 0.000108 [to be the increase produced] by a rise in pressure of 1 m. of mercury.

To obtain the increase of the capacity of the bulb we must subtract the amount the water is compressed for each meter's pressure, that is, about 0.000064, according to MM. Colladon and Sturm; this yields 0.000044 for the expansion of the bulb for an increase of pressure of 1 m. of mercury.

Thus to make the correction in our determinations, it will suffice to add to the coefficient δT of the expansion of the bulb by heat, the expansion produced by the rise of pressure, which is 0.000044 $\frac{H' + h' - H - h}{1000}$.

In the above experiments the change in the capacity of the bulb through an increase of pressure was determined at ordinary temperature; yet it is really its value at the temperature of 100° that we need to know in order to allow for it in our determinations of the rate of expansion of gases, and it might be objected that at 100° this change would not be the same. Yet it will be noted that this introduces a very minute correction which may be neglected since, at most, it changes the fourth decimal of the coefficient of expansion. Thus it may be assumed without inaccuracy that the compressibility of glass is the same at 100° as at the ordinary temperature.

The formula in accordance with which the determinations have been calculated is the following:

$$1 + \alpha T = \frac{(H' + h') \left(1 + \delta T + 0.000044 \frac{H' + h' - H - h}{1000} \right)}{H + h + \frac{v}{V} \frac{1}{1 + \alpha t} (H + h) - \frac{v'}{V} \frac{1}{1 + \alpha t'} (H' + h')}$$

The following table contains the results obtained with these two forms of apparatus.

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Table of Experiments made upon Air under Pressures greater than the Atmospheric.

H	t	h	$\frac{v}{V}$	$H+h$	H'	T'	t'	k'	$H'+k'$	$\frac{v'}{V}$	$1+100 a$	Mean
m m.	—	m m.	—	m m.	m m.	—	—	m m.	m m.	—	—	—
755.31	12.4°	923.13	0.00369	1678.44	755.23	99.82°	15.0°	1530.60	2283.83	0.00360	1.36734	1.36760
755.46	12.5	922.90	0.00367	1678.36	755.45	99.83	16.1	1530.89	2286.34	0.00371	1.36786	1.36760
756.67	12.8	935.87	0.00380	1692.54	756.61	99.87	15.6	1549.10	2305.71	0.00380	1.36777	1.36760
756.67	12.8	935.87	0.00380	1692.54	756.84	99.88	15.5	1549.64	2306.48	0.00371	1.36803	1.36760
756.89	13.6	935.50	0.00380	1692.39	757.09	99.89	15.4	1540.30	2304.39	0.00390	1.36824	1.36760
756.98	13.2	935.65	0.00383	1692.63	757.13	99.89	15.7	1549.21	2306.34	0.00380	1.36795	1.36800
759.21	15.4	1385.04	0.00372	2144.25	759.21	99.97	17.3	2164.61	2923.82	0.00380	1.36880	1.36894
759.23	15.1	1384.87	0.00372	2144.10	759.17	99.97	17.7	2165.09	2924.26	0.00380	1.36907	1.36894

APPARATUS II.											
748.26	9.2	2907.39	0.00183	3655.65	748.62	99.57	9.8	4242.03	4990.65	0.00184	1.37068
748.13	9.2	2907.37	0.00184	3655.50	748.65	99.57	9.7	4243.58	4992.23	0.00184	1.37116
748.30	9.2	2907.27	0.00183	3655.57	748.70	99.58	9.8	4243.50	4992.20	0.00164	1.37074
748.42	9.3	2907.09	0.00185	3655.51	748.76	99.58	9.8	4244.52	4993.28	0.00165	1.37104
											1.37091

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This Table shows that the coefficient of expansion of dry air increases in a marked way with the pressure, and consequently confirms the result already reached by the determinations, page 56 [page 126], made under pressures lower than that of the atmosphere.

Summing up, we have found the following figures for the value of the coefficient of expansion of air under various pressures :

Pressure at 0°.	Pressure at 100°	Density of air at 0°, that of air at 0° under a pressure of 760 mm. being taken as unity.	$1 + 100 \alpha$
109.72	149.31	0.1444	1.36482
174.36	237.17	0.2294	1.36513
266.06	395.07	0.3501	1.36542
374.67	510.35	0.4930	1.36587
375.23	510.97	0.4937	1.36572
760.00	1.0000	1.36650
1678.40	2286.09	2.2084	1.36760
1692.53	2306.23	2.2270	1.36800
2144.18	2924.04	2.8213	1.36894
3655.56	4992.09	4.8100	1.37091

The third column of the table comprises the densities of the gas at the temperature of melting ice ; it will be seen that these vary from 0.1444 up to 4.8100, that is, from 1 to 33.3, and for so great a change in density, the coefficient of expansion of the gas changes only from 0.3648 to 0.3709.

The above determinations therefore prove that the law assumed correct by physicists, viz., that air expands [on heating] the same fraction of its volume at 0°, whatever its density, is not accurate ; air expands, between the same temperature-limits, by amounts which are greater in proportion as the density of the gas is higher, or, in other words, as the molecules are closer together.

Similar determinations were made with carbonic acid gas by means of the two pieces of apparatus described : they gave the following results :

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	Apparatus I.		Apparatus II.	
H	759.94 mm.	760.03 mm.	757.69 mm.	757.79 mm.
t	14.5°	13.9°	11.3°	11.2°
h	982.75 mm.	982.74 mm.	2831.37 mm.	2831.19 mm.
v	0.00361	0.00362	0.00190	0.00190
\bar{v}				
$H+h$	1742.69 mm.	1742.77 mm.	3589.06 mm.	3588.98 mm.
H'	759.86	759.83	758.11	758.41
T'	100.0°	99.99°	99.93°	99.94°
t'	15.8	15.6	11.3	11.4
h'	1627.81 mm.	1627.95 mm.	4200.50 mm.	4201.05 mm. .
$H'+h'$..	2387.67	2387.78	4958.61	4959.46
v'	0.00366	0.00367	0.00190	0.00190
\bar{v}'				
$1+100\alpha$	1.37520	1.37525	1.38586	1.38609

Combining these results with those given in the earlier memoir, volume IV, pages 57 and 60 [pages 109 and 113], we have for carbonic acid gas :

Pressure at 0°.	Pressure at 100°.	Density of the gas at 0°.	1 + 100 α
758.47 m m.	1034.54 m m.	1.0000	1.36856
901.09	1230.37	1.1879	1.36943
1742.73	2387.72	2.2976	1.37523
3589.07	4759.03	4.7318	1.38598

It is evident that the rate of expansion of carbonic acid gas increases more rapidly with the pressure than does that of atmospheric air.

