William John Macquorn Rankine

Thermodynamics, heat conversion, and fluid mechanics

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Resumen

William John Macquorn Rankine (1820-1870) fue un científico, educador e ingeniero muy prolífico y multifuncional, un pionero en el esfuerzo de llevar los recursos de las matemáticas y la física a los problemas prácticos de la ciencia y la ingeniería. Sus contribuciones abarcan un amplio intervalo de actividades: termodinámica, conversión del calor, mecánica de fluidos, construcción de barcos, mecánica de los sólidos y de los suelos, así como temas filosóficos. Él es particularmente famoso por sus contribuciones a la termodinámica, al entendimiento de las máquinas térmicas y al desarrollo de la segunda ley. Entre sus contribuciones en esta área tenemos la escala Rankine de temperaturas y el ciclo de vapor Rankine para la conversión de calor en trabajo. Fue el primero que definió tensión y esfuerzo rigurosamente.

Abstract

William John Macquorn Rankine (1820-1870) was a very prolific and multifaceted scientist, educator, and engineer, a pioneer in the effort to bring the resources of mathematics and physical science to the practical problems of the scientist and engineer. His contributions embrace a wide range of fields: thermodynamics, heat conversion, fluid mechanics, shipbuilding, mechanics of solids and soils, and philosophical subjects. He is particularly famous for his contributions to thermodynamics, to the understanding of the heat engine and development of the Second law. Among his contributions in this area we have the Rankine scale of temperatures and the Rankine vapour cycle for the conversion of heat into work. He was the first to define stress and strain rigorously.

Life and career

William John Macquorn Rankine (Figure 1) was born in Edinburgh on July 5, 1820, the youngest of the two sons of David Rankine of the Riffle Brigade, a former army lieutenant and then civil engineer, and Barbara Grahame, the elder daughter of Archibald Grahame, banker in Glasgow. His brother died in childhood. Rankine records of himself, "My earliest recollection is that of my mother teaching the Lord's Prayer, next to my father explaining to me the character of Jesus Christ;" and further he records, "My early instruction in arithmetic and elementary mechanics and physics was mainly obtained from my father." The mutual dependency thus begun continued through as beautiful a life of mutual devotion between parents and son as can be pictured; for the three were rarely separate during the fifty years the parents liver after his birth (Gordon, 1875).

Rankine's formal schooling appears to have been brief. He started his education at the Ayr Academy in 1828, and afterwards to the high school of Glasgow in 1830. In that year the family moved to Edinburgh, but Rankine did not return to school because of ill health. For the next six years his education was finished at home, first by his father and then by private tutors. Afterwards he went to Edinburgh, where he studied geometry under George Lees; but his knowledge of the higher mathematics was chiefly obtained by private study. He records that in 1834, when he was fourteen years old, "My uncle Archibald Grahame gave me a copy of *Newton's Principia*, which I read carefully; this was the foundation of my knowledge of the higher mathematics and dynamics and physics." He read the Principia in the original Latin, and in after life recommended his pupils so to read this work of paramount authority and reputation; "for", said he, "modern science had added no new principle to the dynamics of Newton, what it has done is to extend the applications of dynamical principles to phenomena to which they had not been previously applied; in fact, to the correlation of the physical sciences, or, in other words, what is denoted by the convertibility of energy" (Gordon, 1875).

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In 1836 he studied practical and theoretical chemistry under David Boswell Reid (1805-1863) before entering the University of Edinburgh. In the following two years, 1836 to 1838, he took the courses of Natural Philosophy, Chemistry under Reid, Natural History under Jameson, and Botany under Graham. He continued for two years under Professor James David Forbes (1809-1868); and in his the first year (1836) he was awarded the gold medal for "An Essay on the Undulatory Theory of Light" and in his second year (1838) the extra prize (gold medal) for"An Essay in Methods of Physical Investigation". At this period, too, he read much metaphysics, chiefly Aristotle (384-322 BCE), John Locke (1632-1704), David Hume (1711-1776), Dugald Stewart (1753-1828), and Joseph-Marie Degerando (1772-1842). As told by Gordon the whole tendency of his mind was to the digestion and assimilation of the highest possible human knowledge. On quitting the University of Edinburgh, without a degree, he chose for himself the profession of a civil engineer (Gordon, 1875; Small, 1956).

For a short time he worked with his father, who was superintendent of the Edinburgh and Dalkeith Railway and then he became an apprentice at the office of Sir John Benjamin McNeill(1790-1880), an eminent Irish civil engineer of the 19th century, closely associated with Thomas Telford (1757-1834), whose most notable projects were railway schemes in Ireland and Northern Ireland. From 1838 to 1842 Rankine was engaged on a variety of engineering projects, which ranged from surveying and railroad construction, river improvements, water works, and harbour works, and on the Dublin and Drogheda Railway. In this work he invented and practiced a technique, later known as Rankine's method, for laying out railway curves. This technique, the first to be based on the use of a theodolite, was more accurate and faster to use than any other then available. After this training period he returned to Edinburgh, and was occupied for some time, in collaboration with his father, in the preparation and publication of an "Experimental Inquiry Into the Advantages Attending the Use of Cylindrical Wheels on Railways" in which he recommended that trains be provided with cylindrical wheels instead of circular because they would retain their shape for the longest time (Gordon, 1875). From 1844 to 1848 Rankine was employed by the engineering firm of Joseph Locke (1805-1860) and John Edward Errington (1806-1862) in the construction of the Clydesdale Junction Railway, and subsequently on various railway projects promoted by the Caledonian Railway Company, of which his father had become secretary. In 1845-1846 he engineered and proposed the Edinburgh and Leith Water Works, a project that was rejected because of the opposition of the Edinburgh Water Company. In 1852, he, in conjunction with the late John Thomson (son of the late Professor William Thomson of Glasgow University), engineered a water supply for Glasgow from Loch Katrine.

