La química en la historia, para la enseñanza.

Émile-Hilaire Amagat and the laws of fluids

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Resumen
Émile Hilaire Amagat (1841-1915) es bien conocido por sus investigaciones de las leyes de los fluidos y el comportamiento a alta presión de gases y líquidos. Él desarrolló nuevos aparatos e instrumentos que permitieron alcanzar presiones a más de 3,000 atmósferas, dos órdenes de magnitud superiores a las alcanzadas previamente. Hizo un estudio detallado de la variación del producto *Pv* para un gran número de gases, así como acerca del efecto de operar variables en el mínimo de *Pv*. Realizó mediciones extensas y precisas del coeficiente de expansión de gases, líquidos y sólidos, y propuso una ecuación de estado para los gases reales basado en el concepto de éter que consideraba correcciones para la presión y el volumen.

Abstract
Émile Hilaire Amagat (1841-1915) is well-known for his researches on the laws of fluids and the high-pressure behavior of gases and liquids. He developed new apparatus and instruments that allowed reaching pressures of more than 3,000 atmospheres, over two orders of magnitude larger than was possible before. He made a detailed study of the variation of the product *Pv* for a large number of gases and the effect of operating variables on the minimum of *Pv*. He made extensive and very accurate measurements of the coefficient of expansion of gases, liquids and solids, and proposed an equation of state for real gases based on the concept of æther that considered corrections for the pressure and the volume.

Life and career
There is almost no information about the life and early education of Amagat. The little available comes from an appendix in the book by Barus (Barus, 1899).

Émile-Hilaire Amagat was born on January 2, 1841 at Saint-Satur, a village in the Sancerre district, in the department of Cher, France. His first intention was to be a technical chemist, but he abandoned this career almost at the very beginning in preference for one in pure science. For several years he was préparateur of Marcelin Berthelot (1827-1907) at the Collège de France. Between 1867 and 1872, he served as professor of mathematics and physics at the Lycée de Fribourg, in Switzerland. There he completed his thése de doctorate and received his degree docteur-ès-sciences from the Faculté de Sciences de Paris in February 1872. After his return to France he was appointed professor at the Lycée d'Alençon, then at the École Normale Spéciale de Cluny, and in 1877 professor of physics in the Faculté Libre des Sciences of Lyons. In this institution he created the department of physics and in it conducted his most famous researches. He left Lyons in 1891 for Paris to take the position of examinateur at the École Polytechnique. He was elected a corresponding member of the Académie des Sciences (Section of Physics) on May 5, 1890, and promoted to full member on June 9, 1902.

Amagat received many honors for his contributions to science. He was appointed foreign member of the Royal Society of London (1897) and of the Royal Society of Edinburgh (1897); honorary member of the Sociéte Hollandaise des Sciences, of the Société Scientifique de Bruxelles, of the Philosophical Society of Manchester, etc., etc. In 1893 the Académie des Sciences awarded him the Prix Lacaze pour la Physique.

Amagat died in Saint-Satur on February 16, 1915.

Scientific contribution
Amagat was a very prolific scientist that occupied himself on a wide variety of subjects: the behavior of fluids, thermodynamics, equations of state, corresponding states, determination of the absolute zero of temperature, physics, pyrometry, measuring instruments, magnetism and electricity, etc., etc. Here we describe only a few of them that show that he was not only an outstanding experimentalist, but also looked for a theoretical explanation of the phenomena he observed and measured. A list of his publica-

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tions appears in the book by Barus (Barus, 1899) and in the summary of activities that he presented to the Académie des Sciences at the time of his candidacy (Anonymous, 1896).

1. Expansion and compressibility of gases

The earliest known attempts to attain high pressures and to study various properties of matter under the influence of these pressures date from the beginning and middle of the seventeenth century (Boyle, 1660). The experiments, which were carried out by extremely primitive methods, aimed in the first place at throwing light on the compressibility of liquids. These investigations did not become of a more scientific and systematic nature until the beginning of nineteenth century, although at first they had the same limited aims as before. However, they were gradually extended to other fields. As an example we may mention attempts to compress a number of gases at high pressure, when great deviations from Boyle's law revealed themselves, and further, investigations of the effect of pressure on the refractivity of water, the effect of pressure on the resistance of an electric conductor, etc.

