ART. XXVII.—*On a possible cause of variation in the proportion of Oxygen in the Air;* by EDW. W. MORLEY, M.D., PH.D., Professor of Chemistry in Western Reserve College, Hudson, Ohio.

PROFESSOR LOOMIS has proposed the theory that certain great and sudden depressions of temperature at the surface of the earth are caused, not by the transfer of cold air from higher to lower latitudes, but by the vertical descent of air from cold elevated parts of the atmosphere. The evidence supporting this theory was published in this Journal in January and July, 1875. It occurred to the writer some time since that if this theory were true, as the evidence makes very probable, the air at the surface of the earth during such a great and sudden depression of temperature might well contain a smaller proportion of oxygen than the average. Dalton, reasoning from the fact that oxygen has a greater specific gravity than nitrogen, argued that the proportion of oxygen to nitrogen in the atmosphere should decrease with increasing altitude above the earth's surface; whether he clearly enough recognized that such a regular decrease would be realized only in an atmosphere in a state of equilibrium undisturbed by convection currents, the writer does not know, not having seen Dalton's memoir. Such a decrease of atmospheric oxygen with increasing altitude has not yet been detected by analysis, although the amount of decrease, on the theory that oxygen and nitrogen are distributed in the atmosphere according to the law which would prevail in case of equilibrium, is so rapid that it would be detected with ease, even in altitudes attained in every holiday ascent of a balloon. This decrease may be calculated from the formula $R=R_0 0{\cdot}9832960^{H}$, where H denotes the height above the earth's surface expressed in kilometers, R_0 denotes the ratio of the tension of oxygen to that of nitrogen at the surface of the earth, and R denotes the same ratio for the height H. The constant is computed from the determinations by Regnault of the weights of a litre of oxygen and of nitrogen, and of the specific gravity of mercury. The following table gives in the second column the ratio of the tension of oxygen to that of nitrogen at the height in kilometers given in the first column, and the per cent of oxygen at the same height in the third column. The per centage of oxygen at the earth's surface assumed in the table is that used in the tables for gas analysis in Bunsen's Gasometrische Methoden.

It will be seen that the composition here calculated for a height of a single kilometer is so different from that at the surface that analysis of no very refined accuracy would detect the variation with ease. But no such variation has been detected even in samples of air collected at the greatest elevations attainable.

Height, Kilometers.	Ratio of O to N.	Per cent of O.	Height, Kilometers.	Ratio of O to N.	Per cent of O.
0	26·52 %	20·96 %	10	22·41 %	18·31 %
1	26·08	20·68	20	18·93	15·92
2	25·64	20·41	30	16·00	13·79
3	25·21	20·14	40	13·52	11·91
4	24·79	19·87	50	11·42	10·25
5	24·38	19·60	60	9·65	8·30
6	23·97	19·34	70	8·16	7·54
7	23·57	19·07	80	6·89	6·45
8	23·18	18·82	90	5·82	5·50
9	22·79	18·56	100	4·92	4·69

But although this is the case, it is certain that in the atmosphere of the same place at different times the oxygen varies by more than one-fortieth of its average amount. Variations so large as this are rare, but variations of the one-hundredth or two-hundredth part are common. It therefore seemed to the writer proper to examine whether facts bear out the conjecture that certain great and sudden local depressions of temperature are caused by the descent of cold air from the upper part of the atmosphere, and that such air may by its poverty in oxygen throw some light on a question in meteorology and a question concerning the physics of a mixture of different gases.

In the number of Wiedemann's Annalen for April of the current year, Jolly has published the results of numerous and very accurate analyses of atmospheric air. He asserts a connection between the variations in composition detected and the direction of the winds when the sample was collected. He considers himself justified in concluding that the atmosphere of tropical regions is poorer in oxygen than that of polar regions, and supposes that at the equator more oxygen is consumed in processes of oxidation than is set free by those of reduction, while the opposite is true near the poles. Since no difference in the composition of the atmosphere at the equator and at the poles has been detected, while on this theory the difference must be one large enough to account for the extreme variations found in temperate regions, and to account for them after such abnormal air had been exposed to admixture with air of a different composition during a passage of thousands of miles, the writer fears that the theory of Jolly will need further proof. Other reasons for a similar doubt will suggest themselves.

