Pierre Louis Dulong

*Jaime Wisniak**

Resumen
Dulong es un ejemplo de una persona que tuvo una juventud desventajosa pero un espíritu fuerte que le ayudó a desarrollar una rica y exitosa carrera en las ciencias. Él fue un diestro experimentador que descubrió compuestos químicos nuevos como el cloruro de nitrógeno y el ácido hipofosfórico. Asimismo, determinó solo (o con Petit) el calor específico de muchos sólidos, la presión de vapor del agua, la densidad absoluta del mercurio, y trabajó en la fisiología de la respiración.

Abstract
Dulong is an example of a person that had a disadvantaged youth but a determined spirit and went on to a rich and successful career in science. He was a skillful experimenter that discovered new chemical compounds like nitrogen chloride and hypophosphoric acid, carefully determined (alone or with Petit) the specific heat of many solids, the vapor pressure of water, the absolute density of mercury, and worked on the physiology of respiration.

Chemists, chemical engineers, and physicists are familiar with Dulong through Dulong-Petit's rule, a rule stating that atoms of all simple bodies have exactly the same capacity for heat. They are generally unaware of his rich contributions in other scientific areas such as chemistry, determination of heat capacities, and the physiology of respiration. Here we describe his personal life and career, his scientific achievements, and, in particular, the results of his fruitful collaboration with Petit.

Life and career [Crosland, 1967; Fox, 1968-1969, 1971; Lemoine, 1895]

Pierre Louis Dulong was born on February 2, 1785, at Rouen, Department of the Seine-Inférieure, the son of Jean Pierre Dulong and Madeleine Peyrot, who earned their living from a small shop in Rouen. Dulong became orphaned at the age of four. After this tragedy, fortunately, he was adopted by an understanding aunt, Mme. Fauraux, who took him to her home in Auxerre and provided him with the necessary warmth and family hospitality. The aunt saw to it that the bright child be given the proper educational opportunities. He attended the *École Centrale* in Auxerre where his two teachers of mathematics, C. L. Bonnard (1765-1819) and Roux, awakened his interest in science. Mostly on his own efforts, he prepared and passed in 1801 the entrance examinations for the *École Polytechnique*, at the minimum statutory age of 16.

His career seemed assured but it was not so, his first year at the École was plagued by sick leaves. Eventually his health situation did not allow his admission into the Artillery Corps and in 1802 he was forced to abandon the École, without completing the course. He switched then to medicine as a career because the formal requirements for the same were minimum. Nevertheless, while he pursued his medical studies he took particular interest in chemistry giving in his home a public course on experimental chemistry (1807) and organizing a laboratory in the Arbalète street (1808).

Dulong married Émelie Augustine Rivière on October 29, 1803, and in the middle of all the uncertainties he had now to face the expenses of maintaining a family. His wife gave him three sons. One went to the École Polytechnique, became an Artillery captain, and went then to work in the railroad industry. The second became a professor of design at the *École des Ponts et Chaussées*, the third was a navy cadet who died very young.

After graduation Dulong practiced medicine at the quarter of the École in Paris but his excessive generosity to needy patients almost ruined him. He was always willing to help the unfortunate and was a familiar figure in one of the poorest sections of Paris. His economical situation was further impaired after he opened an account at a local pharmacy to provide medicines for the poor.

Dulong was always especially attracted to science and after a short practice of medicine he decided to become a chemist. He began as *répétiteur* (assistant) to Louis-Jacques Thénard (1777-1857) who

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*Department of Chemical Engineering.
Ben-Gurion University of the Negev, Beer-Sheva, Israel 84105.
Correo electrónico: wisniak@bgumail.bgu.ac.il
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in turn brought his talents to the attention of Claude-Louis Berthollet (1748-1822). In 1811 Berthollet invited Dulong to become a member of the *Societé de l'Arcueil.* Dulong was the last scientist admitted by Berthollet to the Society [Crosland, 1967].

As a member of the famous Societé de l'Arcueil, Dulong became friend with Berthollet, Pierre-Simon Laplace (1749-1827), Siméon-Denis Poisson (1781-1840), Joseph-Louis Gay-Lussac (1778-1856), Thénard, Jean-Baptiste Biot (1774-1862), François Arago (1785-1853), and Alexander von Humboldt (1769-1859). His scientific career was assured, in 1812 he became *maître de conferences* at the École Normale Supèrieure, directed by Thénard; in 1813 *professeur de chimie* at the École de l'Alfort; *examinateur temporaire* at the École Polytechnique for admission into public services (1813-1820); professor of chemistry at Sorbonne (1820); professor of physics at École Polytechnique replacing Alexis-Thérèse Petit (1791-1820) in 1820, and finally, Director of Studies at the same École.

