César-Mansuéte Despretz

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RESUMEN. César-Mansuéte Despretz (1791-1863) estudió fenómenos relacionados con termodinámica, transferencia de calor, sonido, electricidad, combustión, y las propiedades de los fluidos. En el área de termodinámica investigó la naturaleza del calor latente, la presión de vapor de líquidos, y la compresibilidad de los gases. Demostró que la ley de los gases ideales no era exacta, que la compresibilidad de los líquidos decrecía con el aumento de la presión, que la densidad del agua y disoluciones salinas presentaba un valor máximo, que para el agua era 4 °C y que para disoluciones salinas el valor máximo disminuía con el aumento de la concentración. Construyó el primer horno de arco y lo combinó con una lente y la llama de un soplete de oxígeno-hidrógeno para llevar a cabo la difusión, fusión, y volatilización de cuerpos refractarios. Usó la descarga del arco de Ruhmkorff para aproximar la transformación de carbón puro de azúcar en cristales que tenían todas las propiedades del diamante pulverizado.

ABSTRACT. César-Mansuéte Despretz (1791-1863) studied phenomena related to thermodynamics, heat transfer, sound, electricity, combustion, and the properties of fluids. In the field of thermodynamics he researched the nature of latent heat, the vapor pressure of liquids, and the compressibility of gases. He proved that the law of ideal gases was not exact, that the compressibility of liquids decreased as the pressure was increased, that the density of water and saline solutions presented a maximum value, which for water occurred at 4 °C, and that for saline solutions the maximum decreased with concentration. He built the first electric arc oven and combined its action with that of a very large burning glass and a blowpipe to realize the diffusion, fusion, and volatilization of refractory bodies. Using the discharge of the Ruhmkorff coil he approximated the transformation of pure sugar carbon into crystals having all the properties of pulverized diamond.

LIFE AND CAREER

César-Mansuète Despretz was born at Lessines, Hainaut, Belgium, on May 11, 1791. Not much is known about his early life, except that he was appointed master of studies in the *lyceum* of Bruges and afterwards went to Paris to complete his studies. There he attracted the attention of Joseph-Louis Gay-Lussac (1778-1850), who had him appointed *répétiteur* for the course on chemistry, which he was then giving at the *École Polytechnique*. Despretz replaced Claude Pouillet (1790-1868) at the *Chaire de Physique* at the *École Polytechnique*. In 1824 Despretz was made adjunct and in 1837 promoted to titular professor of physics at the *College Henri IV*; in 1847 he received the chair of physics at the Sorbonne. He was naturalized as a Frenchman in 1838 and on May 5, 1841, he was elected to the *Académie des Sciences*, in the division of general physics, replacing Felix Savart (1791-1841), who had died recently [1]; in 1857 and 1858 he served as vice president and president of the institution, and in 1858 he was elected foreign member of the Royal Society of London.[1-2]

During forty years Despretz studied phenomena related to thermodynamics, heat transfer, sound, electricity, combustion, and the properties of fluids. In the field of thermodynamics he investigated galvanic phenomena,[4] the density of vapors,[5] the nature of latent heat,[6] the vapor pressure of vapors, and the compressibility of gases. He proved that the law of ideal gases was not exact,[7] that the compressibility of liquids decreased as the pressure was increased,[8] that the density of water and saline solutions presented a maximum value, which for water occurred at 4 °C, that for saline solutions the maximum decreased with concentration more rapidly than the decrease of the freezing point,[9-12] and that a liquid substance never solidifies at the same temperature where the corresponding solid melts.[13] He also observed the displacement of the zero in the mercury thermometer[14] and in acoustics he searched the limits of percep-

Note 1. The list of candidates proposed by the Physics Section included Charles Cagniard de la Tour (1777-1859), Jean Claude Eugène Péclet (1793-1857), Jean Charles Athanase Peltier (1785-1845), and Lechevalier. In the first round Despretz obtained 24 votes, Péclet 22, Cagniard Latour 3, and Peltier 2. In the second round Despretz obtained 28 votes against 23 of Péclet and hence was selected as the candidate, subject to the approval by the King, Louis-Philippe I (1773-1850).

tion of sound.[15] In 1824 the *Académie* awarded him the Grand Prix des Sciences Physiques for his memoir on the causes of animal heat.[16] In the same year, while studying the reaction between ethylene and sulfur chloride, he accidentally discovered mustard gas (2,2-dichlorodiethyl sulfide), without recognizing its toxic properties. The strange smelling liquid reminded him of horseradish or mustard.[17]

He devoted much time to the study of the voltaic cell and the voltaic arc. In 1849 he built the first electric arc oven and combined its action with that of a very large burning glass and a blowpipe (oxy-hydrogen flame) to realize the diffusion, fusion, and volatilization of refractory bodies, thus performing some experiments of remarkable interest in those days when electricity was not so highly developed as at the present time. Using the discharge of the Ruhmkorff coil he approximated the transformation of pure sugar carbon into crystals having all the properties of pulverized diamond.[18-23] The experiments he conducted in these areas during his public course at the Sorbonne were spectacular, outstanding by the size of the diapason and voltaic arc he employed.

