Pierre Paul Dehérain

Jaime Wisniak

Department of Chemical Engineering, Ben-Gurion University of the Negev, Beer-Sheva, Israel 84105
wisniak@exchange.bgu.ac.il

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Life and career[1,2]

Paul Pierre Dehérain was born in Paris, on April 19, 1830. He took his basic education of the *Collège Municipal* Chaptal and after receiving his diplomas of *bachelier ès lettres* (1847), and *bachelier ès sciences* (1849), he entered the recently created *École de Administration* but he was stopped suddenly by the suppression the *École*. He then moved to the *École de Mines* and in 1850 entered the laboratory of Edmond Frémy (1814-1894) at the *Muséum d'Historie Naturelle*. Afterwards he was appointed *préparateur* of the course on Zoology applied to Agriculture (1854-1864), taught by the agronomist Émile Baudement (1816-1863) at the *Conservatoire des Art et Métiers*, where Jean Baptiste Boussingault (1802-1887) was also teaching. During his studies he found time to teach chemistry at the *Collège* Chaptal, and continued doing for 24 years (1856-1880). In 1856 he received his degree of *Licencié ès Sciences* and in 1859, at the age of 29, he received his degree of *Docteur ès Sciences* after defending his theses about chlorine salts (*Les Combinaisons Formées par des Chlorures sont-elles des Sels?*) and the use of phosphates in agriculture (Recherches sur l'Emploi Agricole des Phosphates). In 1865 he was invited by Joseph de Mornay (1804-1868), Minister of Agriculture, to become *professeur suppléant at the École d'Agriculture de Grignon*, and promoted to *professeur titulaire* in 1869. In 1872 he returned to the *Muséum as aide naturaliste* to the Chair of Culture, and between 1873 and 1879 he deputized for Joseph Decaisne (1807-1882) in the course on farming. In 1880 he was promoted to the rank of professor and occupied the chair Plant Physiology Applied to Agriculture. During the same period he also taught a course of Agricultural Chemistry at the *École de Grignon*, where he was later appointed professor. In 1880 he was appointed by *decree professeur administrateur* of the Vegetable Physiology Applied to Agriculture Chair at the *Muséum*. In 1887 he was elected to the *Académie de Sciences* (section agriculture rurale) replacing Boussingault who had just passed away. In 1875 he founded the journal *Annales Agronomiques*, under the auspices of the Ministry of Agriculture,

Dehérain passed away on December 7, 1902, and was buried in the Père Lachaise cemetery (65^e^ division, 3^e^ ligne, AA, 4).

Dehérain's main research activities were in the areas of plant physiology (at the *Muséum*) and practical agriculture (at Grignon). Among them the author can mention the assimilation of minerals substances by plants (which led him to win the Bordin Prize for 1866), fertilization of soils, transpiration and respiration by leaves and roots and the effect of artificial light, absorption of CO_2, carbon assimilation, nitrification, wheat and sugar beet cultivation, crop rotation, and many other subjects of practical agriculture.

Scientific contribution

Dehérain published more than 60 memoirs and books[3-9] in the different areas of his interests. He also published a large number of papers in journals devoted to popularize science. As was customary for candidates to the *Académie des Sciences*, he published a summary of his experimental projects and results.[10]

Here the author describes a few of Deherain´s researches.

Evaporation of water and decomposition of CO_2 by plants

In 1869 Dehérain reported the results of an extensive research on the decomposition of CO_2 and evaporation of water by the leaves of plants.[11] In his short historical review he indicated that in 1691 John Woodward had submerged the stem of a leaf in water and measured the amount of water transpired after a few days.[12] In 1727 Stephen Hales (1677-1761) experimented with full plants and found that perennial trees released less water than the intermittent ones.[13] In 1748 and 1749 Jean Etienne Guettard (1715-1786)[14] found that light was the controlling factor on the amount of water transpired by leaves. In 1836 Charles Giles Daubeny (1795-1867) studied the influence of rays of different colors and reported that the transpiration phenomenon depended on the combination of heat and light, coupled with certain mechanical factors, which operated on dead as well as living organic matter.[15] Julius Sachs (1832-1897) had reached a similar, although more restricted conclusion: light was the most important factor affecting transpiration, although it was not possible to determine if it acted alone or in intimate union with the increase in temperature caused by exposition to direct sunlight.[16]

