La química en la historia, para la enseñanza. Empezamos hoy una serie de tres artículos preparados por Jaime Wisniak, sobre tres personajes franceses del siglo XIX: Regnault, Dulong y Petit. Nos gustaría que nos hicieran llegar su opinión sobre los mismos.

The heat man
Henri-Victor Regnault

Jaime Wisniak[1]

Resumen

Regnault fue un investigador diestro, minucioso, y paciente, que determinó (o redeterminó) cuidadosamente el calor específico de un gran número de sólidos, gases y líquidos, la presión de vapor del agua y de otros líquidos volátiles, así como sus calores latentes a varias temperaturas. Él demostró en forma definitiva que cada gas tiene un coeficiente de expansión distinto, y que el gas ideal de Mariotte y Boyle es sólo un modelo aproximado para los gases reales. Sus resultados sobre las propiedades del agua y del vapor pueden ser considerados como la primera versión de las tablas de vapor.

Aun cuando Regnault fue un experimentador sobresaliente, no tuvo la originalidad brillante de muchos de los físicos de su época y no nos dejó un legado de resultados teóricos. Él dedicó toda su vida a la ejecución de mediciones muy precisas y puso en las manos del químico y físico moderno una colección muy valiosa de constantes, que hoy en día siguen siendo usadas no sólo en el laboratorio sino también en la industria.

Regnault fue víctima de una fatalidad implacable que azotó su vida con tragedias personales, sin embargo, sólo en los últimos años de su vida esa fatalidad quebró su espíritu.

Abstract

Regnault was a skillful, thorough, and patient experimenter that carefully determined (or redetermined) the specific heat of many solids, liquids, gases, the vapor pressure of water and other volatile liquids, as well as their latent heat at different temperatures. He proved conclusively that all gases have a different coefficient of expansion and that the ideal gas of Mariotte and Boyle is a model only approximately true for real gases. His results on the properties of water and steam should be considered the first version of the steam tables.

Although an outstanding experimentalist, Regnault did not possess the brilliant originality of many of his fellow physicists and did not leave us with lasting theoretical results. He devoted all his life to perform very accurate measurements and placed in the hands of the modern physicist and chemist an invaluable collection of constants, which presently are in daily use not only in the laboratory but also for a large variety of industrial purposes.

Regnault was the victim of an implacable fatality that filled his life with personal tragedy, but only in the last years of his life he let it overcome him.

Chemists and chemical engineers are familiar with Regnault through the mass of data he measured, the constants he determined, and the equipment he designed, particularly his calorimeter. They are generally unaware of his rich contributions in other scientific areas such as the quantitative analysis of the phenomenon of respiration, the safe operation of steam engines, the use of the gas thermometer, the flow of gases, the speed of sound, the manufacture of porcelain, and others. Here we describe his personal life and career, his scientific achievements and how these have influenced different scientific and engineering ideas and applications.

Life and career

Victor Regnault was born on July 21, 1810, in Aix-la-Chapelle, France, the son of André-Privat Regnault and Marie-Thérèse Massardo. His father, a captain in the corps of army engineers, was killed in 1812 during the Russian campaign. His mother died shortly after, leaving Victor, who was then two years old, and his sister orphans and without economical means of support. Fortunately, Jean-Baptiste Clément, a close friend of arms of his father took the two children under his care and supervised their education. Clément's wife, the daughter of Alexander Dumas, a member of the Académie des Sciences became their second mother (Dumas, 1882).[1] Regnault's youth was spent in a hard battle against poverty to maintain not only himself but also his

[1] Department of Chemical Engineering,
Ben-Gurion University of the Negev, Beer-Sheva, Israel 84105.
E-mail: wisniak@bgumail.bgu.ac.il

[1] Eventually Regnault married Clément's daughter.

sister. When he was 18 years old, his adoptive father found him employment in the drapery establishment Le Grand Condé in Paris. Despite the heavy financial hardship, Regnault found the time during the evenings to take lessons at a school that prepared candidates for the entrance examinations of the École Polytechnique. At this school he was a brilliant student and was appointed *répétiteur*. Jean Baptiste André Dumas (1800-1884) mentioned (Dumas, 1882) that from his salary Regnault opened a saving account, as a dowry for his sister, to which he kept adding until she got married. At the time of the entrance examinations Regnault was affected by a serious illness that put him in the last place of the waiting list for the oral examinations. Dumas (Dumas, 1882) wrote that his examiner, Lefébure de Fourcy, was extremely impressed by the knowledge exhibited by Regnault and approved his exam. In 1830, at the age of 20, Regnault fulfilled his dream to become a student at École Polytechnique.

During his stay at the École tragedy struck him again. During the July 27-29 revolution of 1830 (*Les Trois Glorieuses*) public protest turned into insurrection, Paris fell in the hands of the rebels and plans for a new regime crystallized rapidly. The constitutional monarchists wanted to replace the King Charles X with Louis-Philippe, Duke d'Orléans. Because of the political situation, the students at École were given arms. While carrying his rifle Regnault made a wrong movement and hit a lamp, some of its falling pieces entered his left eye and almost cost him the organ.

According to Jules Jamin (1818-1886) (Discours, 1878) Regnault was one the most famous graduates of École Polytechnique and had the fortune to take the Physics course given by Dulong. Regnault graduated 1832 with second seniority, and transferred to the Écoles des Mines in Paris for two more years of studies as *élève ingénieur*. After graduation from the Écoles des Mines he traveled extensively in Europe to study mining techniques and metallurgical processes. As a result of these trips he wrote four Mémoires that he deposited in the library of the École des Mines. These Mémoires described the manufacture and extraction procedures at coal mines located near Aix-le-Chapelle, the salt mines in Würtemberg, and the steel plants at the Furstemberg principality.

