V.—On the Composition of Air from Mont Blanc.

By DR. E. FRANKLAND, F.R.S.

THE greatly increased perfection of gasometric analysis and the numerous minute investigations made by Regnault, Bunsen and others during the past ten or fifteen years, have rendered our knowledge of the composition of atmospheric air exceedingly complete, as far at least as its two chief constituents are concerned. The earliest analyses of air led chemists to believe that the relative proportions of these constituents were liable to very considerable fluctuations. As the processes employed, however, became more accurate, these discrepancies gradually disappeared; until, at length, carefully conducted experiments showed an apparent uniformity in the composition of samples of air taken from the most widely different localities; but it remained for subsequent and far more delicate methods of research to demonstrate that, notwithstanding these apparently accordant results, the composition of the atmosphere does in reality exhibit certain fluctuations, confined, however, within very narrow limits.

The first series of experiments belonging to the latter category, and which may be said to have first established the variability of the percentage of atmospheric oxygen, are those of Bunsen, made

upon samples of air collected at Marburg on ten different days, and exhibiting, when freed from carbonic acid, a percentage of oxygen varying from 20·973 to 20·840, whilst no two analyses of the same sample differed more than ·031 per cent. from each other.

Then followed a most elaborate series of determinations by Regnault, begun in December, 1847, upon the air of Paris, and continued in January, 1848. The variations in the percentage of oxygen here observed were, in December, 1847, from 20·90 to 21·00, and in January, 1848, from 20·89 to 20·99.

Lewy collected air near the surface of the sea, on the 18th December, 1847, at 3 P.M., in lat. $21^{\circ} 9' N.$ and long. $42^{\circ} 52' W.$ of Paris, temperature $24^{\circ} C.$ and found it to contain :—

Nitrogen	.	.	.	78·886
Oxygen	.	.	.	21·060
Carbonic Acid	.	.	.	·054
				<hr/>
				100·000

Another specimen collected December 4th, 1847, at 3 A.M. in lat. $47^{\circ} N.$ and long. $13^{\circ} W.$, temperature $13^{\circ} C.$ contained :—

Nitrogen	.	.	.	79·006
Oxygen	.	.	.	20·961
Carbonic Acid	.	.	.	·033
				<hr/>
				100·000

A large number of analyses by the same chemist demonstrate that the air near the surface of the sea contains about the same proportion of carbonic acid as that resting upon the land, and that the sea air is richer, both in oxygen and carbonic acid by day than by night; a fact which he explains by assuming that dissolved air is liberated during the day from the heated surface-layer of the ocean, such dissolved air being, as is well-known, much richer than atmospheric air in the two gases just named. Lewy also made a very extended series of analyses of air collected at New Granada and Bogota, during the dry and rainy seasons. The mean of eleven analyses of air from New Granada gave :—

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Nitrogen	.	.	.	78·946
Oxygen	.	.	.	21·014
Carbonic Acid	.	.	.	·040
				<hr/>
				100·000

Analyses of air from Bogota collected during the dry and rainy seasons gave the following mean numbers :—

	Dry Season.	Rainy Season.
Nitrogen	. . 78·932	78·966
Oxygen.	. . 21·022	20·996
Carbonic Acid	. . ·046	·038
		<hr/>
		100·000
		<hr/>
		100·000

On some occasions, the air of New Grenada was found to contain as much as 0·49 per cent. of carbonic acid, on which occasions the percentage of oxygen fell as low as 20·331. This abnormal composition is ascribed to volcanic eruptions and extensive conflagrations. In nearly all cases, Lewy seems to have found that an increased amount of carbonic acid in the air was accompanied by an increase in the percentage of oxygen.

Messrs. H. and A. Schlagintweit determined, by weighing, the amount of carbonic acid in the air at great elevations in the Eastern Alps by absorption with potash; but as the increase in weight of the potash apparatus was only from 3 to 6 milligrammes in each experiment, and as the two weighings were made at intervals of nearly two months, these determinations can only be regarded as approximative. Messrs. Schlagintweit found the volume of carbonic acid to vary from ·032 to ·058 per cent. Up to an altitude of 11,043 feet, they found a gradual increase of carbonic acid, but at this elevation they conceived that a constant maximum was arrived at. In some later experiments on the air of Monte Rosa, at heights varying from 13,374 to 13,858 feet, the same experimenters found a mean percentage of carbonic acid equal to ·079 and a maximum of ·095.