Initially, Dehérain studied the evaporation of water from a leaf by putting it in a tube swept by a current of air, but discarded the procedure after finding that the phenomenon continued indefinitely in a saturated atmosphere. The final procedure was similar to the one used by Guettard: A healthy leaf was enclosed in a glass tube and exposed to sunlight for the required time; pretty soon water was seen dripping from the walls of the tube. The effect of the temperature was studied by enclosing the tube in a sleeve through which flowed cold or ice water, and the effect of color, by enclosing the tube in another one containing a colored solution (e.g., a yellow solution of potassium, dichromate, a blue solution of ammoniacal copper, a violet solution of iodine dissolved in carbon disulfide, a red solution of carmine dissolved in ammonia, and a green solution of cupric chloride).[11]

Dehérain found that the both phenomena were promoted by the same factors. Under the action of sunlight, wheat leaves released oxygen and actively transpired; thus, during one hour, 100 g of young leaves of wheat lost 88.02 g of water when exposed to full sunlight, 17.07 g under diffuse light, and 1.01 g in the dark. This simple procedure was used to prove that young leaves lost more water than mature leaves and that temporal leaves lost plenty more water than perennials ones. The numerical data clearly showed that transpiration was mainly influenced by light; nevertheless, under the same conditions of illumination, a higher temperature led to an increased transpiration, for example 100 g of wheat leaves exposed to full sunlight lost 88.2 g of water at 28 ^{0}C and 71.8 % at 22 ^{0}C.[11]

If the tubes were enclosed within a tube containing solutions of different colors, it was found that the rays more efficient for favoring evaporation were exactly the same as those that decomposed CO_2 more energetically. This was tested by collecting and measuring the gas released by aquatic plants submerged in weak solutions of CO_2 and subject to the action of light having their passage modified by solutions of different colors, identical with those used to study the transpiration phenomena. All the different rays were not equally efficient, on the one hand, the rays that acted the most energetically on photographic paper impregnated with silver chloride were the less active for decomposing CO_2, on the other hand, the yellow and red rays that hardly affected silver chloride, strongly activated the decomposition of the gas by the leaves; the blue rays, which strongly decomposed an aqueous solution of silver chloride, were completely inefficient on the vegetable process. The latter phenomenon was also observed when using a violet concentrated solution of iodine in carbon disulfide. The color of the light affected transpiration in a similar manner. Thus, 100 g of corn leaves under direct sunlight and protected by different colored solutions, lost water as follows:

Color	Water loss (g)
Red	51.5
Yellow	60.6
Blue	40.6
Green	33.3

Dehérain results also confirmed the results reported by other scientists, that the upper surface of the leaves, hard and smooth, evaporated more water than that in the under one, and decomposed the largest portion of the CO_2. Different species of plants evolved very different quantities of water under similar conditions, and the proportion of water seemed to increase as the size of the leaf diminished. Thus large leaves of colza evolved between l and 2 % of their weight of water in an hour; smaller leaves 10 or 12 %, leaves of wheat between 70 and 90 %, and of rye between 90 and 100 %.[11]

Aquatic plants in darkness

It was known that when submerged aquatic plants were kept during several days in a place poorly illuminated, they blackened, the water acquired a bad smell and its surface became covered with mould or was seen teeming with protozoa. The water was also found to contain a very high concentration of CO_2. Dehérain decided to study this phenomenon in more detail, using the waterweed (Elodea) that grew in the *Muséum d'Histoire Naturelle*.[17] For this purpose, he put the plant in a vase full of water previously charged with CO_2, and exposed it to sunlight to verify that the respiratory system was functioning in a normal fashion. Almost immediately a multitude of gas bubbles were seen being generated. Analysis of the latter showed that the gas was a mixture of CO_2, oxygen, and nitrogen, proving that the plants were in healthy state. The plants were now put in water containing oxygen and the suspension transferred to two closed flasks. One of these was kept in the dark, and the other exposed to diffuse light. After two days, Dehérain noticed that all plants had died by asphyxia; they had consumed all the oxygen dissolved in the water (as shown by analysis of the same). The plants being unable to breath, their tissues began to disorganize, the surface of the water became covered by a layer of white mould, and an obnoxious smell was felt. Jean-Baptiste Dumas (1800-1884) and Jean-Baptiste Boussingault (1802-1887) had already pointed out the curious metamorphosis that transformed a plant in the darkness into an animal that breathed and absorbed oxygen to discharge CO_2.[18] Dehérain wrote that his results added another proof to this phenomenon: when an aquatic plant was not invigorated by sunlight, it became a poison; it consumed all the oxygen dissolved in the water until it asphyxiated. Its tissues disorganized and the accompanying corruption was accompanied by the bad odor that followed the putrefaction of an animal. Hence, aquatic plants could be a source of healthiness or putrefaction: growing in well-illuminated water they charged it with oxygen; growing in the dark they depleted the oxygen.[17]