By mid-nineteenth century, all but six of the known gases hand been liquefied, and temperatures below 170 K had been achieved by evaporating a Thilorier mixture of solid CO_2 and diethyl ether. The six remaining gases (oxygen, nitrogen, carbon monoxide, nitrous oxide, methane, and hydrogen) were called *permanent gases* and believed to be non-condensable. Helium was not considered then because this gas was discovered only in 1869 when observing the sun and identified by a bright yellow line in a spectrum analysis of the sun's corona. William Ramsay (1852-1916) discovered the first deposits in the earth in a sample of pitchblende, a dark rock containing radium and uranium.

Temperature was measured using the gas thermometer, based on the dilation of gases with temperature and thus it accuracy depended on the correct 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

$$V = V_0(1+\alpha t) \qquad (1)$$

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

$$\alpha = \frac{1}{v}\left(\frac{\partial v}{\partial T}\right)_P \qquad (2)$$

Gay-Lussac claimed (Gay-Lussac, 1789) that in the range of temperature 0° to 100°C all gases and vapors had the same coefficient of expansion (0.00375 K^{-1}), as long as they were not near their saturation temperature. Most physicists adopted Gay-Lussac's value until Rudberg showed that it was too high and that its real value in the above temperature interval was between 0.00364 and 0.00365 K^{-1}. Regnault wrote (Regnault, 1841) 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. He repeated Rudberg's measurement and found that in the range 0 to 100°C the coefficient for air was actually 0.003665 K^{-1}, a value substantially higher than that reported by Rudberg. Further experiments with CO_2 yielded values between 0.0036850 and 0.0036896 K^{-1}.

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 for CO_2, SO_2, NO, HCl, and C_2N_2 it was substantially higher (Regnault, 1842). The results for NH_3 were also higher but not reliable because the gas reacted apparently with the mercury in the manometer. Regnault also measured the coefficient of expansion of liquid mercury in the range 0° to 350°C (Regnault, 1847-1870).

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 (P_1V/P_0V_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

$$z = \frac{Pv}{RT} \qquad (3)$$

were v is the specific volume of the gas and T the absolute temperature. From equation (3) we see that the old definition of compressibility represents the ratio measured at the same temperature. Since at standard conditions the value of z 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 be constant with a value of one, that is, the density of the gas (ρ) should be proportional to its pressure ($\rho \propto P$). Later work by François Arago (1785-1853) and Pierre-Louis Dulong (1785-1838) (Arago and Dulong, 1831) showed that this relation was valid only at low pressures, although for air it was so up to about 30 atm.

Regnault (Regnault, 1846) 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. His results indicated that air, N_2, and CO_2 presented a similar compressibility, which not only was larger than the one predicted by Mariotte-Boyle's law, but 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 today we call the *Boyle temperature* (T_B), the temperature at which the following relation is valid

$$\lim_{p \to 0} \left(\frac{\partial Pv}{\partial P} \right) T_B = 0 \tag{4}$$

Experimental evidence indicates that for temperatures below T_B the compressibility will first decrease with increasing pressure until it reaches 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.

Based on his findings on the behavior of the compressibility of gases Regnault predicted, and was later proven correct, 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.

A significant advance took place in 1869 when Thomas Andrews's (1813-1885) published his famous memoir on the continuity of the liquid and gaseous state and his findings about the critical phenomena in gases (Andrews, 1869, 1876). Andrews determined several isotherms of CO_2 between 10 and 50°C and up to 110 atm, that is, in the region were the graph Pv vs P for CO_2 goes through a minimum value. At moderate pressures he found that below a certain temperature the gas no longer obeyed Boyle's law. Indeed below the "critical temperature" the gas liquefied as the pressure increased without any further cooling. He studied the behavior of gases under high pressures and different temperatures and was able to formulate the concept of coexistence of the vapor and liquid phases and the constancy of temperature during a phase change (Andrew's isotherms). Andrews demonstrated that for every gas there exists a temperature (the *critical temperature*) above which it is impossible to condense the gas, no matter how high a pressure is applied. For this purpose he used CO_2 because of the easiness with which it can be produced in a pure state and because of its low critical temperature (31°C). Regnault had already shown (Regnault, 1847-1870) that CO_2 deviated sensibly from Boyle's law, even at temperatures well above the critical one.

Andrews used the concept of critical temperature to differentiate between a vapor and a gas, a distinction that was based previously on the boiling point, a clearly arbitrary definition. Another important experimental result was that the gaseous and liquid states of matter could be transformed into one another by a series of continuous and unbroken changes. In 1873 the continuity of the gas and liquid state would be the subject of Johannes Diderik van der Waals's (1837-1923) doctoral thesis (van der Waals, 1873).