In 1835 Regnault entered Pierre Berthier's (1782-1861) laboratory at the Écoles des Mines and in 1838 he was made Joint Professor of Assaying and Adjoint Director of the laboratory at Lyons. While many of the chemists of his day were engaged in theoretical disputes and the battle between the electrochemical theory and the newly advocated type theory was being hotly waged, Regnault devoted himself to the accumulation of the facts needed by the disputants on both sides (Gladstone, 1878; Norton, 1878). After short periods of research under Justus von Liebig (1803-1873) at Giessen and Jean-Baptiste Boussingault (1802-1887, who helped identify the nitrogen cycle) he applied to the École Polytechnique for a position of *répétiteur* for the chair of Joseph-Louis Gay-Lussac (1778-1856). In the beginning Gay-Lussac felt that the preferred candidate should be Auguste Laurent (1803-1857), who had no job in Paris, rather than Regnault who was employed at the École des Mines. The unanimous preference of the *Conseil d'Instruction* of the École Polytechnique for Regnault, a graduate of the school, convinced Gay-Lussac that he also should support him. Once on the staff of the École Polytechnique, Regnault sometimes took over Gay-Lussac's lectures, became one of his associates, and in 1840 succeeded him in the chair of chemistry. He furthered Gay-Lussac's work on the thermal expansion of gases, giving it greater precision; indeed he became obsessed with problems of accurate measurement (Crosland, 1978).

In 1837 and the following years he published several important papers dealing with the action of superheated steam on metals and sulfides (that lead to a new classification of metals); with mineral fuels, considered according to their geological age, their composition, and uses; on mineralogy (about diallage and mica); and on the dosage of carbon in iron furnaces. The experiments he performed in 1839 on the specific heats of isomers attracted particularly the attention of his colleagues.

In 1840, at the age of thirty, he was elected to the Chemical Section of the Académie des Sciences, replacing Pierre-Jean Robiquet (1780-1840, who in 1832 isolated codeine from opium). His interests were already in physics and in the following year, 1841, he was elected to the chair of physics at the Collège de France, where he performed his most important experimental work for the next thirteen years.

In 1854 Regnault was appointed Director of the famous porcelain factory of Sévres replacing Jacques Joseph Ebelmen (1814-1852), and therein devoted much of his time to improve the ceramic processes. He introduced some important new techniques in the production of porcelain by vacuum molding, and the application of gas burners for the high-temperature firing of porcelain decorated with metal oxides. While in Sèvres he found time to continue his research on the heat effect accompanying the expansion of gases. In 1856, he suffered a fall at the factory that resulted in a cerebral commotion that left him fighting for his life, for almost one month, and with a permanent facial rictus. The Franco-Prussian war forced him to abandon Sévres and suspend his research efforts. After the declaration of peace he returned to his laboratory in Sévres to find that in 1870, during the siege of Paris, the Prussian soldiers had destroyed his instruments, his calibration apparatus, and notes, containing the results of over 600 experiments. Dumas visited the laboratory shortly thereafter and gave the following account of his conversation with Regnault (Dumas, 1882): "You can excuse the Roman soldier that in the fury of the battle killed Archimedes, he did not know him. Regnault shows the ruins of his equipment of Dumas and says: This destruction is the work of a true connoisseur! Pointing then to the ashes of his manuscripts: This is what remains of my glory!" This blow, and the death of his second son Henri (1843-1871) at the siege of Buzenval (one of the last battles on the siege of Paris, late in the Franco-Prussian war), a promising artist and universal favorite in Paris, left Regnault a broken man; his last years were clouded by grief and personal disability and meant the end of his scientific career. He retired to Lassigneau, near Gèneve, to an isolated life. But tragedy hit him again: His sister came to visit him at Lassigneau and while there she suffered a fatal heart stroke. As a result Regnault suffered in 1873 a stroke of apoplexy that left him paralytic, followed by years of long, slow agony. He died on January 19, 1878, the anniversary of his son's death.

At Regnault's funeral, Jamin said (Discours, 1878): "*Il y a des hommes dont l'esprit est assez vaste pour embrasser plusieurs sciences à la fois, et que pourraient avec la même convenance appartenir à plusieurs classes d'une même Académie. Regnault fut l'un de ces hommes privilégiés*" (There are men who have such a vast spirit that they can embrace simultaneously several sciences, and that at the same time they can belong to many of the Sections of a same Academy. Regnault was one of these privileged men).

Regnault received many honors in France and abroad, he was appointed Ingénieur en Chef des Mines (1847), awarded the order of Commandeur de la Legion of Honor (1850), nominated Fellow of the Royal Society (1852), and awarded the Rumford (1848) and the Copley (1869) medals of the Royal Society. In 1840 he was appointed to the Board of the journal *Annales de Chimie et Physique*, together with other important French scientists such as François Arago (1786-1853), Michele-Eugéne Chevreul (1786-1889), Dumas, Gay-Lussac, and Théophile-Julius Pelouze (1807-1867).

Many famous scientists stayed at his laboratory to learn his experimental techniques, among them Soret, Bede, Blaserna, Lubimoff, Pflaunder, Nordenskiöld, and Kelvin.

Regnault reported his results in two forms. He published eighteen papers in the *Annales de Chimie et de Physique* in which he gave a short description of his main findings and conclusions on specific subjects, and fifty long Memoires containing a detailed description of his experimental equipment and techniques, the results of the measurements, analysis of the experimental errors, graphs, and equations, when required. His most valuable experimental results are collected in volumes 21, 26, and 37 of the *Mémoires de l'Académie des Sciences* (about 2650 pages) (Regnault, 1847; 1862; 1868; 1870).

