[CONTRIBUTION FROM THE NUTRITION LABORATORY OF THE CARNEGIE INSTITUTION OF WASHINGTON]

The Constancy of the Atmosphere with Respect to Carbon Dioxide and Oxygen Content[1]

BY THORNE M. CARPENTER

The constancy of the percentages of carbon dioxide and oxygen in uncontaminated atmospheric air was established by Benedict[2] in 1912 by the use of the Sondén[2,3] gas analysis apparatus. As a control upon the correct functioning of the apparatus, analyses of air compressed in a cylinder were made daily along with the analyses of atmospheric air. Only when it was established that the apparatus would give constant results with the compressed air was it found that the composition of the outdoor air was constant. Since that time there has been developed in this Laboratory an apparatus[4] especially for the determination of the changes in the composition of atmospheric air that may be produced by the respiration of animals or of man in a confined space. The apparatus is constructed with a compensating pipet that takes care of the changes in the volume of a gas due to variations in temperature and in atmospheric pressure. The absorption of carbon dioxide is by the use of 10 to 20% potassium hydroxide and the absorption of oxygen takes place by means of potassium pyrogallate solution. The buret is so constructed that readings may be estimated to 0.001% of the volume.

This apparatus has been employed regularly for metabolism experiments which require the use of respiration apparatus and analysis of air samples. Based upon previous work of Benedict,[2] the standardization of the apparatus was made by frequent analysis of atmospheric air. During the course of several investigations, three series have been accumulated in which a control analysis was made on each day that the apparatus was used for experimental purposes.

The first series consists of 75 analyses between August, 1934, and June, 1935, at the Laboratory for Animal Nutrition in the University of New Hampshire. Another series consists of 790 analyses on nearly as many days from January, 1933, to May, 1936, that were made at Baltimore in the Department of Embryology of the Carnegie Institution of Washington, located in the building of the Johns Hopkins Medical School. The third series consists of 291 analyses on the same number of days from June, 1930, to December, 1932, in this Laboratory.

In Table I are given the averages of the analyses in the three series including the standard deviations and ranges for carbon dioxide and oxygen. For carbon dioxide the averages are identical in all three series and the standard deviations have a narrow range of from 0.0015 to 0.0017%. The ranges for the series at Durham and at Boston are practically identical. The range for the carbon dioxide in the series at Baltimore is wide, due to the inclusion of one analysis of 0.060%. Excluding this value, the range for the remaining 789 was 0.028 to 0.033%. The average per cent. of oxygen in the three series is nearly identical with a range of only 0.002% in the three series. The standard deviations for the groups at Durham and at Boston are practically identical. The standard deviation for the group at Baltimore is somewhat larger due to the inclusion of results on twenty-one days that were outside of the range of 20.930 to 20.950%. Of these, 17 were repeated immediately following the aberrant analysis and an average of 20.937% was found with a standard deviation of 0.0027%. The value of 20.926 for the minimum at Durham was exceptional as the range of the other 74 was from 20.933 to 20.948%.

TABLE I

AVERAGES OF ANALYSES OF ATMOSPHERIC AIR AT DURHAM, N. H., BALTIMORE, MD., AND BOSTON, MASS.

	No.	Average	S. D.[a]	Range
		Per cent. Carbon Dioxide		
Durham	75	0.031	0.0016	0.027–0.035
Baltimore	790	.031	.0015	.028–0.060
Boston	291	.031	.0017	.026–0.035
		Per cent. Oxygen		
Durham	75	20.939	.0032	20.926–20.948
Baltimore	790	20.938	.0046	20.909–20.957
Boston	291	20.940	.0033	20.931–20.947

[a] S. D. = Standard deviation.

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(1) Presented at the Pittsburgh meeting of the American Chemical Society, September, 1936.

(2) F. G. Benedict, "The Composition of the Atmosphere with Special Reference to its Oxygen Content." Pub. No. 166, Carnegie Institution of Washington, 1912.

(3) Sondén, *Z. Instrumentenk.*, **9**, 472 (1889).

(4) Carpenter, *J. Metabolic Research*, **4**, 1 (1923); Carpenter, Fox and Sereque, *J. Biol. Chem.*, **83**, 211 (1929); Carpenter, Lee and Finnerty, *Wiss. Arch. Landw.*, Abt. B., **4**, 1 (1930); Carpenter, Abderhalden's "Handbuch der biolog. Arbeitsmethoden," Abt. IV. T. **13**, **593** (1933).