Despretz carried on in Paris a secluded and solitary life; he was known to walk every morning through the gardens of Luxemburg, and then go to the Sorbonne for five hours of teaching and research. Despretz died in Paris on March 15, 1863, of a brain and pulmonary congestion. He was replaced by Alexander Edmond Becquerel (1820-1891) at the Académie, by Jules Jamin (1818-1886) at the Chaire de Physique II in Sorbonne, and by Gabriel Lamé (1795-1870) at the *Chaire de Physique* at the *École Polytechnique*.[2]

SCIENTIFIC ACHIEVEMENTS

Despretz published some fifty memoirs between 1817 and 1863. As customary for all candidates to the Académie, he published a booklet describing his research achievements.[1] Among his books we may mention *Mémoire sur le Refroidissement de Quelques Métaux, pour Déterminer leur Chaleur Spécifique et leur Conductibilité Extérieure*,[24] *Mémoire sur la Conductibilité de Plusieurs Substances Solides*,[25] *Recherches Expérimentales sur les Causes de la Chaleur Animale*,[26] *Traité Élémentaire de Physique*,[27] *Eléments de Chimie Théorique et Pratique*,[28] *Recherches sur la Propagation de la Chaleur dans les Liquides*,[29] and a short book about public instruction, *Des Collèges, de l'Instruction Professionnelle, des Facultés*.[30]

Animal heat

In 1822 the *Académie* awarded Despretz the prize on the question of animal heat, a memoir that attracted the attention not only of physicians but also of physiologists.[16,26] Despretz's results indicated that (a) Respiration was the principal source of animal heat; assimilation, the flow of blood, the friction of different members, and the nervous system, accounted for the small remaining part, (b) besides the fraction of oxygen used in the formation of CO_2, a more significant portion disappeared simultaneously; more oxygen disappeared in the respiration of young animals than in the respiration of adult animals, (c) the respiration of carnivorous and herbivorous animals or birds was accompanied by exhalation of nitrogen, which was larger in the case of carnivorous species, and (d) the respiration of carnivorous animals produced substantially less heat than that of herbivorous animals. The same results held for birds and mammals.

Between 1822 and 1824 Despretz performed more than 200 experiments on young and adult birds and mammals (young and mature ducks, chicken, roosters, hens, pigeons, owls, magpies, dogs, and cats). All the results proved that the heat of respiration contributed between 70 and 90 % of the total heat emitted by the animal. The measuring apparatus was such that the gas breathed was immediately received over mercury, thus avoiding the loss of CO_2 by water. Despretz's experimental work represented the first time that larger volumes of air were received over mercury, and his many chemical analyses indicated that air contained 21 % volume oxygen and 79 % volume nitrogen. The apparatus was built of three principal elements: a gas meter that provided the air to the animals, a box that held the specimen tested, and a second gas meter receiving the air consumed. The inlet gas meter allowed measuring the air flow, which was held constant, and its temperature and pressure. The exit gas meter allowed measuring the exit flow, temperature and pressure.

The specifications of the *Académie* for the award requested a comparison between the heat developed by a warm blood animal, within a certain period of time, with the heat developed during the production of CO_2 and water, during the same period of time, that is, a precise measurement of the heat of combustion of carbon and hydrogen. Despretz also addressed other related questions, such as the influence of the purity of air, the respiration of reptiles, etc. The results of more than 100 experiments with tadpoles proved that in the breathing of these animals, CO_2 was formed, a known fact, but that also oxygen disappeared and nitrogen was released (both unknown facts, until then).

During his experiments, Despretz also measured the body temperature of men of different ages, His findings indicated that (a) from 20 years on, the body temperature remained essentially constant at about 37.12 °C (b) newly born infants (1 to 10 d old), had a body temperature about two degrees below that of men, that is, about 35 °C, (c) mature men had a body temperature higher than those of infants; the same result was present with young animals, (d) after several weeks, the age of infants approached that of adults, (e) paralyzed members had the same temperature as healthy members, and (f) the temperature of fish was higher than that of the water in which they inhabited.

This memoir was awarded the 1822 *Grand Prix des Sciences Physiques by the Académie.*

Despretz's results were severely criticized by Victor Regnault (1810-1878) in his masterpiece investigation about animal respiration.[31]

Animal electricity

The problem with using a galvanometer to detect animal electricity was that the very contact between the electrodes and the tissue being investigated generated an electric current. This artifact had led to confusion at the turn of the century, and it was not until Alexander von Humboldt (1769-1859) succeeded in demonstrating animal electricity in an experiment free of metal that the controversy ended.[32] In 1849 Emil Heinrich du Bois Reimond (1818-1896) invited Humboldt to observe his experiments on the electricity developed during muscular contraction. The experiments consisted in immersing the poles of a very sensible galvanometer in a saline solution into which one finger of each hand was then immersed (important advantages of the galvanometer were that the needle responded to current, enabling it to show direction, intensity, and variation in the electricity being measured). When the fingers were immersed, a pronounced deviation of the needle was observed, without any particular law. When one of the fingers had a wound, the deviation was stronger and corresponded to the same direction as the finger behaving as zinc in a zinc-copper arc. Du Bois Reimond also observed the deviation produced when contracting the muscles of one arm or the other. The deviations were stronger when the muscles were contracted more.[33,34]

Humboldt was so impressed by these experiments that he communicated them to François Arago (1785-1853) in a letter sent on April 1849, and which Arago promptly transmitted to the Académie des Sciences in the same month, in these words:[35] *"M. Du Bois is the skilled experimenter, which for the first time and alone, has succeeded in deviating a astatic needle by human power, that is, by the electric current produced by molecular effort, the tension of our members. This deviation operates at large distances and stops when the muscle is no longer tensed"*.[33,34]