In 1847 he published his *Traité de Chimie* on chemistry, which passed through many editions in France, and was translated into German, English, Dutch, and Italian.

As a suitable epilogue we can mention 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. 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. Regnault's name is located on the third facade, overlooking the Military Academy (figure 1).

Scientific achievements

As a scientific investigator, Regnault did not possess the brilliant originality of many of his fellow scientists. It was as a patient, thorough, and conscientious observer that he won his way to the foremost rank. Speculations and discussions of theory are noticeable absent from Regnault's published work, as they are from his surviving notebooks. But in 1853 he declared his acceptance of the principle of conservation of energy, and later he measured the mechanical equivalent of heat, although with only moderate success (by his own words). In declaring his support for the principle, Regnault stated that he had subs-

Figure 1. Regnault's name in Eiffel's tower.

cribed to the mechanical theory of heat "for a long time" and that he had been led to it independently through his own experiments (Regnault, 1853; Fox, 1971).

In 1840, with his reputation as an experimenter established, Regnault was appointed by the Minister of Public Works to determine definitely all the experimental data that would conceivably be required in the theory and practice of steam engines and other heat engines. To do so he also had to do research on the thermal properties of gases for which he is now best known. The result, as it emerged over the next twenty-five years, was the most precisely done yet the most unimaginative of compilations (Regnault, 1847; 1862; 1868; 1870; Fox, 1971). According to Fox (Fox, 1971) it is not at all obvious why this brilliant graduate of the École Polytechnique should have chosen to devote the greater part of his life to the detailed and laborious experimental researches for which he is now remembered rather than to one of the more obviously branches of chemistry, like organic chemistry. Anyhow, when Regnault ceased his experimental work about 1870, he had provided authoritative answers to nearly all the most important problems relating to the study of heat that had been tackled, with such limited success, since the middle of the eighteenth century. That his answers have undergone only minor modifications to this day bears witness to the excellence of his work.

As mentioned before, the most important of Regnault's experimental investigations were related to measuring the coefficient of expansion for air and other gases, as well their compressibility. Between 1841 and 1842 Regnault showed not only that the expansion coefficient for gases determined by Gay-Lussac was too high but also that the coefficient varied both with the nature of the gas and with its initial pressure (Regnault, 1842). Afterwards he demonstrated the approximate nature of the laws of Nicolas Clément (1779-1841) and Charles Bernard Desormes (1777-1862), and of Robert Boyle (1627-1691) (Regnault, 1846).

It was natural for Regnault to participate in the research areas being promoted by Dumas. The latter had long advocated the idea that measurement of specific heats was an important tool for determining the atomic composition of substances. Pierre Louis Dulong (1785-1838) and Alexis Thérèse Petit's (1791-1820) had already measured the specific heat of a number of the elements and obtained data sufficiently accurate to establish their law that the product of the specific heat of an element and its atomic weight was constant. Regnault decided to submit this law to additional test and began a systematic experimental study of the specific heats of a wide range of solids and liquids. Regnault found that the calorimeter used by Dulong and Petit was useless for the exact determination of the specific heat of solids and invented in its place the calorimeter bearing his name. Between 1839 and 1842 Regnault conclusively demonstrated that Dulong and Petit's law (Dulong and Petit, 1819) was only approximate and confirmed the validity, within the same limits of accuracy, of Franz Ernst Neumann's (1798-1895) extension of the law from elements to compounds. From his results he deduced that for all compounds of the same formula and similar chemical composition the product of the specific heat and the atomic weight was the same (Regnault used the expression atomic weight instead of molecular weight). He also measured the specific heat of about thirty-five gases and vapors and established the two important laws, (1) that the specific heat of any gas at constant pressure, whether simple or compound, was the same at all pressures and temperatures (a result that today is known to be wrong); and, (2) that the specific heats of different simple gases were in the inverse ratio of their relative densities. His results helped dispel one of the basic tenets of the supporters of the caloric theory that the specific heat of a gas decreased as it was compressed (Fox, 1971). Regnault also prepared a table of the specific heats of various substances in the solid, liquid, and gaseous forms, from which it appeared that the specific heat of a body was commonly greater in the liquid than in the solid state, and always greater than in the gaseous state.

An important experimental result obtained by Regnault was that the specific heat should always be measured at constant volume. In the case of a constant volume calorimeter all the heat added appeared as an increase in temperature, whilst for the constant pressure calorimeter part of the energy was used to overcome friction and effect the expansion. The later two phenomena carried experimental errors that were very difficulty to quantify.

According to Jamin (Discours, 1878) the equipment designed by Regnault to determine (or redetermine) physical properties was extremely simple when compared to that used by his predecessors. Such a complex equipment was accompanied by a large number of error sources that could be corrected only approximately. Regnault's equipment was designed to eliminate or substantially decrease the source of these errors. For example, a comparison of the equipment used by Dulong and Petit and by Regnault to determine specific heats showed that Dulong and Petit considered only general laws and not the multiplying effect of small perturbations. A common denominator of Regnault *modus operandi* was that before designing his equipment he would make a careful analysis of the sources and magnitude of the probable experimental errors in the equipment used by others.

Let us now discuss in certain detail some of Regnault's most important contributions.

Organic chemistry

In his chemical work, nearly all of which dates from 1835 to 1839, Regnault followed no unified program of research. It was, however, his contribution in organic chemistry, most notably his studies on the action of chlorine on ethers and the research that lead him to the discovery of vinyl chloride, dichloroethylene, trichloroethylene, and carbon tetrachloride, which quickly won him an international reputation and the high esteem of such chemists as Justus von Liebig (1803-1873) and Jean Baptiste André Dumas.