It is important to note the significant influence that the *Académie des Sciences* had on the academic life of France. For example, in the École Polytechnique the Académie was influential in electing representatives to the *Counseil de Perfectionnement* and nominating the Director of Studies. It was through academician Gay Lussac that Dulong was recommended and nominated to the latter post.

At Arcueil Dulong carried out the first of his many chemical studies. He studied the decomposition of insoluble salts by alkaline carbonates and showed that insoluble salts are capable of exchanging constituents with soluble salts, for example, if barium sulfate is decomposed by sodium carbonate then barium carbonate is decomposed by sodium sulfate [Dulong, 1812]. These experiences were inspired by Berthollet's ideas, extended later by Faustino Malagutti (1802-1878), and gave the first examples of chemical equilibrium that would follow. Today, the results of this research are the basis for the analysis of mineral substances that are compact and insoluble.

With his future further assured by his teaching posts at the École Normal in Paris and the Alfort veterinary school, Dulong began to make his name as a chemist, notably by his discovery of nitrogen trichloride and by some important work on metal oxalates. In this work he proceeded according to Berthollet's principles and without reference to such controversial matters as the atomic theory [Fox, 1968-1969].

There has been much speculation about the reasons of why Dulong and Petit joined forces. Petit had graduated from École Polytechnique and afterwards was appointed as professor of physics at the École. It was very common for the teaching staff at the École to participate in common research projects. This is probably one the reasons for the collaboration between Dulong and Petit, others may have been their common interest in physics and very similar personalities. The actual cooperation seems to have begun early in 1815, almost certainly as a result of the prize competition in physics that was announced by the First Class of the Institute on January 9, 1815. Competitors were asked to measure the expansion of mercury in a thermometer between –20° and 200°C and then to determine the rate at which the body cooled both in a vacuum and in various specified gases at different temperatures and pressures.

Their paper was published in three parts [Dulong and Petit, 1818a, b, c] under the general title *Recherches Sur la Mesure des Temperatures et sur les Lois de la Communication de la Chaleur* (Studies on the Measurement of Temperatures and the Laws of the Communication of Heat). The first part was acclaimed as a model of experimental method by such authorities as August Comte (1798-1857), Poisson, Gabriel Lamé (1795-1870), and William Whewell (1794-1866). In 1818, as a result of this work, Dulong and Petit were awarded the annual prize in physics, consisting of a gold medal valued at 3,000 francs.

After Petit's death Dulong continued alone the experimental work. Now he devoted himself to the measurement of the refractive power of gases and the speed of sound. The latter was associated to the question of specific heats because the sound speed on a gas was related to the ratio of the specific heats, c_P/c_V.

Additional work was done in collaboration with Arago on Mariotte's law and the vapor pressure of water [Arago and Dulong, 1830]. They were performed as part of the work of a Commission of the Académie, named in 1824, at the invitation of the French government. Dulong performed most of the experiments (during the four years of the project) where the vapor pressure of water was measured up to 24 atm.

Dulong received several awards and honors during his lifetime, the most important being the 1818 physics prize to his work with Petit. In 1823 he was admitted to the Académie des Sciences after two unsuccessful trials defeating Fresnel by thirty-six to twenty votes. In 1827 he was elected vice-president of the Académie, president in 1828, and in 1832 permanent secretary, replacing Georges Cuvier (1769-1832). In 1833 he resigned his position at the Académie due to poor health. In 1830 Dulong was elected associate in the Swedish Academy of Sciences.

Dulong was basically a researcher, a scientist; he devoted all his life to science and the École and never mixed his research with his administrative or political duties. His life was distributed between his scientific work and his family. Every evening, after dinner, he would play music during one or two hours and would then return to his laboratory for further work.

His students claim that only once did they see him lose his temper: A royal order came suddenly naming him member of the Académie, after the same was reorganized following the Restoration. Dulong reacted angrily saying *"Je ne veux pas être membre de l'Institute par ordonnace royale; si je le deviens, ce sera par mes travaux et par le choix spontané de l'Académie"* (I do not want to become a member of the Institute by a royal order, if I do it will by my work and the spontaneous desire of the Academy). His protest led to an annulment of the order. Eventually, in 1823, Dulong was admitted to the Académie in the manner he believed to be the appropriate one.