Andrews's report was published in France in 1870, and this research was the only one, at the time, reporting the P-V behavior of a gas at varying temperatures. Johann Augustus Natterer (1821-1901) had discovered the Pv vs. P minimum in 1851 and shown that for hydrogen the product Pv increased with pressure without going through a minimum value, a fact that was also known from Regnault's experiences. Natterer's and Regnault's experiments were done only at room temperature and it was left to Amagat to repeat them at several temperatures.

Amagat became very interested in Andrew's results and from 1869 to 1872 he embarked in a very ambitious research project involving the determination of the behavior of gases at different pressures and temperatures. Eventually, all his results evolved into his doctoral thesis (Amagat, 1872). His first scientific papers on the subject were published between

1879 and 1882 (Amagat, 1869, 1870, 1871, 1873ab, 1876, 1877, 1879, 1880abc, 1881, 1883ab) and reported among other things, the network of isotherms of nitrogen, oxygen, air, methane, ethylene, carbon monoxide, and carbon dioxide between 0 and 100°C, and up to a little more than 400 atmospheres (the pressure limit that the most resistant glass tubes could withstand when compressed internally), using a nitrogen manometer. In the first stage he studied the behavior of the gases up to 80 atmospheres using for this purpose a column of mercury that he installed on the side of one of the towers of the Églisse de Fourvière in Lyon, having 63 meters from the ground to the summit of the cross. He then extended the pressure limit to about 430 atmospheres employing the shaft of a coalmine located at Verpilleux, near Saint-Étienne (Amagar, 1879). In particular, Amagat used a mercury column 327 meters high to measure the compressibility coefficient of nitrogen. His results were of such quality that immediately they were used everywhere for calibrating gas manometers. To understand the significance of Amagat's results it is necessary to realize that at that time the only available data for nitrogen were Regnault's measurements up to 30 atm. Netterer's figures were enough for measuring only qualitatively the minimum value of *Pv*, but his measuring methods were not safe enough. Andrews in his research had simply applied the law of ideal gases to an air manometer compressed up to 100 atmospheres, a very gross approximation indeed.

In a representative publication of this activity (Amagat, 1881) Amagat included extensive tables and graphs giving the values of the product *Pv* in the pressure range 30 to 320 meters of mercury, at different temperatures, for nitrogen (17.7° to 100.1°C), hydrogen (17.7° to 100.1°C), methane (14.7° to 100.1°C), ethylene (16.3° to 100.1°C), and carbon dioxide (18.2° to 100.0°C).

The curves show that the families of isotherms may be divided into two extreme and certain intermediate types (for example, methane and nitrogen, which are located at temperatures farther from their critical state than ethylene or carbon dioxide). For hydrogen the curves are straight parallel lines, showing that this gas has reached a limiting state characterized by their direction. At all the temperatures studied the values of *Pv* increased proportionally to the pressure.

Carbon dioxide and ethylene constituted the contrasting type. At first their *Pv* products decrease very rapidly, reaching a minimum and thereafter increase indefinitely. These variations of *Pv*, very rapid at temperatures near the critical point, show a marked diminution when the temperature is raised. The point of the curve at which the ordinate is a minimum moves regularly away from the origin. The minimum appears to move away from the origin less rapidly after passing a certain temperature, after which it apparently retrogrades. This result is seen very clearly for methane and nitrogen. For carbon dioxide and ethylene, at temperatures in the neighborhood of the critical point, the initial branches of the curves (or those which precede the minimum ordinate) are concave towards the axis of pressure. The concavity is well marked, it appears to be prolonged quite into the region of small pressures, and disappears as the temperature is increased. For gases other than ethylene and carbon dioxide, the concavity disappears completely even at ordinary temperatures. For temperatures in the neighborhood of the critical point, the curve turns rapidly after passing the ordinate in question, and changes almost at once into a nearly straight line.

Analysis of the results and the form of the curves led Amagat to the following conclusions regarding the compressibility of gases:

(a) For pressures lower than the critical pressure and continually increasing temperatures, the divergence from Mariotte's law, is initially positive at sufficiently low temperatures, it then passes through zero and eventually becomes negative. Beyond a certain negative value, however, the discrepancy diminishes indefinitely without changing sign.

(b) For pressures below the critical value and a superior limit peculiar to each gas, the range during which the deviation is positive is preceded at still lower temperatures by a range for which it is negative, in such a way that the discrepancy changes sign twice.

(c) Beyond the superior limit indicated in the preceding law, the discrepancy is negative at all temperatures. In general, it diminishes as the temperature increases, always excepting those pressures, which are too near to the limit specified. There the variation is more complicated.

