Benoit Paul Emile Clapeyron: A Short Bibliographical Sketch

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Abstract: Clapeyron is well known in thermodynamics through the Clausius–Clapeyron equation that describes the variation of the vapor pressure with temperature; few are aware that he made his career as a railroad engineer and locomotive designer. Here we give a description of his life and his scientific and professional achievements as an engineer in a turbulent epoch in the history of France and Russia. It is shown that Clapeyron was able to develop his equation without making use of the second law and the concepts of absolute temperature and entropy, ideas unknown in his time.

Every student of thermodynamics becomes familiar with the equation of Clausius–Clapeyron when learning about the influence of temperature on the vapor pressure of a pure compound

$$\frac{dP}{dT} = \frac{\Delta H}{T\Delta V} \tag{1}$$

where ΔH and ΔV are the changes in enthalpy and volume, respectively, that take place during the phase change. The name Clausius appears several times during the discussion of the second law and its consequences, but not so that of Clapeyron, in spite of his being one the three C's (Carnot, Clapeyron, Clausius) [1] who set the fundamentals of thermodynamics on their definite basis. The purpose of this paper is to provide background on the life of Clapeyron, to describe his scientific and engineering activities, and to show the critical relevance of his paper [2] that put the second law of thermodynamics on a solid basis.

Benoit-Pierre-Emile Clapeyron (Figure 1) was born in Paris on 26 February 1799 and died there on 28 January 1864. He graduated from the École Polytechnique in 1818 and then attended the École de Mines. After the defeat of Napoleon in 1814 the Emperor of Russia, Alexander I, realized that scientific knowledge and its application in military techniques and industrial development were essential to keep the country strong and powerful. To advance these ideas he set up a team of engineers to improve the roads and bridges of Russia, and in 1820 he requested some engineers from the French government to provide a nucleus for this corps as well as to engage in instruction. The École Polytechnique selected Clapeyron and his friend and classmate Gabriel Lamé for this purpose; they were sent to Russia immediately after their graduation from the École de Mines in 1820.

Having strong liberal ideas, both Clapeyron and Lamé had participated actively in the political events that took place during the regime of Napoleon. After Napoleon's fall and the return of the monarchy, they barely avoided expulsion from the École and, for that reason, took the opportunity to go to Russia as a voluntary exile. The two young engineers taught geometry, calculus, applied physics, surveying, and the art of construction at the Institute of Ways of Communication (Institut Putei Soobshchneniya) of Saint Petersburg and engaged simultaneously in construction work. The school aimed at graduating civil engineers rather than military engineers; its students trained for six years at the end of which they were commissioned as lieutenants.

Both Clapeyron and Lamé remained in Russia for 10 years, and during that time, they published the first results of their joint mathematical and engineering efforts in a number of journals like the *Journal de Voies de Communication de Saint Petersburg*, the *Journal du Génie Civil*, and the *Bulletin des Sciences Mathématique de Férussac*, as well as various works published in France and Germany. In particular, Navier recommended that a paper on the internal equilibrium in solids subject to external forces should appear in the *Recueil des Savants Étrangers* [3], published by the Académie des Sciences for communications from nonmembers. In this paper they made a theoretical analysis of the stress and stability problems they faced when designing the new dome of the reconstructed St. Isaac Cathedral of Saint Petersburg.

While in Russia, Clapeyron and Lamé enjoyed the friendship of Eugène Flachat, another exiled engineering graduate from the École Polytechnique, who would play an important role on locomotive design in France. The revolutions of 1830 in Poland and France and the stiffening of the position of the new czar Nicholas I made unsustainable the position of foreign scientists, in particular of Clapeyron and Lamé, because of their well-known liberal positions. In 1831 they returned to France. A fascinating description of Lamé and Clapeyron's stay in Russia is found in a paper by Bradley [4].

