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On the Dependence of the Refractive Index of Gases on Temperature

George W. Walker

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XI. *On the Dependence of the Refractive Index of Gases on Temperature.*

By GEORGE W. WALKER, *M.A.*, *A.R.C.Sc.*, *Fellow of Trinity College, Cambridge.*

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THE importance of this question was first impressed on me in the course of some theoretical investigations on refraction in gases and the closely related property of electric susceptibility.

A comparison of the actual temperature effect on a property of a body, with a theoretical formula professing to explain the property, is a very severe test, and one which has proved fatal to many theories.

According to GLADSTONE and DALE'S law, of which most theories of refraction are particular cases, the refractive power of a gas is proportional to its density; or, as a formula,

$$\mu - 1 = \kappa\rho,$$

where μ is the refractive index,
ρ is the density,

and κ a constant depending on the gas, but independent of temperature. If, then, the gas closely obeys BOYLE'S and CHARLES' laws, we must have

$$\frac{(\mu - 1)(1 + \alpha t)}{p} = \frac{(\mu_0 - 1)(1 + \alpha t_0)}{p_0},$$

where p is the pressure, t is the temperature, and α the coefficient of expansion of the gas at constant pressure.

If the pressure is kept constant, we must have

$$\mu - 1 \propto \frac{1}{1 + \alpha t} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1).$$

Several observers have attempted to test this point.

MASCART,* LORENZ,† BENOÎT,‡ VON LANGE§ made observations on the refractive

* 'Annales de l'École Normale Supérieure,' Series 2, vol. 6, 1877, p. 9.

† WIEDEMANN, 'Annalen der Physik,' vol. 11, 1880.

‡ 'Travaux et Mémoires du Bureau International des Poids et Mesures,' vol. 6 1888.

§ POGGENDORFF, 'Annalen der Physik,' vol. 153, p. 488.

index of air at different temperatures and made use of the formula (1) to calculate α. Their results are briefly as follows: LORENZ and BENOÎT obtained a value of α equal to the ordinary coefficient of expansion for air, VON LANGE obtained a value considerably less, while MASCART obtained a value considerably greater. LORENZ does not indicate what degree of accuracy he obtained, while BENOÎT and VON LANGE do not appear to have obtained as great accuracy as MASCART.

MASCART experimented on a number of gases, and in almost every case obtained a value of α appreciably greater than the corresponding coefficient of expansion of the gas. This range of temperature was from about 5° C. to 40° C.

The disagreement between the results of the above-mentioned experimenters in the case of air, and the somewhat limited range of temperature used by MASCART, led me to think that a repetition of the experiments on a few gases would be of value. I set myself the task of obtaining an accuracy of 1 in 500 over a range of temperature from 10° C. to 90° C., and I think the results show that this accuracy has been attained and in some cases surpassed.

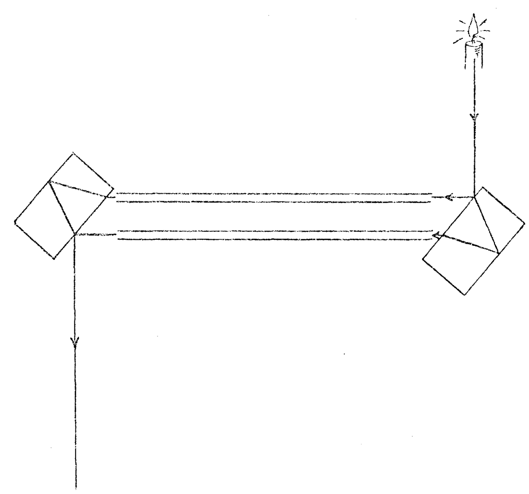

Fig. 1.

The method used was JAMIN'S interference method, which I shall briefly describe, although it is well known (see fig. 1). The rays of light from a monochromatic flame fall on a thick glass block, whose faces are optically plane and parallel, the back face being silvered. Two parallel beams of light are thus produced and proceed through the two tubes filled with the gas and reach a second block of glass identical with the first. The two beams unite on emerging from the second glass block and produce interference bands, which may be observed through a telescope. When the pressure in one of the tubes is altered, the bands move across the field of view. As will be proved later, the number of bands displaced for a given difference of pressure enables us to calculate the refractive index of the gas.

The glass blocks which I used were made by REINFELDER UND HERTEL in Munich. The dimensions were 6 × 4 × 3 centims., the faces, 6 × 3, being optically plane and parallel. One of the blocks was placed on an adjustable screw stand, so that the necessary adjustments might be made. The other block was placed on a heavy block of hard wood.

The tubes for holding the gas were made of brass, and were about 100 centims. long and 1 centim. diameter, and had soldered to them at each end a stuffing box B (see fig. 2). The tubes were soldered to an outer jacket E, which was also made of brass, and was tightly wound on the outside with a thick layer of cotton wool. The vertical tubes *F* at each end of the jacket admitted the introduction of a thermometer fitted through a rubber cork. Steam or water entered at *G* and was pumped out at the corresponding hole at the other end of the jacket. *C* is an optically plane and parallel plate of glass, 17 millims. diameter, 1·5 millims. thick. The four plates were all cut from the same plate of worked glass by REINFELDER UND HERTEL. *D* is a piece of hollow cork to reduce eddies of cold air.

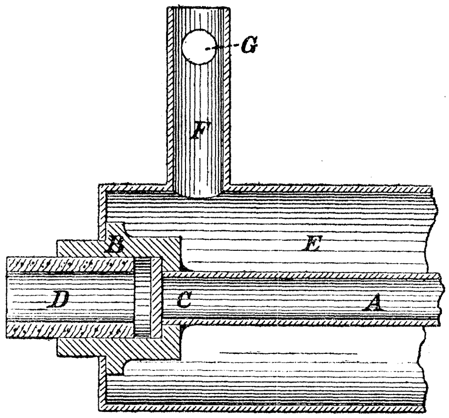

Fig. 2.

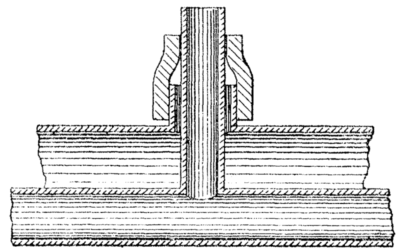

Fig. 3.

I experienced very great difficulty in making the joints between the glass plates and the brass tubes absolutely air-tight under the varying conditions of temperature and pressure. I succeeded finally by using a rubber washer $\frac{1}{5}$ millim. thick between the glass and the brass, and then painting bicycle enamel round the junction. This material dries rapidly and hardens, but still with sufficient elasticity to avoid straining of the glass. It is not porous, nor does it melt or even soften at 100° C. It is, moreover, soluble in ether, so that the glass plate can be recovered unimpaired.

Small brass tubes (see fig. 3) passed through the side of the jacket and were screwed and soldered, one to each of the long brass tubes. These served to connect the tubes with the manometer for recording the pressure.

These small brass tubes passed through short brass tubes of slightly larger diameter, soldered to the jacket, thus allowing play during alteration of temperature. The joint was made by a short piece of thick rubber tube, wired, and painted over with black enamel.

The steady temperatures required were obtained as follows:—Tap water was drawn through the jacket by means of a water pump. This gave temperatures about 10° C. Higher temperatures, such as 20° C., or 30° C., were obtained by drawing the water through lead spirals of different sizes, immersed in a saucepan of water kept boiling. Temperatures from 50° C. to 100° C. were obtained by boiling water under reduced pressure in an old mercury bottle, and drawing the steam through the jacket by the water pump.

