

Heat Radiation Law—From Newton to Stefan

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The understanding and quantification of the phenomenon of heat radiation has gone through many phases, parallel to the interpretation of the concept of heat.

The nature of radiant heat

The physiological sensation of heat and cold has accompanied mankind from the very beginning. Noah, tenth generation after Adam, is told, once he has come out of the Ark, that the natural order before the Deluge will return: "While the earth remaineth, seed time and harvest, and cold and heat, and summer and winter, and day and night, shall not cease" (Genesis 8:22). Observations of various natural and man-made phenomena led the ancients to postulate theories that led to our modern concepts on the nature of heat and heat transfer. Up to the nineteenth century two rival hypotheses regarding the nature of heat were in vogue. The *caloric* theory postulated that heat was an imponderable elastic fluid that permeated the pores of the bodies, and filled the interstices between the molecules of the matter. The *wave* (ondulatory) theory of heat claimed that heat was the vibration of an ethereal fluid that filled all space, and which transmitted vibrational motion from one atom to another. Heat was thus attributed to motion. The theory negated that atomic vibrations alone could account for the phenomena of heat; the role of the ether was essential. In addition, atoms in a gas could not move freely through space, they were constrained to vibrate about fixed equilibrium positions. The particles were held by in position by repulsive forces that were thought to exist between them. These repulsive forces were attributed to the presence of the subtle weightless and highly elastic fluid of heat (caloric).

The wave theory was based on the fact that heat and light travelled through space with a definite velocity and that it could not be conceived in another way by which an influence, travelling in time, could be propagated from one body to another situated at a

distance. Radiant heat like light, was supposed to be due to wave motion in the ether. The molecules of a body were in a state of very rapid vibration, or were the centre of rapid periodic disturbances of some sort, and these vibrations or perturbations gave place to waves that travelled through the ambient ether. These waves moved through the ether at the speed of light and upon falling on the body of a person they were absorbed, generating internal motions in the molecules and the corresponding feeling of warmth. The body of a person was excited by these heat waves in the same manner as the eye was excited by the waves coming from a luminous body, or as the ear was, affected by the aerial waves originating by a sounding body.

The wave theory was supported by many of the outstanding scientists of that time, among them Francis Bacon (1561-1626), Robert Boyle (1627-1691), Isaac Newton (1642-1727), Sadi Carnot (1796-1832), Joseph Fourier (1768-1830), Pierre-Simon Laplace (1749-1827), and Thomas Young (1773-1829).

Bacon in his book *Novum Organum*¹, analysed all the available information on heat and its effect and stated that it could only be explained by heat being motion: "from the instances taken collectively, as well as singly, the nature of whose if heat appears to be motion. This is chiefly exhibited in flame, which is in constant motion, and in warm or boiling liquids, which are like wise in constant motion. The very essence of heat, or the substantial self of heat is motion and nothing else".

Similarly, in 1665 Boyle wrote an extensive treatise on the experimental history of cold in which he claimed, among other things, that wind was the cause of cold².

Newton believed that heat consisted in a minute vibratory motion of the particles of bodies, and that

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this motion was communicated through an apparent vacuum, by the undulations of an elastic medium, which was also involved in the phenomena of light. It was easy to imagine that such vibrations may be excited in the component parts of bodies, by percussion, by friction, or by destruction of the equilibrium of cohesion and repulsion. In his book *Opticks*³ Newton wrote: "Do not all fixed bodies, when heated beyond a certain degree, emit light and shine, and is not this emission performed by the vibrating motions of the parts? Is not Fire a Body heated so hot as to emit Light copiously? Is not the Heat of the warm Room conveyed through the Vacuum by the Vibrations of a much subtler Medium than Air, which after the Air was drawn out remained in the Vacuum? And is not this Medium the same with that Medium by which Light is refracted and reflected, and but whose Vibrations Light communicates Heat to Bodies and is put into Fits of easy reflection and easy Transmission? And do not hot Bodies communicate their heat to contiguous cold ones, by the Vibrations of this medium propagated from them into the cold ones"?