Figure 1: William John Macquorn Rankine (1820-1870).

In the first quarter of 1855, Rankine participated in the teaching of the courses given by Professor Lewis Gordon, Regius Professor of Civil Engineering and Mechanics in the University of Glasgow, lecturing on "Applied Mechanics" and the "Applications of Thermodynamic to the Theory of the Steam Engine." His lectures were so successful that he was nominated to replace Gordon after his resignation and on November 7, 1855, the Queen's commision appointed him Regius Professor of Civil Engineering and Mechanics. In November 1856 he gave the lecture "On the Science of the Engineer", which he concluded with words "Let the young engineer be convinced that the profession which he studies is not a mere profitable business, but a liberal and a noble art, tending towards great and good ends, and that to strive to the utmost to perfect himself in that art, and in the sciences on which it depends, is not merely a matter of inclination or of policy, but a sacred duty" (Gordon, 1875).

One important paper in civil engineering published by Rankine in 1872 related to the design and construction of masonry dams (Rankine, 1872). At that time he had been consulted about a damn to be constructed on the Periyar river in India He made a theoretical study of the general problem and developed a profile for a dam, which almost completely eliminated tensile strength on horizontal sections, the first time this had been achieved by the application of scientific principles to dam design.

From then until his death in 1872 he devoted his energies, as both educationalist and consultant, to the vitalization of scientific engineering, opposing the popular view that engineering was an inappropriate subject for university studies, and exploring the possibilities of applying theoretical science to engineering problems. A product of these activities was the publishing of his *Steam Engine and Other Prime Movers* (Rankine, 1859), a thorough survey of all heat engines. This extraordinary manual became a classic (selling17 editions until 1908 when the experimental data Rankine used went out of date) and established a general framework for the thermodynamic analysis of heat engines, which has been followed ever since. Throughout, he was especially careful to present his results in a form, which would be of the greatest use to the practicing engineer (Hutchinson, 1981ab).

In 1865 he was appointed consulting engineer of the Highland and Agricultural Society of Scotland, and from that time became a regular contributor to the pages of *The Engineer.* For several years he lectured to the Royal School of Naval Architecture.

In an 1855 paper called "Outlines of the Science of Energetics" (Rankine, 1855) Rankine took his ideas further. Physicists, he indicated, were forever trying to reduce the number of fundamental principles in their subject. "Mechanical hypotheses could assist with this reduction because they effectively reduced the postulates of one seemingly distinct branch of physics (such as thermodynamics) from those of mechanics…Being framed by induction from the facts alone this system will be free from the uncertainty which must always attach… to mechanical hypotheses" (Hutchinson, 1981).

Rankine explicitly introduced the entropy function in 1854 (Hutchinson, 1981ab).

Rankine was a patriotic Briton. In 1859 he entered into the Volunteer movement, and was commissioned as Captain of the 2nd Lankarshire Rifle Volunteers, and subsequently, as Major of the 1st Regiment. In that capacity he was in attendance on Her Majesty at the opening of the Loch Katrine Water Works. He attended a course of musketry instruction at Hythe for the purpose of qualifying himself to assist in the instruction of the corps.

Rankine was fond of music and poetry and composed some himself. He occupied himself much with the theory of music, and played the piano and violoncello. His most famous composition was a song in defense of the British system of units and measures against a possible introduction of the metric system. A stanza in that song ran as follows (Raman, 1973):

"Some talk of millimeters and some of kilograms,

And some of deciliters, to measure their beer
and rams;

But I'm a British Workman, too old to go to
school

So by pounds I eat, and by quarters I' drink, and

I'll work by the three-foot rule."

The loss of his father in 1870 and of his mother the following year marked the decay of his vigorous health. After his mother death he was for a time quite absorbed by his grieved for her loss. His health deteriorated more and more, his eyesight became very weak and during 1872 he had to employ an amanuensis and an assistant in his class work. He recovered enough to participate in the meeting of the British Association for the Advancement of Science at Brighton, in August 1870 but those who saw him there could not help observing that he was no longer his old self. Another serious attack of illness (assumed to be diabetes) put him to bed him again in October, but he once more seemed to regain his health, and his condition excited no great alarm until a few days before Christmas, when he rapidly lost power of speech and the sensibility of the right side. He never rallied, and his death occurred on December 24, 1870 (Small, 1956).

Honors and awards

Rankine received many honors for his contributions to science and industry. He was nominated Fellow of the Royal Scottish Society of Arts (1842), Fellow of the Royal Society of Edinburgh (1849), Fellow of the Royal Society of London (1853), Associate of the Institution of Civil Engineers (1843), Member of the Royal Academy of Sweden (1868), and Member of the Philosophical Society of Glasgow (1845). In 1850 he acted as secretary to Section A of the British Association for the Advancement of Science.

In March 1854 he was awarded the Keith Medal of the Royal Society of Edinburgh for researches in thermodynamics. In 1855 he was appointed one of the Visitors of Edinburgh Observatory; and in November of the same year, Regius Professor of Civil Engineering and Mechanics in the University of Glasgow. In 1856 he received the honorary degree of LL.D. fromTrinity College, Dublin, and delivered the opening address as the first President of the Institution of Engineers in Scotland.