The arrangements for altering the pressure in the tubes of gas and measuring the differences are shown in fig. 4. The glass tube *D* connected the brass tube *M* with

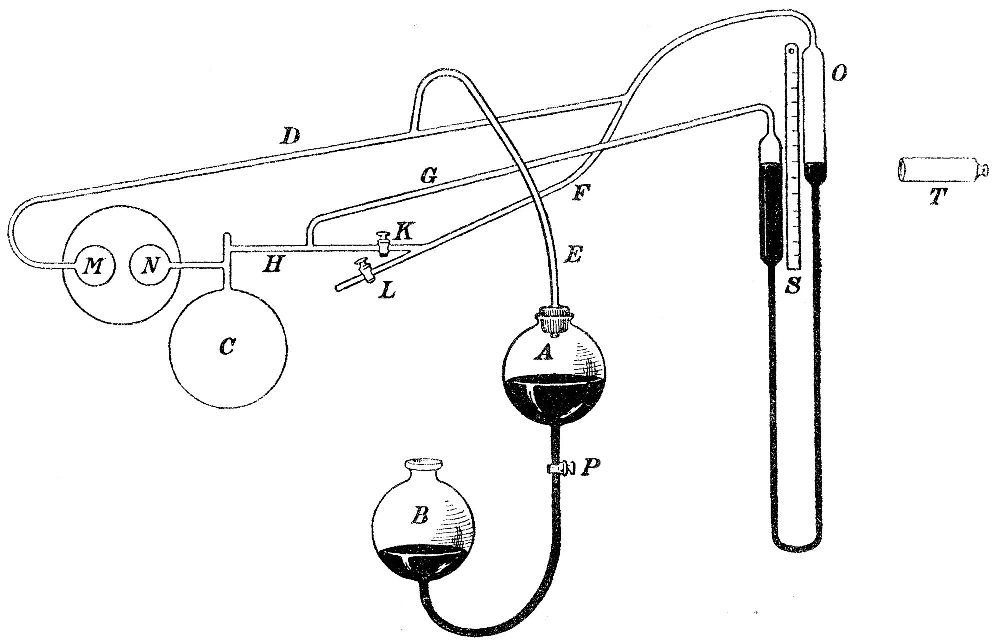

Fig. 4.

one limb of the manometer. The branch *F* led to a tap *L*, through which different gases could be passed into the apparatus.

The branch *H* led to the second brass tube *N*, and from *H* the branch *G* led to the second limb of the manometer. The branch *E* was connected to a glass reservoir *A* of about $\frac{3}{4}$ litre capacity, the tube being drawn to a fine capillary just before entering the reservoir. *A* was connected with a second reservoir *B* by a rubber tube. On lowering *B*, mercury ran from *A* to *B*, and thus the pressure could be altered. The tap *K* being shut, a difference of pressure in the two brass tubes was produced, which could be measured on the manometer. *C* is a glass bulb introduced to keep the pressure in *N* more nearly constant than it would otherwise be. The manometer was over an inch in diameter in the wide portions, and thus capillary error was avoided. A steel scale *S* was hung between the two limbs and the level of the mercury, read by means of a telescope of a cathetometer placed in front of the manometer and about 150 centims. from it.

Wherever it was possible, the glass joints were made by means of a blow-pipe, and the only other joints were at the reservoir *A* and at the small tubes connected with *M* and *N*. These were made with thick rubber tube, wired, and painted with black enamel. The glass taps *K* and *L* were fitted with mercury seals. Very great care was taken in testing to see that the whole apparatus was absolutely air-tight.

As a source of light, I used an ordinary Bunsen burner, placed about 150 centims. from the first glass block, and a small piece of bicarbonate of soda was held in the flame. This gave a brilliant yellow flame for a long time. The position of the interference bands was observed in a telescope with a micrometer scale in the eye-piece.

Theory of the Measurement.

MASCART and others have established that for pressures in the vicinity of atmospheric pressure the refractive power is proportional to the pressure, or

$$\mu = 1 + \kappa p,$$

where κ is a function of the temperature.

This is only true in cases where BOYLE'S law practically holds. In the case of such gases as ammonia, where the deviation from BOYLE'S law is appreciable, a correction is required.

Let d be the length of either tube,

λ the wave-length of Na light,

p_0 the initial pressure in the tubes,

p_1 the final pressure in first tube,

p_2 the final pressure in second tube, and

n the number of bands displaced, then

$$\kappa = \frac{n \times \lambda}{(p_1 - p_2)\, d}.$$

The measurements were made as follows:—Steam or water was allowed to run through the jacket for over an hour until the temperature was steady, and no drift of the bands was observed when the tap K was open. The bands were then adjusted so that a band was on the cross wire in the telescope. The two limbs of the manometer were read, and also the two thermometers in the jacket, and the thermometer hung beside the manometer. The tap K was then shut, the reservoir B lowered, and the tap P opened. When about 100 bands had passed, the tap P was shut and the position of the band observed, the manometer read, and also the three thermometers. B was then raised, the tap P opened, and the mercury allowed to flow back to A. The tap P was shut when the original position was attained and the readings again made. This method provides a test of any possible drift of the bands in one direction due to creeping changes of temperature. The proper temperature to take is readily seen to be the temperature as recorded when the pressure has been reduced, and not the mean of the initial and final temperatures.

With regard to the accuracy I consider that I was able to estimate $\frac{1}{10}$ millim. on the manometer scale. An interference band being a fuzzy thing and not sharp, I found it impossible to estimate more than $\frac{1}{10}$th of a band. The bands appeared about

5 millims. apart in the eye-piece, and the breadth of a band about 1 millim., or $\frac{1}{5}$th of the distance between two bands. It is therefore useless to have a screw micrometer reading to $\frac{1}{100}$th of a band when the eye cannot judge more than $\frac{1}{10}$th. In the case of air at 10° C., 100 bands corresponds to a difference in level in the limbs of the manometer of about 16 centims. We may therefore consider the quantity $\frac{\text{bands}}{\text{pressure}}$ to be accurate to 1 part in 500.

With regard to the thermometers, they were made by R. MITTELBACH, in Göttingen, and divided in half degrees from 0° C. to 100° C. They could easily be read to $\frac{1}{10}$th of a degree, but this accuracy is not necessary. I had one of the thermometers standardised at Kew and compared the others with it under the same conditions as in the experiments. The thermometers used in the experiments were placed in a bath at constant temperature, the same amount of stem being exposed as in the actual experiments, while the standardised thermometer was completely immersed.

Atmospheric Air.

The air in the laboratory was used, and dried by means of phosphoric pentoxide. The tap L was kept shut so that the same air was in the apparatus throughout the experiments.

It would serve little purpose to give all the readings taken; and I shall confine myself to a few specimens. Throughout the initial pressure was as nearly as possible atmospheric pressure.

The thermometers in the jacket were marked 7 and 9, and the thermometer placed under the scale of the manometer marked 6.

15th November, 1901.