Carnot also supported these ideas. According to him "at present, light is generally regarded as the result of a vibratory movement of the ethereal fluid. Light produces heat, or at least accompanies the radiant heat and moves with the same velocity as heat. Radiant heat is, therefore, a vibratory movement. It would be ridiculous to suppose that it is an emission of matter while the light, which accompanies it, could only be movement. Could a motion (that of radiant heat) produce matter (caloric)? Undoubtedly not, it can only produce motion. Heat is then the result of a motion"⁴.

Carnot also referred to the nature of heat transmission: "Is heat the result of a vibratory motion of molecules? If this is so, quantity of heat is simply quantity of motive power. As long as motive power is used to produce vibratory movements, the quantity of heat must be unchangeable; which seems to follow from experiments in calorimeters; but when it passes into movements of sensible extent, the quantity of heat can no longer remain constant"⁴.

Fourier in his famous book, *Analytical Theory of Heat*⁵ stated that "of all the modes of presenting to us the action of heat, that which seemed simplest, and most conformable to observation, consisted in comparing it to that of light. Molecules separated from one another reciprocally communicated across empty space, their rays of heat, just as shining bodies

transmitted their light. All bodies had the property of emitting heat through their surface; the hotter they were the more they emitted and the intensity of the emitted rays changed very considerably with the state of the surface".

According to Fourier although heat that was radiated in all directions from a part of the surface of a solid travelled through air to very distant points it was emitted only by those molecules of the body, which located very close to its surface. This observation was applicable to all the points, which were near enough to the surface to take part in the emission of heat. The obvious conclusion was then that the total amount of heat, which escaped from the surface in the normal direction, was much greater than that whose direction was oblique.

In addition, if a number of bodies, each at a different temperature, were put inside an enclosure closed in all directions and maintained by some external cause at a constant temperature, they would receive and transmit rays of heat and their temperature would vary in a continuous manner until eventually each would reach the fixed temperature of the enclosure.

According to Fourier, "the free state of heat was the same as that of light; the active state of this element was then entirely different from that of gaseous substances. Heat acted in the same manner in a vacuum, in elastic fluids, and in liquid or solid masses; it propagated only by way of radiation, but its sensible effects differed according to the nature of bodies. Heat was the origin of all elasticity; it was the repulsive force, which preserved the form of solid masses and the volume of liquids"⁵.

One of the arguments for the materiality of heat at the beginning of the nineteenth century was the fact that heat can apparently travel through empty space without any accompanying movement of matter; hence it could not be simply molecular motion.

The arguments supporting the wave theory led necessarily to a challenging question: Were there two distinct sets of waves in the ether? Were there heat and light waves, or were these waves of the same nature and type? The fact that light also possessed heating power at once led to suspect that there was no essential difference in character between the wave motion that affected our sense of heat and that which affected our sense of vision⁶.

In the period 1800-1835, experiments on radiant heat by William Herschel (1738-1822), John Leslie (1726-1832), Macedonio Melloni (1798-1854), and others showed that radiant heat had most if not all of

the properties of light. Melloni, in particular, demonstrated that radiant heat shared all the qualitative properties of light: reflection, refraction, diffraction, polarization, interference, etc. This led to a widespread belief that heat and light were essentially the same phenomenon, i.e., superficially different manifestation of the same physical agent. Maxwell's electromagnetic theory indicated that heat radiation would be viewed as a special case of electromagnetic waves (infrared radiation), which produced thermal effects when absorbed by matter⁷.

By 1830 the wave theory of heat was being seriously considered as an alternative to, or modification of, the caloric theory. The first extended discussion of heat was two papers published by Ampère in 1832 and 1835^{8,9}. He began his memoir by stating that "thanks to the findings of Edward Young (1681-1765), François Arago (1785-1853), and Augustin Fresnel (1789-1827), it is well known that light is produced by the vibrations of a fluid distributed all over the space and named *ether*. Radiant heat, that follows the same laws in propagating, can be explained in the same manner. But, when heat is transferred from the hottest part of a body to that that is colder, the propagation laws are very different: Instead of a vibrational movement transferred by waves (*ondes*), we have now a movement that propagates gradually, so that the part that is initially hotter (and consequently, the one more agitated when heat is explained by vibrations), although losing heat by degrees, it conserves more than the parts to which it is transmitting heat. This fact gives place to an objection to heat being transferred by vibratory movements"⁸.