SECOND PART.

Experiments to determine the Rate of Expansion of Gases under Constant Pressure.

In all the experiments described up to the present the rate of expansion of the gas has been determined indirectly. We measure directly the increase in the tension which the gas, maintained at a constant volume, exerts by reason of the rise in temperature, and from this we calculate the rate of expansion on the basis of Mariotte's Law. Yet it may be objected that it has not been shown that this law is absolutely exact even for air, and, consequently, that the increments determined in the rates of expansion under different pressures may

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only point to the fact that Mariotte's Law is not rigorously true.

This objection does not seem to me to be justified, for several reasons. As a matter of fact Dulong and Arago did not in their brilliant research discover any constant variation even at pressures as high as 27 atmospheres, which in any case shows that, between the limits of pressure of 1 and 27 atmospheres, Mariotte's Law is practically exact; hence we may conclude that it would be rigorously accurate for differences of pressure as small as those observed in our researches on any given gas, at 0° and at 100° . It is clear that, were there a variation which such small differences of pressure could render evident in measurements of the rate of expansion, this variation would certainly be revealed in a very marked degree by the great differences of pressure in determinations made with as much care as those of the distinguished physicists I have named.

I should state, too, that my experiments were carried out under precisely those conditions which would be most favorable for exactness in Mariotte's Law, since it is the gas heated to the temperature of 100° —consequently, at the very time when it is farthest removed from its condensation point—that it is subjected to the greatest pressure.

Finally, it should be noted that, in the parallel determinations made upon the compressibility of different gases under one and the same pressure, it was shown that the gases which do not follow Mariotte's Law show a greater diminution of volume than should take place according to the Law. Therefore in my experiments, neglecting the changes occurring in the molecular forces on account of the difference in temperature, the volume of the gas at 100° ought to be smaller than what exactly accords with Mariotte's Law; so that the variation in Mariotte's Law would tend to diminish the coefficient of expansion with [increase of] the pressure, instead of increasing it as we have found in our experiments.

After all, to avoid leaving any doubt upon this important point in the dynamical theory of gases, I made a new series of determinations by a method in which the increase in the volume of the gas is measured directly, while it remains under practically the same pressure at 0° and at 100° . This method

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is clearly the only one that can be used with gases which do not follow Mariotte's Law for slight changes of pressure.

I shall describe briefly the apparatus I have used in these determinations and which is based upon the same principle as that used by M. Pouillet in his air pyrometer. It is shown in *Fig. 3*.

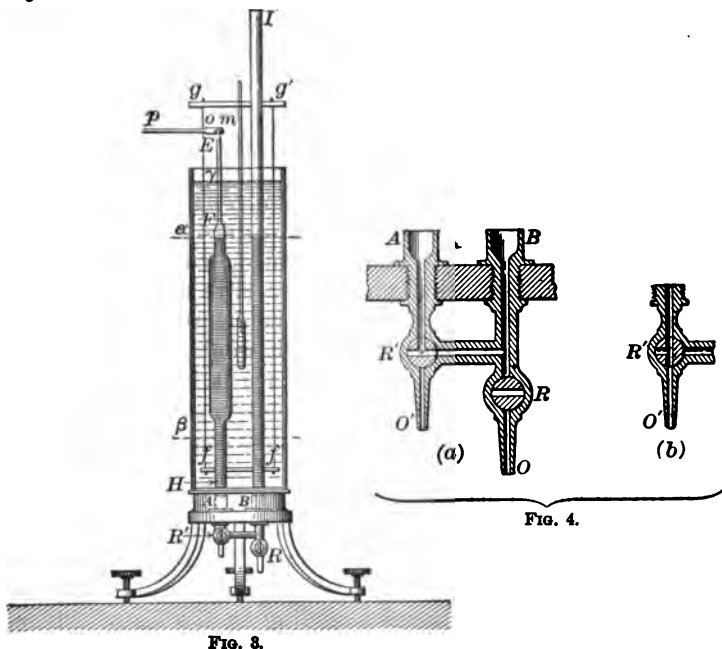


FIG. 3.

FIG. 4.

A glass bulb sealed to a capillary tube is placed in a tin-plate vessel *MN* (*Fig. 13*, Volume IV) [page 96]. The tube is cemented into the little three-way tube *mno*. In the side-tubulure *o* is cemented a short straight piece of capillary tubing, or else a tube of the shape of *abcd*, *Fig. 1*, Volume V [page 128], and containing some pellets of gum mastic,—according as we must work under pressures lower or higher than that of the atmosphere. Into the third tubulure *n* is cemented the bent capillary tube *EF* connecting with the tube *FH* in which the increase of volume of the air is measured. The latter is so chosen that the quantity of air which fills it to *a* when the bulb

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is in melting ice, occupies, when the bulb is in [the vapor of] boiling water, most of the space down to a mark s made upon the narrower tube below. The tube FH is cemented with mastic into the tubulure A of an iron support provided with taps. Into the second tubulure B is cemented a glass tube BI , a meter long in experiments made under atmospheric pressure. This tube was replaced by one of 3 meters' length when working with greater pressures.

The iron support has two taps R and R' . The first tap R is traversed by a single hole and serves to draw off a part of the mercury contained in the apparatus. The second tap R' is bored with two holes at right angles to each other, and serves to connect the tube FH , according to the position given it, with the barometric tube BI , or directly with the outside. This arrangement is clearly seen in *Fig. 4* [page 138], which represents a vertical section of the support and the two positions (a) and (b) of the tap R' . This support is fastened to a cast tripod provided with levelling screws, upon which is fitted a glass jacket filled with water for keeping the expansion reservoir at a known temperature. This jacket consists of a rectangular box two of whose opposite sides are made of glass.

The experiment is then made as follows:

The bulb being surrounded with melting ice, the tube op open and connected with the apparatus which was used before to dry the air, mercury is poured into the tube BI until it reaches the level of a . The tap R' being in position (a), the mercury of course rises to the same level in the two communicating tubes. The tube op is closed by means of a lamp, [the height of] the barometer is recorded, as is also the temperature of the water in the jacket, which has been carefully stirred from time to time by means of the stirrer $ff'gg'$ which is moved up and down in a vertical plane so as to make it pass through all strata of the liquid.