	Readings of thermometers in degrees Centigrade.			Readings of manometer in centimetres.		Number of bands.	Differences.		Ratio, $\frac{\text{bands}}{\text{pressure}}$
	9	7	6	Right limb.	Left limb.		Pressure.	Bands.	
	10·3	10	13·4	15·60	15·60	—	—	—	—
(1) . .	10·3	10	13·5	23·49	7·58	100	15·91	100	6·285
(2) . .	10·2	9·9	13·5	15·65	15·57	99·4	15·83	99·4	6·279
	10·2	9·9	13·5	15·60	15·60	—	—	—	—
(3) . .	10·3	10	13·5	23·48	7·58	100	15·90	100	6·289
(4) . .	10·4	10·1	13·5	15·60	15·60	99·8	15·90	99·8	6·276
	10·4	10·1	13·5	15·60	15·60	—	—	—	—
(5) . .	10·4	10·1	13·7	21·88	9·2	79·6	12·68	79·6	6·277
(6) . .	10·4	10·1	13·7	15·81	15·37	76·6	12·24	76·6	6·258

The correction for each of the thermometers at this temperature was + ·4° C.

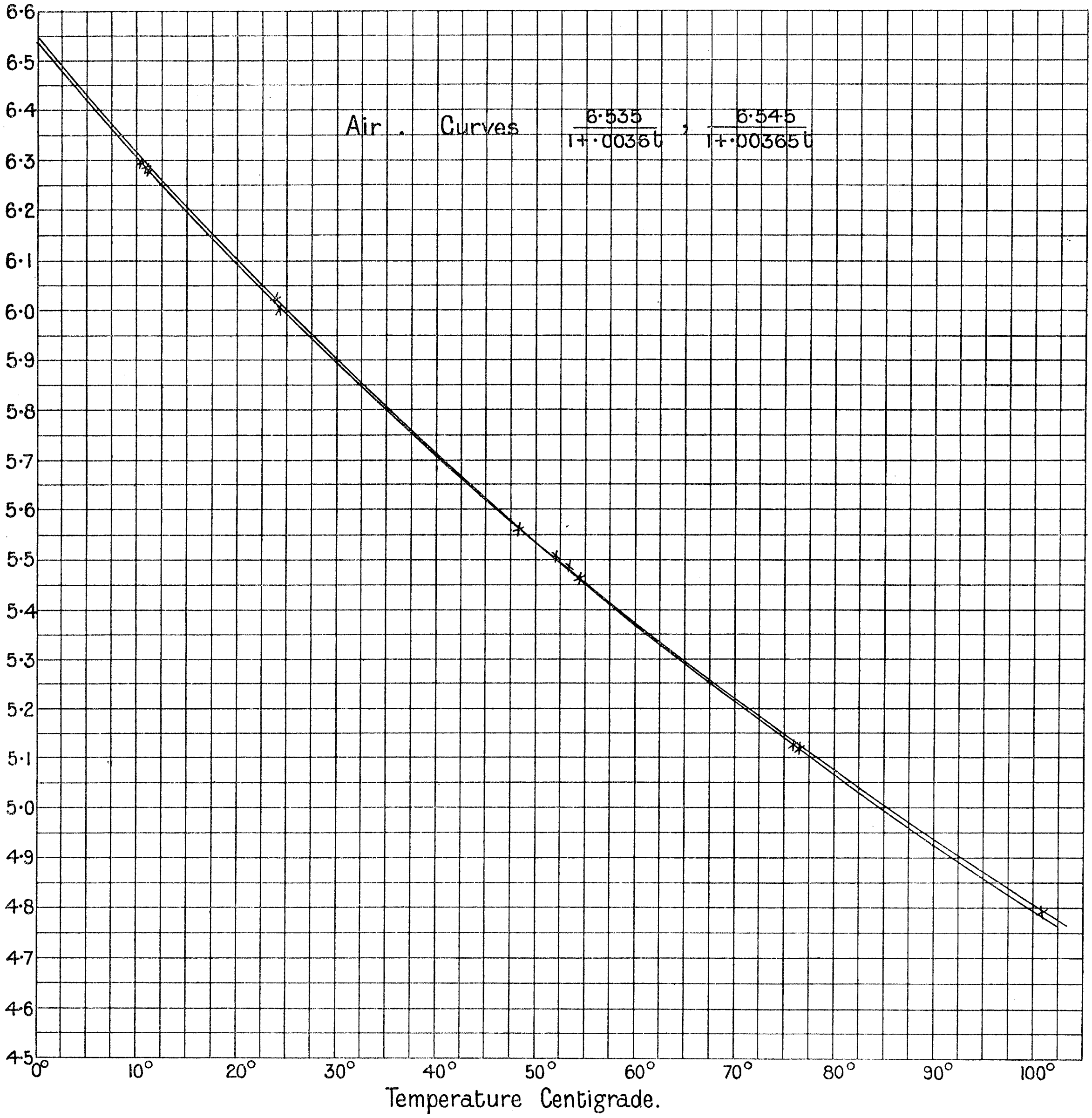

Diagram I.

Taking means we get

	Ratio.	Mean temperature of jacket, ° C.	Temperature of manometer, ° C.
From (1) and (2) . . .	6·282	10·55	13·9
,, (3) ,, (4) . . .	6·282	10·55	13·9
,, (5) ,, (6) . . .	6·267	10·65	14·1

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19th November, 1901.

	Readings of thermometers in degrees Centigrade.			Readings of manometer in centimetres.		Number of bands.	Differences.		Ratio, bands / pressure
	9	7	6	Right limb.	Left limb.		Pressure.	Bands.	
	51·6	52·2	16·5	15·61	15·61	—	—	—	—
(1) . .	51·4	52·1	16·5	22·39	8·70	75·2	13·69	75·2	5·493
(2) . .	51·4	52	16·4	15·61	15·58	75·2	13·66	75·2	5·505
	51·4	52·1	16·4	15·61	15·61	—	—	—	—
(3) . .	51·6	52·2	16·3	22·37	8·71	75	13·66	75	5·490
(4) . .	51·9	52·6	16·3	15·61	15·61	75·2	13·66	75·2	5·505

Making the necessary corrections on thermometer readings we get

	Ratio.	Mean temperature of jacket, ° C.	Temperature of manometer, ° C.
From (1) and (2) . . .	5·499	52·0	16·9
,, (3) ,, (4) . . .	5·497	52·1	16·7

25th November, 1901.

	Readings of thermometers in degrees Centigrade.			Readings of manometer in centimetres.		Number of bands.	Differences.		Ratio, bands / pressure.
	9	7	6	Right limb.	Left limb.		Pressure.	Bands.	
	100	100	12·2	15·60	15·60	—	—	—	—
(1) . .	100	100	12·4	23·90	7·13	80·4	16·77	80·4	4·794
(2) . .	100	100	12·6	15·61	15·57	80	16·73	80	4·781
	100	100	12·6	15·60	15·60	—	—	—	—
(3) . .	100·1	100	13	23·35	7·69	75·2	15·66	75·2	4·803
(4) . .	100·2	100·2	13	15·54	15·62	75·2	15·74	75·2	4·777

	Ratio.	Mean temperature of jacket, ° C.	Temperature of manometer, ° C.
From (1) and (2) . . .	4·787	100·9	12·8
,, (3) ,, (4) . . .	4·790	100·95	13·4
Mean . .	4·788	100·9	13·1

The next table gives a complete statement of the values of the ratio $\frac{\text{bands}}{\text{pressure}}$ at different temperatures.

It is convenient to reduce these values to what they would be if the mercury in the manometer was at 0° C. and the tubes of the length at 0° C.

The coefficient of expansion of brass was taken as ·000019.