On the writer's theory, a sample of air collected at the center of an area covered by a descending current of cold air would at some given instant be a sample fresh from the upper part of the atmosphere, but little exposed to admixture on the way. If before its descent it had remained at a great height for a long time, it might well have lost some of the oxygen which it contained when it was at some previous time at the level of the sea, and the difference might be enough to be detected. An observer at one side of this central point would have samples more or less mingled with surface air; but even then, a deficiency of oxygen might be detected by accurate analysis.

The writer hopes to make arrangements for the regular collection of samples at points which Professor Loomis has indicated as regions of frequent descent of cold air from great heights. But while laying plans for the work, he has thought best to ascertain whether some light on the changes in the constitution of the atmosphere might be obtained by analyzing samples of air collected at home. Having an apparatus for gas analysis lately constructed for the study of the gas issuing from the numerous gas wells of his vicinity, he used this for such determinations. In general, the apparatus is constructed on the plan of McLeod's modification of Frankland and Ward's apparatus. But some important modifications have been introduced, and excellent workmanship was bestowed on details. Some such points but slightly concern analyses by explosion. The connection between the eudiometer and absorption tubes is novel, and has worked well. This will be described in some proper connection. Here will be described everything necessary for a judgment of the accuracy of the analyses to be cited.

The eudiometer and pressure tubes were made from the writer's drawings by Geissler, whose recent death is a loss to science, and a personal loss to so many who have been aided by him. The stop-stocks at the top of these tubes will retain a Torricellian vacuum for weeks. The internal diameters of the tubes are 20·9 and 10·7 millimeters. At the lower end of the eudiometer tube is a glass stop-cock, the use of which is simply to permit the ready cleaning of the tube. Its glass plug is withdrawn, and in place of it is put one of vulcanite so bored that acids or water can be aspirated through the eudiometer without dismounting it and without drawing off the mercury from the pressure tube. The stop-cock at the top of the eudiometer tube is also provided with a similar plug for the same purpose. The pressure and eudiometer tubes are surrounded by a stream of water entering at the top of the pressure tube and running away from near the bottom of the two. The level of water is kept constant by a device similar to that of Thomas, described in a late number of the Journal of the Chemical Society, but perhaps superior to his in some respects. The flow of mercury to and from the movable reservoir is controlled by an iron stop-cock which is attached to the iron tripod support of the whole apparatus. The plug of this stop-cock is vertical, and is prolonged by a shaft which puts it within easy reach of the observer. By means of a long handle on this shaft, the stop-cock can be moved with the greatest delicacy. From this stop-cock, an iron tube, cast in the same piece, extends under the ends of the glass tubes of the apparatus, and two small iron tubes rise from this horizontal tube; these last meet the glass tubes and are connected with them by short tubes of patent black rubber containing no free sulphur. The connectors are tied so as to endure the pressure of mercury having a head of several feet, and are surrounded with mercury so as to be absolutely air-tight. The plug of the iron stop-cock is also so surrounded with mercury that the entrance of air is absolutely impossible, and the same precaution was taken at the junction of the two small iron tubes with the horizontal tube. The cast iron of this tube and stop-cock is well japanned, and no leakage through its pores has occurred.

The measurement of the volume of gas in such an apparatus demands an accurate adjustment of the level of the mercury in the eudiometer tube to one of the marks of the graduations. Such an adjustment can be accurately made by admitting mercury very slowly from the reservoir, and closing the stop-cock at the required moment. But if now the temperature of the gas be not quite constant, the adjustment can be renewed for a second reading only by letting in or out a column of mercury of several millimeters, again permitting it very slowly to approach the proper level, and stopping at the instant of contact. It is quite impossible to open the stop-cock, admit the twentieth or fortieth of a millimeter of mercury, note the right instant, and then again close the stop-cock. But for accurate work, the means of altering the level of the mercury by such small quantities, and of doing it by a continuous movement, seemed important. In the end, therefore, of the horizontal iron tube, there works a plunger, packed with great care, which can be moved in or out by a screw. By means of this micrometric movement, the level of the mercury which has been adjusted by the stop-cock can be altered with the greatest delicacy, and readjusted till perfect steadiness is attained. Danger of leakage through the washers around the plunger was prevented by providing a seat into which, when the plunger is screwed quite home, it fits so as to cut off connection between the pressure tube and the rest of the apparatus. The mercury in the pressure tube is, by the use of this valve, always kept at such a height that any possible leakage is that of mercury outward, and not of air inward.