In the 1862 year he acted as a juror in Class VIII, "Machinery in General," at the International Exhibition in London. In 1863 he was awarded the gold medal of the Institution of Engineers in Scotland for a paper upon the "Liquefaction of Steam."

During 1857-1859 Rankine was the first President of the Institution of Civil Engineers, and then, between 1869-1870, he served again in the same position. An 8-kilometer diameter lunar crater, located at 3.9 S, 71 SE, is named after him.

In December 1870, he was appointed a member of the Committee for Shipsof War. In 1871 he was elected a Vice-President of the Royal Society of Edinburgh. In 1872, along with Stevenson Macadam (1829-1901), professor of chemistry at the University of Edinburgh, he examined and reported into the causes of explosions in grain mills, in connection with the disaster at the flourTradeston Mills.

Books

Rankine was the author of exhaustive treatises on thermodynamics, civil engineering, applied mechanics, and shipbuilding, among them: *Manual of the Steam Engine* (Rankine, 1859); *Manual of Civil Engineering* (Rankine, 1862); *Applied Mechanics* (Rankine, 1858); *Machinery and Millwork* (Rankine, 1869); and *Shipbuilding, Theoretical and Practical* (Rankine, 1866). The range and content of these manuals reflect both Rankine's versatility and the multifarious facets of his career.

Scientific and engineering contribution

Rankine was a very prolific and multifaceted scientist and engineer, publishing more than 150 papers (127 of them in the period 1853-1873) in philosophical journals, mechanics' magazines, and to *The Engineeer* in particular. He also published about ten books and mane professional reports. Here we will describe only part of some of his most significant contributions to thermodynamics and fluid mechanics, to show the wide scope of his activities.

Thermodynamics

Rankine's first paper of the principles on the mechanical action of heat was based on what he called "the hypothesis of molecular vortices;" one of the first comprehensive theories of matter. The vortex model was designed to explain both radiant and sensible heat.

In this model Rankine adopted the hypothesis that real matter was a mixture of a scattering of nuclei, acting through forces at a distance, while embedded in an atmosphere of elastic fluid, exerting an intrinsic pressure of contact. Each atom of matter consisted of a nucleus or central point enveloped by an elastic atmosphere and that the elasticity due to heat arose from the centrifugal force of the atmospheres revolving or oscillating about their nucleus. Although the nature of the nucleus was left vague, Rankine assumed it to be a small central body, which could be either a real nucleus or a center of condensation and force. Light and heat were the consequence of the motion of the atomic nuclei or centers, and were propagated by means of the mutual attraction and repulsion of the nuclei. Absorption of light and heat consisted in the transference of motion from the nuclei to their atmospheres, and conversely, the emission of light and heat was the transference of motion in the opposite direction. The immense velocity of light and radiant heat implicated that the vibrating nuclei were extremely small in comparison with the forces exerted by them. The atmosphere consisted of innumerable vortices, or circulating streams of matter, with their axes of rotation directed towards the scattered nuclei. The vortices accounted for the pressure and temperature; the absolute temperature of an atom being proportional to the square of the vortical velocity. A mechanism was established that connected macroscopic elasticity with microscopic rotation. Rankine assumed further that the *vis viva* (kinetic energy) of the microscopic rotation represented the heat contained in the substance. The mechanism in question established a connection between heat and work (Rankine, 1851, 1853a).

The stream of the vortices were circular and in single planes with axis of rotation along radii of spheres: "Any such motion of the particles of a portion of matter confined in a limited space will in general give rise to a centrifugal tendency with respect to that space." The stability of the rotating streamlines required the presence of a pressure gradient acting toward the center of each vortex. Hence, the pressure at the periphery of the vortex would be higher that the average pressure within the spherical layer where it was located. In the first version of his theory Rankine simplified the problem by stating that in order for an spherical layer containing any number of vortices of any diameter to be in equilibrium, it was necessary that the velocities in all the these vortices should be equal. This condition was necessary in order for the lateral pressures to be identical. In other words, if every stream in a vortex moved with the same linear speed the size of the vortex would have no influence on the magnitude of the peripheral pressure. Every vortex in a given spherical stratum would give the same value (Rankine, 1851, 1853a).

As stated by Gordon (Gordon, 1875) the vortex theory led to some important definitions and consequences: (a) the *quantity of heat* in a body is the energy of its molecular vortices, (b) the *absolute temperature* of the body is the same energy divided by a specific coefficient for each particular substance, (c) a *perfect gas* is a substance in which the elastic pressure is that which varies with the centrifugal forces of the vortices only, (d) the strength of the pressure, according to the principles of mechanics, is proportional directly to the energy of the vortices, and inversely proportional to the space they occupy, (e) in *imperfect gases*, attractive or cohesive forces modify the elasticity. For small deviations from perfect gases the effects of attractive forces may be approximately represented by series, in terms of the reciprocal of the absolute temperature, (f) *sensible heat* is the energy used in varying the velocity of the rotating particles, (g) *latent heat* is the work done in varying the dimensions of particle orbits, when the volumes and figures of the spaces in which they turn are changed, (h) the force, which keeps any particle in its orbit, is equal and opposite to the centrifugal force; therefore the work done in varying the orbits of the particles is proportional to their centrifugal forces, therefore to the energy of the particles, therefore to the absolute temperature, and (i) the quantity of work, or latent heat required to change the dimensions of a body by a given amount is given by the product of the absolute and the corresponding variation of a certain function of the dimensions and elasticity of the body. This function is computed by taking the rate of variation with temperature of the external work done during the kind of change of dimensions under consideration.

