Pierre Hippolyte Boutigny. The Spheroidal State of Matter Theory

Pierre Hippolyte Boutigny. Teoría del estado de la materia esferoidal

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Resumen

Pierre Hippolyte Boutigny (1798-1884), químico francés, fue el primer científico que estudió en detalle y por muchos años, el comportamiento de una gota de agua arrojada sobre una superficie caliente. El postuló que el resultado era un nuevo estado de la materia que bautizó con el nombre estado esferoidal. Hoy en día, este fenómeno se conoce con el nombre de efecto Leidenfrost.

Palabras clave
Carbón; combustión; efecto de variables; estado esferoidal, trementina.

Abstract

Pierre Hippolyte Boutigny (1798-1884), a French chemist, was the first scientist to study in detail, and for many years, the behavior of a liquid drop thrown over a heated surface. He postulated that the result was an additional state of matter that he named spheroidal state. Today this phenomenon is called the Leidenfrost effect.

Keywords
Coal; combustion; effect of variables; spheroidal state; turpentine.
Pierre Hippolyte Boutigny (1798-1884) was probably the first scientist to study in detail the physical phenomenon in which a liquid, close to a surface that is significantly hotter than the liquid’s boiling point, produced an insulating vapor layer that kept the liquid from boiling rapidly (Boutigny, 1840, 1841, 1843b, 1845, 1847b, 1850abc, 1855, 1856, 1860, 1861abc, 1880). Unfortunately, he reached the wrong conclusions and postulated that this insulated drop, which he named *spheroidal state*, was a new state of matter. Boutigny used the spheroidal state to explain a series of physical and chemical phenomena (i.e., Boutigny, 1843a, 1845, 1850a, 1855).

In his first paper, Boutigny wrote that although many persons had observed the peculiar behavior of water when drops of it were thrown over a very hot metal plate, very few scientists had paid attention to it (Boutigny, 1840). He mentioned that Johann Theodor Eller (1679-1760) seemed to have been the first scientist to describe it, although very superficially (Eller, 1746). Johann Gottlob Leidenfrost (1715-1794) had written that a drop of water projected over into an iron spoon heated reddish white, took a long time to evaporate and formed a globule, which turned on itself or remained motionless and transparent like a small sphere of crystal (Leidenfrost, 1756). In 1801, Martin Heinrich Klaproth (1743-1817) carried this experiment in a comparative manner, by putting a drop of water in capsules made of iron, platinum, and silver heated reddish white. The three drops behaved as described by Leidenfrost, except that the length of evaporation varied from one metal to the other (Klaproth, 1801). Benjamin Thompson (Count Rumford, 1753-1814), trying to recognize the cause of this phenomenon, exposed the inside of a silver spoon to the flame of a candle to coat it with black smoke. A drop of water poured into the spoon at ordinary temperature, rounded into a globule and was unable to wet the blackened surface. Rumford heated the spoon until he could not hold it by its end, without the drop of water being noticeably heated.

Rumford concluded from this result that the drop of water reflected the heat and prevented it from penetrating into its interior (Rumford, 1806). More recently, Claude-Servais-Mathias Pouillet (1790-1868) conducted many experiments trying to identify the electricity that developed during a chemical reaction [as postulated by Antoine César Becquerel (1788-1878) (Becquerel, 1825)], and reported that he had been able to fill with water one half of a platinum spoon heated red, white, and keep it without movement or contraction, for 15 minutes. He also found that water darkened with ink or with fine carbon powder, evaporated very rapidly. According to Pouillet, these results indicated that in the first case the heat radiated by the spoon at red, white passed through the pure water without being absorbed, but was absorbed in the second case (Pouillet, 1827). V. (Lechevalier, 1830), an army officer, also found the same result as Pouillet; a drop of water held in a platinum spoon heated red, white could be kept for a long time without evaporation, but heated red brown, it began boiling immediately and transformed promptly into steam. In addition, putting water in an incandescent flask, followed by closing it with a stopper of the same metal, and then opening again, did not change the vapor pressure, indicating that the temperature had not changed. Alexander Edouard Baudrimont (1806-1880) had verified Lechevalier’s experiment and justified the result stating that the amounts of vapor formed were able to lift the liquid if they were formed fast enough to avoid its adherence to the flask. This liquid was heated by radiation and constantly produced the vapor that avoided its heating by direct contact, and its boiling (Baudrimont, 1830). August Laurent (1807-1853) also carried experiments on the subject and claimed that the water did not touch
continuously the wall of the crucible but did it in an oscillatory manner, in the same manner that a ball dropped over a horizontal surface did. The water drop was subject to a variable vibratory motion produced by the vapor generated at the bottom surface each time the drop touched the crucible, and thus successively (Laurent, 1836).

