ART. LV.—*On Jolly's Hypothesis as to the Cause of the Variations in the Proportion of Oxygen in the Atmosphere*; by EDWARD W. MORLEY, M.D., Ph.D., Hurlbut Professor of Chemistry in Western Reserve College.

JOLLY has suggested a certain hypothesis as to the cause of those variations in the ratio of oxygen to nitrogen which are from time to time observed in the atmosphere of a given place. He supposes that the volumes of air which exhibit the deficiency of oxygen are brought by currents from the tropical regions, that the deficiency of oxygen was caused in those regions, that it was caused by the consumption of oxygen in the oxidation of organic matter, and that at some places within the tropics this consumption is therefore considerably greater than the liberation of oxygen in the processes of vegetation.

I have proposed a second hypothesis. I suppose that the volumes of air deficient in oxygen are brought by currents from an elevation above the surface of the earth, that the deficiency of oxygen was caused while these volumes were at this elevation, and that it was caused by that assumed physical action according to which, in a high vertical column of a mixture of two gases, the heavier will tend to become less abundant at the top of the column.

The labor of establishing either hypothesis by experiment will probably be considerable. I propose to mention some reasons which seem to indicate that Jolly's hypothesis is the less probable.

1. There is no direct evidence that the atmosphere near the equator is poorer in oxygen than the air of higher latitudes. Numerous analyses agree in this result. Lewy's analyses of air, collected at Guadeloupe, show that the mean ratio of oxygen to nitrogen there is the same as that at Paris.

2. It is difficult to ascribe to the cause assumed by Jolly a magnitude sufficient to produce the observed effect.

If a volume of air at latitude fifty degrees is deficient in oxygen by 0.004 or 0.005, the deficiency must have originally been far greater, if this air has come from the tropics, and has thus for many hundreds of miles been exposed to admixture with normal air. We must either, in the first place, believe that at some parts of the tropical regions there are not very seldom immense volumes of air, deficient in oxygen to the amount of 0.01 or more; or, in the second place, we must assert that the analyses which show deficiencies of oxygen at latitude fifty degrees amounting to 0.004 or 0.005 are grossly in error, and that the actual deficiencies are very much less; or, in the third place, we must abandon the hypothesis. If the analyses are

trustworthy we must abandon the hypothesis, or else attribute to its supposed cause a magnitude altogether incredible. I will examine some of the experimental evidence, that the oxygen in the atmosphere sometimes falls below the mean by as much as 0.004 or 0.005.

I will not cite any analyses made before the year 1841. In that year Dumas and Boussingault found it necessary to resolve by experiment the doubt as to whether the true proportion of oxygen in the air were exactly one-fifth, or were about twenty-one per cent, or were a variable quantity. If this was the uncertainty as to the mean of multitudes of analyses, it is obvious that we can by no means attribute to a single analysis a degree of precision sufficient to aid in the present inquiry. But in that year, Dumas and Boussingault used a new method of analysis, by means of which sufficient accuracy was obtained, and proposed an elaborate system of analyses on air collected simultaneously at different places. Lewy went to Copenhagen to take part in this system, carrying with him apparatus from the laboratory of Dumas and Boussingault. He had the coöperation of Oersted, and his results were communicated to the Academie des Sciences by Dumas and Boussingault. Four of his results on four samples of air, collected at sea on the voyage to Copenhagen, showed a proportion of oxygen as low as 0.2045.

Regnault's results will command entire confidence. A sample collected in the Bay of Algiers, June 5, 1851, gave 0.2042 and 0.2040 oxygen. A sample collected in the Bay of Bengal, February 1, 1849, gave 0.2046 and 0.2045 oxygen.

Jolly has used a new method equally accurate with the common process, by explosion with hydrogen, and very valuable as confirming the latter. He measures the tension of a confined volume of air while it is at the freezing-point. He then absorbs the oxygen from this air by means of a copper spiral heated by electricity, and again measures the tension at the freezing-point. The absorption and measurement are repeated till no more absorption takes place. A sample of air collected at Munich, June 15, 1877, gave 0.2053 oxygen, one collected July 19, gave 0.2056, and one collected November 10, gave 0.2056. Also at six other dates during the same months he found the amount of oxygen in the air less than 0.207.

A sample taken at this place, September 20, 1878, gave 0.2049 and 0.2049 oxygen. A sample taken February 26, 1879, gave 0.2045. The other analysis of this sample was lost by the accidental use of hydrogen containing a little air. But even this analysis, which of course gave the proportion of oxygen too high, gave only 0.2049.

The analyses of Macagno, at Palermo, made by absorbing oxygen with pyrogallol, I forbear to cite.

It is difficult to resist the conclusion that these analyses show that sometimes the deficiency of oxygen observed in the atmosphere at such latitudes as fifty-two, forty-eight, and forty-two degrees, may amount to 0.004 or 0.005. Then we must either suppose that not very seldom there might be observed within the tropics immense volumes of air in which the deficiency should be several times as great as this, or we must abandon the hypothesis in question.

If processes of oxidation preponderate over processes of reduction within the tropics, there must be a transportation of organic matter from colder climates toward the equator, there to be oxidized, but

3. No such amount of transportation as is required by the hypothesis takes place through the air. For, in the first place, experiment has repeatedly shown that after a volume of air has been freed from carbonic acid, there is left in it but a minute trace of matter capable of undergoing oxidation. Now, if a given volume of air contained an amount of organic matter capable, in its oxidation, of absorbing from this volume of air 0.005 of oxygen; and if further this organic matter was as rich in hydrogen as is marsh gas, even then the carbonic acid produced in some of these experiments would have been ten times as much as the carbonic acid already existing in the air. And secondly, if the observed deficiency of oxygen in the atmosphere had been produced by the oxidation of organic matter previously contained in it, the missing oxygen would be replaced in part by the carbonic acid produced, which, on the most favorable assumption, would amount to half the deficiency of oxygen. But experiment has shown that no such amount of carbonic acid is ever found in air uncontaminated by local causes, though a very large number of determinations has been made.