According to Finkelstein, the Académie reacted with disbelief and sent word back to Berlin requesting an explanation of du Bois-Reymond's results. On May 17, Humboldt sent to Arago a short description of the experiment that du Bois-Reymond drafted for the *Académie*'s benefit. Humboldt added the comment that *"the experience, a result of one's will, does not leave a shadow of doubt. In spite of my advanced age and the little force left in my arms, the deviations of the needle were quite strong…To facilitate the experience its is convenient to immerse the index of each hand in the water and to press the palms in order to stiffen the muscles of the arm one desires to act."* [33-35]

Despretz and Antoine César Becquerel (1788-1878) were the first scientists who attempted to reproduce du Bois-Reymond's results[33,34] but failed to do so because they did not follow the laboratory protocol that du Bois-Reymond had detailed. Despretz concluded that du Bois-Reymond had been deceived by contact electricity and went on to question the rest of the work. Shortly thereafter, Despretz reported his experiences repeating those described by du Bois-Reymond. He used a highly sensitive galvanometer manufactured by Heinrich Ruhmkorff (1803-1877) and performed many experiences under different conditions, for example, changing the nature of the conductors (gold, silver, platinum, copper etc., nude or plated with another metal). Contraction of one arm produced deviations of the needle in one or the other direction. He also replaced the galvanometer by a frog and tried to stimulate it by touching different parts of the body with the two hands, one of them contracted strongly, with negative results. However, holding in one hand a copper wire and in the other a zinc one, and then touching the animal, produced strong convulsions. When sticking the two gold blades of the galvanometer into a potato, an apple, a piece of cabbage, beef meat, or touching different wet skin locations, currents were observed. Withdrawing one of the blades, washing it and then sticking it back, generated a current in the opposite direction; burying the blade more or less than before, also resulted in an inversion of the direction.[33,34]

According to Despretz, it was possible that the convulsions observed in the frog were due to the heterogeneous liquids that wetted its skin. It was also possible that the constancy of the direction of the current observed was due to a different alterability of the extremities of the animal caused by the different solutions employed in the experiences. Another important experience consisted connecting a chain of frogs in the same manner as ordering the couples of voltaic piles. Despretz failed to observe an appreciable effect when joining or separating the ends of the chain. He concluded that his experiments did not prove or disprove the existence of electrical currents in frogs or in vegetables.[33,34]

Latent heats

In 1818 Despretz read to the *Académie* a memoir about the latent heat of different vapors (water, alcohol, sulfuric ether, carbon disulfide, and turpentine).[6] His results indicated that the latent heats varied in an inverse way with the density of the liquid at its boiling point, or in other words, that equal volumes of vapors contained essentially the same amount of latent heat. Although this was an approximation, it could be used in industrial applications, for example, as a guide in the construction of equipment destined to the distillation of liquids more volatile than water. It was easy to understand that for all other factors held equal, it was advantageous to replace water in a steam engine by a more volatile liquid, such as ether. The memoir included a table reporting the total heat and latent heat, measured by condensing the vapor by a liquid of the same nature, the total heat content, the latent heat of water and density of its vapor at 0 °C, and at the normal boiling point. The heat content of other liquids was calculated assuming that the heat capacity of water (for comparison) was unity.

Vapor pressure and energy content of vapors

Until then it was accepted in France (according to Dalton) that vapors had the same pressure at temperatures equally distant from the boiling point of the liquids that generated them. Despretz proved this result to be wrong; vapors had equal pressures at temperature equally nondistant from the boiling points of their liquids.[6] This conclusion was afterwards used by some researchers to determine the boiling point of a substance available in very small amounts.

In their *Mémoire sur la Théorie des Machines à Feu*, read to the *Académie des Sciences* of August 16 and 23, 1819,[37] Charles-Bernard Desormes (1777-1862) and Nicolás Clément (1779-1842) addressed the basic question of how to extract the maximum mechanical power from heat (what today we call the thermal efficiency of a heat engine). The answer to the question was fundamental at a time when steam engines were developing very fast and represented the tool for technological supremacy. In the first part of this memoir they described their experiments to determine the amount of caloric (heat content) present in steam at different temperatures and pressures, and their (wrong) conclusion that for saturated steam this amount was independent of the pressure and temperature. In other words, a given mass of steam could expand or condense without losing its elastic state, independently of the modifications that is volume might experiment. It is interesting to indicate that this "law" was accepted as true until Despretz proved it to be wrong. In his *Traité Élémentaire de Physique,*[27] Despretz stated that he had shown experimentally that Clément and Desormes´s law for steam, could be also applied to the vapors of other liquids (alcohol, turpentine, and ether), but in later editions of his book (after 1836) he wrote that he had repeated his experiences at higher temperatures (up to 160 °C) an found that the total heat content actually *increased* as the temperature was raised. This conclusion had already been presented in the pamphlet he published when being considered for membership in the *Académie des Sciences*.[1]