In the year 1852, M. Regnault published an extensive series of determinations of the percentage of oxygen in samples of air,

deprived of carbonic acid, from different localities. The following is a condensed summary of his results :

		Percentage of Oxygen.	
100 specimens from Paris and neighbourhood			
	(1848)	20·913	20·999
9	„ „ Lyons, Montpellier & St. Martin-aux-Arbres .	20·918	20·966
30	„ „ Berlin (1848 & 1849) .	20·908	20·998
10	„ „ Madrid (1848) .	20·916	20·982
23	„ „ Geneva, Mont Salève and Mont Buet .	20·909	20·993
15	„ „ Toulon, the Mediterranean and Algiers .	20·912	20·982
5	„ taken during a voyage from Liverpool to Vera-Cruz .	20·918	20·965
1	„ from Guallalamba, South America	20·960	
2	„ „ the summit of Pichincha (15,924 feet) - . .	20·949	20·988

In this investigation, a few remarkable deviations from these normal amounts of oxygen were observed, viz. :—

	Percentage of Oxygen.	
Air collected in the Harbour of Algiers, June 5th, 1851	20·42	20·395
Air from Bay of Bengal, February 1st, 1849 .	20·46	20·45
Air from Ganges, March 8th, 1849. Temperature 35° C., foggy weather, much decomposing organic matter in the water. Commencement of an outbreak of cholera . .	20·390	20·387

It would be interesting to know how far these results were really abnormal, as regards the relative proportions of oxygen and nitrogen, since it is not improbable that the apparently small percentage of oxygen indicated, was in reality due to the presence of gaseous organic matters in larger quantity than usual ; the ignition of these with excess of hydrogen, in the mode adopted in these analyses would have the effect of converting the carbon of such organic matters into carbonic oxide, thus diminishing the contraction of volume on explosion and consequently the apparent

percentage of oxygen. Should such abnormal specimens of air be again encountered, it would be desirable, subsequently to the analysis made in the usual manner, to ignite other portions of them with an equal volume of mixed electrolytic gases, so as to convert the carbon of any organic matter that might be present into carbonic acid which could then be estimated in the usual manner by absorption with potash.

Dr. Miller examined air collected during a balloon ascent in August, 1852, at a height of 18,000 feet, and also a sample collected near the surface of the earth at the same time, with the following results :

	Air from altitude of 18,000 feet.	Air near the earth.
Percentage of Oxygen .	20·88	20·92

After these numerous and minute analyses, establishing as they do, with few exceptions, the slight, but still undoubted, variations in the relative proportions of the two chief atmospheric gases, any further contributions to this particular branch of our knowledge can only be of comparatively small value. Nevertheless, as an opportunity was afforded me for collecting specimens of air whilst accompanying Dr. Tyndall, during the past summer, in his ascent of Mont Blanc for the establishment of thermometric stations, I did not regard a few further experiments upon air from great altitudes as entirely superfluous ; since the discovery of the causes determining the variations in the composition of the atmosphere will probably only be arrived at by the accumulation of vast numbers of observations made at various points at and above the earth's surface. It will also be perceived, on reference to the various analytical results above given, that, with the exception of M. Lewy, no experimenter has made contemporaneous determinations of the three chief gaseous constituents of the air ; and I was therefore anxious, if possible, to render these samples available for the determination of carbonic acid, as well as of the two other chief gases.

The very minute changes of volume, which the instrument I use for gaseous analysis is capable of registering, led me to hope that it might not be impossible to make direct determinations of carbonic acid in the few cubic inches of air which are usually sealed up for analysis ; and a number of estimations of the carbonic acid in air, collected at St. Bartholomew's Hospital, proved that

this gas can be thus estimated, by absorption with caustic potash. Such an amount of air was taken for each determination, as was capable of supporting a column of mercury, from 600 to 800 millimeters high, which rendered any diminution of volume, to the extent of about $\frac{1}{7000}$ part, distinctly appreciable. The following results were obtained, those on the 26th of January, being seven successive determinations, extending over about three hours :

Date.				Percentage of Carbonic Acid.
Dec. 7, 1859	.	.	.	·042
Jan. 10, 1860	.	.	.	·064
„ „	.	.	.	·077
26, „	.	.	.	·098
„ „	.	.	.	·087
„ „	.	.	.	·098
„ „	.	.	.	·085
„ „	.	.	.	·098
„ „	.	.	.	·110
„ „	.	.	.	·101

Although it cannot be doubted that there are other methods by which carbonic acid can be more minutely and accurately determined, whenever they can be carried out with the usual conveniences of a laboratory at hand, yet it is very questionable, whether any of these processes can rival this purely eudiometrical one, in cases where the operations have to be performed in the midst of all the inconveniences attending an experimenter at great altitudes. Any such estimations, involving the weighing of potash tubes at intervals of several days, or even weeks, are obviously not worthy of implicit confidence. In the above mode of determination, the actual change of volume, self-corrected for temperature, aqueous vapour, &c., being actually observed by the operator, an error exceeding ·01 per cent., is probably rarely or never committed.