An interesting issue of Rankine's paper on the vortex theory (Rankine, 1851, p. 520) is that it contains a very clear definition of temperature, which may be also thought about as a statement of the Zeroth law of thermodynamics (although in a complicated manner): "To bodies A, B, are said to be at the same temperature, when there is no tendency for one to become hotter by abstracting heat from the other, that is to say, when there is either no tendency to transmission of heat between them, or when A transmits as much heat to B as B does to A…Any surface or other thing which affects the transmission of heat being placed between B and A, has exactly the same influence upon the same quantity of heat passing in either direction…"

In 1853 (Rankine,1853bcd) Rankine named this function *heat potential*, afterwards he added to it an additional term dependent on changes of temperature, and named the new function *thermodynamic function*. From that year on he made frequent use of his thermodynamic function, which he later identified with the entropy of Rudolf Julius Emanuel Clausius (1822-1888) (Gordon, 1875).

One of the first results of the vortex theory was the derivation of the perfect gas law for substances where the action-at-a-distance forces are negligible, together with an indication of the form of the equation of state for imperfect substances: "In any two perfect gases, the respective values of the quotient of the pressure by the density corresponding to the same temperature, bear to each other a constant ratio for all temperatures" (Rankine, 1851, 1853a). Consequently, the pressure of a gas at constant density or its volume at a given pressure, were the most convenient measure of the temperature. In other words, for perfect gases the ratio P/D should be a linear function of Q, the heat content per unit mass. From the definition of Q it follows that if v is the mean velocity of the thermal motion, then (Rankine, 1851, 1853a)

$$Q = \frac{1}{2} v^2 \tag{1}$$

Rankine often distinguished between this v from θ, the actual (as opposed to mean) velocity of vortex rotation. He claimed that θ is constant throughout any particular equilibrium sample of a substance, and that v and θ, were related by a state function k, where

$$k = \frac{v^2}{\theta^2} \tag{2}$$

so that

$$Q = \frac{1}{2} k \theta^2 \tag{3}$$

The state function k "being the ratio of the *vis viva* of motion of a peculiar kind to the whole *vis viva* impressed on the atomic atmospheres by the action of their nuclei, may be conjectured to have a specific value for each substance" (Hutchinson, 1981ab).

Rankine, then developed the following general equation of state for all gases:

$$P = \left(bD\frac{\theta^2}{3b} + 1\right)[1 - F(D,\theta)] + f(D) =$$

$$D\left(\frac{Q}{3k} + b\right)[1 - F(D,Q)] + f(D) \tag{4}$$

where $f(D)$ is a function associated with the gas, which decreases as D becomes small, and $F(D)$ is another function related to the gas, becoming small as D becomes small and θ becomes large, according to the series (Rankine, 1851, 1853a)

$$F(D,\upsilon) = \frac{A_1(D)}{\upsilon^2} + \frac{A_2(D)}{\theta^3} + \dots \tag{5}$$

where the coefficients A_i (D) are functions that decreases as D becomes smaller; the series being quickly convergent. For an ideal gas there are no forces acting through the distance so that both F and f vanish and

$$P = D\left(\frac{2Q}{3k} + b\right) \tag{6}$$

Further on Rankine arrived at the relation

$$T = \frac{2x}{3kb}Q \tag{7}$$

where x is a constant, that is, the temperature is *directly proportional* to the heat content.

Rankine imagined that the atomic vortice would accelerate under compression because these centripetal forces would perform work in the movement toward the center. Not all this work would appear as heat since changes in the density distribution within the atmosphere could occur and consume energy. Expressing the centripetal force as a function of that density distribution and allowing that distribution to vary under an infinitesimal compression, Rankine arrived at the following expression for the heat developed by compression (Daub, 1967):

$$dQ = -\frac{T - k}{CnM}\left[\left(\frac{1}{V} - \frac{dU}{dV}\right)dV - \frac{dU}{dT}dT\right] \tag{8}$$

where U was some function of the density distribution, CnM was Rankine's form of the gas constant where M represented the whole mass of the atom, n the number of atoms that filled a unit volume under the temperature and pressure of melting ice, and k that represented the number of degrees above the absolute zero on the gas thermometer at which the point of zero heat occurred (see below).

Rankine evaluated the differential coefficients of the unknown function U by adopting Joule's principle of the equivalence of heat and work in a cyclic process consisting work built of two isochores and two isothermal processes. He obtained the relations

$$\frac{dP}{dT} = \frac{1}{CnM}\left(\frac{1}{V} - \frac{dU}{dV}\right) \tag{10}$$

$$U = \phi(T) + \int\left(\frac{1}{V} - \frac{dU}{dV}\right)dV \tag{11}$$

and, by claiming that the value of U for a perfect gas would be k/T, he established that

$$\frac{dU}{dT} = -{\frac{k}{T}}^{2} - CnM\int{\frac{d^2P}{dT}}^{2}dV \tag{12}$$

Neglecting the term with k we obtain the key equation for all of Rankine's thermodynamic thought, since

$$dQ - dQ = dQ + T\left[\int\frac{d^2P}{dT^2}dV\right] + T\frac{dp}{dT}dV \tag{13}$$

A question, which engaged the attention of many investigators during the nineteenth century, was the determination of the vapor pressure of various liquids as a function the temperature (Wisniak, 2001). Rankine gave the formula (Rankine, 1849)

$$\ln P = \alpha - \frac{\beta}{t} - {\frac{\gamma}{t}}^{2} \tag{14}$$

stating that "P is the maximum pressure of a vapour in contact with its liquid, t the temperature, measured on the air thermometer, from a point which may be called the absolute temperature, and which is (a) 274.6° of the centigrade scale below the freezing point of water, (b) 462.28° of Fahrenheit's scale, below the ordinary zero of that scale so that 180° of Fahrenheit may be exactly equal to 100° centigrade degrees, and (c) 461.93° below the ordinary cero of Fahrenheit's scaleso that 180° of Fahrenheit being then equal to 100.0735° of the centigrade scale."