Density of vapors and gases

In 1821 Despretz read a memoir about the density of vapors and gases, which showed that in a certain pressure interval the vapors of alcohol, sulfuric ether, and carbon disulfide were more compressible than indicated by the ideal gas law.[5] In another paper, published in 1827, Despretz reported additional measurements on the compressibility of air, carbon dioxide, ammonia, sulfur dioxide, hydrogen sulfide, cyanogen, and hydrogen, perfectly dry, at several pressures, and compared the results against air, assuming the latter to be ideal, as believed by scientists of the time. Once again, his results indicated that all the gases deviated from the law of ideal gases. Carbon dioxide, ammonia, sulfur dioxide, hydrogen sulfide, and cyanogen were more compressible than air and their compressibility increased with increasing pressure, each in a different amount. Hydrogen was found to be less compressible than air. The memoir included detailed tables of the compressibility of ammonia and hydrogen sulfide. From these experiments Despretz concluded that Avogadro's hypothesis that equal volumes of a gas at the same pressure and temperature contained the same number of molecules, was incorrect; that the unequal compressibility carried with it unequal dilatability, and that the law of gaseous combination in most cases is not rigorous.[7]

Heat of combustion

In 1821 Despretz published a memoir about the combustion of carbon, hydrogen, phosphorus, and many metals (iron, zinc, tin); this was he first time that a metal had been made to burn in the atmosphere. Among the results he reported that tin and his monoxide developed the same amount of heat for the same amount of oxygen absorbed. His calorimeter consisted of a copper box, enclosing another copper box wrapped with a coil; oxygen entered the box by one end of the coil and left from the other end. This calorimeter had the advantage of serving equally to determine the heat released during the combustion of any body, including powder, and was preferable to the one used by Benjamin Thomson (Count Rumford, 1753-1814) because it gave more accurate results and could burn coal, which was not possible with Rumford's apparatus. In a memoir read on October 16th, 1827, he reported the same results. The measurements indicated that for 1° of oxygen, hydrogen developed 2 578°, carbon 2 967° and iron 5 325°. It resulted that among all the substance hydrogen was the one that developed the less amount of heat for the same amount of oxygen absorbed. Metals were the ones that developed the most heat. It was interesting that carbon, which did not change the volume of oxygen, developed an amount of heat 3/5 of the one developed by iron and metals in general, which reduced oxygen to the solid state (it became part of the oxide).

In a following work,[38] Despretz reported that the amount of heat released by a substance that did not change the volume of oxygen, was the same for all densities. For example, 1 kg of carbon when transformed into CO_2, released an amount of heat capable of increasing by 1° the temperature of 7 914 kg of water. This result was the same at all pressures, that is to say, the heat of combination without change in volume in a gas was the same for all vivacities of the combination.

Maximum density of liquids

In a paper published in 1837, Despretz presented the results of his experiments for determining the maximum density of water.[9] In the first part of this work he described the determination of the temperature of the maximum density of pure water and the expansion of the same after the maximum and up to the boiling point. The second part concerned the maximum density of seawater and the existence of the same phenomenon in different aqueous solutions of salts, acids, alkalis, and alcohols, at different concentrations. Despretz proved that the density of saline solutions went through a maximum value, the same as water did. The question for seawater was particularly important because of the change in temperature of polar and the equinoctial seas, and well as with depth. The maximum for pure water was important for the determination of the gram. Previous results by other scientists had indicated the value (4.1 ± 0,3) °C .

The procedure used by Despretz consisted in following the simultaneous reading of a water and a mercury thermometer. For this purpose he built six water thermometers and four mercury ones, equally graduated in order to eliminate the error caused by the conicity of the tubes, and arranged in such a way that the variation in the diameter of the tubes varied alternatively in one or the other direction. In the first series of experiments the thermometers were placed in a liquid bath, which was cooled gradually, and after exceeding the apparent maximum value, the liquid was left to heat by natural convection until the thermometers returned to their original readings. Thermal inertia was provided by inserting the thermometers in a copper vase and submerging the latter in a large earthenware vase, containing water at different initial temperatures. The experiments lasted for about 10 h, during which 8 to 20 readings were taken. Since the exact determination of the absolute maximum required knowledge of the expansion of the glass thermometers, Despretz developed a new a procedure independent of the expansion of the glass, based on the fact that in a liquid mass in which the layers are at different temperatures, the molecules that are at the temperature of the maximum temperature tend to descend while the others tend to raise. The memoir includes a detailed description of the experimental procedure used to follow the temperatures of the upper and the lower layer as a function of time, by locating the thermometers horizontally in the liquid. The intersection of the curves describing the temperature history gave the temperature of the maximum density.[9]

The average of many heating measurements was 4.058 °C . Since the thermometers had been graduated in the vertical position and in the experiments they were used horizontally, the readings had to be corrected due to the pressure of the mercury and the action of air on the stems. The corrected result was 3.969 °C . Similar experiments with cooling gave a corrected vale of 3.982 °C, a difference of 0.026 °C with the previous one, which was understandable since on cooling or on heating the temperature of a liquid was not exactly the one read by the thermometer: For cooling the reading was higher, and for heating it was lower.[9]

Despretz took especial care in verifying the zero of each thermometer before and during its use, because he had already noticed that the position of the zero varied when the instruments were maintained for a long time at a high or a low temperature.[14]

This work was followed by another concerning the case of saline solutions. All solutions studied (seawater, sodium chloride, calcium chloride, potassium carbonate, sodium carbonate, potassium sulfate, sodium sulfate, cupric sulfate, potassium hydroxide, sulfuric acid, and alcohol) were found to present a maximum density, which varied with the concentration of the solute. The results pointed clearly to a decrease of the temperature of maximum density and that of freezing, as the solution became concentrated.[10,11] This result became known as Despretz's law.