At the time of Lamé and Clapeyron's return home the Liverpool-Manchester railroad had just been commissioned, but in France railways were just beginning to be constructed, and early ventures had been economic failures. In 1826 Seguin and Biot had been assigned the construction of the Saint-Étienne-Lyon line, which did not consider the transport of passengers. Clapeyron and Lamé had the vision to see the great future reserved to railways as a new means of transportation, and immediately thereafter Clapeyron engaged in railroad engineering, specializing in the design and construction of steam locomotives.

The first important railroad built in France was the short line from Paris to Le Pecq, generally called the railroad from Paris to Saint Germain, authorized by law in 1835. The section of the railway to Saint Germain was not completed until 1847

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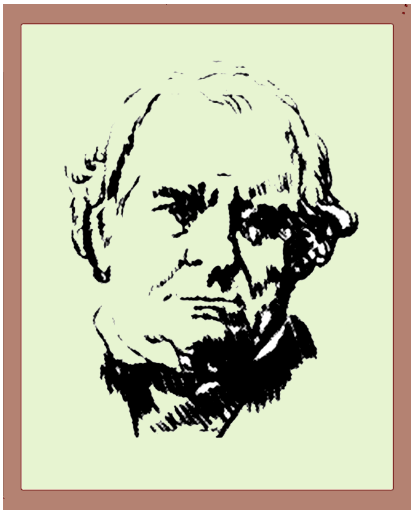

Figure 1. Portrait of Clapeyron.

because the Seine had to be crossed and the track had to overcome the particularly long-continuous-grade hill upon which the town of Saint Germain stands. Clapeyron and Lamé were strong promoters of this line and in 1835, together with other engineers were put in charge of it.

In 1836 Clapeyron and Émile Péreire traveled to England to order some locomotives that would negotiate the ascent to Saint Germain. Robert Stephenson, the most famous of the builders of locomotives (the Rocket), was approached for this task, but he found Clapeyron's designs too difficult and declined the contract. Sharp, Roberts, and Company, a firm that made railway locomotives in one of the earliest applications of the use of interchangeable parts, agreed to take the contract and built the engines according to Clapeyron's design [3]. According to Dunham [5], the ascent problem could be solved thanks to the invention of the atmospheric engine by E. Flachat and its construction by Hallet de Arras.

Lamé was offered the chair of physics at the École Polytechnique shortly after they began their work, and Clapeyron was left to head the railroad project. The Paris–Saint Germain line had an unqualified financial success and was the first to win the support of the future railroad czar, the Baron James Rothschild, a partner in the society put up to exploit the concession given to Péreire in 1835. Between 1837 and 1845 Clapeyron was busy with the study and design of railroads in the north of France, took part in their construction and remained until his death, as consultant engineer of the company that took charge of the concession [3]. In 1852 he took part in the building of other railroads, like the ones in Midi, Bordeaux–Cette, and Bordeaux–Bayonne.

Clapeyron not only dedicated himself to the design and building of railroads, he was also active in many different aspects of mechanical engineering. Metallic bridges, like the ones over the Seine at Asnières, over the Garonne, Lot, and Tarn, were built according to his designs which included an easy and elegant method for calculating the supporting elements of a girder that carries a uniformly distributed load and is supported at any number of points. Clapeyron's publication on the internal equilibrium in solids subject to external forces gave place later to a series of practical rules for the design of springs in engines and train cars. These rules were the subject of Clapeyron's inaugural conference given on the occasion of his being elected to the Académie des Sciences in 1858, replacing Cauchy. He served in numerous committees of the Academy, including the one that awarded the prize in mechanics, the investigation of the project of piercing the Isthmus of Suez, and the application of steam to the Navy.

Clapeyron's election to the Académie has several twists of destiny. He had to run twice to be elected, first in 1847 when he lost to Charles Combes, a mining engineer, and second, in 1848 when he won by an ample majority over three other candidates, one of them being Léon Foucault who received three votes. The winner of the first round, Charles Combes, was fated to be the one to read the eulogy to Clapeyron at the Académie after his death in 1864 [3]. Foucault was a physician turned physicist who invented the pendulum that carries his name, which showed experimentally for the first time that the Earth spins on its axis. Foucault was also presented three times as a candidate to the Académie until he finally succeeded in being elected in 1868.