When King Charles X (1757-1836) visited the École Polytechnique he found that Dulong was the only professor there without a ribbon in his buttonhole and decorated him on the spot.

Dulong died, rather suddenly, of cancer of the stomach on July 19, 1838. The funeral was held the next day at the Père Lachaise cemetery (the same cemetery were Petit is buried). The obelisk that marks his tomb was erected with funds contributed by his fellow academicians.

As a suitable epilogue we can remark that when Gustave Eiffel built his famous tower in 1889, he decided to honor 72 distinguished French scientists by putting their names in the structure. This 'invocation of science', as Eiffel called it, reflected his worry over accusations that the tower was useless and wasteless.

There are eighteen names per side of the tower, all positioned just below the first platform of the structure, on the outside. The letters in the names are 60 cm high. Dulong's name is located on the first facade, opposite the Trocadero (Figure 1). It befits the subject of this paper, to mention that the tower was inaugurated in 1889 during the presidency of Sadi Carnot, the nephew of Sadi Carnot related to the Second law of thermodynamics.

Figure 1. Dulong's name on Eiffel Tower. © Anthony Atkielski, reprinted by permission.

Scientific work

We will now describe in detail some of the contributions of Dulong to chemistry, physics, and other areas.

Chemistry

The discovery of nitrogen chloride in October 1811 is probably Dulong's most important contribution to chemistry [Dulong, 1813]. He was unaware that the product was shock-sensitive and the discovery cost him dearly, he lost a finger during the first experiences and almost lost an eye during the analysis of the product. Dulong prepared nitrogen chloride by reacting chlorine with ammonia. The compound was a new substance that not only had explosive powders, it also had theoretical interest because its synthesis took place with heat storage from the energy released by a parallel reaction. Thus during the action of ammonia on chlorine, nitrogen chloride was formed because of the simultaneous reaction of hydrogen and chloride, a reaction that provided the necessary energy. This stored heat was the energy released during the decomposition of nitrogen chloride, with serious consequences.

Dulong abandoned this project after the second accident.

Today we know that nitrogen chloride, or trichloroamine, is the only stable pure ammonia halamine. It is a shock-sensitive yellow liquid that boils at 71°C and has a volatility similar to that of chloroform. In the gas phase it can be completely decomposed to nitrogen and chlorine by spark initiation at a concentration of only a few percentage in air.

During the period 1813-1815 Dulong investigated the action of heat on metal oxalates. Analysis of the results of the decomposition led him to conclude that oxalic acid consisted of hydrogen and carbon dioxide, and hence proposed calling it *hydrocarbonic acid.* Dulong's results were important because they ran against the chemical ideas of his time according to which only metals in the form of oxides could combine with acids. This work was also significant because it played a part in the eventual establishment of the fact that an acid is simply a particular type of compound containing hydrogen that is replaceable by a metal.

Another important section of Dulong's work had to do with the chemistry of phosphorus and its compounds [Dulong, 1816a]. Dulong investigated the slow oxidation of phosphorus and found that the reaction would cease after a certain proportion of oxygen had been taken up. He remarked that the product reacted only with oxides and thus came to believe that a new acid was formed. At the beginning Humphry Davy (1778-1819) claimed that the product of the slow oxidation was a mixture of phosphorous and phosphoric acid. Dulong was not convinced arguing that if this was so then the oxidation should not stop but should continue until all the material was converted into phosphoric acid. Not only that, every time the product was prepared he had obtained the same ratio of oxygen to phosphorus. Thus the acid was a new compound that he suggested naming *acide phosphatique* (phosphatic acid). Eventually Davy performed all the analytical work and proved that Dulong's phosphatic acid was in fact a mixture of phosphorous and phosphoric acid.

Dulong's most important contribution to the chemistry of phosphorus was his discovery of a new phosphorous acid [Dulong, 1816a]. According to his results the combination of phosphorus with oxygen gave origin to four different acids. He proposed that the acid with the minimum amount of oxygen be named *hypo-phosphoreux* (hypophosphoric). Hypophosphoric acid was prepared by neutralizing the liquor that remained from the action of barium phosphide and water. The filtrate from the reaction product was concentrated by evaporation yielding a very acid viscous liquid that could not be crystallized. Heating this acid produced phosphine, a little of phosphorus sublimated, and a remaining liquid that was essentially phosphoric acid. Analysis of the acid indicated that it contained 72.75% wt phosphorus and 27.25 oxygen (on a water-free basis). The prefix *hypo* was thus introduced into the chemical nomenclature by Dulong.