Later work by Wright[39] extended that of Despretz, proving, in addition, that the lowering produced by a highly ionized binary electrolyte is produced by two separate independent effects, one due to the acid radical and the other due to the basic radical of the electrolyte.

In a following memoir Despretz reported on the fitting of his experimental measurements of the density, using a third-degree polynomial:[12]

$$y = ax^3 + bx^2 + cx + d$$

where *y* represents the volume and *x* the temperature.

The temperature of maximum density (minimum volume) was found by equating to zero the first derivative of the equation. This procedure yielded 4.004 °C for water, compared with 3.995 °C, using the graphical procedure described above.

Despretz also studied the melting of organic substances such as margaric acid, oleic acid, stearin, olive oil, cetin, paraffin, and naphthalene, which, solidified with a substantial decrease in volume but did not present the phenomenon of density maximum. They contracted in the liquid state when cooled below their freezing point.[13]

Oscillations of the zero of the mercury thermometer

The ascent of the zero of a thermometer after its construction was a well-known phenomenon. Despretz experiments indicated that the zero of a thermometer was an ever oscillating phenomenon. If a mercury thermometer was held in a given medium at a temperature below zero (for example ice and salt), the position of the zero ascended, more of less. On the contrary, if it was maintained for the same length of time at 100 °C or higher, the zero descended. In either case, when the thermometer was withdrawn from the cold or hot source, the zero moved very slowly towards the zero determined before the change. For a given thermometer, the phenomenon could last for several years. The results indicated the zero of a thermometer used to measure atmospheric temperature ascended in winter and descended in summer. Consequently, when performing highly precise experiments it was necessary to verify the zero continuously because it might change considerably.[14]

It is of interest to mention that James Joule (1818-1889) kept record for 40 years of the drift of the zero point of his thermometers.[40]

Heat transfer

The problem of heat transfer between two solid substances had been analyzed theoretically by Siméon-Denis Poisson (1781-1840) in his book *Théorie Mathématique de la Chaleur*.[41] Despretz decided to study the problem experimentally to determine if the contact surface between the two bodies represented an obstacle to heat transfer the same like it does for electricity. In the latter case it was known that electricity changed its rate when the conductivity of the medium was changed. For this purpose he used a wood vise to join longitudinally by pressure two square bars, 20.05 mm side, 40 cm long, one made of tin and the other of copper. Since it was not possible to measure the temperature of the joint of the two bars, it was calculated using the relations developed by Poisson. Despretz's results indicated that the temperature of the copper bar surface through which heat passed into the tin bar had an excess temperature of 1.47 °C above that of tin. Inserting a very thin piece of paper between the two bars increased this temperature to 5.5 °C . In other words, the rate of heat exchange behaved in the same manner as the transfer of electricity.[42]

Until 1838 there was little information regarding the transfer of heats through liquids, until Despretz read a memoir in which he reported not only about the direct transfer of heat in a liquid, but also about the laws regulating the phenomenon.[43] His results indicated that if a long enough liquid cylinder was heated from the top with a copper vase to which were added equal amounts of boiling water at equal time intervals, the values of the difference between the temperature of equidistant points in the axis and the ambient temperature, formed a geometric decreasing series, similar to the one taking place in a metallic bar. In a horizontal plane, the temperature decreased from the axis to the surface of the wood cylinder in which the water was contained. This decrease in temperature of the liquid was small, but became notable at the liquid at the surface, a result indicating that it was not the wall that transferred heat into the liquid.

Another interesting result was that the value of the logarithm of the ratio of the geometrical progressions provided by two cylinders of different diameters, varied inversely as the square root of the diameters.

In another memoir Despretz reported the results of additional experiences on heat transfer using pure and salty water, iron, cast iron, marble, lithographic stone, wood, etc., arranged as cylinders 0.225 m diameter and 0.60 m long.[44] His new observations indicated that addition of a salt or acid did not modify in a sensible way the heat conducting ability of water, a result that suggested that in this situation the transfer of heat differed completely from that of electricity. In addition, transfer of heat through poor conductors shaped as bars 2-cm side, did not yield the converging series or geometric progression of temperatures given rigorously by good conductors, but did so when built of sufficiently large dimensions. According to Despretz, his results proved that the fundamental laws of heat transfer were true for all solid and liquid bodies.

Another area of interest was determination of the conductivity of the main common solid bodies, such as gold, platinum, silver, copper, iron, lead, tin, marble, porcelain, the earth of furnaces and bricks, as well as the influence of matter, more or less conductive, on the regularity of the laws of heat conduction.[45] For this purpose, Despretz shaped each of the substances he wanted to study, as a square bar, 21 mm side. Cavities, 14 mm deep and 5 mm long, separated 10 cm from their centers; were carved to carry very sensitive thermometers. The center of the thermometer reservoir was located on the axis of the bar and the little space left between the reservoir and the cavity was filled with oil. All bars were covered with a layer of the same varnish, in order to present the same radiating power. Each bar was heated on one end with the aid of an oil lamp. Experiences lasted 5-6 h; it required at least 2-3 h for each thermometer to reach a constant reading, that is, for the bar to reach an equilibrium state. Interpretation of the results indicated that (a) good conducting substances, such as copper, silver, gold, platinum, iron and tin, gave the same geometrical series as predicted by calculations, (b) for mediocre conducting metals, such as lead, the measurements were not exactly as predicted, (c) with poor conducting substances, such as marble, porcelain, earths, etc., the results were not concurrent, unless the thermometers were located more far apart. The relative conductivities were as follows: gold, 1.000 (reference); platinum, 0.981; silver, 0.973; copper, 0.898 2; iron, 0.374 3; zinc, 0.363 0; tin, 0.303 9; lead, 0.179 6; marble, 0.023 6; porcelain, 0.012 2; and earths, 0.011 4.