Boutigny thought that all the explanations given so far were inadmissible; the purpose of this first publication was not to offer another one but to present his preliminary results and indicate his intention to conduct enough experiments to reach an explanation that harmonized the known facts and a supported a proper theory. Boutigny suggested naming the phenomenon *calefaction* (Boutigny, 1840).

It was generally accepted that water presented this phenomenon only at very high temperature and in a crucible made of lead. Lead melted at 260 °C, indicating that water could be “calefacted” (heated) up to a temperature slightly below this temperature. Boutigny believed that calefaction played an important role in the explosion of boilers and was intent in studying this possibility in detail. He also investigated the existence of this phenomenon in a variety of liquids, among them, alcohol in different concentrations, ether, anhydrous sulfur dioxide, essence of turpentine and of lemon, basic or acid saline solutions, acids, etc. (Boutigny, 1840).

Boutigny observed that ether distilled dropwise in a platinum crucible heated almost red, “calefacted” (heated) as well as water; that is, the mass turned round, without showing any sign of boiling. Then it stirred and did not seem to wet the crucible. Interesting enough, its quantity was always decreasing, but much less promptly than if the vessel had been cold. During this slow vaporization a very penetrating vapor was released, which had nothing in common with that of ether. Boutigny attributed it to the formation of an aldehyde, which developed only in the presence of air (Boutigny, 1840).

Another remarkable case was that of anhydrous sulfur dioxide, a very volatile compound, which could only be kept liquid in well-sealed vessels. Nevertheless, Boutigny observed that projecting a few drops of sulfur dioxide in a small platinum crucible heated almost red, this compound behaved in the same manner as water and ether. It was agitated strongly at first, then becoming rounded and motionless, and even seemed to crystallize. Boutigny first thought that sulfur dioxide absorbed the oxygen of the air and transformed into sulfuric trioxide, but this idea was not justified by the results; he supposed afterwards that the high heat of vaporization of sulfur dioxide led to a sufficiently great drop in temperature to solidify it (itself or the humidity of the air) (Boutigny, 1840).

The review committee of this paper composed by François Arago (1785-1853), Théophile-Jules Pelouze (1807-1867), and Pierre Jean Robiquet (1780-1840), considered the results of this paper very important and suggested that the Académie des Sciences recommend Boutigny to extend his research efforts on the subject.

In his following publication (Boutigny, 1841), Boutigny stated 22 physico-chemical propositions about calefaction and the spheroidal state of substances, among them: (1) Although three states were usually admitted for substances (solid, liquid, and gas), there was a fourth one, the *spheroidal state*, located between the liquid and the gaseous ones; (2) all substances that generated a vapor without decomposing, could pass to the spheroidal one until they vaporized completely; to do so, it was enough to project them over a plate heated about their boiling point. For water, this temperature was 200 °C. In this state, these substances did not touch the heating surface and remained at a temperature below
their boiling point. The pertinent temperature was 96 °C for water, 34 °C for diethyl ether, and -10.50 °C for sulfur dioxide; (3) the temperature of the vapor of these substances was always equal to that of the vases where they formed. Their vapor pressure was related to that of their vapor and not to that of the spheroidal that created it; (4) in the case of a substance that passed directly from the solid to the spheroidal state, the temperature of the latter increased immediately above that of the melting point, while the temperature of the substance remained at the initial temperature; (5) when gravity prevailed over the force, which determined the spheroidal state of bodies, they took the ellipsoidal form, which in this particular case was only a modification of the spheroidal form; (6) the reasons for the spheroidal state was to be found in the competition between centripetal and centrifugal forces, or on the preponderance of the attraction of adhesion in the body being heated and the heating one, which prevented the contact and, consequently, the chemical action, or in the existence of caloric fluids, the positive and the negative, like in electricity; and (7) nowadays, there were not enough arguments to select one of these hypotheses, nevertheless, the third one seemed the most attractive one. Maybe these three hypotheses were modifications of a single cause or force (Boutigny, 1841).