Ampère recognized at the outset a major difficulty in using the same theory to explain the transmission of radiant heat through space and the conduction of heat through material bodies: "Instead of a vibratory motion propagated by waves (*ondes*) in such a manner that every wave leaves at rest the fluid which sets it in motion at the instant of its passage, we have a motion propagated gradually in such a manner that the part which originally was the hottest, and consequently the most agitated, although losing heat by degrees, preserves, however, more than the parts to which it is communicating heat". In modern terms, the problem was to reconcile the propagation of heat by waves (second-order differential equation in time) in free space, with its propagation as described by Fourier's heat conduction equation (first-order time

derivative). But Ampère thought he could answer this and other objections to the theory⁷.

Ampère postulated that the total *vis viva* of the system was conserved, *vis viva* being defined as the "somme des produits de toutes les masses de ses molécules par les carrés de leurs vitesses à un instant donné, et qu'on y ajoute le double de l'intégrale de la somme des produits des forces multipliées par les différentielles des espaces parcourus dans le sens de ces forces par chaque molécule, cette intégrale qui ne dépend que de la position relative des molécules étant prise de manière qu'elle soit nulle dans la position d'équilibre autour de la laquelle se fait la vibration" (the summation of the products of the masses of all its molecules by the squares of their velocities at a given moment, adding double the integral of the sum of the products of the forces multiplied by the differentials of the spaces described, in the direction of those forces, by each molecule" $[\sum mv^2 + 2[\sum F \cdot dx]$. This integral depends only on the relative position of the molecules and is taken in such a manner that it be zero for the equilibrium position about which vibrations take place). If the atoms vibrate while immersed in a fluid, they will gradually lose *vis viva* to it; if initially one atom is vibrating and the others are at rest, then the fluid will transfer some *vis viva* to these other. However, the total *vis viva* of all the atoms will decrease as waves are propagated through the fluid out of the system, unless we suppose it to be enclosed in a container of vibrators (*diapasons*), which are maintained in a state of vibration at a constant *vis viva*. Then eventually all the vibrators will approach the same *vis viva*.

Ampère rejected firmly a doctrine that had dominated atomic speculation during the preceding half-century: "Now, it is clear that if we admit the phenomena of heat to be produced by vibrations, it is a contradiction to attribute to heat the repulsive force of the atoms requisite to enable them to vibrate".

Ampère tried to answer to this objection by showing to which kind of movement were these phenomena due. His explanation was based on the distinction that he made among particles, molecules, and atoms. He defined as *particle* an infinitely small part of a body, having its same nature, so that a particle of a solid was a solid, that of a liquid a liquid, and that of a gas had the aeriform state. Particles were constituted of molecules maintained at a distance by attractive and repulsive forces; by the repulsion that established among them the vibratory movement of the intercalated ether; and by the attraction, in direct

ratio to their masses and the inverse of the square of their distance. According to Ampère *molecules* were an assembly of atoms maintained at a distance by the attractive and repulsive forces proper of each atom, forces that he accepted were substantially larger than those in the previous category. He called *atom* the material points from where these forces emanated and stated his belief that atoms were absolutely indivisible so that although space could be divided infinitely, matter could not.

Ampère distinguished between molecular vibrations and atomic vibrations. In the first, molecules vibrated in mass when they approached or separated alternatively one from the other. Molecules either vibrated or they were at rest. Atoms of each molecule were always vibrating while they approached or separated one from the other, but always attached to the same molecules. These latter vibrations constituted what he called atomic vibrations. He attributed to molecular vibrations and to their *spatial* propagation all sound phenomena and to atomic vibrations and their propagation in *ether* all heat and light phenomena⁹.

In 1845 Ernst Wilhelm Brücke (1819-1892) published a critical review of the evidence against the identity of heat and light, in connection with his studies on the physical properties of the eye; he apparently wanted to believe in this identity and to accept the wave theory of heat, though there were still some obstacles¹⁰. Hermann von Helmholtz (1821-1894) in a memoir published in 1847 on the conservation of force, concluded that heat must be explained in terms of motion, preferably by a wave theory such as that of Ampère¹¹.