After removing the ice, the water in the vessel M is brought to boiling. To keep the two columns of mercury at about the same point, it becomes necessary to draw off mercury by opening the tap R . A part of the air in the bulb thus passes into the tube FH ; the two columns are brought approximately to the same level s , and the difference of height is determined

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accurately by means of the cathetometer; ¹ at the same time the [height of the] barometer and the temperature of the jacket are recorded. The water filling the jacket was continuously stirred for at least a quarter of an hour before beginning the observations, to give it a uniform temperature which would at the same time be that of the air enclosed in the tube *FH*.

To be able from this experiment to calculate the coefficient of expansion of air, we must know the capacity of the bulb, the volume v from *E* to α of the air in the tube *FH* when the bulb is in melting ice, and the volume v' from *E* to β which is filled by air when the bulb is in [the vapor of] boiling water. The first is easily found by filling the bulb with mercury at 0°, after having made it boil for a while in the apparatus. (See volume IV, page 22 [page 82].)

The two volumes v and v' are determined in the following way:

The drawn-out end of the tube *op* is broken off to allow communication between the interior and the outside air, ² and mercury is poured into the tube *BI* until this liquid entirely fills the tube *FH* as far as γ on the capillary tube. The tap *R'* is turned into the position (*b*). There is then no connection between the tubes *FH* and *BI*, but the mercury from *FH* flows out by the opening *O'*. This mercury is caught in a flask. Mercury is allowed to run out until the meniscus comes exactly

¹ There was danger lest the jacket full of water would give rise, on account of refraction, to deviations of the rays which come from the menisci: a very simple test showed me there was no appreciable deviation, at any rate in the places where the readings were made. The tube *op* being open, the mercury meniscus was adjusted at points all along the tube *FH* in succession. It was seen, with the aid of the glass of the cathetometer, that in all these positions the menisci were at the same level in the two tubes *FH* and *BI*.

² To prevent the entrance of moist air into the apparatus, care is taken first to connect the tube *op* with the drying apparatus by means of a rubber tube. In many experiments, chiefly those made upon gases other than atmospheric air, the point of the tube *op* is not broken off. The bulb being in the [vapor of] boiling water, mercury is poured into the tube *BI* so that the liquid rises into the capillary part *EF* of the tube *FH*; the volumes v and v' are then calibrated as usual.

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to the position at α that it had in the first part of the experiment: this is done with great precision with the aid of the glass of the cathetometer.¹ The mercury which has flowed out is weighed, and from this the volume v is calculated.

The mercury is then run out until the meniscus coincides with β . The weight of mercury drawn off, added to that which gave the volume v , will give us the volume v' . It is clear there is a correction to be made on account of the temperature; if p and p' represent the weights of mercury drawn off and t the temperature of the water of the jacket at the time of the calibration, the weights of mercury at 0° which will occupy the volumes v and v' , and which, consequently, actually represent these volumes, are $p \left(1 + \frac{t}{5550}\right)$ and $p' \left(1 + \frac{t}{5550}\right)$.

It is necessary to add to these volumes v and v' the small volume of the capillary tubing outside the vessel in which the water is boiling. This volume was determined by a preliminary calibration. On the other hand, since the temperature of the air contained in these tubes is somewhat uncertain, it is desirable that this volume should be extremely small. In my apparatus it never exceeded $\frac{1}{2000}$ of the capacity of the bulb.

In order to adapt the same apparatus for measuring the rate of expansion of air under high pressures, the lateral tube op is replaced by the twice-bent tube $abcd$ of *Fig. 1* [page 128], and dry air is forced into the bulb, while mercury is poured into the tube BI . When the desired pressure has been got in the bulb, the gum mastic in the tube $abcd$ is melted so as to close the apparatus hermetically; the bulb is surrounded with melting ice and the meniscus is adjusted to the mark α with the aid of a cathetometer. The meniscus in the tube BI is brought in line with a second cathetometer. In these measurements the precautions noted on page 59 [page 129] are followed closely.

After removing the ice, the water in the vessel is raised to boiling, and mercury is drawn off so as to make the level coincide with β .

The height of the raised column of mercury is measured; it

¹ The flow of the mercury is made as slow as may be desired by turning the tap to the proper extent: it is easy to adjust the meniscus in this way within about $\frac{1}{10}$ of a millimeter.

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is practically the same as that of the first part of the determination.

If H and H' represent the barometric heights at the time of the readings for [the temperatures of] melting ice and boiling water, and h and h' the differences of level of the menisci in the tubes of the apparatus, we evidently have the equation

$$\left(V \frac{1 + \delta T}{1 + \alpha T} + v' \frac{1}{1 + \alpha t'} \right) (H' + h') = \left(V + v \frac{1}{1 + \alpha t} \right) H + h$$

hence

$$1 + \alpha T = \frac{(H' + h') (1 + \delta T)}{(H + h) + \frac{v}{V} \frac{H + h}{1 + \alpha t} - \frac{v'}{V} \frac{H' + h'}{1 + \alpha t'}}$$

The quantity α enters into the denominator of the second member ; but as it affects the result only slightly, we make use of the method of successive approximations, that is, an approximate value is given α , from this the value of α in the first member is calculated and this is then substituted in the second member and yields the final value of $1 + \alpha T$.

In this method the greatest care must be exercised in the determination of the volumes V , v and v' , and, even more, in the determination of the temperature t' . There is, finally, another very important matter—the perfect drying of the tube FH . This tube has a large capacity and, on account of the arrangement of the apparatus, cannot be heated while it is exhausted. In my experiments this tube was thoroughly dried at a high temperature before being cemented into its tubulure, and, when the apparatus was completely set up, a little mercury was poured into the communicating tubes; the tap R' was turned to a position intermediate between (a) and (b), and the apparatus exhausted, the bulb being surrounded by the vapor of boiling water. By exhausting a great many times and then allowing dry air to enter slowly, the moisture should not only be completely removed from the bulb but also from the tube in which the expansion is measured.

The table below contains the results obtained in the experiments made by this method, at atmospheric pressure, upon air, hydrogen, carbonic acid gas, protoxide of nitrogen, oxide of carbon, sulphurous acid gas, and cyanogen.

The second part of the table contains [the results of] experi-

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ments made upon atmospheric air, hydrogen, and carbonic acid gas under higher pressures.