According to Boutigny, analysis of these propositions forced one to accept that the laws of heat transfer as known, were not applicable to bodies in the spheroidal state. To the question what is the spheroidal state? Boutigny answered that it was a particular state of matter, with properties different from those that characterized the three standard states. So, the thermal and tension equilibrium present in the solid, liquid, and gas states, was never established in the spheroidal state, simply because it was inherent to bodies in the spheroidal state (Boutigny, 1841).

The next publication gave an even more detailed description of the phenomena that characterized the behavior of the substances projected over a hot surface, based on the results of 34 experiments conducted under a wide variety of conditions (Boutigny, 1843b, 1847b). The basic purpose of this memoir pretended to answer the following questions: (1) the ultimate limit of temperature, at which this phenomenon took place; (2) the law of the evaporation of water in its spheroidal condition; (3) the temperature of the liquids in their spheroidal state, as well as that of their vapors; (4) if the radiated caloric traversed the spheroids or was reflected; (5) if all bodies could pass to the spheroidal condition; (6) if there was contact between bodies in their spheroidal condition and the surfaces upon which they were formed; and finally (7) if this phenomenon played any part in the explosions of steam boilers (Boutigny, 1843b, 1847b).

(1) According to most physicists, the white temperature was necessary for the water to exhibit the phenomenon in question, and it ceased near the temperature of red-brown where the liquid spread over the surface of the capsule, wetting it and evaporating rapidly. According to Boutigny, this was not so. Four experiments were conducted to justify this claim. For example, a drop of water in the spheroidal state over a polished silver capsule heated to 200 °C, was carefully transferred to an oil bath heated to 150 °C; the water was found to maintain its spheroidal condition until the temperature of the bath descended to 142 °C; afterwards it was seen to moisten the surface and evaporate rapidly. This then had been found to be the lowest temperature at which water maintained the spheroidal state (previous experiments had shown that water passed to the spherical state at 171 °C). If the quantity of water consisted of several drops, its sphericity was lost at 153 °C. Additional experiments showed that the same temperature proportions were valid for alcohol and
for ether: alcohol passed into the spheroidal state at 134 °C and ether at 61 °C. Anhydrous sulfur dioxide did not follow this law, but it was not an easy substance to experiment with: Although it assumed and retained the spheroidal condition much below the boiling point of water, it soon become hydrated by absorbing and solidifying the air humidity. Boutigny commented that in this singular phenomenon water vapor solidified in boiling water. The above result established that the temperature necessary to cause a body to pass to the spheroidal state was higher as its boiling point was greater (Boutigny, 1843b, 1847b).

The next series of experiments were to ascertain the law of the evaporation of the water while in its spheroidal condition. At 200 °C, 0.10 g of water took 3.30 minutes to evaporate; at 400 °C, the same quantity of water was evaporated in 1.31 minutes; at a dull red heat, in 1.13 minutes; and at a bright red, in 0.50 minutes. Boutigny commented that his results could vary, within certain limits, with the humidity of the air, its pressure, the possible presence of local air currents, the form of the capsule, its degree of polish, the thickness of the wall, etc. Anyhow, they clearly opposed those reported by Klaproth that the rate of evaporation decreased with increased temperature. Boutigny believed that the difference was since Klaproth had carried his experiments in iron vessels and that the adherence of the oxide of the metal had interfered with the accuracy of the results. Anyhow, Boutigny’s results established clearly that bodies in their spherical condition remained constantly at a temperature lower than that of their ebullition, without regard to the temperature of the containing vessel, being, for example, for water, +96.7 °C; absolute alcohol, +75.5 °C; ether, +34.25 °C; ethyl chloride, +10.5 °C, and sulfur dioxide, -10.5 °C (Boutigny, 1843b, 1847b).