On the materials studied by Despretz, only incomplete results of Jean Ingenhousz (1730-1799) were available. Ingenhousz's procedure was very primitive: baguettes of the different materials were covered with a layer of wax; one end of the baguette was put in contact with boiling water and the rate of heat transfer followed by the advance of the melting zone. Ingenhousz found that silver, gold, copper, and tin were more or equally good conductors, while platinum, steel, and lead was less conducting.

Compressibility of liquids

In 1823 Despretz reported to the *Académie* his results regarding the compressibility of liquids, in response to a prize contest of the *Académie*. Years later,[8] Despretz acknowledged that his memoir had not been significant enough to deserve the prize, nevertheless, it contained two facts that in 1823 were important: (1) An experimental apparatus different from the one used by Kanton and Hans Christian Ørsted (1777-1851), (2) the experiments done with four liquids (water, alcohol, sulfuric ether, and mercury) indicated that the compressibility decreased as the pressure was increased, a finding contrary to the one reported by other contestants. Since the four liquids employed were quite different in nature, Despretz believed that his results could be considered to be general. According to Despretz, Kanton and Oerstedt's apparatus could not be used when the tube was submerged in a liquid, as required when studying the progress of the compression. In Despretz's apparatus (there is a drawing) index M of the mercury, ending the liquid column, was separated from the liquid environment by a space filled with air, so that if during an experiment, the index, forced by a compressive force, penetrated into the liquid, the volume of this liquid was at all times enclosed in the piezometer were the tube was graduated. Thus it was always possible to estimate the decrease in volume corresponding to the applied pressure. In addition, means were provided to avoid the precipitation of water caused by the condensation of the air.

In the same opportunity Despretz proposed a method for measuring the heat released during the compression of liquids, consisting in compressing strongly the liquid and then submerging it in a large mass of water until cooled to the original temperature while the pressure was released to atmospheric. The cold produced by the expansion was equal to the heat disengaged during the compression.[8]

Volatilization of solids

Work on the electric arc and pile represents the most extensive and intensive activities of Despretz. Despretz was looking for a practical way of achieving the fusion or volatilization of substances. Initially he used a battery of 120 Bunsen piles [2], built by Louis-Joseph Deleuil (1795-1862) [3] with the zinc at its center, to which he added another battery of 45 Bunsen piles, built by Henri Adolphe Archereau (1819- 1893) [4], and having carbon at its center. The latter was substantially larger that the first one and could be considered equivalent to about 65 pairs. Thus, 185 Bunsen piles represented the total pile. An annular burning lens of about 90 cm diameter provided additional heating. The blowpipe used hydrogen, which Despretz replaced by methane to achieve a more intense heat. The power of the pile was increased by addition of magnesia, hard and compact, which under the action of the pile alone, volatilized immediately into white fumes, aided by the pile and the lens.[18]

Despretz tested the power of the arrangement on a rod of almost pure anthracite. The rod became curved under the double heating action of the pile and the lens. A second rod fused and fell when put under the combined action of the pile, lens, and blowpipe. Despretz felt that the three combined sources were appropriate for determining the fusion and volatilization of substances already oxidized or that hardly burned in contact with air. For coal, it was better to operate only with the pile and the lens in vacuum or in the presence of nitrogen, and to replace the blowpipe by a number of voltaic elements. He believed that rods made of well-ground anthracite or sugar carbon, well prepared, melted completely. In air, a well-ground rod disappeared almost immediately; thicker rods resisted the action of air and did not heat enough to melt.[18]

Note 2. Bunsen pile: an early electrical battery using multiple cells constituted of a zinc anode in dilute sulfuric acid and a carbon cathode in nitric acid zinc, with a porous separator between the liquids. This device generates a potential of 1.89 V . Later versions added potassium dichromate as a depolarizer.

Note 3. Deleuil was an engineer specializing in optics and in the construction of instruments. In 1844 he carried on the first public lighting over the roof of a house located in the Quai de Conti, and afterwards of the Place de la Concorde.

Note 4. Archereau was a French scientist that had an active participation in the beginning of electrical lighting by building one of the first arc bulbs and developing industrial techniques for the agglomeration of carbon powder.

"Extrait des Comptes rendus des séances de l'Académie des Sciences, tome XXVII, séance du 28 mai 1849."

The discovery of yperite. Peronnet, M. J. Pharm. Chim., 23, 290-292, 1936.

The record of the discovery by Despretz in Ann. Chim. Phys. 21, 428-, 1822, was pointed out in 1927 by Hanslian (cf. C.A. 21, 3404).

Calculation of the Despretz-Trouton constant. Berthelot, D., *Compt. Rendus*, 160, 657-60, 1915.

The value of Q/T, where Q is the latent heat of vaporization and T the abs. temp., as calcd. from the integral of the equation Q = .intg.nt (a/v2)dv, with the help of van der Waals' equation, was only 9 cal, in place of the usual 20 or 22. If the Berthelot equation be used in place of the van der Waals equation, the value 18 cal may be obtained, making the same assumptions as before.