His first publication was related to the Dutch liquid (ethylene dichloride, $C_2H_4Cl_2$) a combination of chlorine and acetylene, whose composition had been determined by Dumas. Regnault found Dumas' results correct against the arguments of Liebig, because the latter did not take into account all the reactions that were taking place. Among his investigations at this time may be mentioned those on the composition of meconine, piperine, cantharidine, and other alkaloids; the composition of pectic acid; the identity of esquisetic with maleic acid; the properties of naphthalene sulfonic acid, etc. (Norton, 1878). He treated ethylene with sulfuric acid and obtained the carbyl sulfate $C_2H_4S_2O_6$, which Henrich Gustav Magnus (1802-1870) prepared later from ethanol. His most valuable researches, however, were on the halogen derivatives of the ethyl group. Among these compounds were monochloroethylene chloride, $CH_2ClCHCl_2$, obtained by the action of chlorine on ethylene chloride, as well as the higher chlorinated derivatives, which offered a brilliant example of successive substitution. These were followed by his classical investigation on the action of chlorine on ethyl chloride C_2H_5Cl, in which one by one all the hydrogen atoms were successively replaced by chlorine, until the limit C_2Cl_6 was reached (Regnault, 1838). Regnault showed that the isomeric substitution products obtained from ethyl ether chloride and from Dutch liquid, possessed very different properties, a fact that proved that the substitution effected did not destroy the molecular grouping of the original substances. To do so, Regnault distilled each compound in the presence of metallic potassium. Diethyl ether distilled without affecting the potassium, but the Dutch liquor released hydrogen chloride and produced a precipitate of potassium chloride. Particularly important was the total chlorination of ethyl ether,$C_4H_{10}O$, into perchlorinated ether, $C_4Cl_{10}O$. Regnault first showed that the reaction occurred only in the presence of light and then proceeded to demonstrate that dichlorodiethyl ether and the Dutch liquid were isomers. They had the same composition but very different properties. Regnault also found that treating both compounds with chlorine in an illuminated reactor, gave two parallel series of substituted derivatives, equally isomeric.

Regnault proved, in this form, that incomplete substitution, respected the molecular groups present in the original compounds.

Another interesting series of preparations gave the substituted ethylenes by the action of alcoholic solution of alkalis on saturated halogen derivatives, ethylene bromide, for example, yielding vinyl bromide and hydrobromic acid

$$C_2H_4Br_2 + KOH \rightarrow C_2H_3Br + KBr + H_2O \quad (1)$$

By this method Regnault discovered vinyl bromide, vinyl iodide, and vinyl chloride, dichloroethylene, and trichloroethylene. Finally, he also discovered carbon tetrachloride by passing chloride into boiling chloroform.

Regnault also noted that exposure of vinyl chloride to the sunlight caused it to turn into a white powder or polymerize.

Coefficient of expansion of gases

The gas thermometer was based on the dilation of gases with temperature and thus it accuracy depended on the accurate knowledge of the expansion of gases with temperature. When heated from 0 to 100°C, at constant pressure, a perfect gas increases its volume according to

$$V = V_0(1 + \alpha t) \quad (2)$$

where V_0, V, are the initial and final volumes and *a* the coefficient of expansion. Today we use the *coefficient of thermal compressibility* to express the effect of thermal expansion as

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P \quad (3)$$

The results reported in Regnault's time and before should be read carefully because sometimes the value of the coefficient of expansion was given in either global form for the 100°C temperature interval (for example, 0.3646), or per degree (0.003646).

In a first publication (Regnault, 1841b) Regnault indicated that Rudberg had reported the coefficient of expansion of gases as 0.3646 (100^o interval) and that he believed that new experiences were necessary to confirm the validity of this value. He reported his preliminary results for air for four series of experiments, two of them using approximately Rudberg's procedure. These gave essentially the same results obtained by Rudberg and gave Regnault the opportunity to recognize a series of possible sources of error, for example, the thermal expansion of glass and the measurement of atmospheric pressure. In the next two series, in which he minimized the errors of these sources, he found that in the range 0 to 100°C the coefficient for air was 0.3665, substantially higher than that reported by Rudberg. He repeated his experiments using this time CO_2 and found that the coefficient of this gas varied between 0.36850 and 0.36896.

In a second publication Regnault (Regnault, 1842) went into more details. He indicated that the coefficient of expansion of air was probably the variable that had been subject to the largest number of determinations (because of the air thermometer). Nevertheless, it could well be said that it was not known with enough accuracy. Gay-Lussac claimed that in the range of temperature 0° to 100°C all gases and vapors had the same coefficient (0.375), as long as they were not near their saturation temperature. All physicists adopted Gay-Lussac's value until Rudberg showed that it was too high and that its real value was between 0.364 and 0.365.

Regnault then proceeded to repeat the measurements for ten other gases (N_2, O_2, H_2, CO, CO_2, SO_2, NH_3, NO, HCl, and C_2N_2) and found that N_2, O_2, and CO had essentially the same coefficient of expansion as air, but that of CO_2, SO_2, NO, HCl, and C_2N_2 were substantially higher. The results for NH_3 were also higher but not reliable because the gas reacted apparently with the mercury in the manometer.

In a following Mémoire (Regnault, 1847; pages 15-150) Regnault gave full details of his experimental procedures and results for the above gases and the coefficient of expansion of liquid mercury in the range 0° to 350°C (Regnault, 1847; pages 271-328).