The eudiometer and pressure tubes are cemented into the brass cap of the glass cylinder containing the water intended to keep all parts of the apparatus at the same temperature. The level of the two graduations with respect to each other is therefore constant.

When the writer planned to make analyses of air in order to detect if possible some law in its variations of composition, he expected to have to do with quantities but little larger than the errors of observations. Some thought was therefore given to the methods of keeping such errors as small as possible. It was hoped that if the probable error of a determination of oxygen with this apparatus was not larger than the probable error of the analyses made by Bunsen in January and February, 1846, the object of the analyses would be attained. Such analyses as those of Bunsen would abundantly serve to establish variations of the four hundredth part of the average amount of oxygen contained in the atmosphere. The writer expected to have commonly to do with such variations, and therefore computed the comparative accuracy of analyses of air made with the long eudiometer of Bunsen's experiments, and with the apparatus used in the present work. In the first analysis by Bunsen of the air of January ninth, the length of the column of gas in the eudiometer was in round numbers, 840 millimeters, and its tension 510. The tension was determined by four readings, and the apparent volume of air taken by one reading. An error in the last reading would produce also an error of the same sign in the observed tension, so that these two errors are not independent. Their influence on the result is therefore computed by simply adding them; the other errors are independent of this joint error and of each other. And the influence of the four independent errors on the result is computed by taking the square root of the sum of their squares. If we repeat this computation for the different volumes and tensions of the second and third measurements, referring all the probable errors to the volume of air first taken, and obtain the probable errors of the three measurements, we may obtain the probable error of the final result by adding the square of the first probable error to the squares of the third parts of the second and third, and taking the square root of the sum.

The probable error of a single reading of the level of the mercury in Bunsen's experiments is not given; but we may compare the two methods by assuming arbitrarily some probable error, provided that we assume the same error in both computations. The first column of the following table gives the influence of a probable error of one-tenth of a millimeter in a single reading in each of the three measurements of the analysis quoted from Bunsen.

In the measurement of a volume of gas with the Frankland and Ward or McLeod apparatus, the mercury is brought to that mark in the eudiometer tube which will give a suitable tension, and the height in the pressure tube at which the mercury stands is determined. An error in determining the volume of gas in the eudiometer tube involves an error of the same sign in the observed tension. If we add these two dependent errors we have one of the two independent errors affecting this mode of measurement, the other being the error probably made in determining the upper level of the mercury in the pressure tube. Adding the squares of these two and taking the square root, we have the probable error of a measurement with the apparatus. If we treat the second and third measurement in the same way, and compute the effect of these three probable errors on the final result, we get the numbers in the second column of the following table.

Probable errors of measurements of gas, and of final results, occasioned by a probable error of the tenth of a millimeter in each reading.

	In Analysis cited from Bunsen.	With Frankland and Ward apparatus.
In measurement of air taken	0·046 %	0·034 %
In measurement of air and hydrogen	0·050	0·042
In measurement after explosion	0·039	0·031
Probable error of result	0·051	0·038

It is obvious that with the same error probable in each reading, the use of the rapidly working apparatus involves no sacrifice of accuracy to convenience, as far as the conditions of *observation* are concerned.