The values of the corrected ratio are given in the fifth column. The next columns are the values obtained by multiplying the corrected ratio by the factors $(1+{\cdot}00355t)$, $(1+{\cdot}00360t)$ and $(1+{\cdot}00365t)$ respectively, t being the temperature Centigrade.

The values are calculated to the nearest 5 in the third decimal place.

DRY Atmospheric Air.

Date.	Temperature of tubes.	Temperature of manometer.	Ratio.	Corrected ratio.	Multiplied by		
					$1+{\cdot}00355t$.	$1+{\cdot}00360t$.	$1+{\cdot}00365t$.
	° C.	° C.					
15th Nov.	10·55	13·9	6·282	6·295	6·530	6·535	6·540
15th "	10·65	14·1	6·267	6·280	6·515	6·520	6·525
22nd "	11·0	15·8	6·267	6·285	6·530	6·535	6·540
22nd "	11·05	16·4	6·262	6·280	6·525	6·530	6·535
22nd "	11·05	16·9	6·270	6·290	6·535	6·540	6·545
26th "	23·9	13·6	6·011	6·025	6·540	6·545	6·550
26th "	24·3	14·0	5·989	6·000	6·520	6·525	6·530
19th "	48·4	15·9	5·551	5·560	6·515	6·530	6·540
19th "	52·0	16·9	5·499	5·510	6·515	6·530	6·545
19th "	52·1	16·7	5·497	5·510	6·515	6·530	6·545
18th "	54·3	14·4	5·450	5·460	6·510	6·525	6·540
18th "	53·2	14·9	5·482	5·490	6·525	6·540	6·555
18th "	53·0	14·9	5·489	5·495	6·530	6·545	6·560
21st "	76·5	18·4	5·109	5·120	6·510	6·530	6·550
21st "	76·1	18·1	5·115	5·125	6·510	6·530	6·550
25th "	100·9	13·1	4·788	4·790	6·505	6·530	6·555
				Mean	6·520	6·535	6·545
				Greatest variation . . .	+ ·020 − ·015	+ ·010 − ·015	+ ·015 − ·020

The superiority of the coefficient ·00360 is clear from the numbers. The results are also shown in the diagram on page 441. Moreover, the agreement between the results on the 15th and 22nd shows that no measurable alteration in the gas had taken place.

I think the numbers justify one in taking the ratio as

$$\frac{6{\cdot}535 \pm {\cdot}005}{1 + t({\cdot}00360 \pm {\cdot}00003)}.$$

The length of each tube was 99·9 centims. between the inner surfaces of the glass plates.

The wave-length for Na light may be taken as 5890×10^{-10} metre.

The standard atmosphere as 76 centims. of mercury at 0° C.

Hence we get for the refractive index of dry atmospheric air

$$\mu = 1 + \frac{\cdot 0002928 \pm \cdot 0000003}{\{1 + t(\cdot 00360 \pm \cdot 00003)\}} \frac{p}{76}.$$

Carbon Dioxide.

The gas was made by warming a bulb containing sodium bicarbonate and drying by means of phosphoric pentoxide. The whole apparatus was exhausted to under 1 centim. pressure by means of an oil-pump, and then the bulb containing the bicarbonate gently warmed until atmospheric pressure was attained. This process of exhausting and refilling was repeated about six times, so that the apparatus might be considered filled with practically pure CO_2.

Observing for nearly a week at about 10° C., I noticed a gradual diminution in the value of the refractive index, which was comparatively rapid at first and became very slow in a few days. The whole change was about 1 per cent. I consider that this was due to gas, probably air, coming off the walls slowly, and later results seem to support this view.

I refilled with pure CO_2, and now there appeared no change. The results are given in the following table. Throughout the initial pressure was maintained as nearly as possible at atmospheric pressure by adjusting the reservoir B.

CARBON Dioxide, put in 28th February, 1902.

Date.	Temperature of tubes.	Temperature of manometer.	Ratio.	Corrected ratio.	Multiplied by		
					$1 + \cdot 00375t$.	$1 + \cdot 00380t$.	$1 + \cdot 00385t$.
	° C.	° C.					
5th March	9·7	15·8	9·687	9·715	10·070	10·075	10·080
5th "	9·65	16·1	9·698	9·725	10·075	10·080	10·085
5th "	9·6	16·4	9·698	9·725	10·075	10·080	10·085
5th "	9·65	17·1	9·698	9·725	10·075	10·080	10·085
6th "	60·7	18·9	8·159	8·175	10·035	10·060	10·085
7th "	61·3	18·1	8·165	8·180	10·060	10·085	10·110
12th "	84·1	17·3	7·619	7·630	10·040	10·070	10·100
12th "	84·5	17·4	7·609	7·620	10·040	10·070	10·100
12th "	84·6	17·6	7·613	7·625	10·045	10·075	10·105
14th "	77·1	17·7	7·773	7·785	10·035	10·065	10·095
14th "	76·9	17·8	7·740	7·755	9·990	10·020	10·050
17th "	18·5	16·8	9·310	9·335	9·980	9·990	10·000
17th "	18·5	17·1	9·307	9·330	9·975	9·985	9·995
17th "	18·6	17·3	9·280	9·305	9·955	9·965	9·975
Mean, excluding 14th and 17th					10·055	10·075	10·090
Greatest variation					+ ·020 − ·020	+ ·010 − ·015	+ ·02 − ·01

The results on 14th and 17th March are quite anomalous and beyond ordinary error of observation, and my inference is that more impure gas had come off at the highest temperature. I therefore refilled with fresh CO_2, keeping the tubes at about 80° C. while filling.

The following table gives the results obtained on the new gas.

New Carbon Dioxide, put in 18th March, 1902.

Date.	Temperature of tubes.	Temperature of manometer.	Ratio.	Corrected ratio.	Multiplied by		
					$1+\cdot00375t$.	$1+\cdot00380t$.	$1+\cdot00385t$.
	° C.	° C.					
19th March	10·5	17·3	9·673	9·700	10·080	10·085	10·090
19th "	10·5	17·4	9·659	9·685	10·075	10·070	10·075
20th "	74·8	17·3	7·832	7·845	10·045	10·075	10·105
20th "	74·9	17·4	7·833	7·845	10·045	10·075	10·105
21st "	21·7	16·7	9·259	9·285	10·040	10·050	10·060
21st "	21·7	17·0	9·276	9·300	10·055	10·065	10·075
24th "	31·55	14·4	8·955	8·975	10·035	10·050	10·065
24th "	31·45	14·4	8·984	9·000	10·060	10·075	10·090
				Mean	10·055	10·070	10·085
				Greatest variation . . .	+ ·025 − ·020	+ ·015 − ·020	+ ·020 − ·025

No alteration appears to have taken place in the gas during the experiments. The results are also in very close agreement with the results on the former gas. Both sets are shown on the curve for CO_2.

We may take the ratio as

$$\frac{10\cdot070 \pm \cdot01}{1 + t(\cdot00380 \pm \cdot00003)}$$

and the refractive index for CO_2 is

$$\mu = 1 + \frac{\cdot0004510 \pm \cdot0000005}{\{1 + t(\cdot00380 \pm \cdot00003)\}}\,\frac{p}{76}.$$

Hydrogen.

The gas was prepared from zinc and moderately diluted hydrochloric acid. The apparatus was exhausted and filled about seven or eight times at the temperature of the room. The gas was dried by phosphoric pentoxide.