In a following work, Dehérain extended his findings to the situation present in the Grignon agronomical station. The institution was located in a valley having a sizable pond at its bottom. This pond was inhabited by many submerged aquatic species, among them, *Potamogeton pectinatus* (sago pondweed) and *Ceratophyllum submersum* (soft hornwort). Lately, a large amount of *Lemna minor* (common duckweed) had begun to accumulate on the surface, forming a very thick layer that prevented penetration of sunlight. This had led to the sudden death of all the fish in the pond and to a very strong smell of hydrogen sulfide. Dehérain made a careful analysis of the water and found that there was absolutely no dissolved oxygen present, and hence, the fish had died by asphyxia. The poisonous gas had not killed them because many varieties of birds continued to use the duckweed as a floating platform. The aquatic plants had wilted by the exclusion of light caused by the Lemna growth, and had absorbed what oxygen was available.[19]

Effect of artificial light

Charles François Hervé-Mangon (1821-1888) was one of the first to demonstrate that electric light was capable of producing chlorophyll in plants; during four days he submitted several rye seeds to the action of artificial light produced by a carbon lamp and observed that the seedlings were green and inclined in the direction of the light source (heliotropism). The same type of seeds grown in the dark, presented the yellow color of wilted.[20] In 1869 Edouard Prillieux (1829-1915) showed that electric light produced by different sources acted energetically on chlorophyll and gave it the capability of decomposing CO_2 and generating oxygen. He placed branches of *Helodea canadiensis* in water loaded with CO_2; when the arrangement was exposed to artificial light, he noticed small trickles of bubbles escaping from the branches, which he assumed was oxygen.[21] Carl Wilhelm Siemens (1823-1883) was the first to carry on a detailed research project on the possibility that light produced by an electric arc might be sufficiently powerful to promote vegetation.[22] For this purpose he used a Siemens dynamo machine connected to a carbon lamp capable of producing a light equivalent to 1400 candles. He took of large number of pots, planted with quick-growing seeds and plants (e.g. mustard, carrots, turnips, beans, cucumbers, and melons), and divided them into four groups. One group was kept entirely in the dark; another was exposed to the influence of electric light only, another to the influence of daylight only, and the fourth one, exposed successively to both day and electric light. The electric light was supplied for six hours, from 5 to 11 each evening, and the plant left in the dark during the remainder of the night. His results indicated that the plants of the first group were pale yellow and soon died; the ones of the second group had light green leaves and were sufficiently strong to survive. The ones in the third group had darker green leaves and were more vigorous, while the ones in the fourth group clearly showed a better development. After many experiments done under different conditions, Siemens concluded that (a) electric light had the power to form chlorophyll in the leaves of plants and in promoting growth; (b) an electric source of light equivalent to 1400 candles, placed at 2 m from growing plants, was as effective as average daylight; (c) plants did not appear to require of period of rest during the 24-hours of the day, but developed strongly if subject during daytime to sunlight and during the night to electric light; (d) the heat radiated from such lamps helped offset the effect of night frost, and (e) the addition of electric light enabled plants to stand a higher temperature in a greenhouse.[22]

An additional set of experiments proved that light from the electric arc could be used to hasten the ripening of fruits.[22]

Dehérain and his doctoral student Léon-Gervais-Marie Maquenne (1853 -1925) believed that the information available was not enough to establish the actual phenomena, which took place. Branches of vegetables always contained a certain amount of gas; the heating effect of electrical light sufficed to disengage the attached air; it was also possible that part of the bubbles originated from a decomposition of the CO_2, etc. It was clear that to properly study the assimilation phenomenon it was necessary to supply the plant with enough light to cause the disengagement of a volume of oxygen at least equal to the one consumed by respiration. To do so it was necessary to approach enough the light source to the leaf, taking into consideration that below a certain distance the heat radiation would become intense enough to damage chlorophyll and stop its proper functioning. They believed that in Prillieux's experiences, the water behaved as a body that absorbed dark radiation, and hence it reduced the radiation of artificial light to a composition similar to that of solar radiation.[23]

Based on these observations, and to facilitate the measurement and analysis of the released gas, they placed the leaves of different species in a gaseous environment loaded with CO_2 (contained in a glass tube) and protected from the heating action of radiation by a layer of water 1-2 cm thick. The plants considered where tulip, orange lily, wheat, oats, Aleppo sorghum, etc.; and the electric light was provided a Drummond lamp (emitted by an incandescent refractory block heated by an oxyhydric torch), or a Bourbouze lamp (carbon arc lamp). A set of experiences was conducted covering the glass tube with a sleeve containing benzene or chloroform (both more diathermal than water), instead of water.[23]