Dulong also prepared a large number of salts of hypophosphoric acid and found them to be extremely soluble in either water or rectified ethanol.

One important conclusion of Dulong's work on phosphorus compounds was that phosphites and phosphates were quite analogous to nitrites and nitrates in the proportion of their components and that the same conclusion was applicable to acids formed by phosphorus and nitrogen. These results led Dulong to study the acids derived from nitrogen, within which he synthesized nitrogen peroxide and discovered the series of color changes that this compound exhibits with changing temperature: colorless at –20°C, pale greenish at –10°C, pale yellow at 0° to 10°C, and orange at 15° to 28°C [Dulong, 1816b].

Physics

The first joint paper by Petit and Dulong was related to the laws of expansion of solid, liquids, and elastic fluids, and the exact measurement of temperature [Dulong and Petit, 1816]. In their opening statement Dulong and Petit stated that in order to find the true laws of cooling it was necessary first to know the exact relation between the reading of a thermometer and the amount of heat added or subtracted. Since all thermometers were based on the change of volume of a substance with temperature, this required knowing with the maximum accuracy the laws that regulated the expansion. In the first part of their work they immersed a mercury thermometer and an air column in a thermostated bath and proceeded to compare the reading of the thermometer with the temperature deduced from the expansion of the air enclosed in a tube, as predicted by Mariotte's law. Their results indicated that above 100°C the reading of the mercury thermometer was always the higher and that the difference between both values increased from 0 to 8.23°C as the temperature increased from 100° to 300°C. Dulong and Petit repeated the same experiments using different metals (Pt, Cu and Fe) and found, contrary to the accepted opinion, that the temperature calculated from the expansion coefficient of the metal was even higher than that of mercury. Not only that, they were surprised to find that glass gave an even higher temperature. In other words, if the temperature was calculated from the expansion of air, then the respective values were in the order $t_{glass} > t_{metal} > t_{Hg} > t_{air}$.

Their procedure for measuring the expansion of air was very clever. The gas was kept in a dry tube that ended in capillary having a negligible volume. The tube was submerged horizontally in an oil bath. Once it had achieved the pertinent temperature, the capillary was sealed, the tube taken out, left to equilibrate with the temperature of atmospheric air, and then submerged in mercury. The tip of the capillary was broken and the amount of mercury that entered the tube noted. A comparison of its weight with that of the mercury necessary to fill the tube completely permitted calculating the air expansion.

An interesting point is that Gay-Lussac at the beginning of his career had compared the mercury and air thermometers over the temperature range 0° to 100°C. The report of Dulong and Petit for a higher temperature range was presented to the First Class of the Institute and evaluated by Gay-Lussac and Biot [Gay-Lussac and Biot, 1815].

Thermometry and heat transfer

On 1817, the Académie announced the annual competition for the prize in physics [Anonimous, 1817]. The stated topic was in three parts: (a) to determine the movement of the mercury thermometer as compared to that of an air thermometer from –20° to 200°C; (b) to determine the laws of cooling in a vacuum; (c) to determine the laws of cooling in air, in hydrogen and in carbonic acid (today CO_2), at different degrees of temperature and for different states of rarefaction.

The competition announcement stimulated Dulong and Petit to continue the work they had previously done on the subject [Dulong and Petit, 1816] and resulted in three fascinating publications, notable for the originality of the approach, hence theoretical and hence experimental [Dulong and Petit, 1818a, b, c].

In their first publication [Dulong and Petit, 1818a] Dulong and Petit approached the problem of measuring the coefficient of expansion of mercury by a very ingenious procedure, based on the principle of communicating vessels. Two vertical columns of mercury, one hot and one cold, were connected by a thin horizontal tube of negligible volume. At the equilibrium the columns were balanced, the pressures were identical, and thus

$$h_1 : d_1 = h_2 : d_2 \tag{1}$$

were h and d were the height and density in the respective column. The height could be measured easily and very precisely with the help of a cathetometer. Since density is inversely proportional to the volume, a simple and accurate method was now available for measuring the expansion of mercury, without reference to the material and shape of the vessel. The only care to be taken was that the bore of the tube should be constant and sufficiently large to make the capillary effect negligible.

Numerical calculations by this method indicated that the expansion of mercury increased from 0 at 0°C to 1/5,300 at 300°C.