The many experiences performed previously provided Despretz with clear evidence of the fusion of carbon. Given that the largest part of carbon disappeared in air under the triple action of the arc, pile, and blowpipe and not having yet equipment with which he could operate in the absence of air, Despretz looked for the possibility of increasing the number of elements in his battery. With the help of his colleagues, he was able to collect 500 elements. Having learned by experience that a flat element of zinc could provide the same energy as a cylindrical one, he did the pertinent replacement in all the piles he had gathered. In order to find what the battery alone was capable of performing he arranged 496 elements in four parallel series, giving him the equivalent of almost 124 elements about four times larger. He introduced into the apparatus, which he named *oeuf éléctrique* (electrical egg) a rod-shaped piece of sugar carbon, of about 4 mm diameter and 5 cm long, and connected it between the two poles. After evacuating the equipment to about 5 mmHg, and making the electrical connection, the carbon rod became incandescent almost immediately and the inside of the container became covered with a dry black crystalline powder.[19]

When the carbon was now fixed to the negative pole, it become blazing white, deposited on the walls of the vessel some white rays, and all of the sudden it vaporized. All the part of the apparatus near the hearth became covered with a dry crystalline black powder. The experiment was repeated inside a crystal bell, separated in the inside of the hearth by a metallic web. This time a layer of bright powdered carbon was deposited on the upper part of the lateral wall. Everyone who observed the experiences became convinced that carbon had volatilized.[19]

In a following publication Despretz reported his results on the vaporization of silicon, boron, titanium, tungsten, palladium, and platinum.[20] Under the action of the electric arc, silicon melted easily, forming a globule, slightly vitreous on the surface. When sandpapered with emery powder its surface acquired the polish of a very dark glass. The material scratched glass. Boron melted into a globule having a slightly vitreous surface, more fusible and volatile than silicon. The inside of the globule was green black, similar to carbon. Titanium, prepared from titanium tetrachloride, volatilized and deposited in the form of a thin layer capsule, or as small globules. The material was scratched by tungsten and scratched quartz and zircon. Tungsten behaved similarly to titanium, depositing as a film or very hard globules able to wear down a file, and to scratch quartz, precious stones, and natural or artificial ruby. The particular hardness suggested his potential use in polishing precious stones, cutting tools for glass, etc. Palladium melted very easily under the action of the electric pile. The product was easily laminated yielding a highly homogenous and malleable substance. Platinum nodules also melted easily. The volatilization manifested itself by the formation of a black cloud originating on all the surface of the carbon, and depositing mostly on the walls of the vessel containing the carbon joining the two poles. This volatilization took place in vacuum or in a gaseous atmosphere, in a way that varied according to the purity of the material. For example, platinum volatilized in air, iron in vacuum or in the presence of a gas, etc. Despretz indicated that he had tested the volatilization of many substances, and he had found all to volatilize; he believed that his results were of particular interest to the study of certain geological phenomena.[21] Despretz concluded that he had found a new application of the pile for industrial practice.[20]

Since everyone considered carbon to be fixed and infusible Despretz carried on additional experiments on the effect of the high temperature obtainable by electrical means using a battery of 600 Bunsen cells, which could be connected up in various ways, according to the nature of the work required.[21] The electrical effects of the battery were tested on different varieties of carbon: retort carbon, anthracite coal, graphite, sugar carbon, carbon obtained by decomposing turpentine in a strongly heated porcelain tube, and finally, on diamond. Despretz avoided combustion of the carbon by carrying it in nitrogen or other non-combustible gas, at a pressure above the atmospheric. The electrical current flowed through a wire connecting both poles or through a gas vacuum. In the case where the current of the pile was made to pass through a rod-shaped piece of carbon, he found that the carbon curved in the form of an arch or an S (the same phenomenon took place with sugar carbon, turpentine carbon, carbon deposited in the cylinders, anthracite, and graphite).[21]

The results indicated that all the carbon structures employed changed into graphite under the strong heat generated by the pile. Despretz described various experiments in which he placed carbon rods between the two electrodes: the current flow led to bending of the rods. Analysis of the rod indicated for the first time formation of graphite: *"The carbon rod, 2 centimeters long and 2 millimeters in diameter, was placed between the electrodes, and the current from the 600 cells, arranged in twelve series of fifty elements, was passed through it with the result that the rod bent and broke, the upper part showing an enlargement at the fracture. This enlarged portion resembled slag and the ends of the carbon were graphite."* Other experiments conducted with sugar carbon powder showed that *"certain globules in the powder had been formed by the heat; and in some cases the transformation of the powder into graphite was complete."* These phenomena were taken as evidence of fusion. The most interesting of these experiments indicated that: *"Some nearly pure anthracite, treated in the same way, spread out on a crucible like a black glass... A much larger piece of this substance treated in the same manner by the battery, which had been weakened by numerous experiments, exfoliated. The part, which received the direct action of the heat, became bluish gray in color and was clearly graphite. The part on the edges of the crucible became less hard but was not yet graphite... I covered and impregnated some acicular rods of carbon with more fusible materials: silica, alumina and magnesia, in order to see if the presence of more fusible substances made the fusion of the carbon easier in the heat from the battery. The silica, alumina and magnesia were dissipated in the form of vapors and the carbon remained behind retaining its (original) properties... I placed an acicular rod of carbon in a clay crucible, filled the latter with well-dried sand, and then passed a current through the carbon, which fused and volatilized. I found a sort of very hard fulminous tube, the inside of which was lined with smoked quartz. The inside diameter was at least ten times that of the carbon"*.[21]