Dehérain and Maquenne concluded as follows: (a) Leaves protected by water and kept at a short distance from the light source were always able to decompose CO_2; the action of the light provided by the Drummond lamp was stronger than that from the Bourbouze lamp; (b) leaves protected by benzene were even more sensitive to the radiation emitted by the Drummond lamp; no additional change was observed with the Bourbouze lamp. In general, the phenomenon of respiration was weaker than the absorption of CO_2; (c) leaves protected by chloroform were less sensitive to the light emitted from a Drummond lamp than when protected by benzene; with the Bourbouze lamp the phenomenon of respiration was stronger that the absorption of CO_2, as shown by a decrease in the concentration of oxygen: and (d) the results clearly showed the different ways of action of luminous radiation and dark radiation (heat). When the former controlled, the chlorophyll was able to decompose CO_2; when the latter predominated, the plant consumed oxygen and emitted CO_2 (for a Bourbouze lamp radiation acting through a layer of benzene or chloroform).[23]

Oxygen absorption and CO_2 release

Scientists already distinguished two different physiological activities, quite different in the external manifestations, although they strived for the same goal: growth of the plant and formation of the reproduction organs.[24] The functions of nutrition, embracing the decomposition of CO_2 and water and the assimilation of nitrogen and minerals principles, had been well studied, the functions of respiration, which manifested themselves in absorption of oxygen and emission of CO_2, had been only partially investigated. Nicolas Théodore de Saussure (1767-1845) had shown that these two actions were not absolutely coupled, and certain plants, such as *Cactus opuntia* (prickly pear), were able to absorb oxygen without simultaneously releasing CO_2.[25] Guerrau had claimed that the oxygen absorbed by a plant in the shadow during daytime is transformed into CO_2, which was partially released (expired). That respiration had the fundamental purpose of removing carbon from certain plant organs and transport it to another location and increase the temperature; during respiration the buds consumed more oxygen than the leaves and the plants more than the buds; leaves during the day, at sunlight or in the shadow, expired CO_2 and the amount expired was larger at higher temperatures; and that leaves in sunlight or in the shadow, exerted two opposite functions, first as fuel, and the other a reducing one, The first function was the dominant one and led to the accumulation of carbon in the plant.[26]

Dehérain and his doctoral student Henri Moissan (1852-1907; 1906 Nobel Prize for Chemistry), decided to study the subject in more detail by determining the amount of CO_2 produced by a given weight of leaves held in the darkness for a specified period of time, and to compare it with the amount of gas produced by the lower animals, to see if this vital function played a similar role in both kingdoms.[24] The memoir they published was divided into three parts. In the first one they analyzed the effect of the species to which the plant belonged, the health state of the leaves, and the temperature at which the phenomenon took place. In the second part they reported the amount of CO_2 released and its ratio against the amount of oxygen absorbed, as well as the effect of other gases present in the gas atmosphere in which the respiration was taking place. In the last par of the memoir Dehérain and Moissan explained their understanding of the physiological role of the internal combustion process represented by the absorption of oxygen and the emission of CO_2.

In their experimental apparatus the leaves were place in a laboratory tube employed for drying gases. The tube was submerged inside a large glass cylinder containing water; the temperature water was changed as desired, by steam flowing through a glass coil. Thus, the leaves could be maintained at the temperature level desired, the gas surrounding them changed at will, and adequate arrangements avoided the entrance of atmospheric CO_2 as well as total absorption of the gas produced (the memoir contains a detailed drawing of the apparatus).[24]

The experimental results were presented in four tables, reporting the nature of the leaves (green or yellow), the length of the experience, the weight of leaves, the temperature, and the amount of CO_2 produced by 100 g of leaves during 10 h, for experiments conducted in atmospheric air or in oxygen, using leaves of tobacco (Tables 1, 2, and 3 in the paper), and of a variety of other leaves (white mustard, rubber plant, sorrel, and pine, Table 4 in the paper).