Construction of a "weight" thermometer is probably one of the most interesting parts of this work and it was also used by Dulong and Petit to determine the expansion of other solids (Pt, Fe, Cu, and glass). It was helpful for determining the dilation of the principal substances and for a rigorous comparison of the different thermometers employed then. Dulong and Petit came in favor of the air thermometer as the ultimate standard, convinced that increments of temperature indicated in this instrument, or indeed on any gas thermometer, were increments in the true temperature.

In the same publication Dulong and Petit reported the measurement of the specific heat of a series solids, by heating the particular material to a certain temperature by submerging it in hot boiling water, boiling mercury, or hot oil, followed by quenching in a large amount of water (mixing method). The results were as follows:

Table 1. Mean specific heat, cal/g°C.

	0 to 100°C	0 to 300°C
Mercury	0.0330	0.0350
Zinc	0.0927	0.1015
Antimony	0.0507	0.0549
Silver	0.0557	0.0611
Copper	0.0949	0.1031
Platinum	0.0355	0.0355
Glass	0.177	0.190

Heating and cooling laws

According to Newton, a hot body subject to cooling by a constant temperature source, like an air stream, should lose heat proportionally to the instant temperature difference, and the heat losses at equal time intervals should form a decreasing geometric progression. John Dalton (1766-1844) and François Delaroche [Delaroche, 1812] did independent experiments at high temperatures (where the main mechanism of heat transfer was radiation) and found that radiation losses were much faster than those predicted by Newton, but did not correlate them by an analytical expression.

With great sagacity Dulong and Petit determined the role played by each of the variables that contributed to the final result: temperature and disposition of the source that emitted heat, temperature and nature of the receiving surrounding; influence of the surrounding gas compared to an empty environment. They realized that it was necessary to separate the heat losses caused by the surrounding fluid (today, convection), from those caused by a heat sink not necessarily in contact with the hot body (radiation). For these reasons they decided to perform separate experiments in vacuum and in the presence of air.

Dulong and Petit considered that the simplest case of cooling was that represented by a body of sufficiently small dimensions to neglect its internal temperature gradient [Dulong and Petit, 1818b]. That is, at any instant the body could be considered to be isothermal. In a brilliant stroke they assumed that the bulb of a mercury thermometer could be used as an example of this situation and went on to measure the cooling rate of three bulbs having a diameter of 2, 4, and 7 cm, as a function of their excess temperature above that of the surrounding air. Analysis of their results brought them to the conclusion that the excess temperature was *independent of the size of the bulb.* They also indicated that they did not determine qualitatively how the heat loss depended on the *area* of the bulb because of the technical difficulties in measuring the area of a bulb blown at the end of a tube. Nevertheless, their approximate measurements indicated that this loss was inversely proportional to the diameter of the bulb.

Additional experiments were performed to determine the influence of the liquid (concentrated sulfuric acid, water, and absolute alcohol), and the shape and material of the bulb (glass or iron) The results indicated that neither the nature of the liquid nor the shape of the bulb did influence the rate, but that a bulb made out of iron cooled faster than a glass one.

Dulong and Petit went on to measure the rate of cooling in vacuum. To do so they used a spherical bulb with a diameter of 3 cm of a mercury thermometer. The bulb was heated up to 300°C and put into a concentric spherical enclosure at a constant temperature of 0°C or 20°C and the cooling rate measured. In some experiments the spherical enclosure was evacuated down to pressures of 2 mmHg. The measured rate of cooling decreased with decreasing pressure and finally the data were extrapolated to zero pressure. It was supposed that by doing this, convection and conduction were avoided and only the cooling by radiation was observed. A mathematical analysis led them to determine *for the first time* a law that described heat transfer by radiation. Their final expression had the form

$$V = -\frac{d\Delta t}{d\theta} = 2.037\ a^{\theta}\ (a^{\Delta t} - 1) \tag{2}$$

where V is the rate of cooling when the difference in temperature is Δt, θ is the temperature of the surroundings, and a is a parameter of the system. Dulong and Petit found that for their setup a was equal to 1.0077 when both Δt and θ were expressed in °C. Since parameter a was *independent* of the nature of the surface equation (2) was a general expression for the rate of cooling in vacuum of all bodies [Dulong and Petit, 1818b].