Statements (b) and (c) represent the definition of the Rankine scale for temperatures. Rankine noted that his equation followed from theory and that the values of the constants α, β, γ, for each fluid were to be determined from experiments. He used Regnault's data (Rankine, 1849; Regnault, 1847) to calculate the value of the constants for water, ethanol, and ethyl ether.

During the first half of the eighteenth century, James Watt(1736-1819) measured the amount of heat required to warm up and then vaporize a same amount of water under different pressures and reached the wrong conclusion that the sum of the sensible and the latent heat was constant, independent if the process was done under vacuum or at atmospheric pressure. This conclusion became known as Watt's total heat principle. For example, if h is the amount of heat necessary to heat a unit mass of water from 0°C to t°C, and L the latent heat of steam at that temperature, then the total heat would be given by $H = h + L$. More precise measurements made afterwards by others suggested that Watt's law was not exact, and that it was L rather than H, which was constant. Precise measurements made by Regnault in 1847 (Regnault, 1847) established an empirical relationship between H and t as follows:

$$H = 606.5 + 0.305t \tag{15}$$

Rankine deduced this relationship from theoretical considerations. In fact, he showed that the difference between the total heats of vapor at any two temperatures t and t' is equal to the specific heat at constant pressure c_P times the temperature difference. Thus according to Rankine:

$$H - H' = c_P(t - t') \tag{16}$$

This relation not only confirmed Regnault's result, but also showed that the coefficient of t in the latter's formula may be interpreted as the specific heat of steam.

In 1951 Rankine published an improved version of this vortex theory in which he eliminated the simplifying assumption that groups of vortices were arranged in spherical layers around the atomic nucleus (Rankine, 1853a). He now considered streamlines of any form size and orientation, which led to even more complicated equations. The final conclusion was that the relations between heat, elasticity, and mechanical work, were identical to the ones developed previously.

Rankine did research on the specific heat of gases and deduced from some measurements on the speed of sound the value $c_P = 0.24$ cal/g°C for air, a result that disagreed with the latest accepted value (0.2669) that had been reported by François Marcet Delaroche (1803-1883) and Jacques-Étienne Bérard (1789-1869). Rankine's prediction was exactly verified three years later by Victor Regnault's (1810-1878) experiments (Gordon, 1875). Within the subject Rankine investigated the expansion of steam and made the surprising discovery that the specific heat of steam at the saturation pressure should be negative, that is, expanding saturated steam would absorb heat while its temperature dropped, or else it would condense. Gustave Adolph Hirn (1815-1890) would later verify this fact experimentally and thus provide an outstanding demonstration of the predictive power of the new theory. Soon Rankine was to make important application of his result in the design of steam engines (Hutchinson, 1981ab).

In a paper published in 1853 (Rankine, 1853b) Rankine stated that all kinds of energy could be distinguished into two kinds, actual or sensible, and potential or latent. Actual energy was measurable and transferable, and its presence caused the substance to change its state in one or more aspects. By the occurrence of these changes actual energy disappeared and was replaced by potential energy, which was measured by the amount of change in the condition of a substance. The exchange between actual and potential energy was reversible, that is, if now the process was effected in the opposite direction, the potential energy that had disappeared would turn into actual energy. This was Rankine's way of expressing the first law of thermodynamics: The sum of the actual and potential energies in the Universe if unchangeable. Although Rankine was aware of the early use of energy in mechanics, his classification was intended to be applicable to all phenomena, not just mechanical. In his paper "Outlines of the Science of Energetics" (Rankine, 1855) he said: "Energy, or the capacity to effect changes, is the common characteristic of the various states of matter to which the several branches of physics relate; if, then, there are general laws respecting energy, such laws must be applicable, *mutatis mutandis*, to every branch of physics, and must express a body of principles as top physical phenomena in general."

Based on these arguments Rankine proceeded to develop a law for the transformation of energy, that is, of actual energy into potential, and vice versa. Calling V a measurable state of a substance, whose magnitude increased as potential energy (U) was developed, and P the force by which V tended to increase, then for an infinitesimal change d o the potential energy developed was

$$dU = PdV = \frac{dU}{dV}dV \tag{17}$$

So that

$$P = \frac{dU}{dV} \tag{18}$$

Calling Q the quantity of actual energy under consideration and assuming it to be divided into an indefinite number small parts dQ, then abstraction of an amount dQ would lead to diminishing the development of power dU by the amount d^2U. The development of potential energy will then be given by $(d^2U/dQdV)dVdQ$. Since each discrete part dQ act of the actual energy exerts an identical and independent influence manner, the total effect should be Q/dQ times that for each element dQ. The contribution of any element dQ to the potential energy change PdV is simply $(d/dQ)(PdV)dQ$ so that $Q(dP/dQ)dV$ becomes the general expression for the transformation of actual into potential energy due to the presence of actual energy Q. Since for Rankine the sensible heat is proportional is proportional to the absolute temperature, the total work performed by the disappearance of heat at constant actual heat (isothermal expansion) becomes, where dP/dT is the partial derivative at constant volume (Daub, 1967).