Besides his professional activities, Clapeyron also devoted part of his time to teaching. In 1844 he was appointed professor at the École des Ponts et Chaussées and remained in that position until 1859. At the École he taught, in particular, the course on steam engines, and he made use of the concepts of the equivalence between heat and work, as well as the Carnot cycle.

The best description of Clapeyron as a human being is probably the one given in the note that his partner, Émile Péreire, gave to Combes just before he read his eulogy: "We were together since 1832, and he never left me. I have never done an important business without consulting him; I have never met someone having such a firm and straight judgment. His modesty was so great and his character was so good that I never met someone who was his enemy" [3].

Clapeyron and Carnot

Sadi Carnot visited his exiled father Lazare in 1821 in Magdeburg where the first steam engine had been installed three years earlier. Lazare Carnot become very interested in the engine's operation and had long discussions with his son on its theory. The subject was so fascinating that Sadi Carnot left Magdeburg filled with enthusiasm to develop a theory for steam engines. According to Mendoza [7], "The problem occupying Carnot was how to design good steam engines. Steam power already had many uses—draining water from mines, excavating ports and rivers, forging iron, grinding grain, and spinning and weaving cloth—but it was inefficient." As early as 1822 Carnot was intent on calculating how much work can be obtained from one kilogram of steam, and he made use of an adiabatic stage followed by an isothermal one. Eventually Carnot summarized all his ideas in a 64-page brochure, *Réflexions sur la puissance motrice du feu et sur les machines propres à developper cette puissance,* published on June 12, 1824. Although very few copies of the book were sold, on July 26 of 1824 Pierre Girard, a prominent engineer, gave a long review of it to the Académie des Sciences in Paris. Among the academicians present were Arago, Fourier, Laplace, Ampère, Fresnel, Legendre, Poisson, Cauchy, Dulong, and Navier. Pierre Girard's review was very positive and was published in the *Revue Encyclopédique*, a literary journal devoted to criticism of the most noteworthy works produced in the sciences, industrial arts, literature, and the fine arts.

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As mentioned above, Carnot's little treatise went practically unnoticed, and no one seems to have been impressed by it. Ten years later (1834), however, Émile Clapeyron published a paper in which he took up some of Carnot's verbal discussions, formulated them in analytical terms [2], and drew for the first time Carnot's cycle, using the Watt indicator diagram, already familiar to engineers. Clapeyron emphasized the fact, already contained in Carnot's work, that the efficiency of a reversible engine depends only on the temperatures of the source and sink. In the introduction to his paper Clapeyron wrote that one of the basic ideas contained in Carnot's work is that "it is impossible to create motive power or heat out of nothing," and that from here one can conclude, for example, that the difference in the heat capacities of a gas ($C_P - C_V$) is the same for all gases.

Clapeyron's paper also appeared in England and Germany so that despite the rarity of the original, Carnot's work was generally available and associated with the name of Clapeyron who was widely recognized as a leading steam engineer. Nevertheless, not only was Clapeyron's original paper ignored by other engineers, but he himself made only one passing reference to it until the work of Kelvin and Clausius made its true significance generally known. According to Kerker [6], the 1853–1854 edition of the class notes of Clapeyron's course (as taken by his students) given at the École des Ponts et Chaussées includes a discussion of the equivalence of heat and work that he attributes to Regnault, without making any reference to the work of Joule, Kelvin, Mayer, and others on the subject. The notes mention Carnot's results and Clapeyron's earlier work, but no attempt is made to reconcile the now accepted principle of the equivalence of heat and work with the treatment of the Carnot cycle that had used the old caloric theory.

As we have seen, Clapeyron worked most of his life on the design and theory of steam engines. His most important research paper dealt with the regulation of the valves in a steam engine to determine the optimum position for the piston at which the different valves should be opened and closed [6]**.** His analysis of the problem was based on the Watt diagram, which Clapeyron had employed in his exposition of Carnot's work [2]. Interestingly enough, the Carnot cycle does not yield a specific solution to this question, but it does give the maximum possible effect that the mechanism can achieve. It is remarkable then that at no point in this paper does Clapeyron gives credit to Carnot.