Dulong and Petit went on to determine the rate of cooling when the bulb of the thermometer was in contact with a gas (air, CO_2, ethylene, and hydrogen) [Dulong and Petit, 1818c]. Experiments performed with the bulb of the thermometer, without or without a silver plating, indicated that the rate of cooling: (1) was independent of the state of the surface, (2) for a given excess temperature it was a function of the temperature and the density of the gas, (3) the cooling power of a gas (Π) varied exponentially with the pressure of the same (P) according to $\Pi P^n = \text{constant}$, where n was a constant typical of the gas ($n_{\text{air}} = 0.45$, $n_{H_2} = 0.38$, $n_{CO_2} = 0.517$, and $n_{\text{ethene}} = 0.501$), and that (4) the total rate of cooling for radiation and convection was given by

$$V = -\frac{d\Delta t}{d\theta} = m(a^{\Delta t} - 1) + n(\Delta t)^{b} \tag{3}$$

where $a = 1.0077$, $b = 1.233$, m was a coefficient that depended on the nature of the contact surface and the temperature of the surrounding medium, and *n* another coefficient that depended on the nature of the gas.

Equation (2) may be considered a good example of a "bad" influence. Dulong and Petit were aware that Newton had stated that the values of the rate of cooling taken at equal time intervals formed a geometric progression. Dulong and Petit had found that the rate was faster, but the idea of some kind a progression was probably behind the mathematical model they used in developing equation (2) (Inspection of the latter shows that it is closely related to the *sum* of an infinite geometric progression). Had Petit used his mathematical skills in another form he could have perhaps put the temperature *as the basis* of the power and arrived at the equation that Josef Stephan (1835-1895) would develop empirically in 1879 stating that the heat radiated was proportional to the difference of the fourth powers of the absolute temperatures [Stephan, 1879]. Stephan's results would be confirmed theoretically by Ludwig Boltzmann (1844-1906, a student of Stefan) within thermodynamics, taking into account Maxwell's result for the pressure of light [Boltzmann, 1884].

Specific heat of solids

In a paper published in 1819 Dulong and Petit reported additional measurements of the heat capacity of solids, using a modified version of the method of cooling they had used before [Dulong and Petit, 1818a]. Analysis of their results led Dulong and Petit to the brilliant idea of reporting the specific heat not on the basis of unit weight but the relative weights of their atoms [Petit and Dulong, 1819] (Table 2).

Table 2. Heat capacity of solids.

Element	Specific heat (A)	Molecular weight (B)	Product (A) × (B)
Bismuth	0.0288	13.30	0.3830
Lead	0.0293	12.95	0.3794
Gold	0.0298	12.43	0.3704
Platinum	0.0314	11.16	0.3740
Tin	0.0514	7.35	0.3779
Silver	0.0557	6.75	0.3759
Zinc	0.0927	4.03	0.3736
Tellurium	0.0912	4.03	0.3675
Copper	0.0949	3.957	0.3755
Nickel	0.1035	3.69	0.3819
Iron	0.1100	3.392	0.3731
Cobalt	0.1498	2.46	0.3685
Sulfur	0.1880	2.011	0.3780

The values in column A were based on assigning a value of one to the heat capacity of water and those of column B assuming that the weight of the oxygen atom was equal to one. Dulong and Petit calculated the atomic weights using the idea that for equal weights of substances the number of particles (atoms) should be reciprocally proportional to the densities of the atoms.

Inspection of the results presented in the last column of the table led them to the conclusion that "*les atomes de tous les corps simples ont exactement la même capacité pour le chaleur*" (atoms of all simple bodies have exactly the same capacity for heat). Their results for thirteen substances (twelve metals + sulfur) gave a value that varied between 0.3675 and 0.3830. This conclusion became known as *Dulong-Petit's law.*

Dulong and Petit's law appeared primarily as convincing evidence of the physical reality of atoms but it also had a possible application as an alternative method of determining atomic weights. Dulong and Petit were confident that accurate measurements of specific heat would lead to values of the molecular weight that were wholly trustworthy in their own right without reference to the better-established chemical methods. Unfortunately, the exactness of their law was never sufficiently established for their hope to be completely fulfilled but there was no doubt that atomic weight and specific heat were closely related.

Dulong-Petit's law, the same as that of Gay-Lussac on the equal dilation of gases, was the subject of much discussion. In papers read to the Académie in 1840 and 1841 Victor Regnault (1810-1878) demonstrated the approximate nature of Dulong-Petit's law when applied to solids and then the validity, within certain limitations, of Franz Ernst Neumann's (1798-1895) attempt to extend the law to compounds [Regnault, 1840, 1841]. According to Regnault, at the time of Dulong and Petit atomic weights were not know with enough precision and several values were available for a given substance. Dulong and Petit had naturally selected the value that went best with their claims.