(d) Beyond a sufficiently high temperature the law of compressibility of a gas can be represented by the equation $P(V-\alpha) =$ constant where α is the smallest volume to which the gas can be reduced. In other words, α may be considered the *absolute volume* of the constituent matter. The above relation implies that beyond a certain sufficiently high temperature all the curves become straight lines.

Amagat then proceeded to discuss the concept of *covolume* or *atomic volume*. Since the curves Pv vs. P eventually become straight lines we can write

$$Pv = \alpha P + b \tag{5}$$

the initial ordinate b is the value of Pv at the limit when the pressure goes to zero. Assuming b and α constants then

$$(v - \alpha) = \frac{a}{P} \tag{6}$$

and v tends to α when P tends to infinity. This means that α should be considered the volume that the gas eventually takes when pressure is increased indefinitely, that is, the absolute volume of matter within the gas, supposing that the molecules will ultimately touch each other. Amagat calculated the atomic volume (referred to the unit volume of the gas at 0°C and 760 mmHg) of hydrogen (0.00078), carbon dioxide (0.00170) and ethylene (0.00232). Amagat remarked that this conclusion was similar to the one reached by Athanase Louis Victoire Dupré (1808-1869) and Gustave Adolphe Hirn (1815-1890). Dupré, from the fundamental formulas on the mechanical theory of heat (Dupré, 1869), had deduced the following law which he called the *law of covolumes*, as an approximation of higher order of accuracy to the law of Mariotte: "At constant temperature the pressure of a mass of gas varies inversely as the volume is diminished by a small constant quantity $c_o u_o$. This is to be called the *covolume* when the volume u_o under normal conditions is the unit of volume."

Thus, according to Dupré the covolume of nitrogen, carbon dioxide, and air was positive, while for hydrogen it was negative. Dupré's law presupposed that the curve representing the experimental values should always be straight, a condition negated by experience for nitrogen and carbon dioxide, unless it was limited to temperatures and pressures for which the covolume became precisely contrary in sign to that deduced by Dupré. Hence, according to Amagat, it was necessary to reject Dupré's law and his interpretation of the covolume.

Hirn, in his book *Exposition Analytique et Expérimentale de la Théorie Méchanique de la Chaleur* (Hirn, 1862), published an elaborate analysis of the same subject and expressed the opinion that in Mariotte's law it was the variable part of the volume which ought to be considered, a conclusion which for Amagat was far from being evident. For the case in which the interactions of the molecules was not negligible, Hirn introduced an *internal pressure p* to be added to the external pressure in such a way that the equation of state for a real gas became

$$(P + p)\,(V - \alpha) = (P' + p')\,(V' - \alpha) \tag{7}$$

For hydrogen p and p' would be approximately zero, whence $P(v - \alpha)$ would be become constant, an expression which Hirn verified with the aid of Regnault's data. The observant reader will note that eq. (7) is a primitive form of van der Waals's equation of state.

Amagat believed that even after making full allowance for the atomic volume, the occurrence of an internal pressure representing a mere addition to the external pressure, was not enough to account for the variations from ideality and additional factors had to be taken into account. With the new results he had reached, he was able to make this fact much more evident. The so-called internal pressure could be admitted into gaseous kinetics in so far as this pressure depended only on the mean distance between molecules, i.e., it was a function of the volume only. But Amagat's results indicated that it was also a function of the temperature. Taken as a whole, Amagat believed that his results showed clearly that a special theory for gases and another for liquids was unacceptable. His question was (Amagat, 1881): "Considering, for example, the isotherms for hydrogen, how is it possible to admit one theory to explain the facts represented by one part of the curve and another theory to explain the rest, seeing that their form shows conclusively that a phenomenon of perfect continuity is being observed?"

Amagat proceeded to study the two hypotheses: attraction between molecules and unequal distribution of the *force vive* (kinetic energy) of the molecules. The first hypothesis had been proven above to be insufficient to explain the deviations from ideal behavior. In the kinetic hypothesis molecules possess kinetic energy that represents thermal energy. The force vive can be decomposed in two parts, the force vive of translation of the molecules and the internal force vive. The latter can also decompose into a series of components. The force vive of translation is solely responsible for pressure and volume; we do not know the laws that rule the distribution of internal force vive, particularly in the state of non-ideal gas. In his derivation of the virial theorem Clausius (Clausius, 1870) demonstrated that the force vive of translation and the volume and the pressure are related as follows

$$Pv = \frac{2}{3}\frac{nu^2}{2} \qquad (8)$$

where *m* is the average mass, *u* the average velocity of the molecules, and *n* their number. Hence, according to Amagat, the ideal gas law was a consequence of eq. (8) if we assume that the right hand side remains constant during a compression process. If this is not so, this quantity varies and so does the product *Pv*.