	H	t	h	v	H+h	H'	T	t'	h'	H'+h'	v'	1+100α	Means.
<i>Experiments at Atmospheric Pressure.</i>													
	m m.	m m.	gr.	m m.	m m.	m m.	99.80°	14.56°	m m.	m m.	gr.		
Atmospheric Air.	757.29	14.27°	0	28.40	757.29	756.76	99.80°	14.56°	-4.38	753.43	1716.06	1.36638	
	754.85	16.00	0	47.57	754.85	754.68	99.81	16.09	-1.25	753.53	1718.22	1.36696	
	756.33	14.10	0	42.06	756.33	756.03	99.86	14.78	-2.70	753.33	1719.06	1.36714	
Hydrogen.....	754.75	17.64	+2.97	30.06	757.72	754.70	99.81	17.52	0	754.70	1719.43	1.36716	1.36706
	755.71	15.21	+3.07	29.13	758.78	755.68	99.84	15.35	0	755.06	1724.79	1.36642	
	755.65	15.46	0	27.43	755.65	755.30	99.82	15.29	-2.49	752.81	1722.06	1.36610	1.36613
Carbonic Acid Gas.	755.63	20.21	+1.88	27.22	757.46	755.29	99.82	20.48	0	755.29	1722.19	1.36566	
	756.31	17.19	+0.80	48.81	756.61	756.36	99.86	16.62	0	756.36	1722.59	1.37048	
	756.14	17.64	0	22.40	756.14	755.79	99.85	19.23	-0.86	754.93	1720.16	1.37068	
	756.13	18.88	+0.86	30.85	756.09	756.57	99.87	18.69	0	756.57	1721.02	1.37100	
	755.52	19.82	+1.92	30.90	757.44	756.10	99.85	19.47	0	756.10	1721.75	1.37094	
Protoxide of Nitrogen	755.46	19.68	0	30.26	755.46	755.43	99.84	20.58	-1.47	753.98	1741.46	1.37164	1.37099
	754.90	15.85	0	30.40	754.90	754.79	100.18	16.44	-2.84	752.45	1731.02	1.37228	
Oxide of Carbon.....	754.45	19.40	0	26.37	754.45	754.32	99.80	19.83	-0.34	753.98	1729.80	1.37167	1.37195
	756.29	18.42	0	27.50	756.29	756.14	99.86	19.59	-2.23	753.91	1724.30	1.36720	
Sulphurous Acid Gas.	754.75	16.11	+1.92	25.30	756.67	754.70	99.81	16.86	-2.66	752.03	1729.07	1.36654	1.36638
	759.58	18.38	0	21.44	759.58	759.40	99.96	19.67	+2.67	762.07	1763.33	1.36904	
	760.41	19.61	-1.54	25.79	758.87	760.66	100.08	19.88	+0.72	761.88	1768.30	1.36987	1.36928
	762.46	17.63	-3.84	22.40	756.12	762.04	100.08	18.63	+0.06	762.10	1754.36	1.36904	
	763.18	20.30	+0.25	32.80	763.43	763.14	100.12	21.24	+0.70	763.54	1765.37	1.36766	
Cyanogen.....	764.19	18.56	-1.44	25.63	762.75	764.06	100.15	19.72	+0.78	764.96	1764.23	1.36768	1.36797
<i>Experiments at High Pressures.</i>													
	m m.	m m.	gr.	m m.	m m.	m m.	99.80°	19.38°	1763.84	2517.71	1727.66	1.36624	
Atmospheric Air I.	754.22	18.61°	1770.40	29.72	2524.62	754.37	99.80°	19.38°	1763.84	2517.71	1727.66	1.36624	
	754.67	18.57	1772.56	20.17	2526.23	754.53	99.80	19.08	1761.90	2516.43	1731.00	1.36663	1.36644
II.....	757.74	16.86	1863.75	23.26	2623.49	757.65	99.91	18.03	1855.05	2512.70	1720.70	1.36941	
	757.04	17.04	1863.86	30.80	2620.40	756.85	99.89	17.94	1868.88	2515.71	1718.77	1.36987	1.36964
Hydrogen.....	747.58	18.31	1763.05	25.69	2545.63	747.62	99.54	19.00	1782.96	2530.58	1728.00	1.36615	
	748.40	17.44	1762.11	87.72	2540.51	747.91	99.55	18.33	1796.16	2534.07	1716.39	1.36628	
	750.40	16.67	1765.07	26.46	2545.47	747.92	99.62	16.44	1770.39	2530.31	1740.27	1.36605	1.36616
Carbonic Acid Gas.	747.43	18.67	1777.06	30.63	2524.51	747.17	99.63	18.55	1786.54	2538.71	1726.40	1.36467	
	750.88	18.34	1772.07	85.15	2522.45	750.76	99.65	17.08	1769.75	2530.51	1761.36	1.36448	1.36455

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Atmospheric air gives figures a little higher than the mean of earlier determinations; yet the difference is inappreciable; it may be attributed also to the fact that air does not conform rigorously to Mariotte's Law.

My earlier determinations gave for hydrogen the same coefficient of expansion as for air. The new experiments assign to hydrogen a coefficient slightly lower than that of air. Hr. Magnus has already reached a similar result (*Annales de Chimie et de Physique*, volume IV, page 334), but the differences are so small that it is difficult to decide the question; they are within the limits of the errors of observation. As a matter of fact, there are in Magnus' determinations with air many figures which are still lower than those he has found for hydrogen; so that the question does not seem to me settled. It will be seen later that the experiments made upon the rate of expansion under higher pressures decide the matter in a very clear way.

The hydrogen was prepared from very pure zinc; it was passed through a wash bottle containing water, two tubes a meter long full of pumice-stone soaked with a concentrated solution of potash, a tube of equal length full of pumice stone soaked with a solution of silver sulphate. Beyond the air pump it traversed two tubes a meter long full of pumice stone soaked with concentrated sulphuric acid, and a tube filled with small bits of caustic potash. The latter was to hold back the small quantity of sulphurous acid gas which might be formed through the interaction of the hydrogen gas and the sulphuric acid. This precaution had been neglected in the determinations of the first memoir, yet I have never perceived any odor from the presence of sulphurous acid in any of these experiments.

Oxide of carbon gave the same figure as in the earlier researches (volume IV, page 52 [page 109]).

The coefficients of expansion of carbonic acid gas and protoxide of nitrogen determined by this method are higher than those obtained by the earlier methods (volume IV, pages 52, 56 and 57 [pages 109, 113, 115]); this is unquestionably due to the fact that these gases do not exactly conform to Mariotte's Law, and that their volumes at 100° , under a pressure higher than

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that to which they are subjected at this temperature in the earlier methods, are smaller than they ought to be according to this Law. We must expect to find similar results with all gases more compressible than air.