Regnault used Berzelius' atomic weights to repeat the calculations of Dulong-Petit and found a different picture: the value of the product (A×B) varied substantially and the variations could not explained by an error in Dulong and Petit's determination of specific heat, they simple reflected the very approximate validity of their law.

Anyhow, today we know that a solid may be considered as consisting of a space lattice of independent atoms vibrating about their equilibrium positions. If the vibrations are considered simple harmonics then each vibrational mode contributes RT to the energy content of a gram atom. Since the atoms are free to vibrate in three dimensions then the energy of the ideal solid will be 3RT and its contribution to the heat capacity at constant volume will be 3R, that is, 5.96 cal/K·g atom. Multiplication of the values in the third column in Table 2 by 16 gives a result very close to the theoretical one.

Specific heat of gases

At the time of Dulong it was felt strongly that to answer a series of theoretical questions (including the nature of caloric), it was necessary to calculate very precisely the amount of heat that corresponded to a given increase in temperature. This meant measuring the specific heat of different substances in different states of aggregation. It was believed that simple or composite gases, at equal volumes, had the same heat capacity. Most of the experimental techniques were based on an observation of the time required to heat (or to cool) a gas a given number of degrees.

After Petit's death Dulong continued his investigations on the specific heat of gases, driven by the feeling that the heat capacity equality they had found was simply circumstantial and due to experimental errors. Not only that, he was convinced that it was not possible to design an experimental setup that would allow calculating the heat capacity from the time required to heat a gas [Dulong, 1829]. He then decided to determine the ratio $\gamma = c_P/c_V$ of the specific heats by measuring the effect of a variation of temperature on the pitch (measured with a diapason) of a sound wave moving through gases contained in a fluted tube. The value of γ was calculated using Laplace's equation for the velocity of sound in a tube:

$$\frac{\nu}{\nu_{gas}} = \frac{\sqrt{(1 + 0.00375t} \sqrt{\gamma \text{ air}/\rho \text{ air}}}{\sqrt{(1 + 0.00375t'} \sqrt{\gamma_{gas}/\rho_{gas}}} \qquad (4)$$

where ν is the frequency of the fundamental note obtained with the gas (or air) in the tube, and t the temperature. No doubt that Dulong's love for music played a role in selecting this technique!

Examination of the numerical results lead Dulong to the following conclusions: (a) equal volumes of all gases, under the same pressure and temperature, when suddenly compressed or expanded to the same fraction of their original volume, gave off or absorbed the same quantity of heat; (b) the resulting variations in temperature were inversely proportional to the specific heats at constant volume.

With these conclusions and the knowledge of γ it was possible to calculate the specific heat c_V for any gas relative to air.

Animal heat

Robert Boyle (1627-1691), Stephen Hales (1677-1761), Giovanni Francesco Cigna (1734-1791), Joseph Black (1728-1799), and Joseph Priestley (1733-1804) had been among the first to observe that respiration exerted a clear effect on atmospheric air, it decreased its volume, changed its composition, and after sometime the air was unable to support life. Between 1777 and 1790 Antoine Laurent de Lavoisier (1743-1794) had explained the respiratory system and inaugurated physiology. In 1785 Lavoisier had declared that respiration was not only carried on by a combustion of carbon but also of the hydrogen contained in blood. The results of respiration were not only generation of carbon dioxide but also of water. Additional findings of Laplace and Armand Séguin (1767-1835) had indicated that nitrogen played not role in the process and that the production of CO_2 and the absorption of oxygen were not constant for a given individual; they were largest during the digestion process, movement, or activity. According to Lavoisier animals were controlled by three processes: (a) respiration that consumed carbon and hydrogen and provided caloric, (b) transpiration, that increased or decreased depending on the need to carry caloric and, (c) digestion, that returned to blood what it had lost during respiration and perspiration. Lavoisier had also found that animals could live several hours in an atmosphere of pure oxygen, or a mixture of hydrogen and oxygen, and that in both cases the production of CO_2 was the same as in pure air.

Lavoisier and Laplace had also found that the amount released by an Indian pig during a certain amount of time, was very close to that released by the amount of carbon and hydrogen burnt during respiration.

In all the reported experimental works the phenomenon of respiration in animals had been following by keeping them on a hermetic cage. The air inside the cage was either left to change as the process took place, or it was slowly renovated by letting in fresh air and withdrawing an equivalent volume of the vitiated atmosphere. The respiration phenomenon was followed by analyzing the air. The classical study by Lavoisier and Laplace had left the subject in an unsatisfactory form since the amount of heat found was less than that computed from the combustion of the carbon and hydrogen. Furthermore, Lavoisier and Laplace had measured the heat produced when the experimental animal was exposed to a temperature of 0°C, and the carbon dioxide produced when the animal was exposed to 18°C.