Boutigny was the first to experiment with sulfur dioxide and notice its remarkable and unexpected behavior on hot surfaces. He heated to white a platinum capsule and poured into it several grams of anhydrous sulfur dioxide. Observing the neck of the flask containing the sulfur dioxide at the part which corresponded to the hand, he noted that the dioxide was boiling very rapidly, and that this phenomenon ceased immediately when it fell in the capsule and presented all the physical phenomena presented by water. While in the capsule, the evaporation took place extremely slowly and without any sign of boiling. When carrying the operation in humid weather, dioxide became opal and lost more and more its transparency until it became solid. Inspection of the solid showed that this solid was almost entirely composed of water. This phenomenon did not occur in dry air: Now the sulfur dioxide did not solidify and evaporated without leaving a residue. Throwing distilled water drop by drop into sulfur dioxide in the spheroidal condition, it froze, even if the capsule was white hot (Boutigny, 1843b, 1847b).

The vapors arising from the spheroidal liquids, had their temperature much elevated; and where water and an iron vessel were used, it was decomposed, furnishing hydrogen gas.

The question if the heat traversed the liquids in their spherical condition without combining or it was reflected, was very important. Up to the time of this paper it was generally accepted that it was traversed. Boutigny proved clearly that the heat was reflected and not transmitted. To do so, he heated a platinum capsule red hot and placed a small glass bulb containing water very near the bottom of the vessel; the radiated heat soon heated the vessel and made the water boil. It was now withdrawn, and water poured in. This water immediately assumed the spheroidal condition, and into it was plunged the small bulb. No signs of boiling were noticed, showing clearly that no heat rays (caloric) penetrated the spheroid of water. Adding small particles of wood, sand, lampblack, or iron to the water, did
not change the result. The iron, much heavier than the water, did not touch the capsule but
remained in the spheroid until its complete evaporation (Boutigny, 1843b, 1847b).

Boutigny claimed that all liquid bodies, including non-volatile oils and volatile solids,
could pass into the spheroidal state. The corresponding temperature had to be as higher as
possible from that of their boiling point. Boutigny proved this claim with iodine. He threw
about one gram of iodine into a capsule heated to redness, the iodine assumed at once the
spheroidal condition and became surrounded with rare and transparent vapors of it vapor.
The source of heat was now withdrawn. Immediately after, the iodine passed to its ordinary
liquid state, the capsule was moistened and the iodine seen to boil violently, releasing an
abundant number of beautiful vapors. According to Boutigny, this experiment demonstrated
clearly the difference existing between the evaporation of a body in its spheroidal condition,
and the evaporation of the same body by boiling (Boutigny, 1843b, 1847b).

This experiment was repeated with various other solid substances. For example, the
two chlorides of mercury in the spheroidal state were transparent like water and did not
decompose. Sodium chloride and ammonium chloride and carbonate did not decompose.
Carbon chloride burned sometimes with a beautiful violet flame. When it evaporated without
inflammation, it left in the capsule a carbon residue. Boutigny remarked that for all compounds
that contained carbon, this substance was the last to burn (Boutigny, 1843b, 1847b).