Compressibility of gases

The determination of the compressibility of a gas has occupied the attention of many scientists in the past and nowadays. Originally this parameter was defined as a function of the equation of state for ideal gases, as $(V_0/V_1)(P_1/P_0)$ where the indexes *0* and *1* represented two isothermal states, and the index zero was assumed the standard state at 0°C and 1 atm. Today the compressibility (factor) z is defined as

$$z = \frac{Pv}{RT} \quad (4)$$

where v is the specific volume of the gas and T the absolute temperature. From equation (4) we see that the old definition of compressibility represents the ratio z_1/z_0. Since at standard conditions the value of z_0 is essentially unity, what was really being measured was the value of z. For gases obeying the ideal gas law the compressibility of all gases at a given temperature should have been constant with a value of one.

Regnault published two papers reporting his measurements of the compressibility of different gases and on the validity of the observations of Mariotte and Boyle (Regnault, 1846; 1847). Previous investigators had assumed that the compressibility of gases at atmospheric temperature was constant, or, in other words, that the density of the gas (ρ) was proportional to its pressure ($\rho \propto P$). Later investigations by Arago and Dulong (Arago and Dulong, 1831) had shown that this relation was valid only at low pressures, although for air it was up to about 30 atm. Regnault felt that these conclusions were not consistent with some measurements he had performed with air. He analyzed the experimental procedure followed by Arago and Dulong and found it at fault: The intention of Arago and Dulong's work had been to measure the vapor pressure of water at high temperatures and had used, for this purpose, a manometer of compressed air calibrated against a mercury column. Regnault considered that Arago and Dulong's apparatus was not built to consider the small variations that took place in the compressibility of air. The vapor pressure of water at the temperatures used was sufficiently high to be unaffected by these small differences and thus it was easy to overlook them.

In the first part of his work (Regnault, 1846) Regnault went on to construct a new set of manometers to measure the compressibility of air, N_2, CO_2, and H_2 at different temperatures and pressures. These manometers were carefully built to eliminate the experimental errors present in Arago and Dulong's work. Regnault's results indicated that air, N_2 and CO_2 presented a similar compressibility, but that not only it was larger than the one predicted by Mariotte-Boyle's law, it also increased with increased pressure. The results for H_2 were surprising in that they presented the opposite behavior. From these results Regnault concluded that the compressibility of a gas depended not only on the pressure and the temperature, but also on the nature of the gas. More than that, he predicted that for every gas there should always be a temperature for which the compressibility was unity. In modern terms, Regnault was advancing the existence of what we call today *Boyle's temperature* (T_B), the temperature at which the following relation is valid

$$\lim_{P \to 0} \left(\frac{\partial Pv}{\partial P} \right)_{T_B} = 0 \tag{5}$$

where P is the pressure and v the specific volume of the gas in question. For temperatures below T_B the compressibility will first decrease with increasing pressure, it will attain a minimum value and then it will increase indefinitely. For temperatures above T_B an increase in pressure will always be accompanied by an increase in the compressibility above the value of one.

In the second part of his work (Regnault, 1847; pages 329-462) Regnault gave a detailed numerical listing of the results he had obtained and added his experimental results on the compressibility of liquid mercury.

Based on his findings on the behavior of the compressibility of gases Regnault predicted, and was later demonstrated, that application of insufficient pressure was the only obstacle for the liquefaction of oxygen and nitrogen. Also, that if hydrogen was cooled, it would show enough compressibility to be liquefied. On December 24, 1877, Regnault sat for the last time in a session of the Académie, he was already very ill and would die a few weeks later. On that opportunity Dumas read Cailletet's communication on the liquefaction of oxygen. A week later Cailletet annonunced that he had also succeeded in liquefying nitrogen.

Specific heats

The meaning of heat and temperature provided the scientists of the seventeenth and eighteenth century with some awkward problems. The question of what was the nature of heat was explained postulating the existence of a fluid, called *caloric*, whose only properties were heat and the ability to pass from one body into another by contact. Its concentration was measured by the thermometer and, as any fluid must, it flowed from higher to lower concentration. The great advantage of this concept of heat was that it permitted quantitative statements. Caloric was conceived as a kind of all-pervading, imponderable, highly elastic fluid the particles of which were attracted by matter and repelled by one another. When two bodies at different temperature came into contact, it was supposed that caloric flowed from the hotter to the colder body until equilibrium was established in the two systems of material and caloric particles. When expansion resulted from heating, the expansion was attributed to the mutual repulsion of the caloric particles that entered the bodies when heated. The idea of caloric as a weightless fluid was finally discarded early in the nineteenth century and replaced with the vibrational theory, according to which heat consisted in the vibrations of the particles of ordinary ponderable matter.

In 1819 Dulong and Petit's law appeared primarily as convincing evidence of the physical reality of atoms, but it had also a possible application as an alternative method of determining atomic weights. Dulong and Petit were confident that given accurate measurements of specific heat it would give values 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.

In papers read to the Académie in 1840 and 1841 Regnault 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; 1841a).

		Molecular weight		Product	
Element	**Specific heat cal/g.°C**	**Dulong-Petit**	**Berzelius**	**Dulong-Petit**	**Berzelius cal/mol°C**
Bismuth	0.0288	1330	887	38.30	*25.53*
Lead	0.0293	1295	1295	37.94	37.94
Gold	0.0298	1243	1243	37.04	37.04
Platinum	0.0314	1116	1233	37.40	38.72
Tin	0.0514	735	735	37.79	37.99
Silver	0.0557	675	1351	37.59	*75.18*
Zinc	0.0927	403	403	37.36	37.36
Tellurium	0.0912	403	806	36.75	*73.50*
Copper	0.0949	395.7	395.7	37.55	37.55
Nickel	0.1035	369	369	38.19	38.19
Iron	0.1100	339.2	339.2	37.31	37.31
Cobalt	0.1498	246	369	36.85	*55.28*
Sulfur	0.1880	201.1	201.1	37.80	37.80

In his first publication Regnault (Regnault, 1840) gave first a historical review of the determination of the specific heat of pure substances and compounds. Dulong and Petit had been the first to determine this property with acceptable precision, in the range 0 to 350°C, and found that it increased with an increase in temperature. Later on they had used their results to determine the Dulong-Petit law: *Les atomes de tous les corps simple ont exactement la même capacité pur le chaleur* (The atoms of all simple bodies have exactly the same capacity for heat) (Dulong and Petit, 1819). Their results for thirteen substances (twelve metals plus sulfur) gave a value that varied between 36.75 and 38.30. 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 went on to say that today the same uncertainties were not present because Berzelius had determined atomic weights very precisely and all chemists accepted his values. Regnault used Berzelius' atomic weights to repeat the calculations of Dulong-Petit and found a different picture.