To obtain the degree of accuracy needed for the present purpose, it is necessary to take account of the expansion of the mercury in the column which measures the pressure, and also of the linear expansion of the scale which measures the tension, and of the cubical expansion of the eudiometer tube. Since all these are at the same temperature with the gas to be measured, it is easy to prepare a table giving the correction not only for the expansion of the gas but also for the expansion of mercury, scale and eudiometer. Such a table, giving on a single page, for every tenth of a centigrade degree from zero to thirty degrees, the logarithmic factor to be added to the logarithms of the observed volume and observed tension, makes the work of reduction very slight. Most tables of correction of the volumes of gas contain a logarithm to be subtracted; for convenience it should be additive; and five places of decimals should not be exceeded. Unless measurements can be made ten times more accurate than Bunsen's, five places of logarithms distinguish smaller differences than observation deals with; five places permit instant interpolation for hundredths of a degree, and a greater number waste time and possess no advantage whatever.

The eudiometer was calibrated by filling it with air-free water, and weighing the quantity expelled as the mercury rose to each successive mark of the graduation. This was done four times for each division; the probable error of a single determination was found to be 8·6 milligrams of water. The results were all reduced to the temperature of melting ice. There were seventeen divisions in the eudiometer tube, now broken, which was used in all the analyses in this paper. The volume of gas to be measured was always brought to one of the two divisions which permitted measurement under the most favorable conditions, and its tension determined; it was then brought to the other division, and its tension again determined. Two independent measurements thus obtained eliminated the chance of error in identifying divisions on the scale, and also afforded the means of ascertaining the probable error of a measurement. In the analyses contained in this paper, the quantity of air taken was unfortunately limited by the circumstance that the collecting tubes at hand were small; the probable error of the results so far obtained is therefore much greater than is due to the care used in observing. In analyses made after the present month this mistake of judgment will be corrected. The mean quantity of air taken in an analysis so far has been 38·9 cubic centimeters measured at zero and 760 millimeters. From 196 pairs of measurements it has been computed that the probable error of a single determination of volume is its 5800th part. Hence the probable error of a determination of oxygen in the air is the 7200th part, and the probable difference of two determinations on the same sample is the 5100th part. A second analysis was always made when the first showed a deficiency of oxygen. A comparison of the results will show whether the accuracy indicated by computation was obtained.* The writer has in hand an entirely new construction of the pressure tube, and some modifications of the optical appliances for reading the level of the mercury in the eudiometer tube, by which he hopes considerably to lessen this probable error.

The samples of air analyzed were collected in the open country in glass vessels with due care as to admixture with the air from the collector's lungs, preserved over mercury, freed from carbonic acid, and exploded with hydrogen, of proved purity, obtained by galvanic decomposition of water. But

* The divergence of the second result of February 26th from the first is due to the fact that in the second analysis the hydrogen used was not pure. As none of the sample remained for a third experiment, the second result is given in confirmation of the first. But this pair of results should not be used in computing probable errors.

some samples were collected in clean stoppered and capped bottles, and kept for a short time by inverting the bottle in the cap which had been filled with water. In this case the air was withdrawn for analysis with a Tœpler's mercury pump.

The table gives in the first column the date, in the second, the mean temperature of the day at this place as determined by three observations. In the third, on the days when analyses were made, the hour of collecting the sample is given, fractions of hours being disregarded. In the last two columns are given the hundredths per cent found by analysis, the figures twenty and the decimal point being suppressed. The figures ninety-six, for instance, in this column mean 20·96 per cent of oxygen. Within the time covered by the analyses now published, there were several well marked great and sudden depressions of temperature, and the figures show the falling off in the proportion of oxygen in the air at these times to be as well marked as the depression of temperature. The deficiency is not proportionate to the depression of temperature; this could not be expected.

It may be said that these analyses were commenced in March, 1878, but in December of that year, a doubt was felt whether it were absolutely certain that in every case the air and hydrogen had been completely mixed before explosion. In test cases, the air and hydrogen had been permitted to diffuse into each other for eighteen hours before explosion, and the results were the same as in the usual course of analysis; but the analyses are not here given, although they contain only evidence perfectly agreeing with that here presented. In all the analyses here printed, the air and hydrogen were known to be thoroughly mixed; they were driven as rapidly as possible through a capillary tube twelve or twenty times. All made between the first and last dates of the table are given without selection, except that some were rejected for obvious instrumental errors.