Rankine considered now the more general case in which both V and Q changed and derived the following equation, which represented the algebraic sum of all energies, actual and potential, acquired by the substance in changing its state from (Q, V) to $(Q + dQ, V + dV)$

$$\frac{H_1 - H_2}{H_i} = \frac{Q_1 - Q_2}{Q_1} \tag{19}$$

where LdQ represents the energy transformed from the actual to the potential form in consequence of the change dQ alone.

Since the change $d\gamma$ is independent of whether the change dQ or the change dV is made first, or both simultaneously (otherwise the law of energy conservation would violated), $d\gamma$ must be an exact differential, that is

$$\frac{dL}{dV} = \frac{d}{dQ}\left(Q\frac{d}{dQ} - 1\right)\frac{dU}{dV} = Q\frac{d^2}{dQ^2}\frac{dU}{dV} \tag{20}$$

or

$$L = f'(Q) + Q\frac{d^2U}{dQ^2} \tag{21}$$

where $f'(Q)$ is a function of Q alone, to be determined experimentally.

The expression of the law of transformation of energy (first law) becomes

$$d\psi = UdQ =$$

$$= \left[1 + f'(Q) + Q\frac{d^2U}{dQ^2}\right] + \left(Q\frac{d}{dQ} - 1\right)\frac{dU}{dV}dV \tag{22}$$

Rankine concluded that an immediate consequence of eq (22) was that if a substance underwent a cyclic change in which the forward process was different that the backward one, then there would be a certain amount of permanent conversion of energy between the actual and potential energies. To calculate the amount of converted he first considered a change of state from V_A to V_B. The actual energy supplied by the system is, then

$$H_1 = Q_1\frac{d}{dQ}\int_{V_B}^{V_A}\frac{dU}{dV}dV = Q_1(F_A - F_B) \tag{23}$$

where

$$F = \frac{d}{dQ}\int\frac{dU}{dV}dV \tag{24}$$

is the *heat potential*.

If the actual energy is reduced by an amount Q_2 transformed totally into the potential form, then $O = dQ = d[Q + f(Q)] + Q$d, and *if* F_C is the value of F at then of the operation

$$F_B - F_C = \int_{Q_1}^{Q_2}\frac{d[Q + f(Q)]}{Q} \tag{25}$$

If now F_C is a fourth value of F such that $F_A - F_D = F_B - F_C$, then $F_C - F_D = F_B - F_A$. At the end of the operation the amount of energy that has been permanently transformed from the actual to the potential form is $H_1 - H_2 = (Q_1 - Q_2)\ (F_B - F_A)$. This amount bears the same proportion to the whole quantity of actual energy received by the substance from outside, that is,

$$\frac{H_1 - H_2}{H_1} = \frac{Q_1 - Q_2}{Q_1} \tag{26}$$

In Rankine's words (Rankine, 1853bd): "The greatest quantity of energy that can be permanently converted from the actual to the potential state by a substance undergoing a cycle of changes, bears the same proportion to the actual energy communicated to the substance from without, which the excess of the actual energy present in the substance during the reception of actual energy, above the actual energy present during the emission of actual energy, bears to the former of these two quantities.” In this complicated language Rankine is giving us the expression for the efficiency of a reversible Carnot heat engine, as a proceeds to show immediately. Again, in his own words: If we admit…that the heat present in a body varies with temperature according to the same law for all substances…the vortices hypothesis leads us to…the quantity of heat in a body…is proportional to the temperature as measured of absolute privation (κ)…then the greatest…proportion of heat rendered effective by any expansive engine, receiving heat at τ_1 and emitting it at τ_2 is $(\tau_1 - \tau_2)/(\tau_1 - \kappa)$.

Rankine used the results of Joule and Thomson to determine that in perfect gases, total privation of heat occurred at 272.5°C below the freezing point of water.

Soon after this Rankine read another paper before the Royal Society of Edinburgh, in which he introduced the concept of heat potential in the following context: “In order to investigate the laws according to which heat is converted into mechanical power, in a machine working by the expansion of an elastic body, it will be convenient to use a function

$$F = \int \frac{dP}{dQ}\, dV \qquad (Q = \text{constant}) \tag{27}$$

of such a nature that the difference between two of its values corresponding to two different volumes of the body at the same total heat, represents the ratio of the heat converted into power by expansion between the two volumes, to the given constant total call this function a *heat potential*” (Raman, 1973).