In the following analyses of air from Mont Blanc, the carbonic acid was absorbed by a single drop of concentrated solution of caustic potash, and the oxygen was then determined by exploding the residual gas with excess of electrolytically prepared hydrogen.

Specimen collected at the Grands Mulets (altitude 11,000 feet), August 20th, 1859, at 6·45 p.m. Wind, north, hail falling, but a moderately clear sky.

Estimation of Carbonic Acid.

I.

	Obs. vol.	Temperature C.
Air used	539.5	5.0°
After absorption of carbonic acid .	538.9	5.0°

Estimations of Oxygen.

II.

	Obs. vol.	Temperature C.
Air used	290.8	5.2°
After admission of hydrogen .	486.5	5.2°
After explosion	304.9	5.2°

III.

	Obs. vol.	Temperature C.
Air used	248.7	5.2°
After admission of hydrogen .	443.8	5.2°
After explosion	288.7	5.2°

Percentage Composition.

	I.	II.	III.	Mean.
Nitrogen	..	79.096	79.124	79.110
Oxygen	..	20.793	20.765	20.779
Carbonic acid	0.111	..	..	0.111
				<hr/> 100.000

Specimen taken at the summit (altitude 15,732 feet), August 21st, at 8.45 A.M. Wind, north; weather bright and sunny; air filled with particles of snow whirled up by the wind.

Estimation of Carbonic Acid.

I.

	Obs. vol.	Temperature C.
Air used	326.1	5.2°
After absorption of carbonic acid .	325.9	5.2°

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Estimations of Oxygen.

II.

	Obs. vol.	Temperature C.
Air used	166·8	5·3°
After admission with hydrogen	273·0	5·3°
After explosion	168·1	5·3°

III.

	Obs. vol.	Temperature C.
Air used	159·9	5·3°
After admission of hydrogen	302·7	5·3°
After explosion	202·7	5·3°

Percentage Composition.

	I.	II.	III.	Mean.
Nitrogen	..	78·989	78·988	78·989
Oxygen	..	20·950	20·951	20·950
Carbonic acid	0·061	..	..	·061
				<hr/> 100·000

Specimen collected at Chamonix (altitude 3000 feet), August 23rd, at 2 P.M. Wind north; sky clear.

Estimation of Carbonic Acid.

I.

	Obs. vol.	Temperature C.
Air used	474·1	5·4°
After absorption of carbonic acid	473·8	5·4°

Estimations of Oxygen.

II.

	Obs. vol.	Temperature C.
Air used	255·6	5·0°
After admission of hydrogen	455·8	5·0°
After explosion	295·5	5·0°

III.

	Obs. vol.	Temperature C.
Air used	217·4	5·0°
After admission of hydrogen . . .	377·3	5·0°
After explosion	241·1	5·0°

Percentage of Composition.

	I.	II.	III.	Mean.
Nitrogen	..	79·045	79·067	79·056
Oxygen	..	20·892	20·870	20·881
Carbonic acid	·063	..	..	·063
				<hr/> 100·000

So far as the nitrogen and oxygen are concerned, the composition of these samples of air falls within the limits of variation noticed by former experimenters; but, although the comparatively high percentage of carbonic acid, at the Grands Mulets, confirms the observations of the Messrs. Schlagintweit, as to the presence of a larger amount of this gas at great elevations, yet the diminution of the quantity to about the normal amount upon the summit, shows, either that this gas attains a maximum at a height of about 11,000 feet, and again diminishes above this altitude, or, as is much more probable, the percentage of carbonic acid is *generally, but not invariably*, greater in the higher regions of the atmosphere. These results also exhibit a correlation between atmospheric oxygen and carbonic acid, for when the one increases the other diminishes,—a fact which will be better seen from the following comparison:—

	Percentage of carbonic acid.	Mean percentage of oxygen, in air free from carbonic acid.
Grands Mulets	·111	20·802
Summit	·061	20·963
Chamounix	·063	20·894

This result, if it be confirmed, cannot be regarded as altogether unexpected, when we consider the effects of vegetation, combustion, and respiration upon the constituents of the atmosphere; but both this and the comparative amount of carbonic acid at great altitudes, are problems, the solution of which must be left to future and more extended inquiries.