The coefficients of expansion of sulphurous acid [gas] and cyanogen are much higher than those of other gases. My earlier researches (volume IV, pages 52 and 57 [pages 109 and 114]) had, on the other hand, assigned them figures very little higher than the coefficient of expansion of atmospheric air. The variations may be attributed to the fact that, sulphurous [acid] gas and cyanogen being much more compressible than air, their volume at 100° , calculated from the change of tension, is much too low and, consequently, gives too small a coefficient of expansion. In an endeavor to verify this supposition by means of direct experiments, and after many trials, I found that there had been a serious error in my former determinations of sulphurous acid [gas] and cyanogen.

I have always had to face the difficulty of drying sulphurous acid gas completely, the presence of a trace of moisture being able, in the case of this very soluble gas, to cause much greater variations than in other gases. My earliest experiments had given for sulphurous acid [gas] figures much higher than those to which I was led in my former research; but I discovered that these figures became lower in proportion as the gas was more slowly admitted into the bulb,—which I most naturally attributed to more perfect drying,—and it was only by having the gas enter extremely slowly, compelling it to remain for a long time in the tubes full of pumice stone soaked with concentrated sulphuric acid before introducing it into the bulb, that I succeeded in securing constant figures. Working in this way, a source of error is introduced which then escaped me; some dry air evidently entered the bulb along with the sulphurous acid gas. The proportion of this air was greater, the slower the introduction of the sulphurous acid gas. Now the presence of a small amount of air is sufficient to lower appreciably the coefficient of expansion of sulphurous acid [gas], since the latter gas expands under these circumstances as if it were under a very low pressure, and the coefficient of expansion of sulphurous acid [gas] falls very rapidly with the pressure.

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I thought at that time that the entrance of air must be due to the fact that the apparatus (perhaps the taps of the pump through the action of the acid gas) had not remained gas-tight during the long time the gas was making its way in. I am not prepared to assert this was not the case, yet I can say that the apparatus was always tested with great care each time before commencing a series of experiments with any particular gas.

Yet there is another source of error against which I was not sufficiently on my guard in my earlier experiments. It lay in the great difficulty met with in freeing the pumice stone and sulphuric acid from air mechanically held or absorbed; thus, I found, in the experiments with sulphurous acid [gas], that after the apparatus had been exhausted three or four times in succession, at least to 1 or 2 centimeters, and sulphurous acid gas had been introduced each time, the gas in the bulb still showed on testing an appreciable amount of air mixed in. In the ordinary determinations with gases other than atmospheric air, I was accustomed to exhaust at least ten or twelve times; in the experiments with sulphurous acid gas I contented myself with only three or four times, because of the very long time required for each filling. In the experiments with cyanogen, only two exhaustions were made, on account of the difficulty of preparing a considerable quantity of this gas in a pure state.

Sulphurous acid gas in the recent determinations was prepared by the action of mercury upon sulphuric acid; the gas passed through a long inclined U-tube full of concentrated sulphuric acid which the bubbles traversed very slowly; from this it made its way to the bulb through a tube connecting with the small air pump. This arrangement permitted the exhaustion, not only of the receiving bulb, but also of the generating apparatus. Besides, it was easy to prove, by means of the communicating tubes *FH* and *BI*, that the apparatus was perfectly gas tight.

The bulb had in this way been filled with perfectly pure sulphurous acid gas. I satisfied myself after the determinations were over, by breaking off the tip of the tube *op* under mercury and driving out part of the gas by pouring mercury into

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the tube *BI*. The gas was completely absorbed by a solution of potash.¹

A similar arrangement was used in the work on cyanogen. This gas was prepared by decomposing cyanide of mercury with the aid of heat; it passed through a long column of concentrated sulphuric acid.

If we adopt the figures found for the coefficients of expansion of the various gases by this last method, which is the only one capable of giving comparable results when we wish to know the rates of expansion of gases which do not follow Mariotte's Law, it is apparent that the various gases show very different coefficients of expansion. We have found, as a matter of fact, for these coefficients:

Hydrogen.....	0.36613
Atmospheric Air.....	0.36706
Oxide of Carbon.....	0.36688
Carbonic Acid Gas..	0.37099
Protoxide of Nitrogen.....	0.37195
Cyanogen.....	0.38767
Sulphurous Acid Gas.....	0.39028

I have already shown above that the coefficients of expansion of carbonic acid gas and protoxide of nitrogen were higher when determined by the last method than when calculated from the changes in tension. The variations are much greater for the very compressible gases, such as cyanogen and sulphurous acid gas, as may be understood from the following results, which have been reached in the same series of determinations as the figures given in the table above. As a matter of fact, in order to obtain, with the apparatus of *Fig. 3* [page 138], the variations of tension in the gas occupying a constant volume, when it is carried from the temperature of melting ice to that of boiling water, it is only necessary to keep the level of the mercury at *a* in the tube *FH* while the bulb is in [the vapor of] boiling water, and to measure the difference of level between *a*

¹ It remains to be decided whether sulphurous acid gas is completely dried by concentrated sulphuric acid, and whether it did not carry with it a minute quantity of the latter acid. This point seemed to be hard to decide by direct experiment; the coefficient of expansion of the gas is perhaps appreciably changed by the presence of an infinitesimal quantity of [water] vapor.

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and the meniscus of the mercury pushed up in the tube *BI*. These determinations were made, in fact, in the three experiments upon gaseous sulphurous acid and in the two experiments upon cyanogen. With the values for *H*, *t*, *h*, *v*, and *H* + *h* of the table above [page 143] it is only necessary to combine the following:

Sulphurous Acid Gas			Cyanogen	
I	II	III	I	II
<i>H'</i>759.31 mm.	760.71 mm.	762.13 mm.	763.07 mm.	764.07 mm.
<i>T'</i> 99.98°	100.03°	100.08°	100.12°	100.15°
<i>t'</i> 19.29°	19.88°	18.42°	20.94°	19.16°
<i>h'</i>288.62 mm.	286.19 mm.	284.30 mm.	289.23 mm.	287.62 mm.
<i>H' + h'</i> .1047.93 mm.	1046.90 mm.	1046.43 mm.	1052.30 mm.	1051.69 mm.
<i>v'</i>21.44 gr.	25.79 gr.	28.20 gr.	22.80 gr.	25.62 gr.
1 + 100 <i>a</i> .. 1.38439	1.38451	1.38470	1.38282	1.38298

Thus, we have found:

For Sulphurous Acid Gas:

By direct measurement of expansion.	By calculation, from the change of tension.
0.39094	0.38439
0.38987	0.38451
0.39004	0.38470
Mean.....0.39028	0.38453 ¹

For Cyanogen:

0.38766	0.38282
0.38768	0.38298
Mean.....0.38767	0.38290

I have stated above that the coefficient of expansion of sulphurous acid gas rises quite rapidly with the pressure; this may be observed in the following experiment, begun by filling the bulb, while cooled with ice, and the expansion-tube *FH* down to β , with sulphurous acid gas. The tube *op* was then sealed with the lamp and, by pouring mercury into the tube *BI*, the gas contained in the tube *FH* was forced back into the bulb.