The Clapeyron Equation

We are all familiar with the standard derivation of the Clausius–Clapeyron equation using the Maxwell relations, but few are aware that Clapeyron derived it in 1834 when the second law was still to be stipulated, entropy was a nonexistent concept, and James Clark Maxwell was only three-years-old. Clapeyron came to his equation as a corollary of his putting the Carnot cycle on a mathematical basis. While discussing the fundamental concepts developed by Carnot, he compared two differential reversible Carnot cycles (Figure 2) that differ in the working substance and in the way heat is added and removed from the cycle. In the first cycle (Figure 2a) an ideal gas goes through a Carnot cycle where the heat source and the heat sink are two isotherms separated by dT, while in the second cycle (Figure 2b) a saturated liquid is first evaporated and then the vapors condensed at a slightly lower temperature. We will first use simple modern concepts to derive Clapeyron's equation and then repeat the procedure along the lines used by Clapeyron himself. Let us consider the cycle performed by an ideal gas. Because the two sources are separated by a differential, we can approximate the adiabatics by isochores and express the heat received, net work produced, and the thermal efficiency of the cycle (η) as follows (Figure 2). The subscripts H and C represent the hot and cold sources, repsectively.

$$Q_{\mathrm{H}} = RT_{\mathrm{H}} \ln \frac{V_2}{V_1} \tag{2}$$

$$W_{\mathrm{net}} = RT_{\mathrm{H}} \ln \frac{V_2}{V_1} - RT_{\mathrm{C}} \ln \frac{V_2}{V_1} \tag{3}$$

$$\eta = \frac{W_{\mathrm{net}}}{Q_{\mathrm{H}}} = \frac{RT_{\mathrm{H}} \ln \frac{V_2}{V_1} - RT_{\mathrm{C}} \ln \frac{V_2}{V_1}}{Q_{\mathrm{H}}} = \frac{R \ln \frac{V_2}{V_1} dT}{RT_{\mathrm{H}} \ln \frac{V_2}{V_1}} = \frac{dT}{T_{\mathrm{H}}} \tag{4}$$

For the second cycle where the two phase changes occur at constant pressure and temperature, and the heat effect is equal to the latent heat, ΔH, we have

$$W_{\mathrm{net}} = P_{\mathrm{H}}(V_2 - V_1) - (P_{\mathrm{H}} - dP)(V_2 - V_1) \tag{5}$$

so that

$$\eta = \frac{W_{\mathrm{net}}}{Q_{\mathrm{H}}} = \frac{(V_2 - V_1)dP}{\Delta H} = \frac{\Delta V dP}{\Delta H} \tag{6}$$

According to Carnot, both engines must have the same efficiency because they are connected to the same reservoirs and operate reversibly. Hence, equating equations 4 and 6 we get

$$\frac{\Delta V dP}{\Delta H} = \frac{dT}{T} \tag{7}$$

$$\frac{dP}{dT} = \frac{\Delta H}{T \Delta V} \tag{8}$$

The actual mathematics in Clapeyron's paper is somewhat less straightforward and reflects the knowledge available at his time. Clapeyron begins his analysis of the cycle that uses an ideal gas (he does not call it ideal) using the Mariotte–Gay-Lussac law in the form

$$Pv = \frac{P_0 v_0}{267 + t_0}(267 + t) \tag{9}$$

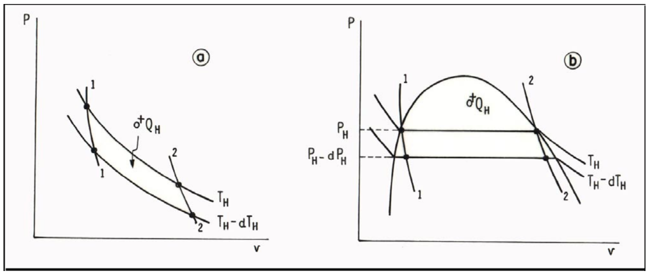

Figure 2. (a) Reversible Carnot cycle using an ideal gas. (b) Reversible Carnot cycle performed within the saturation envelope. 1→1 and 2→2 are adiabatics.