Since the available information was insufficient and not clear, the Académie des Sciences decided in 1821 that the prize in physics for 1823 would be awarded for the best essay on animal heat.

Dulong reasoned that the only way to give a clear answer to the questions raised by the Académie was to measure simultaneously, and for various animal species, the chemical changes in the air caused by respiration and the heat losses by all possible sources. Not only that, the animals had to be kept in an environment as close as possible to their natural habitat. To increase the accuracy of the measurements Dulong devised a respiration calorimeter in which the heat was absorbed by water instead of ice as in Lavoisier's ice calorimeter.

Dulong's conclusions lead to a modification of Lavoisier's ideas by proving that the combustion of carbon by the organism was not enough to account for the observed phenomena. He also found that the volume ratio of CO_2 evolved/oxygen consumed was smaller for dogs than rabbits and fowls and suggested that it was due to the different eating habits of carnivores and herbivores. This research was stopped by Dulong's death and published afterwards [Dulong, 1829].

The final quantification of the phenomena came in 1849 when Regnault and Jules Reiset (1818-1896) published their landmark book on the respiration of animals [Crosland, 1967]. The closed-circuit animal respiration apparatus they invented initiated the idea of the *balance sheet* in metabolism. This concept remained the philosophical basis for the interpretation of metabolic phenomena for nearly one hundred years, until isotopes began to be used for this purpose. The apparatus of Regnault and Reiset was the progenitor of modern closed-circuit equipment for the measurement of respiratory metabolism.

Other contributions

Dulong participated in a series of public activities, mostly in collaboration with Gay-Lussac, as illustrated below for some.

The general principle of lightning conductors had been established in the 18th century by Benjamin Franklin (1706-1790) but the problem continued to be raised from time to time in the 19th century. In 1822 a series of French cathedrals was seriously damaged by thunderstorms and the Minister of the Interior turned to the Académie to draw up specific instructions for the making and fitting of lightning conductors. Gay-Lussac, Poisson, Louis Lèfevre-Gineau (1751-1829), Pierre-Simon Girard (1755-1836), and Dulong were assigned the task and in their report recommended that tall buildings be provided with a rod at least seven meters higher that of the structure, and that the conductor buried deep in moist ground.

During the 1831-1832 cholera epidemic the French government asked the Academy to appoint a commission to examine any possible relationship between the outbreak of cholera and meteorological conditions. A commission composed of Gay-Lussac, Dulong, Arago, Alexis Bouvard (1767-1843), and François Magendie (1783-1855) took responsibility of this assignment but was unable to find the immediate cause of cholera.

Longchamp, a former commissioner of gunpowder had presented in 1823 to the Académie a memoir about a new theory for nitration that postulated that salpetre was formed in the soil not because of any constituent there but uniquely from the elements in the atmosphere. To assess the value of this memoir the Académie appointed a commission consisting of Louis Nicolas Vauquelin (1763-1829), Jean-Antoine Chaptal (1756-1832), Gay-Lussac, Dulong, and Jean D'Arcet (1725-1801). Because of the personality involved the commission avoided the issue and did not write a report.

In 1827 Gay-Lussac and Dulong were appointed by the Académie to examine a memoir by Jean Baptiste André Dumas (1800-1884) on the atomic theory. Both had a particular interest on atomic theory and were known to hold different views on the subject, Gay-Lussac maintaining cautious reserve while Dulong had been in the vanguard of those young Frenchmen who felt that the atomic theory had not been given a fair hearing in France. Yet the report that they drew up represented clearly the opinion of Gay-Lussac.

Dulong collaborated with Jöns Jacob Berzelius (1779-1848) in determining the molecular weight and composition of a series of compounds, among them water. For water they reported a molecular weight of 17.78 and the ratio oxygen:water = 88.9:11.1 [Berzelius and Dulong, 1820].

Conclusions

Dulong's contributions to the advance of chemistry, physics and physiology were notable, and even more those that resulted from a synergistic collaboration with Petit.

Although many of Dulong's (and Dulong-Petit's) results were later substantially improved by Regnault, he did set the right way for determining properties like the specific heat, the vapor pressure of water, the physiology of respiration, and setting the air thermometer as the proper instrument. ◩

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