Observations for a week at about 10° C. indicated a gradual increase in the refractive index, which I attribute to carbon dioxide coming off the walls. When this effect had ceased, the apparatus was exhausted and kept exhausted for a few hours, while the temperature of the tubes was maintained at about 70°. I hoped in this way to remove all impure gas from the walls, but it will be seen from the results that

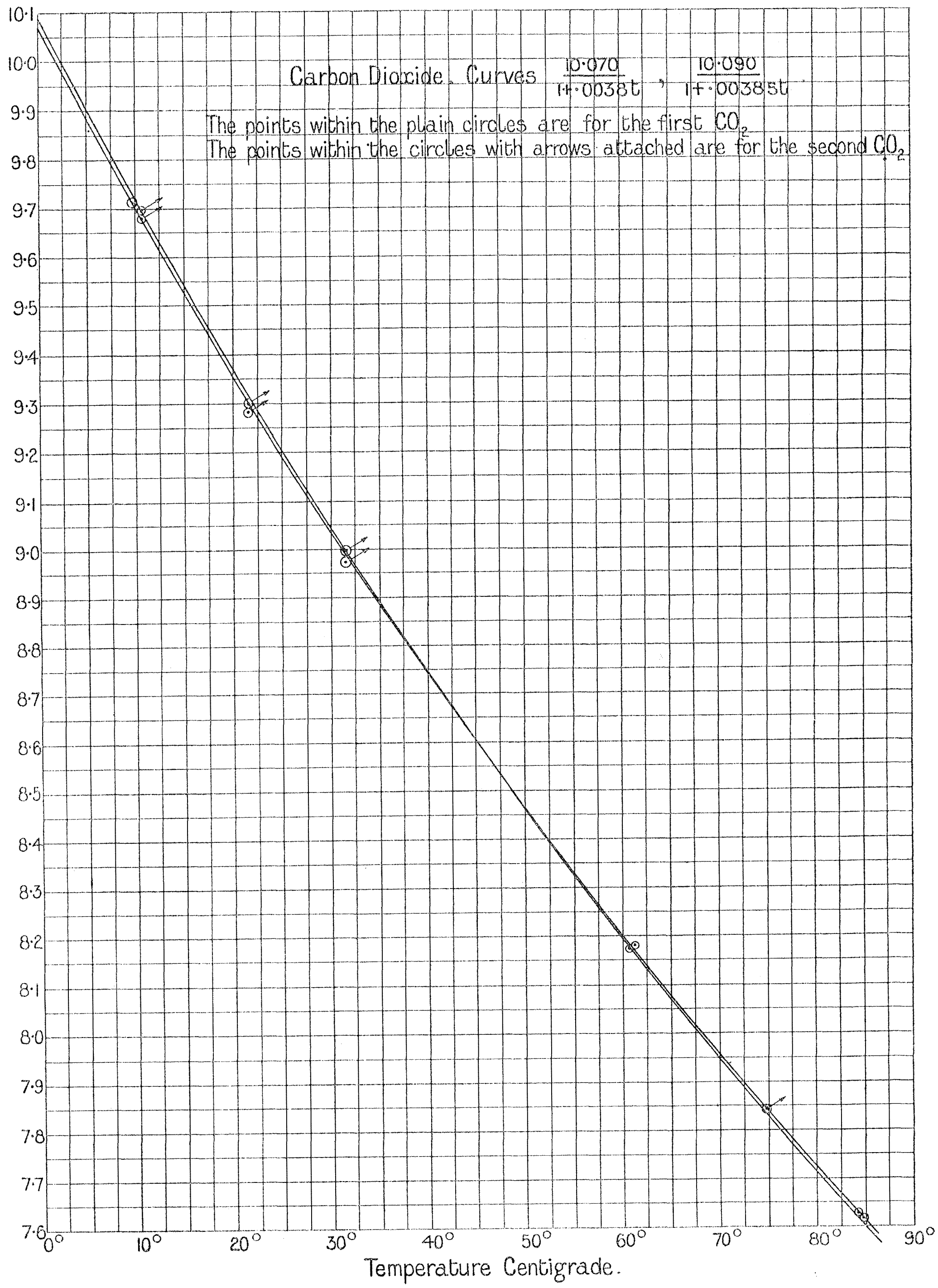

Diagram II.

I was not quite successful. The exhaustion and re-filling with new hydrogen was repeated about four or five times.

The results are given in the following table :—

HYDROGEN put in 21st April, 1902.

Date.	Temperature of tubes.	Temperature of manometer.	Ratio.	Corrected ratio.	Multiplied by		
					$1+\cdot00345t$.	$1+\cdot00350t$.	$1+\cdot00355t$.
	° C.	° C.					
22nd April	11·7	17·4	3·010	3·019	3·142	3·143	3·144
22nd ,,	11·7	17·6	3·007	3·016	3·138	3·139	3·141
23rd ,,	59·7	18·2	2·583	2·588	3·121	3·129	3·137
24th ,,	71·0	19·0	2·509	2·515	3·131	3·140	3·149
25th ,,	83·5	19·8	2·442	2·447	3·156	3·164	3·172
26th ,,	89·7	17·1	2·406	2·409	3·154	3·165	3·176
28th ,,	23·3	16·3	2·913	2·920	3·155	3·158	3·161
28th ,,	22·65	16·3	2·916	2·923	3·152	3·155	3·158
29th ,,	33·0	14·8	2·821	2·827	3·148	3·153	3·158
29th ,,	32·4	15·4	2·822	2·828	3·145	3·149	3·153
29th ,,	32·3	15·4	2·826	2·832	3·147	3·152	3·157
30th ,,	65·8	15·2	2·556	2·560	3·140	3·149	3·158
30th ,,	65·5	15·2	2·561	2·565	3·145	3·153	3·161
1st May	10·8	14·5	3·031	3·038	3·152	3·153	3·154
1st ,,	10·9	14·6	3·033	3·040	3·156	3·157	3·158
2nd ,,	77·5	14·4	2·476	2·479	3·141	3·151	3·161
3rd ,,	84·1	15·3	2·438	2·441	3·148	3·159	3·170
3rd ,,	83·2	15·6	2·442	2·445	3·147	3·157	3·167
5th ,,	81·7	13·2	2·447	2·449	3·139	3·149	3·159
5th ,,	10·65	13·2	3·042	3·048	3·159	3·161	3·163
		Mean			3.148	3·154	3·160
		Greatest variation . . .			+ ·011 − ·008	+ ·007 − ·005	+ ·010 − ·007

The results on the 22nd, 23rd, and 24th April are fairly consistent, but on raising the temperature to over 80° the values are distinctly higher. From the 28th onwards the agreement is quite satisfactory. I conclude that some impurity (CO_2) had come off at the higher temperature, and after that the composition remained constant. The results from the 28th onwards give a ratio

$$\frac{3\cdot154 \pm \cdot003}{1 + t\,(\cdot00350 \pm \cdot00003)}.$$

The value of the ratio at 0° for the original hydrogen may be taken as the mean of the first two observations on 22nd April. This gives 3·141. The amount of impurity is thus 13 in 3141, or 1 part in 240. This would not alter the value of the temperature coefficient to the present order of accuracy. I did not think it worth while to put in new hydrogen, as the absolute purity could hardly be relied on by this method of preparation.