Amagat believed that it was very remarkable that the law given by the equation $P(v-\alpha) =$ constant, which appeared to be the limiting law towards which all gases converged when the temperature was increased, was the same law which was in action in the neighborhood of the critical point, whenever the compressibility of a body was considered throughout increasing pressures. Thus it was rather a law for the liquid than for the gaseous state. He went further and claimed that it was specifically the law of liquids, at least within the limits of actual experimental inquiry, for it appeared, from the family of isotherms, that carbon dioxide at 18°C, which is then truly liquid, followed exactly the same law: A straight line with slope α. At first sight this result appeared quite paradoxical: (a) *Increasing* the temperature transformed the gas into the state of a perfect liquid and, (b) the region of branches of the isotherms situated on the left of the line of minimum coordinates, the region which corresponds accurately to the gaseous state in the ordinary sense of the word, was a period of turbulence terminating in the phenomenon of liquefaction properly so called. This phenomenon disappeared when the temperature was raised indefinitely and the body became a perfect fluid.

At this stage Amagat made the wrong turn and introduced the concept of æther to explain his findings. He stated that the equation $P(v - \alpha) =$ constant could be written in the alternative form $PW =$ constant, were W was the *interatomic* volume. This equation was as simple as that for an ideal gas and one was induced to seek an explanation for the fact that the behavior of a real gas depended on the interatomic volume. The new law could be stated as follows (Amagat, 1880): "The behavior of the fluid during compression is such as if an infinitely subtle fluid rigorously subject to Mariotte's law pervades the whole space between the molecules. The material particles, or the groups, which they form, show only a negligible amount of translation kinetic energy and produce an effect only by their presence, i.e., by the volume which they delimit in the same way as if they are ordinary walls of the region."

"Why may not this fluid be the æther in a certain degree of concentration? Such hypothesis would give a complete account of all observed facts. It does not exclude the theory of molecular impact; it merely restricts the limits within which kinetic action is applicable. It seems probable that the molecules are surrounded in every thermal state, solid, liquid or gaseous, with atmospheres of æther. These atmospheres account for their perfect elasticity, as evidenced in the kinetic theory of gases, an elasticity which it would be very difficult to explain, or which would be even quite inexplicable, if the molecules were simple, i.e., reduced to single atoms. Granting this, let us consider a gas at a low pressure and at a temperature slightly above the critical point and let the gas be compressed initially at a constant temperature. Changes in the distribution of kinetic energy between the motion of molecular translation, the motion within the molecule, and its rotational motion, suffice to explain the discrepancies of the law, to which, in a certain measure, molecular attraction may add its effects. Thus the gas is more compressible than Mariotte's law indicates, even if allowance is made for the absolute volume of the atoms. Very soon, however, these with their atmospheres of æther occupy the major part of the volume, and so hamper each other in their movements of translation that the latter virtually vanish. This occurs in the neighborhood of the minimum ordinate. Finally, for continuously increasing pressures the atmospheres of æther will actually become continuous, and the molecules appear as if suspended therein. *The æther now forms a medium, which is continuous*, and by its reaction produces the observed pressure against the walls of the vessel. If this æther obeys Mariotte's law, which is now regarded as the limiting law of an infinitely subtle fluid, the volume which it occupies is exactly W, and $PW =$ constant, or $P(v - \alpha) =$ constant. Hence, although there has been no liquefaction in the true sense of the word, the body is rather a liquid than a gas, for the reason that the molecular translation motion, which is a criterion for the gaseous state, as vanished."

"At the beginning of the heating process, the æthereal molecular atmospheres will expand simultaneously with the molecules themselves, and the atoms separate more and more fully until decomposition ensues. Inasmuch as the total volume of the æthereal atmospheres is larger, the law $PW=$ constant ought to begin to apply for a given mass of gas at a larger volume than at the lower initial temperatures. This indeed appears very well to account for the fact that for a given mass of gas the volume corresponding to the minimum ordinate increases with temperature. If temperature continually rises, the fraction of the total volume occupied by the æther also continuously increases, and when the effect of the latter preponderates the curves will rise and be gradually transformed into straight lines."