Despretz summarized his results as follows: (a) In a vacuum, carbon manifestly vaporizes at the temperature to which it is raised by a battery of 500 to 600 Bunsen cells connected in five or six series. In a gas the vaporization is more gradual but likewise occurs, (b) carbon brought to the temperature which obtained in the experiments may be bent, welded and fused, (c) carbon of any source which is submitted for a long time to a high temperature becomes proportionally softer and finally transforms into graphite, (d) graphite, like carbon, dissipates little by little under the action heat. The portion that does not volatilize remains as graphite, (e) under the action of a sufficiently strong pile, diamond changes into graphite, like all other species of carbon. Heated for enough time, it yields small fused globules, the same like carbon.[21]

The reader interested in the history of the transformation of carbon into graphite and other derivatives is directed to a detailed paper by Fitzgerald.[46]

Piles

Despretz carried many experiments using a two-liquid pile[22,23,47-53] and concluded that the nature of the light of the pile seemed to be independent of the number and arrangement of the elements. If the beam of electrical light was concentrated in an appropriate manner on a lens, where the blue coincided with one line of the lens, no displacement was noticed, when going from 100 to 600 elements, in series, or of 600 arranged in six parallel series of 100 elements. This was considered to be a situation of refrangibility. Despretz was unable to determine with a rock salt prism if the pitch or the temperature of the heat that accompanies the electric light, changed with the tension of the energy of the pile. He could only assert that this temperature was always high enough to melt alumina or silica when employing 20 or 600 elements. Not withstanding, the size of globule produced was smaller as the pile was built from a small number of elements of the same surface. This experience proved that the temperature of a small number of elements was already high enough. Despretz tried to measure the intensity of the electric light using different methods, by estimating the distance at which it ceased to be read distinctly, and by several photometric methods. The number of elements arranged in series (by tension) exerted a slight influence on the intensity of the light: the intensity increased from 50 to 100, from 100 to 600, but not in a considerable manner. Now, if the elements were connected so as to double, triple, etc. the surface, then a considerable increase in the luminous energy took place, proportionally to the surface of the elements. For example, the illumination produced by 200 elements connected in two series of 100 elements each, was less than the illumination produced by 100 simple elements, and thus successively up to 600 elements, arranged in series of 100 elements. A serious obstacle to the complete success of these experiences was found to be the lack of constancy of the electric light, which varied from moment to moment.[23]

Despretz tried to measure the energy of the pile by observing the oscillations of a tangent galvanometer. The energy generated by a pile arranged in quantity, increased more or less proportionally to the surface. Comparing these experiments with the ones done with the voltaic arc, it was seen that that the number of elements that so much influenced the length of the arc, did not influence the intensity measured with the compass. Extension of the elements reflected in an increase of the intensity, as measured by the compass, by the light, or by the chemical action. Regarding the latter, Despretz found that the amount of zinc dissolved increased as the resistance of the connecting conductor decreased. The alteration of nitric acid, as measured by potassium permanganate, varied as the dissolution of zinc. The amount of zinc destroyed was not represented exactly by the amount of hyponitric acid formed, because of the increasing amount of gases released into the air, as the electric current was more intense. The amount of zinc dissolved by each pair of two piles of the same number of identical elements, joined by the same conductor, represented the amount of gas released at the voltmeter, and was exactly proportional to the intensity of the current measured by the compass. Measurement of the time needed by a pile composed of 4, 8, 16, 32, 64, 128, or 256 identical elements connected in series, produced the same amount of external work; for example, it decomposed the same amount of water. This time decreased rapidly from 2 to 4, from 4 to 8, changed little from 8 to 16, or almost did not change from 32 to 64, or 128 to 256 elements. These results showed that nothing was gained in time by doubling the number of the elements when the pile already contained 8 elements. Since the loss in zinc and acid was the same in each pair for the same amount of external work, there was a real advantage in not exceeding this number of elements.[47,53]

Despretz also compared the chemical changes taking place in the Bunsen and Daniell piles, and concluded that in a two-liquid pile the internal chemical work was equivalent to the external chemical work and that external work in any pile was represented by the zinc dissolved in the inside of the instrument.[23]

Another paper[23] described his experiments and results about the chemical phenomenon and light, taking place in a two-liquid pile: (a) the nature of electrical light seemed to be independent of the number and disposition of the elements. The position of a yellow or blue ray was the same if 100 or 600 elements end to end, or 600 elements arranged in six parallel series of 100 elements, (b) the number of elements arranged end to end influenced little the intensity of the light. It grew from 50 to 100, from 100 to 600, but not by much. If the elements were joined in quantity, so as to double, triple, etc. the surface, the luminous energy grew proportionally. Thus 2 series of 100 elements joined in parallel, lightened about twice more, six series almost 6 times that of a single series, (c) measuring the time necessary for a pile composed of 2, 4, 8, 16, 32, 6, 128, or 256 identical elements joined end to end, to produce the same chemical work, for example, to decompose the same amount of water, showed found that this time decreased rapidly from 2 to 4, from 4 to 8, less from 8 to 16, and almost insensibly from 32 to 64 and 128 to 256. These experiments proved that almost nothing was gained doubling the number of elements when the pile was already built of 8 elements, and since the loss of zinc and acid was the same for each pair for the same chemical work there was really no advantage and exceeding this number of elements (8).

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