Boutigny carried several experiment proving that there was no contact between
bodies in the spheroidal state and the surfaces on which it originated, and that the interval
between them was measurable and permanent. For example, he threw one or two drops
of water on a heated flat silver plate, while putting a candle on one side of the capsule so
that the middle of the flame was at the level of the capsule, From the other side he tried and
succeeded seeing the light of the candle between the spheroid and the capsule. This meant
that the globule remained constantly at a small distance from the wall, or, on the contrary,
that it made rapid oscillations touching and moving away from the wall (as proposed by
Laurent, as mentioned above). Boutigny believed that the first explanation was the correct
one. If the candle was raised, he could see forming, on the other side of the spheroid, a cone
of light whose base was at the half-circumference of the drop of water, the latter acting as a
biconvex lens. For better results, Boutigny recommended carrying this experiment at night
or in a dark apartment (Boutigny, 1843b, 1847b).

Miscellaneous

Ether to aldehyde

Boutigny described in detail the curious transformation of ether into aldehyde in the
presence of air (Boutigny, 1843a). It was common knowledge that adding ether to a metal
crucible, or of another non-porous material, and heating the vessel with an alcohol lamp,
resulted in the immediate vaporization of the ether, without any change in its properties.
But adding the ether to a crucible previously heated, produced an unpredictable result: the
ether assumed a round shape and passed into the spheroidal state: It did not wet and did
not touch the crucible, and its temperature remained below that of its boiling point, while
the vapor that it provided, was always in thermal equilibrium with the walls of the crucible
and not that of the liquid. This aldehyde vapor burned with a flame so transparent that it
could only be seen in a very dark place, and it strongly irritated the nasal mucosa and the conjunctiva (Boutigny, 1843a).

Boutigny could only speculate about the chemical reaction that had transformed the ether into aldehyde. The accepted chemical formula of the ether, $\text{C}_4\text{H}_{10}\text{O}$, contained 4 carbon atoms, 10 hydrogen atoms and 1 oxygen atom, while the aldehyde created contained two 8 hydrogen atoms and 2 oxygen atoms, $\text{C}_4\text{H}_8\text{O}_2$. According to chemistry, for the ether to transform into an aldehyde, it only needed to remove two atoms of hydrogen and absorb one atom of oxygen, and this was indeed what took place in this experiment (Boutigny, 1843a).

Boutigny added that during this experiment he was surrounded by an atmosphere containing abundant aldehyde; he noticed that the resulting breathing gave him the same well-being as drinking a good wine and the feeling of being younger. This led him to speculate about the potential use of this vapor in medicine, particularly for the treatment of airways illnesses (Boutigny, 1843a).

Marsh apparatus spots

According to Boutigny, it was almost impossible to assure that a stain produced by the Marsh apparatus was arsenical. He now reported an artifice that could be easily performed to answer the question (Boutigny, 1845). For this purpose, the stain was separated with a glass rod wet with a solution of 1% nitric acid and put in a glass capsule. A drop of the same acid was added, and the mixture heated slightly. If the spot was arsenical, it disappeared almost immediately because the arsenic had been converted into a colorless mixture of arsenious and arsenic acids. The capsule was allowed to cool, and the colorless spot treated with a stream of hydrogen sulfide obtained by treating ferric sulfide with sulfuric acid. Therefore, the colorless spot turned yellow. According to Boutigny, the release of hydrogen sulfide from iron sulfide was a prerequisite for success. Hydrogen released from the reaction of antimony sulfide with HCl always left a deposit of sulfur, which impaired the sharpness of subsequent reactions (Boutigny, 1845).

The yellow spot was dissolved in one gram of pure aqueous ammonia and added dropwise to a platinum capsule heated red. This transformed the colorless ammoniacal solution into the spheroidal state, which was very flat; it had a horizontal diameter which was constantly diminishing, while its axis or vertical diameter remained invariable. Touching the colorless spheroid with a glass bar wet in HCl turned it yellow; touched with ammonia discolored it again. According to Boutigny, these staining and fading alternatives, which could be repeated almost indefinitely, were typical of arsenic sulfide (Boutigny, 1845).

Boutigny added that he had also applied the spheroidal state to the analysis of a microscopic blood stain and Henri Chambert made another experiment using water in the spheroidal state as an oxidizing agent to burn the organic matter contained in the salts resulting from the evaporation of urine (Chamber, 1845).