According the Amagat the æther hypothesis gave a natural and complete account of the details of the phenomena observed experimentally since it did not exclude those kinetic theories, which were then becoming accepted. It restricted the limits within which the theory of impact was apparently applicable by establishing a transition from the liquid to the gaseous state, which may be passed continuously and the mechanism of which was easily intelligible.

Amagat used his data to calculate the coefficient of expansion, $1/v(\partial v/\partial T)_P$, for ethylene and carbon dioxide (tables are given for the pertinent values within certain temperature ranges). His results indicated that the behavior of the coefficient was rather complex for the region near the locus of the minimum ordinates, but at high pressures or low pressures, the coefficient diminished regularly with temperature. The variation with pressure at constant temperature was clearer: the coefficient at first increased with pressure up to a maximum value and thereafter decreased regularly. The maximum corresponded very nearly to the pressure at which the ordinate was a minimum. Hence, the conclusion was that at this exceptional point the gas *accidentally* obeyed the law of Mariotte (what Amagat meant was that although the gas is real, at certain singular points it may satisfy the equation of state $Pv=RT$). At higher temperature the maximum became more and more indistinct until finally it vanished.

In a further study (Amagat, 1888a, 1893a) Amagat extended his measurements to higher pressures, measuring the values of the volume v and the product Pv, at pressures up to 3,000 atmospheres and various temperatures for oxygen (0° and 15.6°C), hydrogen (0°, 15.4°, and 47.30°C), nitrogen (0°, 16.0°, and 43.6°C), air (0°, 15.70°, and 45.1°C), carbon dioxide (0°, 10.0°, 20°, 30°, 40°, 50°, 60°, 70°, 80°, 90°, 100°, 137°, 198°, and 258°C), and ethylene (0°, 10.0°, 20°, 30°, 40°, 50°, 60°, 70°, 80°, 90°, 100°, 137.5°, and 198.5°C). He also calculated the values of the coefficient of expansion at constant pressure and at constant temperature and . To perform the experimental work he developed his most ingenuous apparatus, a manometer using the ideas of Gally-Cazalat (based on Pascal's principle), of pistons perfectly free to move while at the same obviating leakage. In principle, the Gally-Cazalat manometer is an inverse hydraulic press where the pressure is measured by a mercury column whose height is that of an air manometer in the ratio of the section of the small piston to that of the large one. Before Amagat all the attempts to convert Gally-Cazalt's idea into reality, had failed, they were full of considerable errors. Amagat's instrument was essentially a back-acting hydraulic press made gas-tight by means of viscous liquids such as molasses and castor oil. To secure freedom from leakage Amagat gave the large piston a suitable thickness and replaced the actuating water by a lubricating and, at the same time, viscous liquid (castor oil). He used the same principle for the small piston, except that there he used a sufficiently viscous liquid (molasses). According to Amagat the role of the molasses was somewhat different from that of castor oil; for while the oil continuously lubricated parts, oozing with extreme slowness between them in a way not to interfere with effective action; the molasses penetrated the space around the piston with great difficulty even at very high pressures. Amagat succeeded in essentially eliminating the resistance due to friction by impressing on both pistons a slight movement of rotation. For pressures above 400 atmospheres he measured the volume with the aid piezometers, as suggested to him by Peter Guthrie Tait (1831-1901).

The new apparatus was used to measure the properties of gases (oxygen, hydrogen, nitrogen, air, carbon dioxide, and ethylene) and liquids (water, ether, ethanol, methanol, propanol, allylic alcohol, acetone ethyl chloride, ethyl bromide, ethyl iodide, carbon disulfide, and phosphorus chloride) (Amagat, 1888a, 1893a). Once again, Amagat reported his data as tables and graphs giving the Pv vs P isotherms of two extreme cases (carbon dioxide and hydrogen) and an intermediate one (nitrogen). His conclusions were as follows:

(a) The pressure corresponding to the minimum of the product Pv, for successive isotherms, goes through a maximum value and then decreases. The curve that unites the minima converges to the initial ordinate, that is, the minimum disappears.

(b) The isotherms, within the P and range studied, do not seem to have a rectilinear behavior, they show a slight but clear curvature. This is true for all the gases and liquids studied.

(c) The coefficient of compressibility at constant volume, $(dP/dT)_v$, at all pressures and temperatures, decreases as the pressure increases. At all pressures it increases with the temperature (exception made of water).

(d) The coefficient of expansion at constant pressure, $(dv/dT)_P$, for a given temperature, increases initially as the pressure increases, then goes through a maximum at a pressure slightly below that of the minimum ordinate, and finally decreases. The coefficient initially increases with the temperature, goes through a maximum value, and then decreases. At higher pressures this maximum occurs at temperatures higher and higher and is less conspicuous. The pressure at which the maximum appears for a given temperature differs little from that for which the maximum for a given pressure occurs at the same temperature.