We may take the ratio for the original hydrogen as

$$\frac{3{\cdot}141 \pm {\cdot}003}{1 + t\,({\cdot}00350 \pm {\cdot}00003)},$$

which gives for the refractive index

$$\mu = 1 + \frac{{\cdot}0001407 \pm {\cdot}00000015}{\{1 + t\,({\cdot}00350 \pm {\cdot}00003)\}}\,\frac{p}{76}.$$

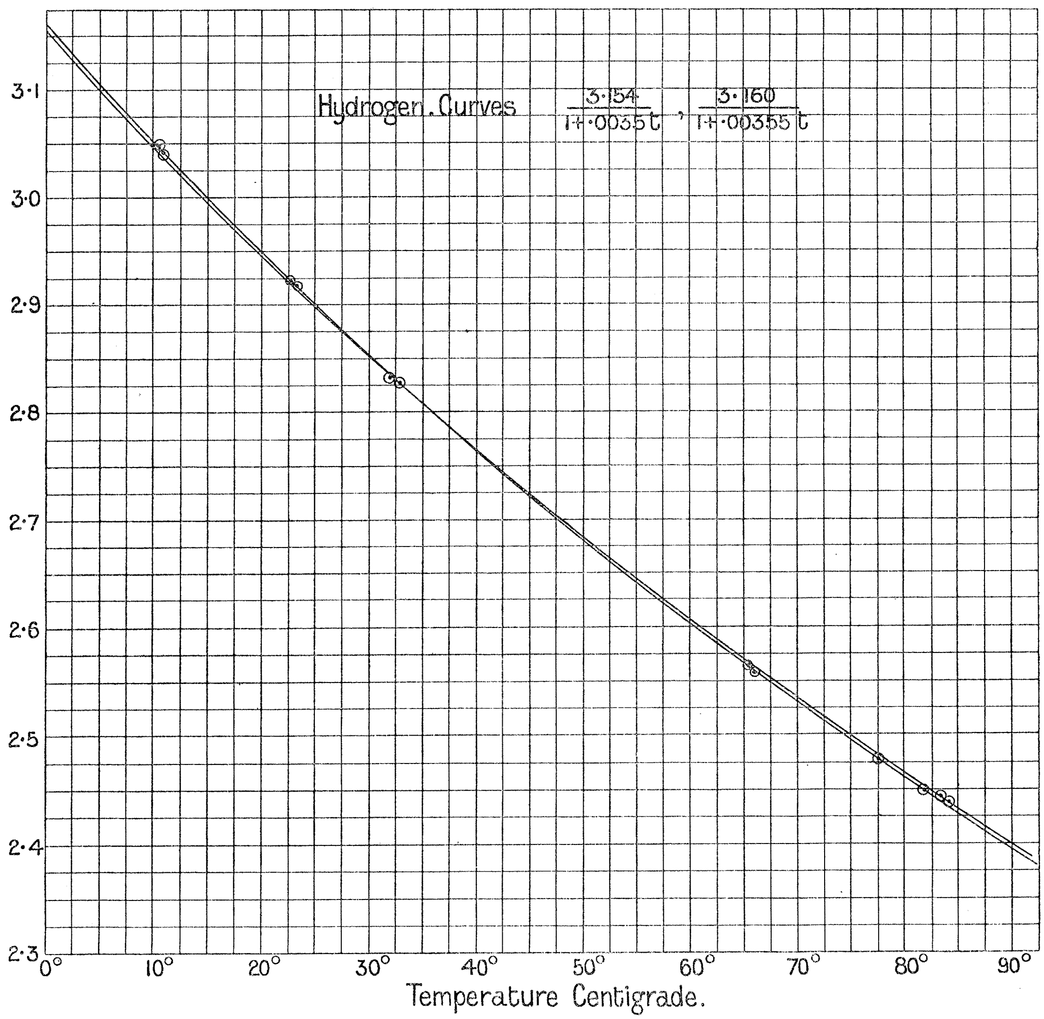

Diagram III.

Ammonia.

The gas was prepared dry by the following method, for which I am indebted to Dr. SCOTT, of the Davy-Faraday Laboratory.

A strong solution of ammonia, in a glass flask, was gently warmed, and the gas passed first through a tube containing dry caustic potash and next through a tube containing dry calcium chloride. The calcium chloride absorbs large quantities of the gas. One end of the tube was then sealed up and the other attached to the apparatus, and the whole exhausted with the oil-pump. On gently warming the calcium chloride tube, the ammonia gas was liberated. The former method, of exhausting and filling several times while the tubes were kept at about 90° C., was adopted; and after the gas had been in the apparatus for a few days, the process was repeated.

More care must be taken in the case of ammonia, since the gas does not strictly follow the ordinary gaseous law.

If p be the pressure and t the temperature, the refractive index may be written

$$\mu = 1 + \frac{\kappa p (1 + \lambda p)}{(1 + \alpha t)}.$$

Hence if p_0 be the initial pressure in the tubes,
p_1 ,, final ,, ,, one tube,
p_2 ,, ,, ,, ,, second tube,

the number of bands displaced

$$\propto \frac{\kappa (p_1 - p_2) \{1 + \lambda (p_1 + p_2)\}}{(1 + \alpha t)}.$$

According to MASCART* λ for ammonia = ·000178 per centimetre of mercury.

We must, therefore, take care that the value of $p_1 + p_2$ does not vary to any extent throughout the series of measurements. This point was carefully attended to, and the value of $(p_1 + p_2)$ was equal to 120 centims. throughout, the variation not exceeding 2 centims.

My main object being the temperature coefficient, and not so much the absolute value of μ, I did not make any measurements with another value of $p_1 + p_2$. This omission I now regret; but MASCART'S value may be used, as he made experiments specially on this point, and had much greater ranges of pressure than my apparatus was arranged for. In his papers I cannot find that he measured the temperature coefficient.

* 'Comptes Rendus,' vol. 86, 1878, p. 321.

AMMONIA Gas, put in 13th June, 1902.

Date.	Temperature of tubes.	Temperature of manometer.	Ratio.	Corrected ratio.	Multiplied by		
					$1+\cdot 00385t$.	$1+\cdot 00390t$.	$1+\cdot 00395t$.
	° C.	° C.					
17th June	11·8	15·5	8·139	8·160	8·530	8·535	8·540
17th "	11·8	15·6	8·140	8·161	8·530	8·535	8·540
18th "	56·25	18·2	6·997	7·012	8·530	8·550	8·570
18th "	56·0	18·2	7·003	7·018	8·530	8·550	8·570
19th "	60·6	20·2	6·887	6·904	8·515	8·535	8·555
19th "	60·3	20·4	6·904	6·921	8·530	8·550	8·570
20th "	75·5	19·4	6·597	6·610	8·530	8·555	8·580
20th "	76·4	19·4	6·572	6·585	8·525	8·550	8·575
20th "	76·8	19·8	6·562	6·575	8·520	8·545	8·570
23rd "	90·5	22·3	6·291	6·305	8·500	8·530	8·560
23rd "	90·5	22·7	6·283	6·298	8·490	8·520	8·550
23rd "	90·4	22·8	6·287	6·302	8·495	8·525	8·555
24th "	32·0	23·6	7·580	7·607	8·545	8·555	8·565
24th "	31·95	23·9	7·574	7·602	8·540	8·550	8·560
24th "	31·75	24·2	7·575	7·603	8·530	8·545	8·555
25th "	23·75	23·9	7·780	7·810	8·525	8·535	8·545
25th "	23·65	23·8	7·777	7·807	8·515	8·525	8·535
25th "	23·75	23·8	7·781	7·811	8·525	8·535	8·545
				Mean	8·523	8·540	8·557
				Greatest variation . . .	+ ·022 − ·033	+ ·015 − ·020	+ ·023 − ·022

I was unable to make a final observation at 12° C., owing to the fact that one of the glass joints had cracked during the night of the 25th June. However, the results of 17th and 25th June are a fairly good test that no change in the gas had taken place.