The results clearly indicated that the amount of CO_2 released by the leaves in the dark were comparable to those produced by inferior animals (frogs, silk caterpillars, beetles, salamanders, and lizards) and increased regularly with an increase in temperature. The amount of oxygen absorbed by the leaves was larger than the amount of CO_2 produced; this difference was particularly noticeably at low temperatures, which seemed to favor the synthesis of compounds partially oxidized, such as fatty acids. Leaves submerged in an atmosphere depleted of oxygen continued to release CO_2 for many days, at the expense of their own tissues. This emission ceased only when all the cells were dead. The resistance to asphyxia was highly dependent on the plant species. The state health of the leaves and their size had a significant influence on the respiratory function, green leaves produced larger amounts of CO_2 than the yellow ones, at all the temperatures considered, in atmospheric air and in an oxygen atmosphere; the perennial leaves released less CO_2 than the temporal ones The respiratory function was little affected by the nature of the gas atmosphere (air, pure oxygen, and presence of CO_2). It was probable that the slow combustion that took place in the leaves generated the heat necessary to form the immediate principles. The emission of CO_2 was favored by dark heat, which also exerted a decided influence upon the rate of growth of the plant. The latter result was well understood by horticulturists; they put their plant in glassed environments, which concentrated the dark heat.[24]

In another project, Dehérain and Maquenne studied the behavior of plants (colza, haricot, *Agarethum cœruleum*, and tobacco), grown in an atmosphere enriched with CO_2.[27] The plants were grown inside three glass bells arranged one next to the other, one was communicated to the atmosphere by a narrow orifice, the second was under a constant flow of atmospheric air, and the third confined to a controlled atmosphere, into which well measured volumes of CO_2 were added, and gas samples take, as desired. The experimental evidence proved that (a) germinating young plants (colza and haricot) did not gain by being grown in an atmosphere enriched with CO_2; their weight was sensibly the same as the same plants grown in atmospheric air; (b) in the case of *Agarethum*, the composition of the gas changed slowly as more CO_2 was consumed. Within one month, the concentration of oxygen had increased from 20.8 to 26.5 %, while that of nitrogen had decreased from 77.3 to 73.5 %. The most significant difference with the plant grown in atmospheric acid was that the leaves of *Agarethum* grown in a CO_2-charged atmosphere contained much more starch, 9.1 % against 6.8 % of the dried material, respectively. Tobacco plants grown in an enclosed atmosphere deprived of CO_2 perished very rapidly, confirming a previous finding from Saussure that the cells containing chlorophyll died in the absence of CO_2. Tobacco plants grown in a CO_2-rich atmosphere contained very large amounts of starch.[27]

Root respiration

Saussure had recognized that oxygen was indispensable for the roots; plants having their roots submerged in a atmosphere deprived of this element perished soon. He had also found that fleshy roots, such as those from sugar beet and carrot, separated from their stems transformed atmospheric oxygen into CO_2. Nevertheless, he had not examined if roots attached to plants continued to absorbed oxygen.[25] Dehérain and Julien Vesque (1848-1895) believed that this question deserved to be answered, and also to find the possible relation between the amounts of oxygen absorbed and CO_2 emitted.[28,29] For this purpose, they placed cuttings of plants such as ivy and veronica (*Veronica speciosa*) in a glass tube filed with pumice stone. The tube was provided with three top openings; the central one for holding the cutting, and another for measuring the internal temperature and pressure. A bottom opening allowed introducing water to chase out the air inside the tube through the third top opening. Pumice stone was used instead of soil to avoid its influence on the absorption of oxygen and release of CO_2 by the roots. Dehérain and Vesque carried three series of experiments, one using atmospheric air; the other using pure oxygen, and the third with an atmosphere deprived of oxygen. The results of the first series indicated that roots functioned as leaves and as buds: they absorbed oxygen and released CO_2. In other words, the roots breathed as other vegetable organs did. The air in contact with the roots was found to contain less oxygen and more nitrogen than normal air; also, the amount of CO_2 gained was substantially different from the amount of oxygen lost. The results of the second series of experiments showed that roots absorbed oxygen but did not allow asserting that this oxygen was vital for their existence. This led to the third series of experiments carried with ivy immersed in an atmosphere deprived of oxygen. Comparative experiments conducted with air containing 33 % CO_2 showed that the plant behaved exactly the same as one grown in normal air; when grown in at atmosphere of pure CO_2 (or nitrogen) the plant perished rapidly. In other words, oxygen was necessary for the roots, it was not enough that the aerial part be submerged in an oxygenated atmosphere, oxygen also had to contact the subterranean organs. The absorption of oxygen observed in the previous experiences was not a simple oxidation of combustible material contained in the roots, it was a breathing act that could not be suppressed without killing the plant.[28,29]

Chemical effects of electrical emissions

In 1881 Dehérain and Maquenne published three papers on the decomposition and synthesis of water by means of electrical emissions.[30-32] In the introduction of the first memoir, they explained that the concept electrical emission did not refer to a unique phenomenon having always the same results, but to a series of effects, which could vary from sparks, a rain of fire or a simple phosphorescence, to an electric exchange showing no luminous appearance. These effects led sometimes to chemical reactions; some of them were unable to carry on the decomposition of water vapor or the combination of hydrogen with oxygen, others were able to produce both phenomena.[30]