The division of the series at Baltimore into yearly results is shown in Table II. The averages of the carbon dioxide for the four years are identical and the standard deviations for three years for carbon dioxide are low, whereas the standard deviation for 1936 is somewhat higher due to the inclusion of one aberrant result of 0.060%. The averages for the percentages of oxygen for the four different years have a range of only 0.003%. The standard deviations are under 0.005% for each of the four years.

TABLE II

YEARLY AVERAGES OF ANALYSES OF ATMOSPHERIC AIR AT BALTIMORE

Year	No.	% CO_2	S. D.[a]	% O_2	S.D.[a]
1933	229	0.031	0.0010	20.938	0.0049
1934	230	.031	.0010	20.936	.0044
1935	230	.031	.0012	20.939	.0038
1936	101	.031	.0032	20.938	.0044

[a] S .D. = Standard deviation.

An example of the monthly averages for a single year is given in Table III. The average carbon dioxide ranges from 0.030 to 0.031; thus there was constancy in the percentage of carbon dioxide throughout the year. The monthly standard deviations of carbon dioxide ranged from 0.0010 to 0.0015%. The average of oxygen percentages by months ranged from 20.938 to 20.940%. The range of the standard deviations for the oxygen percentages by months is slightly larger than in the series by years and is due to the occasional finding of an erroneous result which has been included. Thus at Baltimore it was found that the percentages of both carbon dioxide and oxygen were practically constant over a period of nearly four years. A subdivision into months shows that practically the same constancy remains throughout the year.

TABLE III

MONTHLY AVERAGES OF ANALYSES OF ATMOSPHERIC AIR AT BALTIMORE, 1935

Month	No.	% CO_2	S. D.[a]	% O_2	S. D.[a]
Jan.	23	0.031	0.0010	20.938	0.0045
Feb.	19	.031	.0011	20.939	.0041
Mar.	23	.030	.0010	20.940	.0038
April	22	.030	.0015	20.939	.0046
May	22	.031	.0011	20.939	.0034
June	21	.031	.0011	20.939	.0043
July	22	.031	.0014	20.940	.0041
Aug.	3	.031	...	20.940	...
Sept.	18	.031	.0015	20.938	.0033
Oct.	21	.031	.0011	20.939	.0033
Nov.	18	.031	.0012	20.939	.0032
Dec.	18	.031	.0012	20.939	.0070

[a] S. D. = Standard deviation.

The yearly averages of the analyses at Boston are shown in Table IV. The carbon dioxide percentages are identical for the three years with a value of 0.031%. Similarly the oxygen percentages are practically constant and the standard deviations by years for the oxygen percentages in the series in Boston are under 0.004% for each year. An example of the monthly averages is given in Table V for the year 1931 at Boston.

TABLE IV

YEARLY AVERAGES OF ANALYSES OF ATMOSPHERIC AIR AT BOSTON

Year	No.	% CO_2	S. D.[a]	% O_2	S. D.[a]
1930	79	0.031	0.0016	20.940	0.0032
1931	135	.031	.0017	20.939	.0032
1932	77	.031	.0017	20.940	.0034

[a] S. D. = Standard deviation.

TABLE V

MONTHLY AVERAGES OF ANALYSES OF ATMOSPHERIC AIR AT BOSTON FOR YEAR 1931

Month	No.	% CO_2	S. D.[a]	% O_2	S. D.[a]
Jan.	5	0.031	0.0011	20.941	0.0022
Feb.	17	.031	.0011	20.939	.0023
Mar.	8	.032	.0014	20.939	.0024
April	12	.032	.0017	20.940	.0033
May	7	.031	.0016	20.938	.0033
June	16	.030	.0017	20.940	.0037
July	14	.031	.0016	20.940	.0025
Sept.	5	.032	.0013	20.939	.0012
Oct.	14	.031	.0015	20.939	.0026
Nov.	18	.032	.0021	20.940	.0037
Dec.	19	.031	.0020	20.938	.0038

[a] S. D. = Standard deviation.

No analyses were made in August. The carbon dioxide percentages average from 0.030 to 0.032%, the standard deviation ranging from 0.0011 to 0.0021%. The averages of the oxygen percentages range from 20.938 to 20.941%, the standard deviation ranging from 0.0012 to 0.0038%. Thus the composition of the atmospheric air at Boston with respect to its carbon dioxide and oxygen content was practically constant for the period of time covering nearly three years and a subdivision into monthly groups does not increase the range of the averages.

