which such combinations occur only when the azimuthal quantum number changes by ± 1, and the inner quantum number by 0 or ± 1. In the simple spectra, such as that of sodium, these rules are closely followed, the exceptions being weak lines, produced in the presence of strong electric fields.

In the more complex spectra, the inner quantum rules are still strictly followed, but the azimuth quantum rules suffer changes. In the calcium spectrum, for example, some of the strongest lines arise from combinations between terms, both of which are of type p (Azimuth quantum 2) or of type d (Azimuth quantum 3). Professor Saunders and the writer, in a paper now in press, have advanced evidence, in favor of Bohr's suggestion, that in these "anomalous" states of the atom the two valency electrons are simultaneously shifted to states of higher energy.

A more complicated situation is found in the spectrum of titanium. Investigations of this were begun independently by Dr. and Mrs. Kiess and by the writer. When this fact was realized, it was mutually agreed that those who were first in the field should publish first, and the work of the former authors has just appeared,[1] and will be followed in due time by the writer's. The latter includes the spark spectrum as well as the arc, and brings to light combinational relations of a new type.

The arc spectrum of titanium consists of systems of singlets, triplets and quintets, of which the second is the most extensive. Terms of types s, p, d, f, g, h and i (that is of azimuth quanta 1, 2, 3, 4, 5, 6 and 7) are clearly recognizable. These terms fall sharply into two sets, such that *no two terms in the same set combine with one another,* while any term of one set combines with all terms in the other set for which the azimuth quantum differs by 0 or ± 1. In the spark spectrum, which consists of quartets and pairs, the same division into two sets exists, and, again, terms of the same set do not combine, but a term of one set may combine with any term of the other set for which the azimuth quanta differ by 0, ± 1 or ± 2—thus an f term will combine with p, d, f, g and h terms. The inner quantum rules, and Landé's other rules governing multiplet structure and Zeeman effect are completely observed. The work of Catalan, Meggers and Walters shows that substantially the same set of rules hold in the arc spectra of scandium, vanadium and iron, and the spark spectrum of the first. We have here a quite new form of the first, or "azimuthal" exclusion principle, which appears to hold good in all the more complicated spectra so far analyzed. The relations in the alkaline earths exhibit a transition between the simpler and the more complex rules. Chromium and manganese appear to represent a somewhat later stage in this transition.

It may be remarked also that in the simpler spectra the lowest energy level, or normal state of the atom, is always of small azimuth quantum number (an s term or sometimes a p term), while in the complex spectra so far studied this lowest level is a d or f term of large azimuth quantum.

These relations are likely to have important bearings on the theory of the structure of the outer parts of the atom.

Full details of the writer's work on the titanium spectrum will soon be published in a contribution from this observatory.

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[1] *Journal Optical Society of America, 8,* 607, 1924.

ABSORPTION OF CARBON DIOXIDE THE FIRST STEP IN PHOTOSYNTHESIS

THE classical researches of Brown and Escombe[1] formulated in a clear and concise fashion the laws governing the diffusion of carbon dioxide through the stomata into the leaves during photosynthesis. These investigations demonstrated that the absorption of atmospheric carbon dioxide by an illuminated leaf proceeds at about one half the rate which the same surface of the leaf would possess if it were covered by a constantly renewed film of a solution of caustic alkali. "Or if we assume that the absorption of carbon dioxide in the leaf takes place only through the stomatal openings which occupy at the outside not more than 0.9 per cent. of this leaf area, we arrive at the somewhat remarkable conclusion that during assimilation the absorption per unit area of these openings must be 43 to 64 times as fast as the absorption of a unit area of a freely exposed solution of caustic alkali." Brown and Escombe dealt especially with the purely physical process of the diffusion of carbon dioxide through the stomata. The ascertainment of the agents or leaf constituents which effectuate the absorption constitutes another problem.

While the rate of photosynthesis is governed by the purely physical process of diffusion, the initial stage of the photosynthetic process must depend upon a mechanism which supplies the active centers of photosynthesis with carbon dioxide. Graham stated: "Liquid diffusion of carbonic acid is a slow process compared to its gaseous diffusion, quite as much as days are to minutes." The low partial pressure of CO_2 in the atmosphere and the relatively low solubility of the gas in water have for a long time been recognized as conditions unfavorable for photosynthesis. At 0.03 volume per cent., 1,000 cc of water dissolves at 25° 0.033 cc CO_2. 1,000 grams of *Helianthus* leaves, with an area of 3.3 square meters, contain 850 cc water and would dissolve only 0.027 cc

[1] H. T. Brown and F. Escombe, *Phil. Trans.* Roy. Soc. B. *193,* 223 (1900).