The incombustibility of humans

Boutigny wrote a short paper trying to explain the apparent lack of damage of people seen running over burning coal, submerging their hands in liquid metals, eating fire, etc. by the presence of a protective layer of spheroidal matter (Boutigny, 1849ab, 1850ab).
The origin of coal

In one of his many experiments, Boutigny wrote that all volatile oils in the spheroidal state behaved in the same way, in that the proportion of carbon was always increasing in the spheroid (Boutigny, 1847b; experiment 95). The products, which volatilized differed from each other like the oils themselves and it was understood that an oxygenated oil must give other products than a hydrocarbon. In this experiment he described the results observed when passing the essence of turpentine to the spheroidal state. The oil was seen volatilizing slowly without giving any noticeable vapors, and slowly staining from the lightest yellow to the yellow brown. Afterwards, the vapors became visible because they contained carbon black in suspension. The color of the essence continued darkening, passing from brown to blackish; the spheroid showing signs of signs of boiling, spreading over the capsule and covering it a black varnish very rich in carbon, but still containing essence, becoming a real artificial coal. Naphtha and petroleum behaved in the same manner. Boutigny believed that all hydrocarbons also behaved in the same manner (Boutigny, 1847b).

Boutigny added that the part which volatilized first was the richest in hydrogen, hence the increase in the proportion of carbon in the spheroid and the rise in temperature from its boiling point, so that a moment arrived when the temperature of the capsule was no longer high enough to maintain the dehydrogenated gasoline in a spheroidal state; hence, it spread over the capsule. The liquefaction of the spheroid could be stopped momentarily by raising the temperature of the capsule, but then the vapors enveloping the spheroid would ignite, returning to the phenomenon of ordinary combustion. From here on, Boutigny used geologic arguments to extend this state to the formation of coal deposits (Boutigny, 1847b, 1855).

Summary of the laws that govern matter in the spheroidal state

In 1880, Boutigny, forty years after he began his experiments about spheroidal state, summarized his results as follows (Boutigny, 1880):

**First law.** Temperature. The temperature of bodies in the spheroidal state is always lower than that of their boiling; it is +97 ° for water.

**Second law.** Temperature imbalance. The body in the spheroidal state never comes into thermal equilibrium with the vessel, which contains it. Its temperature is in constant equilibrium, whether it is in a capsule in the open air or in the muffle of a cup furnace. Surprisingly, the vapor which emanates from the spheroidal state is always in thermal equilibrium with the vessel.

**Third law.** Reflection of radiant heat. The matter in the spheroidal state reflects the radiant heat.

**Fourth law.** Volume and mass of spheroids. The volumes of matter in the spheroidal state are in inverse ratio to their density, and their masses are equal.

**Fifth law.** Repulsive force at a sensitive distance. This law is the most important of all, the richest in deductions, because we consider it the antagonist of universal attraction.

This statement was justified with following experiment, On the floor of the Pantheon (Paris), in the axis of the dome, a large platinum capsule was placed on a live charcoal fire, having a temperature as high as possible. Water was then poured from the top of the Pantheon (about 70 m high) into the capsule without wetting it, and which instantly passed
into the spheroidal state. This experiment was repeated when it rained or when hail fell, with identical results. Did these results meant that the water and the hail were supported in the capsule by the vapor which enveloped them? Boutigny’s answer was negative: they were instantly repelled by the repulsive force that the heat created in the capsule (Boutigny 1880).

This experiment was now repeated with non-volatile bodies that cannot be distilled, but are thermally labile, such as small fragments of wax, tallow, stearic or margaric acid, or a few drops of oleic acid or a fixed oil. The capsule was heated as before and small fragments or drops of above material projected onto it. Since molecular movements are not transmitted with a very high speed, the substance in question remained suspended on the capsule without vapor (nonvolatile) and without gas coming from its decomposition. Consequently, the gases released from its decomposition came not from its surface, but from its interior. They ignited and the spheroid disappeared. The only possibility was repulsion by the capsule (Boutigny 1880).

References