As Regnault wrote, inspection of the last column in the table indicated that the Dulong and Petit' conclusion was only approximate. The product for bismuth was now about one third less than that predicted by Dulong and Petit, that of tellurium and silver was double, and for cobalt it was about one third higher. Regnault also mentioned that Dulong and Petit had determined the specific heat of antimony as 0.0507 and that this value did not fit their law (even when using Berzelius' values for the atomic weight). To Regnault the differences could not be explained by an error in Dulong and Petit's determination of specific heat, they simple reflected the very approximate validity of their law. Regnault decided to redetermine the value of this property and again his first step was to analyze the experimental procedure of Dulong and Petit and recognize many possible sources of error. He went on to redesign the experimental equipment and procedure to minimize or eliminate all the sources of error he had identified. In his publication Regnault reported the mean specific heat of very large number of substances that he classified as follows: (a) highly pure elements, for which the experimental value may be considered very accurate, (b) metals not totally reduced and partially carburized, and (c) simple substances in an impure form (indium and manganese). In addition, he also measured the specific heat of mercury. The temperature range of measurement was different for each substance. Regnault indicated that for the substances reported by Dulong and Petit his results were systematically higher.

In a following publication (Regnault, 1841) Regnault addressed himself to the problem of measuring the specific heat of composite materials, in either liquid or solid form. He indicated that many had tried to answer, without success, the question if the specific heat of these substances followed a law similar to that of Dulong and Petit or not, and if there was a relation between the specific heat of the composite material and that of the elements that constituted it. He indicated that the purpose of his measurements was to provide an answer to the second question. He then measured the specific heat for a very large number of substances that he classified in five groups: (a) metallic alloys, (b) oxides (RO, R_2O_3, RO_2, RO_3), (c) sulfides (RS, R_2S_3, RS_2, R_2S, and complex sulfides) (d) chlorides, bromides, and iodides, and (e) salts formed by oxides and oxacides.

Regnault concluded the following:

(a) The specific heat of alloys was equal to the weight average of the metals that compose it.

(b) The specific heat of oxides having the same chemical formula, were in inverse ratio to their atomic weights.

(c) The specific heat of sulfides having one atom of sulfur, were in inverse ratio to their atomic weights.

(e) The law that applied to sulfur was also valid for chlorides, bromides, and iodides.

(f) The specific heat of composite substance containing the same electronegative element and similar atomic composition, were in inverse ratio to their atomic weights.

Regnault generalized all the above conclusions as follows: The specific heat of all composite substances that have the same atomic composition and similar chemical constitution varied in inverse ratio to their atomic weights. This meant that the law of Dulong-Petit was valid for composite substances, as suggested by Neumann.

Regnault ended this publication indicating that he had also measured the specific heat of substances that presented the phenomenon of isomorphism (same molecular weight) and found that this property varied widely from one allotropic state to another.

Steam and steam engines

Regnault resigned his position at École des Mines after being commissioned by the Ministry of Public Works to determine the main physical laws and the numerical properties required for the design of steam engines. In his eulogy Dumas (Dumas, 1882) illustrated the challenge of the problem by saying that at the beginning of the 18th century 3 kg carbon/h were required to produce one horsepower while by the year 1840 only 1 kg carbon/h was required. Encouraged by generous official backing, he embarked immediately on the systematic redetermination of all the experimental data that could conceivably be required in the theory of steam engines and other heat engines.

Regnault redetermined the compressibility of steam in the range –34°C (were the vapor was provided by ice) to 230°C, that is, at a pressure of 28 atm. He determined the specific heat of water from a temperature slightly above 0°C to about 200°C, and its latent heat at different pressures. He determined that at 0°C the heat of condensation of steam was 637.67 cal/g and that the specific heat of water increased from 1.000 units at 0°C to 1.013 unit at 100°C. No doubt that Regnault should be credited with having issued the first version of what today we call steam tables.

The results were one of the most precise compilations available. Regnault's report (Regnault, 1847) contained a detailed description of the experiments made to determine the validity of the gas thermometer. Regnault tested two possibilities: (1) the gas was held at constant pressure and the temperature was determined from the change in volume, and (2) the volume was held constant and the temperature was determined from the change in pressure. The results indicated in the pressure range 400 to 1500 mmHg both procedures gave essentially the same results. Similar results were obtained if the gas was air, hydrogen, or CO_2, as long as their pressures at 0°C did not exceed one atm. The thermometer with SO_2 differed from the others.

In his experiments on the effects of heat Regnault was led to devise methods of measuring high temperatures accurately, and improved the well-known air thermometer, which could be used at all temperatures below that at which glass softened, and the mercury and hydrogen pyrometers, the latter of which permitted measuring the temperature in a furnace at any instant. He also carried out an elaborate series of experiments on the density and absolute expansion of mercury from 10 to 36°C, the results of which were of primary importance in the correction of thermometers and barometers, as well as other physical measurements. He also developed the formula for describing the same.