CO_2 under normal conditions. During photosynthesis there is absorbed about 1,500 cc CO_2 by these leaves per hour. For some time it has appeared to us that the first step in photosynthesis is not a simple splitting of carbonic acid under the influence of light, but that the CO_2 undergoes a primary change through absorption by certain constituents of the leaf.

It has been known that vegetable tissue is capable of absorbing CO_2 in quantities considerably above that accounted for by the solubility of the gas in the water of the tissues.[2] Willstaetter and Stoll demonstrated that this phenomenon is shown not only by living leaves but also by the dried leaf material to which water has again been added.

In order to establish more directly the nature of the absorbing substances in the leaves under conditions similar to those employed in our investigations of photosynthesis we have studied the absorptive capacity of dried leaves. For a number of reasons it was desirable to employ concentrations of CO_2 as near to normal as possible. The experimental difficulties are increased by the fact that the post-mortal respiration of the leaf material is relatively high. The absorptive effects are augmented and the accuracy of the determinations increased by using air enriched in CO_2. Accurate results could be obtained only by the complete avoidance of rubber stoppers and connections in the absorptive flasks. The investigations have been unavoidably interrupted, so that a brief report of the findings to date seems desirable.

(1) Dried and ground leaf material to which the same amount of water has been added as originally contained in the leaves, absorbed CO_2 from the air in the dark. In order to increase the accuracy of the analyses the air was enriched to 1.3 per cent. CO_2.

(2) The manner of drying the leaves greatly affects the absorptive capacity; 55–60° in a rapid stream of dry air seems to be best.

(3) Dried and powdered *Helianthus* leaves, to which the same amount of water was added as originally in the leaves and which had been freed of CO_2 by passing a stream of CO_2— free air over them, absorbed at 25° 4.95 mg CO_2 per gram, more than ten times the amount dissolved in the water present.

(4) Leaf material exhibiting high absorptive capacity also had a high rate of post-mortal respiration and *vice versa.* The post-mortal respiration coefficient (CO_2/O_2) averaged about 1.5.

(5) Extraction of the dried leaves with cold water reduced somewhat the absorptive capacity of the leaf material. Extraction with cold absolute alcohol greatly reduced the absorptive capacity. The material extracted by the cold alcohol absorbed only exceedingly small amounts of CO_2. Similarly, heat tends to destroy the absorptive capacity of the leaf material. Extraction with acetone, thus removing most of the pigments, did not affect the absorptive capacity. Extraction with water saturated with ether at 20° (Chibnall-Schryver method for protein extraction) reduced the absorptive capacity 90 per cent. The residue obtained from evaporating the water-ether extract at reduced pressure and 50° absorbed as much CO_2 as the original leaf material.

(6) We are of the opinion that our experiments support the theory that the leaf absorbs CO_2 from the atmosphere by a mechanism similar to that by which the blood of mammals serves in freeing the tissues of this gas. According to our experiments 100 grams of dry leaf material, when moistened, can absorb at 25° and 1.3 per cent. CO_2, 495 mg CO_2 or 272 cc at standard conditions. The dry material constitutes about 15 per cent. of the leaf in its original condition, so that 100 grams of fresh leaf material would on this basis be able to absorb about 41 cc of CO_2. 100 cc of venous blood contains about 50 cc CO_2; of this amount not more than 20 per cent. is dissolved in the water of the blood, the rest being held by the blood plasma and the inorganic constituents.

In the leaf probably the major portion of the CO_2 is absorbed by the proteins on the basis of the carbamino reaction. The effect of this is to increase the concentration of the CO_2 in the cells and to alter the form in which the CO_2 is present. It remains to be determined whether these carbamino compounds can act as photochemical acceptors in the primary photochemical reaction. Our experiments on the action of ultra-violet light on the simpler carbamino acids have, however, led to the same negative results as to the formation of the formaldehyde as those with carbonic acid. The primary union of CO_2 with the proteins of the leaf as the first chemical step in photosynthesis may be of considerable importance in determining the cause for the asymmetric nature of the synthesis of the carbohydrates in the chlorophyllous plant.

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[2] de Saussure, Ostwald's Klassiker, No. 15, p. 43, Boehm, *Ann. Chem.*, *185*, 248 (1876); Willstaetter and Stoll, "Untersuchungen ueber die Assimilation der Kohlensauere," pp. 172–225, Berlin, 1918; Carey, Physiological Researches, *2*, 407 (1923).

THE ILLINOIS STATE ACADEMY OF SCIENCE

THE Illinois State Academy of Science held a very successful meeting in Elgin, on May 1, 2 and 3, with an attendance of nearly 200 members, besides many friends. The convention opened on May 1, with a