The expression for the heat potential was developed as follows (Daub, 1967): The heat added to a system, *dH*, is equated to the increase in actual energy *kdT* and the work performed *TdF*

$$dH = kdT + TdF \tag{28}$$

where *k* is the proportionality constant between the actual energy *Q* (sensible heat) and the absolute temperature, assumed equal to the specific heat at constant volume of a perfect gas, for under those conditions none of the heat added was considered to convert into work. Differentiation of eq (27) and replacement in eq (28) leads, after some algebraic work to:

$$dH = kdT + T\left[\int_{\infty}^{V} \frac{d^2P}{dT^2}\, dV\right] dT + T\frac{dP}{dT}\, dV \tag{29}$$

The limits of the integral in eq (29) are from the state of perfect gas ($V = \infty$) to the value of the volume at any higher pressure. According to Daub (Daub, 1967) this single differential equation derived by Rankine in 1850, is equivalent to all traditional formulations of thermodynamics in terms of internal energy and entropy differentials and can be demonstrated using standard thermodynamics. Using one the so-called *TdS* equations (Zemansky, 1951)

$$TdS = c_V\, dT + T\left(\frac{\partial P}{\partial T}\right)_V dV \tag{30}$$

and assuming the specific heat at constant volume to be a function of the temperature and volume, we have

$$dc_V = \left(\frac{\partial C_V}{\partial T}\right)_V dT + \left(\frac{\partial P}{\partial T}\right)_V dV \tag{31}$$

$$c_V = \int \left(\frac{\partial c_V}{\partial V}\right)_T dV + f(T) \tag{32}$$

The integrand in eq (32) can be found from the definition of c_V, and the Maxwell relation

$$\left(\frac{\partial c_V}{\partial V}\right)_T = T\left(\frac{\partial^2 P}{\partial T^2}\right)_V \tag{33}$$

Therefore (34)

$$TdS = f(T)\, dT + T\left[\int \left(\frac{\partial^2 P}{\partial T^2}\right)_V dV\right]\left(\frac{dV}{dT}\right) + T\left(\frac{\partial P}{\partial T}\right)_V dV \tag{35}$$

Comparison of eqs (29) and (35) indicates that Rankine’s heat content function *dH* is equal to *TdS* and the constant k is equal to c_V, as indicated above.

Clausius discovered the second law of thermodynamics concurrently with Rankine, using general principles and without assuming any particular hypothesis regarding the structure of matter (Clausius, 1850). Rankine, in an address to the Philosophical Society of Glasgow, concluded an eloquent justification of the mechanical hypothes of molecular vortices, in this words: “I wish it to be clearly understood that although I attach great value and importance to sound mechanical hypotheis as means of advancing physical science, I firmly hold that they can never attain the certainty of observed facts; and accordingly, I have laboured assiduously to show that the two laws of thermodynamics are demonstrated as facts independent of any hypothesis; and in treating the practical application of those laws, I have avoided all reference to hypothesis whatsoever" (Gordon, 1875; Rankine, 1865).

During the nineteenth century, when the atomic hypothesis began to be taken more seriously, physicists and chemists wondered if they had sufficient justification for accepting the existence of entities decidedly beyond their direct perception. Berthelot referred to this possibility sarcastically (Berthelot, 1867): "…En réalité, nous ne voyons pas les molecules, et nous n'avons aucun moyen connu pour les compter…Il y a là deux notions hypothétiques, celle de la molecule et celle de l'atome. Qui a jamais vu, je le répète, une molecule gazeuse ou un atom…" (…In reality we do not see molecules and we do not have any known method of counting them…We have here two hypothetical notions, that of a molecules and that of an atom. Who has ever seen a gaseous molecule or an atom?).

Rankine recognized these intrinsic difficulties and he classified the methods by which physical theories are formulated into two large classes, which he described as the abstractive and hypothetical methods. After defining a physical theory as a "system of principles, with its consequences methodically deduced", he went on to characterize the abstractive method as one in which only what is directly perceivable and discernible to the senses is taken into account. In other words, in the abstractive methods one adopts Newton's motto of *hypothesis non-figa*. On the other hand, in the hypothetical method, one introduces entities "according to a conjectural conception of nature, in a manner not apparent to the senses, by a modification of some other class of objects or phenomena whose laws are already known" (Rankine, 1864; Raman, 1973).

Kelvin had pointed out that in the Universe there was a predominant tendency to the conversion of all forms of physical energy into heat, and to its uniform diffusion throughout matter. That is to say, natural processes were irreversible and as such led to the ultimate thermal death of the Universe, an end of all physical processes. Some philosophers and scientists were upset by such a possibility and attempted to consider possible escapes from such a doom. Rankine accepted that these conclusions were probably true since they were based on experimental data. Nevertheless he assumed that "it was perfectly possible to assume that in some indefinitely distant period, an opposite condition of the world may take place, in which the energy now being diffused may be reconcentrated into foci, and stores of chemical power produced from the inert compounds which were now being formed". To justify his hypothesis he suggested "that there must be between the atmospheres of the heavenly bodies a material medium capable of transmitting light and heat…a medium which is perfectly transparent and diathermanous…This medium should be incapable of acquiring any temperature whatsoever…all the heat that arrives in the conductible form at the limits of a star or planet…will be totally converted, partly into ordinary motion and partly into radiant form" (Rankine, 185).

Maxwell criticized Rankine's statement of the second law of thermodynamics for its lack of clarity; nevertheless he put him among the three founders of the science. In his review of Peter Guthrie Tait (1831-1901) book on thermodynamics (Tait, 1877; Maxwell, 1878), he discussed Rankine's contribution in these words: "Of the three founders of theoretical thermodynamics, Rankine availed himself to the greatest extent of the scientific use of the imagination. His imagination, however, though amply luxuriant, was strictly scientific. Whatever he imagined about molecular vortices, with their nuclei and atmospheres, was so clearly imaged in his mind's eye, that he, as a practical engineer, could see it work…However intricate, therefore, the machinery might be which he imagined to exist in the minute parts of bodies, there was no danger of his going on to explain natural phenomena by any mode of action of this machinery, which was not consistent with the general laws of mechanics, Hence, though the construction and distribution of his vortices may seem to us as complicated and arbitrary as the Cartesian system, his final deductions are simple, necessary, and consistent with facts…Certain phenomena were to be explained, Rankine set himself to imagine the mechanism by which they might be produced. Rankine, long after an explanation of the properties had been founded on the theory of collisions of molecules, published what he supposed to be a proof that the phenomena of heat were invariably due to steady closed streams of continuous fluid matter…When we come to Rankine's Second Law of Thermodynamics we find that though, as to literary form, it seems cast in the same mould, its actual meaning is inscrutable…The student who thinks he can form any idea of the meaning of this sentence is quite capable of explaining on thermodynamic principles (!!) what Tennyson says of the great Duke (Maxwell, 1878):