According to Dumas (Dumas, 1882) the experimental program was plagued by accidents: a pot with boiling sulfur set the laboratory on fire, a flask containing boiling mercury exploded in his face, and finally, a recipient full with liquid CO_2 exploded in his hands. None of these accidents hurt him seriously, he seemed to be invulnerable, until a fourth accident that took place in August 1856, resulted in a cerebral commotion that left him slightly impaired.

The official declaration, published in the newspaper *Moniteur Universel*, on September 14, 1847, after he delivered his first volume of his results (Regnault, 1847), said: "*Les résultats obtenus para se savant Ingénieur constituent l'un des plus remarquables travaux de Physique expérimentale qui aient été exécutés. C'est à la fois un monument scientifique et un travail de la plus haute utilité pour l'industrie, qui honore et son auteur et les corps des Ingénieurs des Mines ¼*' (The results obtained by this sage engineer constitute one of the most remarkable works of experimental physics ever done. It is at the same time a scientific monument and a work of the maximum industrial use, it honors its author, and the corps of Mine Engineers ¼).

The political events in France of 1848 put in doubt the possibility that the State would continue financing the project, but a proposition from the Society of Engineers of London that they would be willing to do it forced the issue and additional French funding was provided for Regnault to continue his work.

In his second report to the Ministry Regnault (Regnault, 1862) described his measurements of the specific heat of 33 gases at atmospheric pressure (oxygen, hydrogen, CO_2, HCl, NH_3, alcohol, acetone, titanium chloride, PCl_3, etc.) and hydrogen, air, and CO_2 at pressures above atmospheric. He also determined the vapor pressures as a function of temperature, for 28 liquids like vinyl alcohol, ether, and CS_2 (Regnault, 1862; pages 42-204), the relative humidity of six substances (in air), the vapor pressure of mixtures of liquids, partially or totally soluble (Regnault, 1862; pages 715-750), the heat of vaporization at different pressures of eight substances (CS_2, ether, ethanol, benzene, CCl_4, CHl_3, acetone, and turpentine) (Regnault, 1862; pages 761-882), and finally, the speed of sound in the atmosphere.

In 1878 Karl Eugene Dühring (1833-1921) used Regnault's results on the vapor pressure of organic compounds to develop what is now known as Dühring's rule, that allows calculating the increase in boiling point caused by a nonvolatile solute (Wisniak, 2001).

Other results of Regnault included the observation that the vapor pressure of a mixture of insoluble liquids was equal to the sum of the vapor pressures of the pure liquids at the same temperature, but the vapor pressure of a mixture of mutually soluble liquids was less than the sum of the individual vapor pressures.

It is interesting to note that in his paper describing the general law of the vapor pressure of solutions (eventually to be known as Raoult's law) (Raoult, 1887) Raoult made no mention of Regnault's results on the subject.

Flow gases and speed of sound

Regnault performed a large number of experiments on the flow characteristics of gases, and on the velocity of sound in the same. One of his objectives was to calculate the ratio c_P/c_V using Laplace's equation for the velocity of sound in a tube

$$\frac{\nu}{\nu_{gas}} = \frac{\sqrt{1 + 0.00375\, t\, \sqrt{\gamma_{air}/\rho_{gas}}}}{\sqrt{(1 + 0.00375\, t'\, \sqrt{\gamma_{gas}/\rho_{gas}}}} \tag{7}$$

where ν, is the frequency of the fundamental note obtained with the gas (or air) in the tube, *t* the temperature, and $g = c_P/c_V$.

The first publication (Regnault, 1868) contained extensive data on the velocity of sound (Regnault, 1870) dealt with the characteristics of flow and heat transfer in different regimes and for different gases. For example, Regnault measured the heat absorbed during the expansion of the gas, through an orifice in a vessel, through capillaries, and when the gas was suddenly stopped. He also took measurements of the temperature and speed profiles along the flow path. An interesting fact is that in some of his experiments on the discharge of a gas through a capillary tube Regnault observed a small cooling effect but he misinterpreted them. This effect appears to have been precisely the same one reported in 1852 by James Prescott Joule (1818-1889) and William Thomson (1824-1907, Lord Kelvin) (Joule and Thomson, 1852) (the Joule-Thomson effect).

Respiration

Hermann von Helmholtz's (1821-1894) law of conservation of energy, embodied in the First law of thermodynamics, had profound influence both on initiating a physicochemical approach to problems in physiology and in coloring viewpoints in all branches of thought. Between 1777 and 1790 Antoine Laurent de Lavoisier (1743-1794) had explained the respiratory system and inaugurated physiology. The quantification of the phenomena came in 1849 Regnault and Jules Reiset (1818-1896) published their landmark book on the respiration of animals (Regnault and Reiset, 1849).

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. Their measurements provided the relationship among dietary carbohydrate, fat, and protein to what Eduard Friedrich Wilhelm Pflüger (1829-1910) would call later the *respiratory quotient*. They also foresaw the principle involved in the law of surface area, where the typical metabolism is considered to be essentially equal in animals having the same body volume, surface, and temperature. The larger the body surface, for equal body volume and temperature, the higher will be the metabolism. We see here an early, clear appreciation of the application of thermodynamics to the analysis of a living organism.

Before Regnault and Reiset the phenomenon of respiration in animals had been followed 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. Regnault and Reiset believed that this procedure was wrong because in the first arrangement the animals were breathing air of changing composition, and in the second, the composition of the air changed very little and the overall results were strongly influenced by analytical errors. In Regnault and Reiset's equipment the specimens were put in an enclosed space where their behavior was respected and could sojourn indefinitely. The air was recirculated and renovated at constant composition, by ingenious mechanisms (see below). In this manner, Regnault and Reiset were able to make a complete material balance of the perspiration phenomena of different species (mammals, birds, reptiles, and insects) that included the effects of breathing, losses through the skin, and wastes. No only that, they were studied under different regimes, like rest, sleeping, well-fed or fasting, and hibernating, and also under air enriched in oxygen, or with the nitrogen replaced by hydrogen. For example, Regnault and Reiset found that for hibernating animals (such as marmots) the body temperatures could descend to 12^{0}C, while the weight increased instead of decreasing. Insects, like the silkworm, were studied in each of their development stages.