4. The transportation of organic matter required by the theory does not take place by the waters of the globe. If Jolly's hypothesis is true a very large part of the organic matter returned to the air in the form of carbonic acid must be supposed to be dissolved or suspended in the water which flows from the land into the sea, to be brought by ocean currents to the equatorial parts of the ocean, and there to be at last oxidized.

It may be noticed that this supposition would permit us to explain the removal of oxygen from the air without the restoration of, a corresponding volume of carbonic acid to the same volume of air, by assuming that the oxidation takes place in the waters of the ocean while near the equator, but that the carbonic acid there produced is restored to the air but slowly, and therefore is not restored to the volume of air which afforded the oxygen.

Now, if this supposed mechanism of oxidation is not consistent with observed facts, the theory that the atmosphere within the tropics sometimes shows a deficiency of oxygen produced by the preponderance of processes of oxidation over those of reduction must be dismissed from consideration. My own knowledge is far from sufficient to enable me to assert that the hypothesis is disproved by facts already observed. But I may mention some of the points in which the theory may be compared with facts capable of easy observation, or perhaps already observed. Those who are familiar with observations on the chemistry of sea-water will be able to judge whether the hypothesis is not overthrown by these facts thus compared.

In the first place, if the supposed process of oxidation is the actual process, it must obviously be about as regular and invariable as the motion of rivers and ocean currents. A vigorous withdrawal of oxygen from the superincumbent air must then go on constantly within certain areas of the ocean. Whenever a volume of air is becalmed over such an area, so that the cause may operate for some time on the same air, such air should be highly deficient in oxygen. Now, can we find any evidence that air over some parts of the tropical oceans is specially deficient in oxygen whenever the winds are slight? If the evidence is of the opposite nature, Jolly's hypothesis lacks confirmation.

Again if the supposed oxidation takes place in the water, a somewhat rapid transfer of oxygen must go on between the air and the water. In the regions in question, whenever the sea is still, then there must be a falling off in the quantity of oxygen at different depths in the ocean. The contrast in this respect between equatorial waters and those at forty-five degrees of latitude ought to be capable of observation. A collation of results already obtained may perhaps afford a decisive test of the theory.

In the third place, if the supposed oxidation takes place through the waters of the sea, the retention of the carbonic acid produced is somewhat protracted. Determinations of carbonic acid in the air are very numerous, but no observer has yet found normal air containing one or two hundredths per cent of carbonic acid more than the average. Then, even when air is exposed long enough to oxygen-absorbing water to lose 0.005 of oxygen, it does not gain a noteworthy amount of carbonic acid. Now if the carbonic acid produced is thus retained, the water of some parts of the equatorial seas must be very abundant in carbonic acid. There must be a gradual diminution toward the poles; and further, within all moderate latitudes, there can be no equilibrium between the tension of carbonic acid in the air and that of carbonic acid in sea-

water. If facts do not agree with these deductions, the supposition that a large part of the processes of oxidation on the surface of the globe takes place in sea-water within the tropics is contrary to the facts.

In the fourth place, it is doubtful whether rivers carry any such amount of organic matter as is required by the theory. Determinations of the amount of oxidizable matter contained in the water of rivers have been chiefly limited to the water supply of towns. But some observations have been made on the water of the Nile. Tidy found by the permanganate process that 0.23 grain of oxygen was given up to a gallon of the water of this river. If we take this result to represent the amount of oxygen absorbed by river water *after the water reaches the tropics*, we shall concede much for argument. Such water could remove 0.001 oxygen from about ten times its own volume of air. Of course it is difficult to suppose that the consumption of oxygen can be localized in a small volume of air. Now, if such water be diluted with sea-water, and if it absorbs oxygen from a hundred times its volume of air, through several degrees of latitude, and if the deficiency of oxygen to be explained is several times 0.001, it is hard to believe that the cause is sufficient.

5. It is very doubtful whether the whole consumption of oxygen on the globe would account for the observed deficiencies of oxygen, even if we suppose this total consumption for a certain short period to be taken from one and the same small volume of air.

Dumas and Boussingault made an approximate estimate of the amount of oxygen used in a century by all process of oxidation. If we take this estimate we shall find that all the oxygen absorbed from the air in a week, if taken from the same volume of air covering but half a square degree of the earth's surface, and containing only the lower third part of the atmosphere, would produce in this limited volume a deficiency of oxygen of but one-eighth of one per cent. But we have to account for deficiencies several times as large, and we cannot suppose the consumption so limited to a small volume. Then the theory fails to agree with the facts.

At the foundation of the hypothesis which I have suggested to account for the observed deficiencies in the oxygen of the atmosphere, there lies the assumption that in a vertical column of a mixture of two gases of different densities, there is a tendency to the accumulation of a greater proportion of the heavier gas toward the bottom, and of a greater proportion of the lighter toward the top. There has not yet been obtained any direct experimental evidence in favor of this theory of

Dalton. Although the assumption is a simple, and, I think, certain inference from the known principles of mechanics as applied to gases, it is desirable that experimental evidence should be supplied. I have planned two forms of apparatus and two series of experiments for this purpose; but the making of a more perfect eudiometric apparatus than had heretofore been used, the carrying on a series of daily analyses in duplicate of samples of air collected at this place, and the providing for the collection of samples at other parts of the continent, have used so much of my time and income that so far it has been impossible to carry out these plans. I hope before long to supply this deficiency.