In their study about the decomposition of water Dehérain and Maquenne used instruments of different design, among them a 0.25 m long coil (producing a spark 0.25 m long), a small Gaiffe induction apparatus (producing a spark 0.004 to 0.005 m long), the apparatus designed by Marcelin Berthelot (1827-1907) for analyzing a given amount of gas;[33] a tube containing a longitudinal platinum wire, etc. In all the experimental arrangements, water vapor was subject to an electric emission for a certain amount of time. In some cases, the resulting mixture was analyzed using a eudiometer and found to detonate. In other experiments the tube also contained starch colored blue by iodine or arsenious acid. In these last two experiments the liberated oxygen oxidized the iodine and bleached the starch, or oxidized the arsenious acid to arsenic acid. According to Dehérain and Maquenne, their result proved that certain electrical emissions were able to decompose water into its elements, even at low pressure.[30]

In a following publication, Dehérain and Maquenne described the result of their experiments to determine if it was possible to cause hydrogen to react with oxygen using an electrical emission. The experiments were carried on using a mixture of hydrogen and oxygen previously dried with phosphorus pentoxide or calcium oxide, or saturated with water. Their results indicated that the humidity state of the mixture deeply affected the nature of the discharge. With dry mixtures, there was no immediate detonation, the chemical combination took place slowly; in the presence of humidity the electrical emission transformed into true sparks with the consequent detonation. In some situation the latter was strong enough to shatter the glass.[31]

The third memoir considered the possibility of decomposing water vapor in the presence of nitrogen, the possible combination of the latter with the products of the decomposition, and the influence of humidity. Again, part of the experiments was conducted in the presence of starch colored blue by iodine, arsenious acid, or calcium carbonate. The results indicated again that in the presence of humidity the emission converted into true sparks, there was a brusque combination of hydrogen and oxygen, and the products of decomposition could combine with nitrogen forming nitric acid, or complex carbon substances (from the carbonate), which were decomposed by alkalis only when heated red.[32]

Assimilation of minerals

It was long accepted that plants of different species, grown one next to the other in the same soil, did not contain the same mineral principles and that their cinders showed a very different composition. Plants selected the substances appropriate for them, without which they could not live or go through the complete growth cycle. It was not known how vegetables selected the materials they absorbed and what was the mechanism of the selection process. Did it depend on the tissue structure of their roots or was the consequence of internal physiological actions? For these reasons in 1863 the *Académie des Sciences* opened a competition for awarding the Bordin Prize to the best memoir providing an experimental proof of the causes why different vegetables absorbed unevenly the saline solutions contained in the soil, and to identify, by an anatomical study of the roots, the possible relation between their tissues and the substances they absorbed or excreted. In 1865, the Prize committee, composed of Joseph Decaisne (1807-1882), Adolphe-Théodore Brongniart (1801-1876), Edmond Frémy (1814-1894), Louis René Tulasne (1815-1885), and Charles Victor Naudin (1815-1899), selected Dehérain's memoir as winner of the prize (the memoir was 200 pages long and included a drawing on vegetable anatomy).[34]

In the first part of his work Dehérain tried to determine the state of the different minerals present in plants. Minerals were found to be combined regularly with the different substances elaborated by the vegetable. Thus, in cactuses, sorrels, raisins, berries, etc., calcium or potassium was found combined with organic acids, mainly oxalic, tartaric, and malic acids. Treating different tissues with weak reagents showed that neutral principles were able to combine and maintain mineral substances. For example, the silica present in the straw of grasses or in the leaves of fern, resisted the action of a diluted boiling alkaline lye; the iodides, and sulfates present in algae resisted continuous washings with boiling water; and the phosphates present in flours were only partially removed by diluted acids. Nevertheless, in other circumstances it was found that common reagents removed easily the mineral materials. The intermediate situation also occurred: certain mineral substances resisted for some time the action of solvents, but eventually they were extracted from the tissues that contained them.[10,34]

Hence, it was possible to distinguish four different states or four different ways in which the mineral substances were present in plants: (a) combined in the usual manner, for example, potassium or calcium with organic acids; (b) attached by capillary affinity in the same manner that dyes are attached to a mordant; for example, iodides and sulfates in algae, silica in grass, (c) retained in the same manner that dyes attached to tissues without the aid of a mordant; for example chlorides on algae, and (d) simply deposited by evaporation, for example calcium carbonate or silica on leaves.[10,34]