¹ This figure differs little from the mean assumed by Hr. Magnus, but from three determinations which gave too divergent figures, viz., 0.3897; 0.3839; 0.3832.

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In other respects the determination is carried out as has been described in volume IV, page 43 [page 99]; we have :

$H = 761.33 \text{ mm.}$	$H' = 761.08 \text{ mm.}$
$t = 18.83^\circ$	$T' = 100.04^\circ$
$h = 221.40 \text{ mm.}$	$t' = 19.10^\circ$
$v = 25.36 \text{ gr.}$	$h' = 228.56 \text{ mm.}$
$H + h = 982.73 \text{ mm.}$	$H' + h' = 987.64 \text{ mm.}$
	$v' = 1780.44 \text{ gr.}$
$1 + .00 \alpha = 1.39804.$	

Thus, for a change in pressure as slight as that from 760 mm. to 980 mm., the coefficient of expansion of sulphurous acid [gas] has changed from 0.3902 to 0.3980, and the gas under the pressure of 980 mm. is not even at 0° near its point of condensation.

It is likely, judging from this, that vapors have coefficients of expansion very different from that of air at points slightly removed from their points of condensation—consequently, under the conditions where we usually meet them in our experiments for determining their densities.

Let us now turn to the second part of the table [page 143] which contains determinations made under a pressure of 2530 mm. (about 3.33 atmos.) with three gases, atmospheric air, hydrogen, and carbonic acid gas. The very striking fact is there apparent that hydrogen has maintained practically the same coefficient of expansion as under atmospheric pressure; whereas air, and, above all, carbonic acid gas show a very marked increase in their coefficients.

The variation in rates of expansion of atmospheric air and carbonic acid gas is far more noteworthy in those experiments where the pressure is the same at 0° and at 100° , than in those where the rates of expansion were calculated from the change of tension.

At the same time it is clear that in proportion as the pressure under which the gases are studied is greater, so much the more marked become the variations among their coefficients of expansion. Hydrogen and atmospheric air, which have practically the same rate of expansion under ordinary barometric pressure, show very marked differences when they are subjected to pressures three or four times as great.

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Conclusions.

To sum up, my determinations do not confirm the two fundamental laws of the theory of gases, assumed up to the present by all physicists to be exact, *viz.* :—

I. All gases expand to the same extent between the same limits of temperature.

II. The rate of expansion of a given gas, between the same limits of temperature, is independent of its original density.

Must these laws be banished from science for the future? I do not think so. I believe that these laws, along with all those which have been discovered for gases, such as the Law of Volumes, etc., are true *at the limit*, that is, that they come nearer to conforming with the results of observation in proportion as we use the gas in a more expanded condition.

These laws hold good for a perfect gaseous state, which the gases that nature places before us, more or less approach, according to their chemical characteristics; according to the temperature at which we study them and which may be, for each in turn, more or less removed from the point where change of state takes place; finally and chiefly, according to their condition of less or greater compression.

**RESEARCHES UPON THE GAS THERMOMETER,
AND THE COMPARISON OF THE GAS THERMOMETER
WITH THE MERCURY THERMOMETER.**

BY P. CHAPPUIS.

(*Abstract*)

Travaux et Memoires du Bureau International des Poids et Mesures, volume 6 (1888); Archives des Sciences (Genève), volume 20, pages 5—36, 153—179, 248—262 (1888).

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RESEARCHES UPON THE GAS THERMOMETER,
AND THE COMPARISON OF THE GAS THERMOMETER
WITH THE MERCURY THERMOMETER.

BY P. CHAPPUIS.

(*Abstract.*)

IN an extended memoir Chappuis describes the means he employed in his attempt to determine with greater accuracy than had hitherto been attained, the relation existing between the rates of expansion of gases and of mercury. In the effort to find an instrument which would be more reliable than the air thermometer of Regnault, he made use of a gas reservoir the material of which was an alloy of platinum and iridium instead of glass, and thereby avoided, in part at least, the difficulties introduced through the uneven expansion of the latter substance. This reservoir was 110 centimeters long, 3.6 centimeters in diameter and had a capacity of a little more than a litre. It was connected by means of a platinum capillary tube a meter long with the manometric apparatus. For experiments at 0° C. and below, as well as at temperatures up to 50° , the gas reservoir was supported in a horizontal position in the inner one of two concentric metal troughs, and the mercury thermometers were disposed symmetrically about it. In this position it could be surrounded with crushed ice, with freezing-mixtures or with liquid baths of any desired temperature; in the last case stirrers driven by a water motor kept the liquid in motion and at a perfectly uniform temperature. Evaporation with consequent temperature-variation was largely avoided by covering the troughs with a large glass plate. For a vapor bath a double-walled vessel was employed and, somewhat as in Regnault's apparatus, the steam, after passing through the inner vessel, reached the condenser by way of the annular space between the double walls.

In Regnault's constant-volume air thermometer the tension of the gas was measured by a simple manometer open to the

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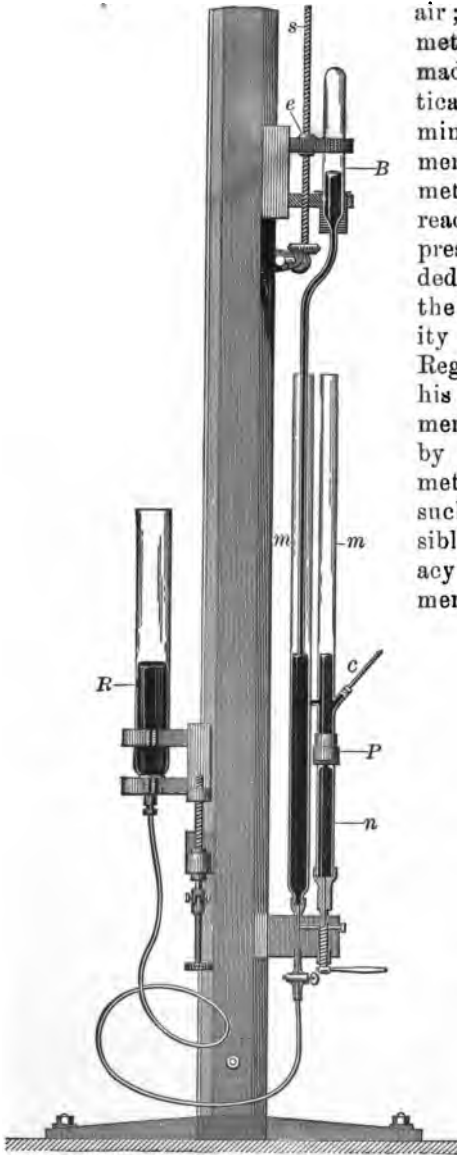