We may take the ratio as

$$\frac{8{\cdot}540 \pm {\cdot}010}{1 + t\,({\cdot}00390 + {\cdot}00003)}.$$

Throughout $p_1 + p_2 = 120$ centims. of mercury

$$\lambda = {\cdot}000178 \text{ per centimetre of mercury (MASCART).}$$

We thus obtain for the refractive index

$$\mu = 1 + \frac{({\cdot}0003743 \pm {\cdot}0000005)\,(1 + {\cdot}000178p)}{1 + t\,({\cdot}00390 \pm {\cdot}00003)}\,\frac{p}{76},$$

p being expressed in centimetres of mercury at 0° C.

At 0° C. and 76 centims. pressure

$$\mu_0 = 1 + {\cdot}0003793 \pm {\cdot}0000005.$$

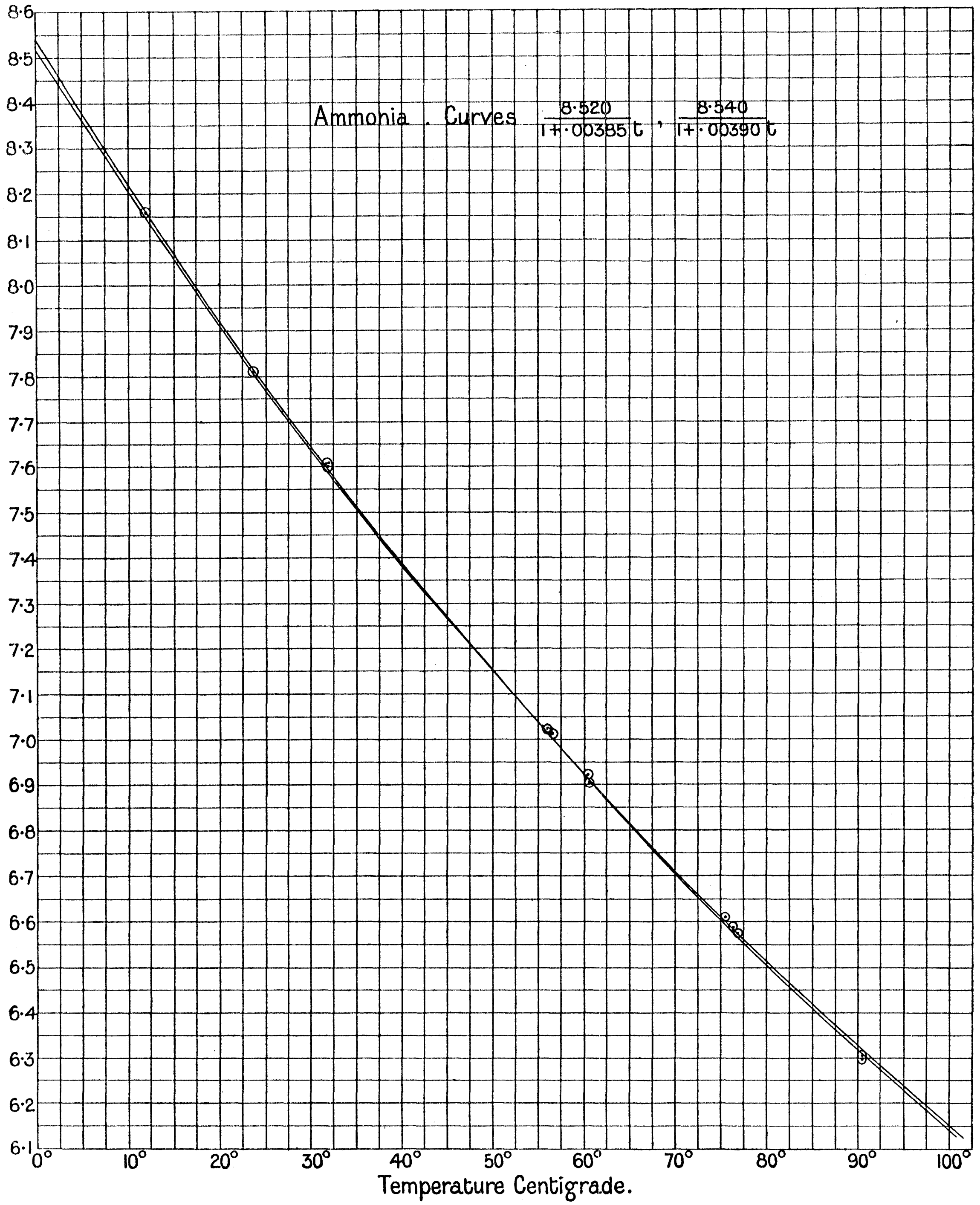

Diagram IV.

Sulphur Dioxide.

The gas was obtained from a syphon of the liquefied gas and dried by means of a phosphoric pentoxide bulb inserted in the apparatus. The former process of exhausting and refilling at a temperature of about 90° C. was adopted.

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As in the case of ammonia, the pressure conditions must remain the same throughout.

My first experiments gave a temperature coefficient about ·00415; but, after having been at a temperature about 90° C., there seemed to have been a considerable absorption of gas, so that I could not obtain the former pressure conditions at lower temperatures. I therefore put in new gas and kept a record of the pressures. There was still a gradual absorption of the gas, although not so great as before. Whether this was due solely to the walls of the apparatus or to the phosphoric pentoxide I am not in a position to say.

NEW Sulphur Dioxide, put in 16th August, 1902.

Date.	Temperature of tubes.	Temperature of manometer.	Ratio.	Corrected ratio.	p_1+p_2.	$\frac{\kappa}{1+\alpha t}$.	Multiplied by		
							$1+\cdot 00415t$.	$1+\cdot 00416t$.	$1+\cdot 00417t$.
	° C.	° C.							
18th Aug.	80·7	21·2	11·524	11·550	137	10·955	14·625	14·635	14·645
18th ,,	81·1	21·3	11·507	11·535	137	10·940	14·620	14·630	14·640
18th ,,	81·2	21·4	11·495	11·520	137	10·925	14·605	14·615	14·625
19th ,,	37·4	22·2	13·278	13·320	130	12·665	14·630	14·635	14·640
19th ,,	37·3	22·4	13·250	13·295	130	12·640	14·595	14·600	14·605
19th ,,	37·5	22·5	13·248	13·295	130	12·640	14·605	14·610	14·615
19th ,,	15·0	22·7	14·409	14·465	126	13·775	14·630	14·635	14·635
19th ,,	14·9	22·7	14·404	14·460	126	13·770	14·620	14·625	14·625
20th ,,	14·15	20·0	14·437	14·485	121	13·820	14·630	14·635	14·635
20th ,,	14·15	20·2	14·442	14·490	121	13·825	14·635	14·640	14·640
20th ,,	14·20	20·4	14·221	14·270	81	13·825	14·635	14·640	14·640
Mean							14·620	14·625	14·630
Greatest variation . . .							+ ·015 − ·025	+ ·015 − ·025	+ ·015 − ·025

The last two observations were made in order to obtain the coefficient of increase with pressure.