In his search for an explanation of the process of assimilation, Dehérain selected a very simple case: a marine algae was constantly bathed by a solution rich in chlorides and poor in iodides. Nevertheless, its tissues accumulated iodides in an insoluble state. Chlorides also penetrated the tissues, but analysis of the cinders of algae indicated that their chloride content was well below that present in seawater; it was clear that iodides were assimilated in much larger proportion that the chlorides. To clarify this anomaly, Dehérain employed the methods used by Jules Jamin (1818-1886) to study the ascent of liquids in vegetable tissues. Dehérain showed that by putting into play simple forces like diffusion and precipitation, it was possible to cause the penetration of unequal amounts of soluble substances into a porous vase, and to imitate by this means, the selective choice practiced by plants living in a complex environment. Dehérain used the following experiment to illustrate his explanation: imagine a glass vase containing a solution of cupric sulfate. Into this solution is immersed a porous vase, similar to the one used in a Bunsen pile, full with distilled water up to the same level as the external vase. There is no transport of liquid between the two vessels but simply diffusion through the porous wall. After a few days 10 cm^3 of the internal vase contain as much salt as 10 cm^3 of the external one, that is, the system has achieved equilibrium. Now, a few drops of barite are added to the internal solution, with the resulting precipitation of the cupric sulfate as barium sulfate and copper oxide. The internal solution becomes more diluted and the equilibrium is broken. A new amount of cupric sulfate transfers from the external vase to the internal one, and the equilibrium is reestablished after a few days. The process can now be repeated until the external solution is exhausted. A salt, for example sodium nitrate or potassium chloride, which is not precipitated by barite, can be added to the copper sulfate solution without changing the results. It is clear that by this procedure, a true selection has been executed by the porous vase, which has become charged with cupric sulfate, while the sodium nitrate of potassium chloride will be at the same concentration than the one they had at the beginning of the experience. The cause of the choice is unique; it is due to the insolubility of cupric sulfate in the presence of baryte. Returning to the example of the algae being washed with a complex solution of chlorides and iodides: the latter resist washes of boiling water, which are strongly retained by the tissues; we can understand that the diffusion is operating through plant cells submerged the same as diffusion through a porous vase. The insolubility of the iodide is enough to assure its accumulation.[10,33]

Thomas Graham (1805-1869) had already demonstrated that the diffusion through a colloid was easier than through water.[35] Hence it is easy to understand that a complex solution diffuses through arable land and penetrates the tissues of the plant by endosmosis, and with the help of evaporation, the different mineral substances that have penetrated the plant, go through the action of the component tissues. If one of them forms an insoluble compound with the vegetable principles, the complex solution becomes impoverished; the external and the internal solution are now in equilibrium. Repetition of the process will result in accumulation of the principle being precipitated.[10,34]

All the mineral substances contained in a vegetable are not engaged in insoluble combinations; potassium is joined with oxalic, citric, malic acids, etc. If these salts are contained in the liquids that soak the vegetable, then the previous explanation is not enough to explain the accumulation the combined mineral principles in vegetable cells. Hence, Dehérain resorted to the same explanation as before: A simply play of physical forces such as diffusion and precipitation is able to cause the penetration of different amount of the various compounds dissolved and imitate the choice selected by plants living in a complex environment. Assume again the two-vase arrangement described in the previous situation, except that now the external vase contains an aqueous mixture of two salts. After a few days both have penetrated in the same amount though the porous wall and equilibrium has been established. What must be done to the diffusion process so as to favor the penetration of one of the two salts into the porous vase? Simple put in it a substance capable of combining with one the two salts. For example, assume that the salts dissolved in the external solution are sodium chloride and potassium carbonate and that the internal solution is diluted sulfuric acid. Clearly potassium carbonate will flow in larger amounts than NaCl, without precipitation taking place. This experience allows understanding how plants that secrete vegetable alkalis draw alkalis. For example, it is known in the tubercles of potatoes and in sugar beet roots, oxalic, citric, and malic acids, are probably generated from the oxidation of neutral principles. The presence of these acids draws in potassium carbonate, so that the secretion of these acids is the cause of the assimilation o potassium or calcium in these vegetables. In the same manner, the combination of phosphates with albuminous substances was the reason that determined the assimilation of this type of salts. When a complex dissolution penetrates the roots by endosmosis, one or more of its components is affixed in the plant and becomes insoluble, while the others remain in the sap, flow back to the roots, and returns to the soil by exosmosis.[10,34]

Dehérain concluded that vegetable fibers were not composed of a unique immediate principle; there existed a large number of celluloses capable of forming with saline solutions veritable combinations or couplings. These couplings were the first manifestation of the chemical affinity that Michele Eugène Chevreul (1786-1889) had named *capillary affinity*.