Between 1876 and 1882 Amagat also studied the elasticity of rarified gases (air, hydrogen and CO_2) at very low pressures (below 3 mmHg) and found that all of them followed the ideal gas law (Amagat, 1876, 1883a).

2. Expansion and compression of liquids and solids

Knowledge regarding the P-V-T behavior of liquids was even more limited. It was believed that besides water, the coefficient of compressibility of liquids increased with the temperature. In 1877 Amagat published an extensive memoir on the subject (Amagat, 1877) where he showed, contrary to the findings of other researchers, that this coefficient actually decreased when the pressure increased. Water was an exception to most of the gas laws described and this was due to the existence of a maximum in the density with temperature. At normal pressures, the coefficient of compressibility of water decreases as the temperature increases up to about 50°C. The experimental evidence had led many scientists (among them Tait and van der Waals) to believe that the maximum in density changed as the pressure increased. These considerations had not been published in France and were unknown to Amagat when he announced in 1887 that under the influence of pressure, he had made the maximum of density to retrograde to temperatures below 0°C. The examination of this phenomenon was made possible after Amagat built the high-pressure apparatus described above. With it he was able to determine the properties of liquid water and liquid ether at 1,100 atmospheres between 0 and 100°C, and at 3,000 atmospheres, between 0 and 50°C.To illustrate the difference between water and ether Amagat drew the pertinent isotherms in the plane P-V and the isobars in the plane P-T. The first figure showed plainly how the isotherms for water diverged as the pressure increases, contrary to what happened with ether and other liquids. The second figure was a clear illustration of the retrogradation of the temperature of the maximum of the density as the pressure increased. The average retrogradation between 0.6 and 4° was 0.0235°C per atmosphere (Amagat, 1893b).

According to Amagat, besides the anomalies of water just mentioned, the laws described previously, applied to both liquids and gases and showed how difficult it was to establish a distinguishing feature between these two states. In particular, in the entire region located at the right of the minima of the PV values, there was no sudden variation of these laws; the values of the coefficients of expansion and compressibility, as well as the densities, became of the same order of magnitude for the gases (nitrogen, oxygen, or carbon dioxide) and for the liquids (alcohol, ether, and water) studied. Amagat's publication (Amagat, 1893a) includes detailed tables giving the specific gravity and the compressibility coefficient of oxygen, nitrogen, air, hydrogen, alcohol, and water at 0°C, from 1 to 3,000 atmospheres, and the average coefficient of expansion between 0 and 20°C. The latter shows clearly how the coefficient for water increases while that of alcohol decreases as the pressure goes up. The compressibility of mercury, weaker than that of other liquids, was of particular interest because it allowed correcting the apparent compressibility of other fluids. The experimental result obtained by Amagat was 0.0000039.

Between 1887 and 1893 Amagat studied the solidification of liquids under pressure (Amagat, 1887, 1893c). He was the first to achieve the solidification of carbon tetrachloride and to confirm Kelvin's theoretical results that the pressure of solidification must increase with temperature. For carbon tetrachloride he found the solidification conditions to be (210 atm, −19.5°C) and (1,160 atm, +19.50°C). An interesting fact is that Amagat photographed the crystallization phenomena and observed that the crystals of carbon tetrachloride belonged apparently to the cubic system; he could distinguish cubes, octahedrons, cubic-octahedrons, etc. He also studied the solidification of water slightly below 0°C, which he achieved by decreasing the pressure on liquid water (Amagat, 1893c).

Between 1889 and 1890 Amagat studied in more detail the elasticity of solids and the compressibility of mercury (Amagat, 1889ab, 1890, 1891). This information was necessary to correct for the deformation of the piezometers with pressure; the variations the vessel dimensions were an important fraction of the variation of the volume of the liquid under pressure. First he determined the validity of the theoretical formulas describing the phenomenon: the coefficient of elongation α and Poisson's coefficient μ (the ratio between lateral contraction and elongation during traction). Mathematical manipulation of the equations allowed him to eliminate these parameters from the equations and obtain relations containing only variables which could be measured experimentally (Amagat, 1889a). Fo example, he was able to demonstrate that for cylinders having a flat base, the variation of the internal volume caused by the external pressure is equal to the variation of external volume caused by the same internal pressure. In this manner he was able to determine the coefficient of cubic compressibility K, α and μ, for glass, crystal, steel, copper, brass, metal delta and lead. Afterwards, in 1889, he was able to build an experimental set up capable of measuring the coefficient of cubic compressibility directly, up to 2,000 atmospheres, and confirm the measurements done indirectly (Amagat, 1888b).