FIG. 1.

air; consequently a barometric reading had to be made at the time the vertical difference was determined between the two mercury levels in the manometer. The number of readings involved in these pressure measurements added to the laboriousness of the work and to the liability to error in the results. Regnault did not regard his readings of heights of mercury columns incorrect by more than 0.01 centimeter, yet he considered such an error always possible. To increase the accuracy of the tension measurements was Chappuis's chief

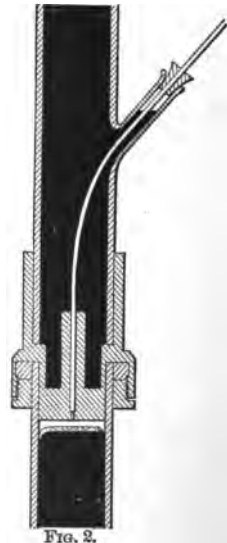


FIG. 2.

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care. For this purpose the apparatus was so arranged that but one reading was necessary to give the total pressure exerted by the gas in the reservoir. The platinum capillary tube (c in *Fig. 1*) leads from the gas reservoir through the close-fitting steel plug into the closed chamber shown in section and on a larger scale in *Fig. 2*. The mercury in this chamber is kept just in contact with a fixed pointer, 0.5 millimeter long, projecting downward from the plane under-surface of the steel plug, by raising or lowering the mercury reservoir R connected with the manometric chamber by a steel tube. This adjustment can be made with the greatest exactness by means of a screw movement attached to R . The difference between the mercury level in the closed chamber and that in the open tubes M , M' and R —which are all in communication with one another—is a measure of the excess of pressure in the gas reservoir over that of the atmosphere.

Dipping in the open well M is a barometer B attached to a movable carriage e which can be displaced along a vertical line by means of the screw-rod s . The barometric chamber is provided with one or more black glass pointers fused to the side, the tips of which turn downward along the line of the axis of the chamber; by means of s the barometer is raised or lowered until the mercury meniscus just touches the tip of the pointer. The apparatus is so constructed that the barometric chamber and the manometric chamber are in the same vertical line; hence the *total* pressure upon the gas in the reservoir is measured by the vertical distance between the menisci in B and n . The tubing of which B , n , M and M' are made is of 2.5 centimeters internal diameter, and hence the menisci show little curvature. The position of the pointer in the manometric chamber with respect to the scale attached to the support being once for all known, a single reading, that of the pointer and meniscus in B , suffices to show the total pressure on the gas in the reservoir.

The fact of the exact adjustment of all these levels was determined by means of cathetometer microscopes fitted with micrometer eyepieces. The heights were read off on a metal scale attached to the manometer-support close to the manometer tubes.

Eight mercury thermometers of hard glass were used: four

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were graduated from -5° to 104° ; the other four from -32° to $+39^{\circ}$ and from 95° to 103° , there being a reservoir on the stem between 39° and 95° . The thermometers of these two kinds were about 70 centimeters and 54 centimeters long, respectively; the divisions corresponding to single degrees were over 5.5 millimeters apart. Prior to the actual determinations most careful calibration-tests were made upon the gas reservoir, the capillary tube, the reading microscopes, the scale, the thermometers, etc. The coefficient of expansion of the reservoir was determined with another tube of the same alloy.

Nitrogen.—The reservoir being filled with pure nitrogen, a series of determinations were made of the pressure upon the gas at 0° . Of the 19 measurements, each the average of 3–7 readings, the highest was 995.967 mm.; lowest, 995.922 mm.; mean, 995.942. These measurements were made on various days extending through two months and a half. At intervals during this period the pressure corresponding to a temperature of 100° was determined; the figures, reduced to 45° latitude and sea level, were:

No.	Pressures	Corresponding temperatures
1. 4 readings	1358.057mm.	100.0548°
2. 6	1357.424	99.8826°
3. 6	1356.479	99.6212°
4. 6	1356.795	99.7160°

From these pressures, assuming the mean value 995.942 mm. for the pressure at 0° , the coefficients deduced are:

1. 0.00367482
2. 0.00367471
3. 0.00367468
4. 0.00367442

Mean, $\alpha = 0.00367466$.

Elaborate comparisons were next made between four of the mercury thermometers and the nitrogen thermometer at 15° , 20° , 25° , 30° , 35° , 40° , 45° , 60.8° (boiling-point of chloroform) and 78° (that of alcohol).

A second series of determinations of the gas pressure at 0° (the room temperature being lower than in the former series), gave, as a mean, 995.888 mm. Comparisons, on the assumption that $\alpha = 0.00367466$, were made with the mercury thermometers

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of the second set at 2.5° , 5° , 10° , 15° , 20° , 25° ,— 4° ,— 24° ,— 20° ,— 15° ,— 10° ,— 5° . The results of these comparisons are shown in the form of a curve on page 158.

Carbon dioxide.—Twelve measurements were made (each the average of 4–8 readings) of the tension of the gas at 0° , and four of the tension at 100° , as in the case of nitrogen. The values deduced for α were :

0.00372458
0.00372483
0.00372481
0.00372486

Mean, $\alpha = 0.00372477$.

Comparisons were again made with the mercury thermometers at— 17° ,— 10° , 10° , 20° , 30° , 40° .

Part of the gas having been allowed to escape from the apparatus, so that the pressure at 0° was reduced from about 1 meter of mercury to about 870 mm., nine measurements were made at 0° which ranged from 870.253 to 870.296 mm., and five at about 100° . The values of α obtained were :

0.00371629
0.00371631
0.00371646
0.00371629
0.00371635

Mean, $\alpha = 0.00371634$.