We have

$$\frac{\kappa}{1+\alpha t}(1+\lambda\, 121) = 14{\cdot}490,$$

$$\frac{\kappa}{1+\alpha t}(1+\lambda\, 81) = 14{\cdot}270.$$

Hence

$$\frac{\kappa}{1+\alpha t} = 13{\cdot}825, \qquad \lambda = {\cdot}000398.$$

The accuracy attained seems much greater than in the case of the former gases; but to be safe we take the ratio as

$$\frac{(14{\cdot}625 \pm {\cdot}01)(1 + {\cdot}000398p)}{1 + t({\cdot}00416 \pm {\cdot}00002)}.$$

This gives for the refractive index

$$\mu = 1 + \frac{({\cdot}0006553 \pm {\cdot}0000005)(1 + {\cdot}000398p)}{1 + t({\cdot}00416 \pm {\cdot}00002)} \frac{p}{76}.$$

At 76 centims. pressure and 0° C.

$$\mu_0 = 1 + {\cdot}0006758 \pm {\cdot}0000005.$$

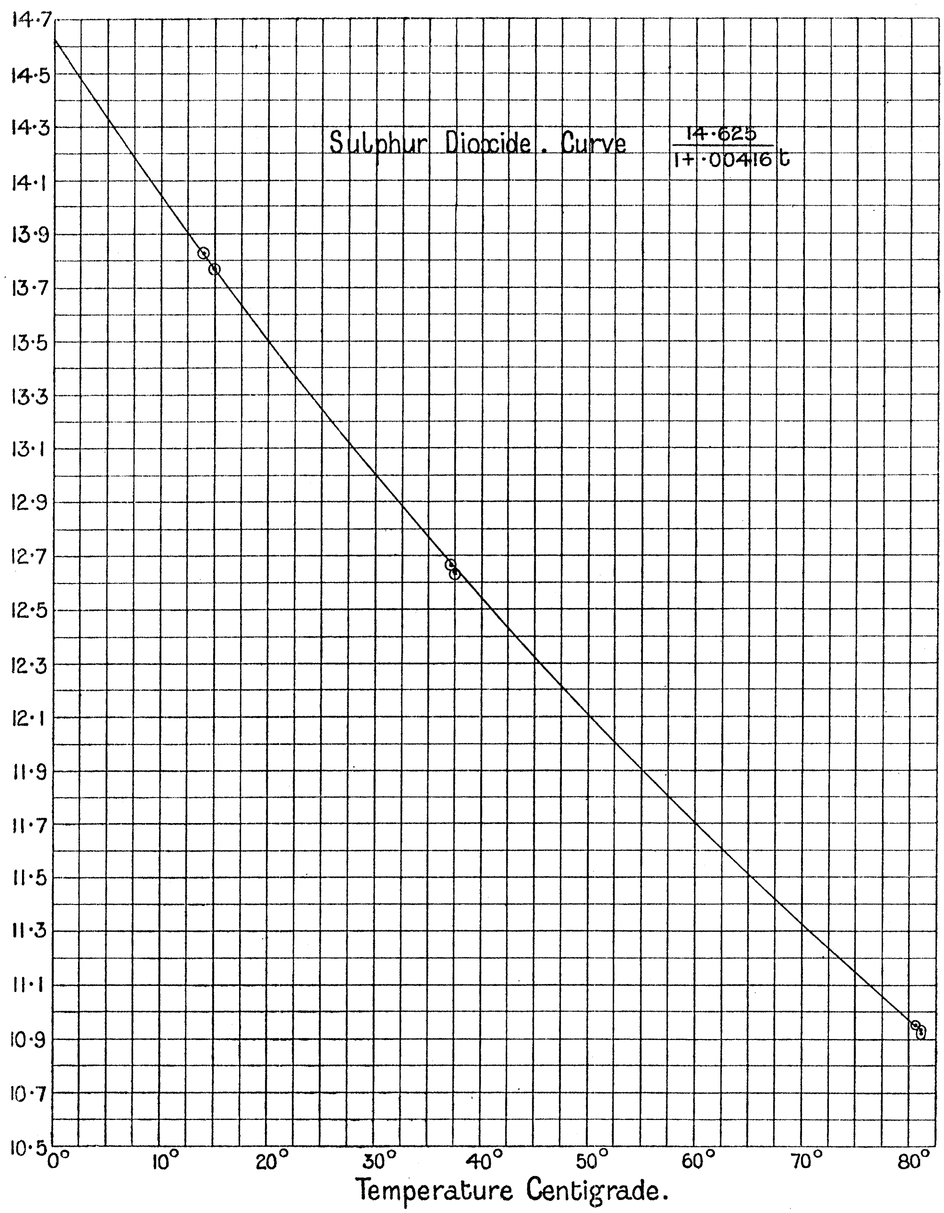

Diagram V.

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The following table gives a comparison of the results with those of former observers* :—

REFRACTIVE Index for Na Light at 76 centims. Pressure and 0° C.

Observer.	Air.	Hydrogen.	Carbon dioxide.	Ammonia.	Sulphur dioxide.
Present	1·0002928 ± 3	1·0001407 ± 15	1·0004510 ± 5	1·0003793 ± 5	1·0006758 ± 5
MASCART	1·0002927	1·000139	1·000454	1·000379	1·0007038
LORENZ	—	1·000139	—	1·000373	—
KETTELER . . .	—	1·000143	1·000449	—	1·000686
DULONG	1·000294	1·000138	1·000449	1·000385	1·000685

The following table gives a comparison of MASCART's temperature coefficients with those obtained in this paper :—

	Air.	Hydrogen.	Carbon dioxide.	Ammonia.	Sulphur dioxide.
Coefficient of expansion . .	·00367	·00366	·00371	—	·00390
MASCART, refractive index coefficient	·00382	·00378	·00406	—	·00460
Present	·00360 ± 3	·00350 ± 3	·00380 ± 3	·00390 ± 3	·00416 ± 2

The values of the temperature coefficient of refractive index obtained are, in every case, less than those obtained by MASCART. It is somewhat futile to attempt to explain the difference; but perhaps the following points are worthy of attention. In my apparatus the tubes were about 1 metre long and the two rubber washers together about $\frac{2}{5}$ millim. thick, while MASCART used tubes about 25 centims. long and his rubber washers were probably 1 millim. thick each. He does not mention the thickness, but LORENZ, who appears to have used an almost identical apparatus, used washers $1\frac{1}{2}$ millims. thick each. The somewhat irregular behaviour of rubber under varying conditions of temperature and pressure may have produced errors in MASCART's observations, from which I consider that mine are entirely free.

I have already referred to the apparent escape of impurities from the walls of the apparatus. MASCART makes no reference to this point, and gives no indication of how he tested the constancy of composition of the gas during the experiments. It is true he analysed the gas chemically after the experiments, but this is hardly accurate enough for the point in view.

* A very useful table of the results of different observers is given by BRÜHL, 'Zeitschrift für Physikalische Chemie,' vol. 7, 1891.

The difference between the temperature coefficient of refraction and the coefficient of expansion has naturally attracted my attention; but I do not propose to discuss the matter theoretically in this paper, mainly because I am now taking up experiments on the temperature coefficients of the dielectric constants, which I hope will give me a more complete basis for generalization.

In conclusion, I wish to express my great obligation to Professor THOMSON for having placed the appliances of the laboratory at my disposal, and for his kind interest in what has necessarily been a very tedious work.

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