In a following work (Amagat, 1890) Amagat determined the coefficient of cubic compressibility for glass and crystal, as a function of the temperature, between 0 and 200°C, and up to 200 atmospheres. He came to the interesting conclusion that for natural rubber, in spite of having a very large coefficient of elongation, the variation of volume when compressed everywhere, is of the same order as that of metals (Amagat, 1884).

3. The ratio $\gamma = c_P/c_V$, its measurement and application

The earliest and simplest method for determining the ratio of the two specific heats is that developed by Nicolás Clément (1779-1842) and Charles-Bernard Desormes (1777-1862) (Desormes and Clément, 1815): A gas is contained in a vessel at room temperature and at a pressure P_i slightly above atmospheric. Suppose that the volume of any small constant mass of the gas is V_i. By rapidly opening and closing a stopcock the small amount of gas under consideration is caused to expand adiabatically until its volume is V_f and its pressure P_0, the temperature dropping slightly below room temperature. Assuming that this expansion is adiabatic and approximately quasistatic, we may write

$$P_i\, V_i^{\gamma} = P_f\, V_f^{\gamma} \tag{9}$$

The gas is allowed to stand for a few minutes at constant volume until its temperature comes back to the initial value, thus causing the pressure to rise to the final value P_f. Since the initial and final temperatures are equal, we have

$$P_i V_i = P_f V_f \tag{10}$$

Eliminating V_i and V_f from the two equations we have

$$\frac{P_i}{P_0} = \left(\frac{P_i}{P_f}\right)^{\gamma} \tag{11}$$

$$\gamma = \frac{\ln\left(\frac{P_i}{P_0}\right)}{\ln\left(\frac{P_i}{P_f}\right)} \tag{12}$$

The pressures are usually measured with an open U-tube manometer containing a convenient light liquid.

The Clément-Desormes is very simple and fast but its accuracy depends on the measurement of the pressure after the adiabatic expansion. The free expansion leads to oscillations of the gaseous mass, a phenomenon discovered by Achiles Auguste Cazin (1832-1877). To diminish this problem to the minimum and thus increase the accuracy, Amagat developed an improved method in which the internal pressure is measured directly in a manometer inserted up to the center of the balloon and the increase in pressure is provided by a cylinder-piston arrangement in which the piston is connected to an oil volume resting on top of a layer of mercury that constitutes the internal manometer. The method permits a very accurate of the pressure and volumes, and hence, calculation of γ using eq (9). Amagat reported the experimental values of γ as 1.397 for air and 1.299 for carbon dioxide.

In 1895 Amagat studied the influence of pressure and temperature on the specific heats of fluids and their ratio (Amagat, 1885, 1895, 1896). His results allowed calculating c_P and c_V when one of them was known. He studied, in particular, carbon dioxide at about 100 atmospheres, and came to the following conclusions: At a constant density (0.124), when the pressure is increased, the value of c_P decreases faster that the values of c_V, hence their ratio γ decreases. At constant temperature, γ increases rapidly with pressure from 1.705 (50°C, 50 atm) to 4.633 (50°C, 100 atm). At constant pressure γ also decreases rapidly when the temperature is increased. The values determined by Amagat allowed predicting that beyond 100 atmospheres γ must go through a maximum and then decrease in a regular fashion, and that these variations must eventually diminish and disappear, as the temperature is increased, confirming the other results obtained for gases closer to the state of ideal gas, such as air and hydrogen.

Amagat utilized his findings on specific heats and their ratio to obtain an improved expression for the differential equation that describes the propagation of sound in a gas (Amagat, 1880b). The expression normally used is that developed by Poisson

$$\frac{d^2u}{dt^2} = a^2 \frac{d^2x}{dt^2} \qquad (13)$$

which assumes a priori that the gas behaves ideally. According to Amagat, the fact that the compression wave may lead to release of heat by condensation, can be taken into account to give a better expression for the constant a in eq. (13). This is done by considering that in traveling a small differential segment the wave produces an adiabatic compression of the gas, which can be handled by eq. (9) above. Amagat's final expression is

$$a^2 = \gamma \frac{P}{\rho} \qquad (14)$$

Comparison of eqs. (13) and (14) indicates that

$$a^2 = \gamma \frac{P}{\rho} \qquad (15)$$

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