The laboratory in New Hampshire is located on the college campus and is not far from a heavily wooded section. The laboratory at Boston is situated about 200 feet (61 meters) from a heat, light and power plant. There are two stacks of 180 feet (55 meters) and 190 feet (58 meters) each and the total fuel consumption varies from 35 to 95 tons of coal per day. In spite of the widely different local conditions of the three laboratories there is no evidence that variations in season or proximity of large consumers of fuel cause any measurable differences in carbon dioxide and oxygen content of the atmospheric air. As pointed out by Benedict,[2] many of the atomic weights are not known beyond the fourth significant figure, but here is a physical mixture of gases, with the percentage content of one of its constituents, namely oxygen, having a constancy beyond the accuracy of many atomic weight determinations.

The analyses were made at Durham by Mrs. H. H. Latimer and Mr. N. F. Colovos, at Baltimore by Mr. K. Koudelka, and at Boston by Mr. E. L. Fox.[5]

Summary

Three series of samples of outdoor air consisting of 75 at Durham, New Hampshire, 790 at Baltimore and 291 at Boston were analyzed for carbon dioxide and oxygen content by means of an apparatus on which readings are estimated to 0.001%. Each series was scattered over nearly the same number of days as there were analyses. The grand average of all three series gave 0.031% for carbon dioxide and 20.939% for oxygen. In spite of widely different local conditions of the three laboratories there was no evidence that variations in season or proximity of large consumers of fuel caused any measurable differences in carbon dioxide and oxygen content of atmospheric air.

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[5] Died Dec. 19, 1934.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF YALE UNIVERSITY]

Note on the Relative Partial Molal Heat Content of Zinc Sulfate in Aqueous Solution

BY HERBERT S. HARNED

Cowperthwaite and La Mer[1] have measured the electromotive forces of the cells

Zn(2-phase amalgam) | $ZnSO_4(m)$ | $PbSO_4$-Pb(2-phase amalgam)

at concentrations from 0.0005 to 0.01 M, and from 0 to 50° at 12.5° intervals. They showed that these results were in conformity with the Gronwall, La Mer and Sandved[2] extension of the Debye and Hückel theory, provided that 3.64 Å. was used for the mean distance of approach of the ions, a. With this equation, they obtained the standard potentials of the cell at the temperatures at which they were measured.

From these data, La Mer and Cowperthwaite[3] have computed the relative partial molal heat content, $\bar{L}_2$. This quantity has also been obtained from calorimetric data by Lange, Monheim, and Robinson,[4] who derived values which differed considerably from those computed from the electromotive forces. Such a discrepancy detracts from the value of Cowperthwaite and La Mer's proof of the validity of the extended theory unless it can be shown that this disagreement disappears upon further consideration of the results.

Following Cowperthwaite and La Mer, we shall employ the quantity E_0', defined by the equation of the cell by

$$E_0' = E + \frac{\gamma RT}{NF}\ln m = E_0 - \frac{\gamma RT}{NF}\ln \gamma \qquad (1)$$

where E is the measured electromotive force corrected for lead sulfate solubility, E_0 the standard potential of the cell, and the other symbols have their usual connotation. The calculation of $\bar{L}_2$ by La Mer and Cowperthwaite is open to two criticisms. In the first place, they employed a five constant power series equation ending in a term containing T^4 to express five results. If one or more of the results are in error, this procedure will not yield an accurate temperature coefficient at a given temperature. Secondly, their results at 50° were obtained with difficulty and in fact seem to be inconsistent with the results at the lower temperatures. Electromotive force measurements as a function of temperature usually may be expressed with high accuracy by a quadratic equation. To test this in the present instance, the first order differences of Cowperthwaite and La Mer's results[1] were plotted against T. These plots are straight lines with the exception of the one which involves the 50° reading, a fact which indicates that a quadratic equation may

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[1] Cowperthwaite and La Mer, THIS JOURNAL, 53, 4333 (1931).

[2] Gronwall, La Mer and Sandved, *Physik. Z.*, 29, 358 (1928).

[3] La Mer and Cowperthwaite, THIS JOURNAL, 55, 1004 (1933).

[4] Lange, Monheim and Robinson, *ibid.*, 55, 4733 (1933).