Figure 3. View of the side of the Eiffel tower with Clapeyron's name. Courtesy of Anthony Atkielski.

and then defines R as

$$\frac{P_0 v_0}{267 + t_0} = R \tag{10}$$

First, we notice that Clapeyron does not use the concept of absolute temperature and second, that the gas law refers to a zero located at 267 °C. Clapeyron goes on to draw a differential Carnot cycle in the PV plane, using the words *heat source* and *impermeable envelope* to define the isotherms and adiabatics. Because the pressure and volume differences are differential, the resulting cycle is a quadrilateral that can be approximated by a parallelogram. By writing the heat balance of the isothermal stage he arrives at the following equation that expresses the heat transferred.

$$Q = R\ (B - C\ \log P) \tag{11}$$

According to Clapeyron, B and C are undetermined functions of the temperature, function B will formally vary from one gas to another but is probably identical for all simple gases. Constant C, in particular, is assumed to be positive and independent of the nature of the gas. Equation 11 is arrived at by making the (wrong) assumption that dQ is an exact differential. Mendoza [7] indicates that in modern terms equation 9 would be written

$$TdS = C_P dT - RT\frac{dP}{P} = C_P dT - RTd\ln P \tag{12}$$

Now, Clapeyron repeats the same reasoning using a saturated vapor as the working substance, that is, he locates the cycle within the saturation dome. He now arrives at the relation

$$k = C\left(1 - \frac{v^L}{v^G}\right)\frac{dP}{dt} \tag{13}$$

where k is the latent heat vaporization (which he calls *latent caloric) per unit volume of vapor*. Clapeyron remarks that k is never infinite but can be zero when both phases have the same density (critical point). Equation 13 is essentially the same as equation 1 if C is taken as the absolute temperature multiplied by the conversion factor between heat and mechanical work units. In his paper Clapeyron indicates that no experimental data are available to determine the value of C except for $t = 0$. Using the value $C_P/C_V = 1.412$ found by Dulong, Clapeyron calculates $1/C$ to be 1.41 at 0 °C and thus the value 386 as the mechanical equivalent kg.m kcal^{-1}.

Although equation 13 had been determined using a cycle in the liquid–vapor envelope, it is clear that the same result would be obtained if the cycle is performed either in the solid–gas or in the solid–liquid envelopes.

The Clausius–Clapeyron equation

Clausius, in a paper published in 1850 [8], uses Carnot's monograph and Clapeyron's paper, as well as new experimental data, to change the expression of Mariotte–Gay-Lussac's law to

$$Pv = \frac{P_0 v_0}{273 + t_0}(a + t) \tag{14}$$

pointing out that the best value for a at that time is 273 °C and that this value will become more precise as better experimental data become available. In addition, Clausius arrives at the conclusion that Clayperon's function C has the structure $C = A$ $(a + t)$ where $1/A$ represents the work equivalent of the unit of heat. He then proceeds to write the Clapeyron equation in the form

$$r = A(a + t)(v^G - v^L)\frac{dP}{dT} \tag{15}$$

where r is the latent heat of vaporization. Clausius uses equation 15 to calculate the value of $1/A$ to be 421 kg m kcal^{-1}, and he compares his results with those of Joule: 460 kg m kcal^{-1} for the heat produced by magneto electricity, 438 kg m kcal^{-1} for the mechanical expansion of a gas, and 425 kg m kcal^{-1} for the heat produced by the friction of water, mercury, and cast iron. All these values are in remarkable agreement with the actual value of 427 kg m kcal^{-1}. Inspection of equation 15 shows that Clausius has already arrived at the definition of absolute temperature and that equation 15 is equivalent to the modern expression for the Clausius–Clapeyron equation.

Epilogue

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 18 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 centimeters high. The name of Clapeyron is located in the fourth facade, facing the city of Paris. There is also a Rue Clapeyron in the 8th Arrondissement of the city.

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