The Prize Committee remarked that although Dehérain had not strictly answered the questions posed by the *Académie*, he had answered in a satisfactory manner the principal one. He had shown that the selective absorption of minerals was not exclusively a physiological phenomenon; it was partly caused by physical forces activated by the live organism.[34]

Influence of atmospheric nitrogen

In 1873 Dehérain published a long memoir analyzing the role played by atmospheric nitrogen on vegetation;[36] there were many examples in nature that would lead one to think that the soil was becoming impoverished in this element. Nevertheless, experience showed that this was not so, for example, the soil of a forest under commercial exploitation showed no decrease in nitrogen content. The same result was found for the soil of prairies located in the high parts of mountains; the only manure they received came from the droppings of animals. When these animals descended to the lower plains, they had increased in weight; the females gave milk, etc., everything carrying the nitrogen from the prairies soil. All these phenomena repeated themselves season after season. Jean-Baptiste Boussingault (1802-1887) had found that rotational crops contained more nitrogen than the one contained in the manure used. Hervé-Magnon had shown that the hay harvested from the irrigated prairies of Mid-France contained more nitrogen than the one provided by the manure and the irrigated water together. These and other examples showed that the nitrogen contained in cultivated soil was increasing instead of decreasing. According to Dehérain, they proved that nature took from atmospheric air the nitrogen deficit caused by vegetation. Hence he decided to investigate the possible reactions that determined the fixation of nitrogen in arable soil.[36]

In the first part of his memoir Dehérain analyzed in detail the possible losses of nitrogen of caused by the main factors involved in cultivation: (a) nitrogen in the crops collected against the nitrogen contained in the manure employed; (b) losses caused in the soil carried away by a water course; (c) nitrate losses originated by infiltration in the subsoil; (d) loss of ammonia by diffusion in the atmosphere; and (e) loss of nitrogen into the atmosphere. Some well-known scientists had proven that in addition to manure, other nitrogenous organic materials lost part of their nitrogen to the atmosphere by decomposition.[36]

The second part of the memoir analyzed the opposite process, the gain in nitrogen by the soil. It was well proven that the amount of nitrogen added by atmospheric phenomena such as snow, rain, dew, and fog, was negligible and that plants were unable to fix the free nitrogen present in the atmosphere. Initially Dehérain looked at the possibility that nitrogen combined with atmospheric nitrogen to form nitric acid (nitrogen dioxide), by a process analog to the one that took place when hydrogen was detonated with atmospheric air: the formation of water was accompanied by that of nitric acid. For these reasons, he looked into the possibility that atmospheric hydrogen was fixed by carbohydrates mixed with alkalis. Hence, he burned substances such as glucose; ulmic material extracted from the soil, and humus of old trees, in the presence of nitrogen and other substances (KOH, NaOH, ammonia, and calcium carbonate), which may favor the reaction. The mixture was put in a glass tube (afterwards he used a glass ampoule), closed, and immersed in a water bath for 5-6 h; the gases present at the beginning and end of the reaction were properly measured. To his surprise, analysis of the results indicated that the nitrogen in the air nitrogen, instead of forming nitric acid (nitrogen dioxide), formed other nitrogenous combinations, may be a nitrogen oxide less rich in oxygen than nitrogen dioxide, may be cyanogen or ammonia, etc. Similar experiments carried at higher temperature gave negative results (no reaction).[36]

Dehérain assumed now that the fixation of nitrogen occurred when organic matter decomposed with release of nascent hydrogen, which combined with atmospheric nitrogen to form ammonia. For this purpose he repeated the above experiences using a large number of organic substances (sawdust, humus, roots, champignons and their mixtures with humus, soil, KOH, calcium carbonate, roots, root hairs, etc.) alone or mixed with KOH, calcium carbonate, pumice stone, tannin, fermented wheat, etc.). Reactions carried on with glucose indicated that this compound decomposed under the influence of an alkali, releasing CO_2 by an internal combustion, and also hydrogen which formed ammonia combined with glucose to form other dark derivatives. The formation of CO_2 seemed to indicate that an atmosphere poor in oxygen favored the other reactions and that nitrogen was able to fix itself to the organic substances present in the soil. According to Dehérain these were actually the conditions present at a certain depth of the soil. There, organic substances decomposed naturally, or their decomposition was accelerated under the influence of calcium carbonate. The decomposition generated hydrogen, which reacted with nitrogen to form ammonia.[36]

According to Dehérain, the experience accumulated at Grignon showed clearly that there were two conditions which led the soil to be become enriched in nitrogen: (a) Abundance of carbonated substances, and (b) Complete rest and absence of operations which favored the penetration of air.[36]

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