The results of Regnault and Reise have a picturesque angle in Jules Verne's book (Verne, 1900) *From the Earth to the Moon*. In chapter eleven Michel Ardan suggested solving the problem of supplying fresh air inside Barbicane's space capsule using Regnault and Reise's results: "The question of provisions and lighting having been solved, there remained the question of the air supply. It was evident that the air confined in the projectile would not be sufficient for the traveler's respiration for four days. Barbicane, his two companions, and the two dogs that he meant to take, would consume every twenty four hour 2,400 liters of oxygen, or a weight equal to seven pounds. The air in the projectile must be renewed. How? By a very simple method, that of Messrs. Reiset and Regnault, indicated by Michel Ardan during the discussion of the meeting ¼ In an enclosed space and after a period of time, all the oxygen is replaced by carbon dioxide, a gas that is essentially toxic. The question comes down to this: ¼(1) to replenish the oxygen, (2) to get rid of the exhaled carbon dioxide. Both are easily accomplished by means of potassium chlorate and potash. Potassium chlorate is a kind of salt that takes the form of white flakes; when brought to a temperature above 400 degrees, it changes into potassium chloride, and the oxygen that it contains is released. So much for replenishing the oxygen. As for the potash, it hungers for the carbon dioxide mixed in the air, and one need simply shake it to absorb the former and create potassium bicarbonate. In combining these two procedures, one can be sure that the vitiated air in the capsule would be made breathable. Two chemists, MM. Reiset and Regnault, have successfully experimented with this. But, it must also be noted that until now all their experiments have taken place *in anima vili*. However precise their results, exactly how this procedure would work on humans was as yet unknown''.

Conclusion

Victor Regnault is probably the scientist that single-handed determined the vastest amount of highly reliable data. The question is sometimes asked why he did not turn his huge database into physical and chemical theories. One possible answer arises from a detailed reading of his papers. All of them follow, more or less, the same pattern, Regnault first described in a highly praising manner the work done by others and then, very politely but without mercy, went on to show their many experimental errors and why their conclusions were at the most qualitative. For example, when discussing the work of Dulong and Petit he wrote that they did not pick the *best value* of the molecular weight available for a given compound (several were available), they simple picked the one that *justified* their law. Regnault then proceeded to explain how he had overcome the shortcomings of previous investigators by improving the experimental equipment and or the experimental equipment. The message seems clear: I can do it better and simpler. This leads to the second possible answer: You can build theories based on imprecise information and have them accepted until someone will discover the error. Regnault did not want to follow this road; he preferred the safe one (the winning one for him) of experimental nature alone.

References

Arago, F., Dulong, P. L., *Mémoires de l'Académie des Sciences*, **1831**, *10*, 193-236.

Crosland, M., *Gay-Lussac - Scientist and Bourgeois*, Cambridge University Press: Cambridge, 1978.

Discours Prononcés par des Membres de l'Académie aux Funérailles de M. Regnault, *Compt. Rendu*, **1878**, *86*, 131-143.

Dulong, P. L., Petit, A. T., *Ann. Chim. Phys.*, **1819**, *10*, 395-13.

Dumas, M. J.-B, *Mémoires de l'Académie des Sciences*, **1882** *42*, xxxvii-lxxv.

Fox, R., *The Caloric Theory of Gases - From Lavoisier to Regnault*, Clarendon Press: Oxford, 1971.

Gladstone, J. H., *J. Chem. Soc.* **1878**, *33*, 235-239.

Joule, J. P., Thomson, W., *Phil. Mag.* 4th ser., **1852**, *4*, 481-492.

Norton, T. H. N., *Nature*, **1878**, *17*, 263-264.

Raoult, F. M., *Compt. Rendu*, **1887**, *104*, 1430-1433.

Regnault, V., *Ann. Chim. Phys.*, **1838**, *71*, 353-430.

Regnault, V., *Ann. Chim. Phys.*, **1840**, *73*, 5-72.

Regnault, V., *Compt. Rendu*, **1841**, *23*, 1077-1079.

Regnault, V., *Ann. Chim. Phys.* 3rd ser., **1841**, *1*, 129-207.

Regnault, V., *Ann. Chim. Phys.* 3rd ser., **1842,** *4*, 5-63.

Regnault, V., *C. r. Hebd. Séanc. Acad. Sci., Paris*, **1846**, *23*, 787-798.

Regnault, V., *Mémoires de l'Académie des Sciences*, **1847**, *21*, 1-767.

Regnault, V., *Compt. Rendu* , **1853**,*36*, 680.

Regnault, V., *Mémoires de l'Académie des Sciences*, **1862**, *26*, 1-928.

Regnault, V., *Mémoires de l'Académie des Sciences*, **1868**, *37*(1), 3-575.

Regnault, V. *Mémoires de l'Académie des Sciences*, **1870**, *37*(2) , 579-968.

Regnault, V., Reiset, J., *Recherches Chimiques sur la Respiration des Animaux des Diverses Classes*, Bachelier: Paris, 1849.

Verne, J., *From the Earth to the Moon*, Ward, Lock. & Co.: London, 1900.

Wisniak, J., Karl Eugene Dühring - A Scientist and Political Extremist, *J. Phase Equil.*, accepted, (2001).