The remarkable deficiency of oxygen observed on the twenty-sixth of February seems affected with no reason for doubt. On Sept. 16, 1878, two very careful analyses of the same sample gave 20·49 and 20·46 per cent of oxygen. On July 19, and Nov. 10, 1877, Jolly found 20·56 per cent. The Neues Handworterbuch der Chemie, i, 856, cites an analysis of air from the Bay of Bengal showing 20·46 per cent, one of air from near Calcutta, showing 20·39 per cent, and one of air from near Algiers, showing 20·41 per cent. That Jolly and the writer have found air almost as deficient in oxygen as the three last will lessen the probability that the air of the surface of the earth in the Torrid zone is normally poor in oxygen. One of the first cases of a supposed descent of cold air from

Analyses of Air,

Showing deficiency of Oxygen attending sudden depression of temperature.

Winter of 1878–1879.

Date.	Mean Tempera-ture. F.	Hour of taking sample.	Oxygen.		Date.	Mean Tempera-ture. F.	Hour of taking sample.	Oxygen.	
Dec. 28	---	4 P. M.	98	96	Feb. 16	26·3	9 A. M.	95	
29	14·8				17	25·7			
30	19·3				18	24·1			
31	16·2				19	23·2			
Jan. 1	23·8				20	18·9	6 P. M.	87	87
2	7·6	4 P. M.	91	92	21	17·9			
"		10 P. M.	90	89	22	---			
3	—7·2	9 A. M.	90	91	23	25·4			
"		1 P. M.	96	97	24	21·5			
4	2·2				25	37·1			
5	7·7				26	22·3	3 P. M.	45	50
6	13·5	3 P. M.	97		27	12·8	9 P. M.	77	80
7	19·3				28	24·1			
8	26·4				Mar. 1	38·7			
9	16·9				2	29·7			
10	9·6	10 A. M.	96		3	34·3			
11	20·6				4	37·2			
12	26·0				5	35·9			
13	27·9				6	41·6			
14	26·3				7	34·1			
15	25·8				8	51·0			
16	28·5				9	61·8			
17	29·1				10	58·4			
18	---				11	54·4			
19	15·9				12	40·3			
20	9·9				13	39·4			
21	26·0				14	29·3			
22	37·7				15	22·8	9 A. M.	88	84
23	28·3				"		9 P. M.	84	86
24	32·5				16	25·3	9 P. M.	92	92
25	32·4				17	24·5	9 A. M.	89	90
26	23·7				18	24·3			
27	44·9				19	28·7			
28	37·4	9 A. M.	96		20	33·1			
29	31·5				21	32·3			
30	---				22	34·6			
31	28·2				23	31·7			
Feb. 1	18·5	9 A. M.		96	24	40·1			
"		9 P. M.	94	94	25	30·1			
2	19·8	9 A. M.	91	93	26	38·2			
"		9 P. M.	82	80	27	35·1			
3	26·8				28	44·8			
4	28·1				29	45·9			
5	31·5				30	33·3			
6	28·3				31	31·9			
7	25·1				Apr. 1	33·7			
8	28·5				2	29·9			
9	24·0				3	25 at	9 A. M.	77	79
10	32·7				"	2 P.M.	9 P. M.	85	87
11	54·4				4	27·1	9 A. M.	80	80
12	26·5				"		9 P. M.	88	85
13	15·6				5	28·2	9 A. M.	77	77
14	5·8				"		9 P. M.	86	82
15	11·1	4 P. M.	88	86	6	39·4			

an elevation mentioned by Loomis occurred in the warmer parts of this country. If his theory finds favor, and the writer's conjecture is correct, it will be presumed that the three samples cited in the Handworterbuch from the still warmer regions of the earth were taken in the midst of such a mass of cold air descending from, and retaining the composition of, the upper parts of the earth's atmosphere.

The analyses here printed should not be used in determining the average composition of the air by combining analyses from all sources. Whether the writer's conjecture is correct or not, it has enabled him to select times for taking samples of air varying widely from the average; and to such times his analyses have been commonly limited, only occasionally including a sample of presumably normal air to serve as a check on the abnormal.

Western Reserve College, Hudson, Ohio, June 12, 1879.