"Whose eighty winters freeze with one rebuke
All great self-seekers trampling on the right."

Fluid mechanics

Another of Rankine's major interest was naval architecture to which he turned his attention about 1855 when James Robert Napier (1791-1876), a marine engineer, and large ship constructor, asked for his technical assistance in the design of a boat to travel at a certain speed. Rankine took the information available for calculating the resistance offered to water in flowing through iron pipes at high velocities and adapted it to give an approximate calculation of the engine-power required by a ship of any given design. More refined analysis led him to his theory of stream-lines, a theory which, with its rigid mathematical demonstration, is, with all its imperfections, far in advance of the elegant guesswork that enters into John Scott Russell's (1808-1882) wave-line system of construction, which revolutionized nineteenth century naval architecture (In the 1960's the significance of the wave line was fully appreciated; it was discovered that many phenomena in physics, electronics, and biology could be described by a mathematical and physical theory of soliton, as Russell's wave is now known).

Rankine was the first to recognize the contribution of William Froude (1810-1879), using scale models, investigations, which were judged skeptically by the naval authorities of his time. Froude was a hydrodynamicist who first formulated reliable laws for the resistance that water offers to ships and for predicting their stability. He also invented the hydraulic dynamometer (1877) for measuring the output of high-power engines. These achievements were fundamental to marine development. His experimental results led him to establish formulas, which would predict the frictional resistance of a hull with accuracy and give an estimate of the power required to drive a hull at a given speed. Froude and formulated a law, carrying his name, that states that the wave-making resistance of similar-shape models varies as the cube of their dimensions, if the speeds are as the square root of their dimensions. These similarity relations are contained in what today we know as Froude's number (v^2/Lg; the ratio between the inertial force and the gravity force) and Froude's law.

In 1861 Froude exposed to the members of the Institution of Naval Architecture his theory of the rolling of ships, the most important advance that had been made in naval architecture for nearly three-quarters of a century. "This question," to employ the words of Russell, "was one which had hitherto absolutely evaded the investigation of mathematicians and the devices of the naval architect" and, consequently, it is not surprising that many eminent scientists did not accept it. Rankine understood the importance of Froude's results and in the next session of the Institution he pointed out that the simplest method of arriving at the differential equation of the ship's motion was to assume the figure of the wave to be trochoidal, instead of adopting the curve of sines hypothesis, which Froude had taken as the basis of his theory. This assumption, as Froude stated when speaking on Rankine's paper, was one which evidently led to a complete and rigorous solution of the whole question. Beginning in 1862 with an independent derivation of the trochoidal shape of waves in deep water, a result already published by Franz Joseph von Gerstner (1793-1840), Rankine examined the rolling, dipping, and heaving motion of ships in waves. Similarly, his two-dimensional analysis of the flow of water around circular and oval bodies enabled him to determine the waterlines of a ship that would create a minimum of friction as it moved through the sea.

From that year on Rankine Rankine contributed to the Transactions of the Institution of Naval Architects some paper of importance to the shipbuilder or marine engineer. In 1866 the folio treatise of his most important results was published. The preparation of this treatise led to a series of additional researches on fluid motion. His memoirs on "Theory of Propagation of Waves", the "Theory of Waves Near the Surface of Deep Water", and his investigations on plane water lines in two dimensions, i.e., of the lines of motion ow water flowing past a ship, advanced the applicatiion of science to naval architecture as much as his discovery of the second law of thermodynamics did that to the theory of the steam engine and other heat engines.

Miscellaneous

In 1842-1843 various papers sent to the Institution of Civil Engineers led to Rankine being awarded the James Walker Premium. In 1843, while working with his father, Rankine proposed a theory to explain fracture that took place tin the axles of trains. This theory would eventually serve August Wöhler (1819-1914) to systematize mechanical calculations, which are in use up to day in mechanical design (Wöhler derived the formula, named equation of three moments, for calculating the sag of lattice girders). In his publication "Fracture of Axles" Rankine showed the importance of form and fibre, thus disproving the hypothesis of spontaneous crystallization, and demonstrated for the first time the danger of abrupt changes in the transverse dimensions of machine parts, and also the danger of the interruption of the fibre of wrought iron forged with sharp re-entrant angles. The conclusions of Rankine's paper were generally accepted and acted upon in the construction of axles (Gordon, 1875). His tests contradicted the theory commonly accepted, that after axles have been run for several years the fibrous texture of their iron deteriorates, gradually becoming crystallized and he proposed to form the journals with a large curve in the shoulder, before going to the lathe so that the fibre would be continuous throughout (Southwell, 1956). Rankine also proposed a theory for the mechanical failure under static loads (Rankine's curve), which is not in use toady but is particularly valid for fragile materials (Rankine, 1843, 1856).

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