Finally, the reservoir was filled with pure hydrogen obtained by electrolysis. Two series of determinations of the tension at 0° were made, comprising a total of 23 measurements, each the average of three readings, and seven determinations at 100° . The calculated values of α were :

0.00366271
0.00366248
0.00366225
0.00366231
0.00366256
0.00366270
0.00366269

Mean, $\alpha = 0.00366254$.

Comparisons of the readings of the hydrogen- and mercury-thermometers were made at 17 different temperatures between— 24° and 78° .

The curves showing the deviations of the nitrogen-, carbon-dioxide- and hydrogen-thermometers from the mercury-ther-

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mometers are exhibited in *Fig. 3*. The maximum deviations are :

For hydrogen, 0.107° at 40° ,

For nitrogen, 0.097° at 40° ,

For carbon dioxide, 0.049° at 35° .

It will be noted that from about 65° to 100° the value of α is practically identical for hydrogen and nitrogen.

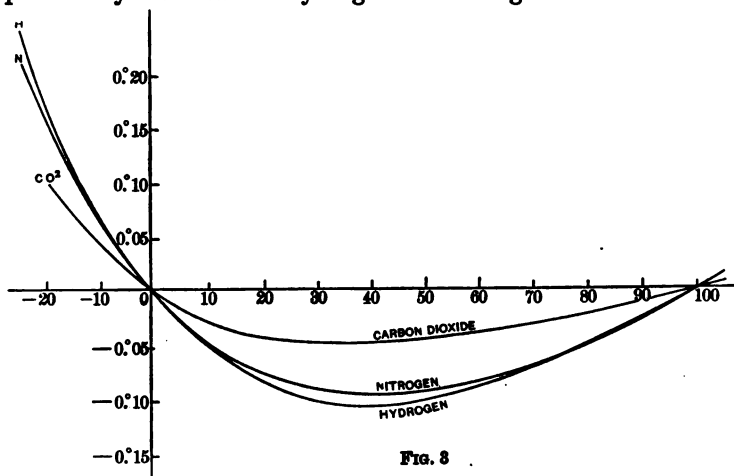


FIG. 3

The coefficients of expansion for nitrogen and carbon dioxide at temperatures ranging from -10° to 100° are thus stated by Chappuis :

Temperature	Nitrogen	Carbon dioxide
-10°	0.00367781	0.00373807
0°	7698	3538
10°	7625	3273
20°	7561	3019
30°	7506	2779
40°	7461	2558
50°	7426	2360
60°		2191
70°		2054
80°		1954
90°		1896
100°		1884

In the case of carbon dioxide, the change of the coefficient of expansion with change of pressure, is given thus :

Initial Pressure	Coefficient
999.18	0.00372477
870.28	0.00371634

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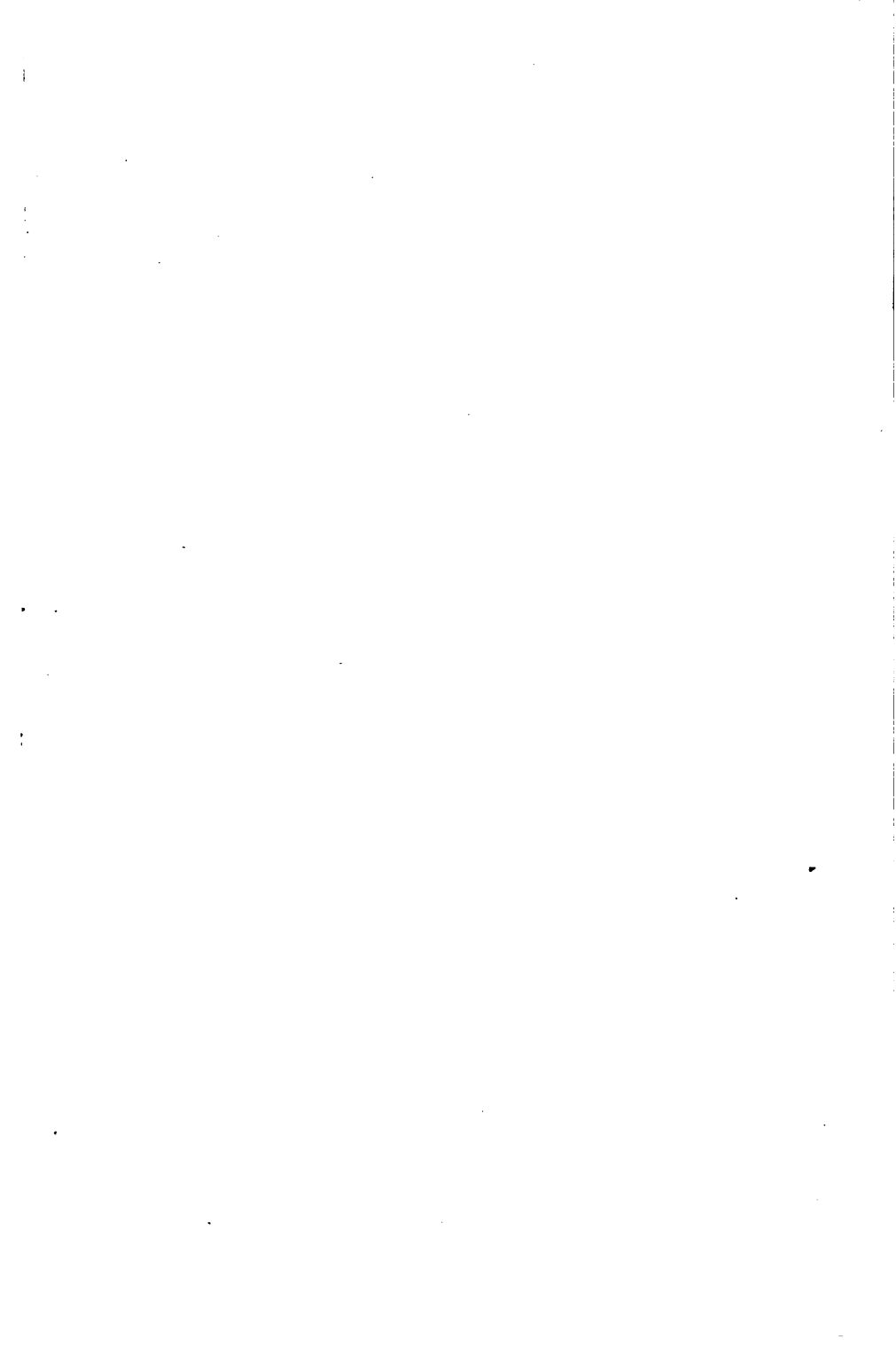
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