It can be seen then that during most of the nineteenth century many leading physicists were led to accept a wave theory of heat. Subsequent development of better experimental techniques to understand the structure of radiant heat, the application of thermodynamic principles, the proof that ether did not exist, and research on thermal black body radiation led to the quantum theory at the beginning of the twentieth century and the demise of the wave theory.

Quantification of the phenomena

Newton seems to have been the first to consider the law of cooling of a body subject to any constant cooling action, such as for example, the influence of a uniform current of air. According to him, during the cooling of incandescent iron in a constant stream of air equal quantities of air were heated by quantities of

heat proportional to those that they removed from the iron (*Opuscula*, II, 423, 1744). In other words, Newton claimed that a hot body subject to cooling by a constant temperature source, like an air stream, should lose heat proportionally to the instant temperature difference, and the heat losses at equal time intervals should form a decreasing *geometric* progression.

Since the rate of cooling was proportional to the excess of the temperature of the body above that of the medium in which it was immersed, if $f(\theta)$ represented the rate of loss by radiation then it must be that $f(\theta) = A\theta + B$; if the temperature was measured from the absolute zero, then $B = 0$; plus the assumption that the total radiation of a body is proportional to its absolute temperature. Hence, for the rate of cooling:

$$f(\theta) - f(\theta_0) = A(\theta - \theta_0) \quad \dots(1)$$

where, $f(\theta_0)$ is the rate of absorption from the surroundings at θ_0 . Now, since the rate of cooling is $-d\theta/dt$ we may write:

$$\frac{d\theta}{dt} = -E(\theta - \theta_0) \quad \dots(2)$$

Georg Wolfgang Kraft (1701-1754) and Georg Wilhelm Richmann (1711-1753) found that Newton's formula was able to represent the facts fairly well for small differences in temperatures (a few degrees). For differences above 40° or 50°C they and other experimenters such as George Martine (1704-1742)¹², Leslie, and John Dalton (1766-1844), found it to deviate seriously from experimental evidence and attempted to replace it with another law according to which the heat losses increase more rapidly than what Newton's law predicted. Richmann¹³ restated Newton's law in the following form: "the speed of cooling is proportional to the difference in temperature between the heated body and the surrounding atmosphere".

Nevertheless, many physicists still considered Newton's law to be exact and tried to adjust it by different means; for example, Dalton thought to save it by introducing a new temperature scale.

Dalton and François Delaroche¹⁴ did independent experiments at high temperatures (where the main mechanism of heat transfer was radiation) and found that radiation losses were much faster than those predicted by Newton, but did not correlate them by an

analytical expression. According to Delaroche: "La quantité de chaleur qu'un corps chaude cède, dans un temps donné par voie de rayonnement, à un corps froid situé à distance, croit, toutes choses égales d'ailleurs, suivant une progression plus rapide que l'excès de la température du premier sur le second" (The quantity of heat which a hot body gives off in a given time by way of radiation to a cold body situated at a distance, increases, other things being equal, in a progression more rapid than the excess of the temperature of the first above that of the second).

Delaroche also found that radiant heat consisted of a mixture of different rays, or a multitude of waves of different lengths, just as a white light consisted of a mixture of differently coloured rays.

Delaroche was aware that the heat losses due to radiation increased more rapidly than in proportion to the temperature difference, but he did not isolate the radiation from the other heat losses, as Pierre-Louis Dulong (1785-1838) and Alexis-Thérèse Petit (1791-1820) attempted to do a few years later. For radiation in empty space Dulong and Petit developed a much more complicated law, introducing an absolute temperature scale and extending Newton's law. As was later seen, however, their law also possessed only limited validity and did not agree with measured results even up to 300°C.

*The work of Dulong and Petit*¹⁵⁻¹⁸

All these discrepancies led Dulong and Petit to undertake an elaborate series of experiments on the cooling of thermometers in an enclosure maintained at constant temperature, and which could be either evacuated or filled with a gas at any pressure desired. Analyses of the experimental results led them to propose the formula $(A\alpha^\theta + B)$ for the function $f(\theta)$. In this formula θ may be taken as the absolute temperature if desired, as the effect is only to alter the value of the coefficient A . If the absolute temperature is chosen, then the radiation will be zero when $\theta = 0$ and we shall have $B = -A$. By the same reasoning as before it will follow that the absorption from the walls of the enclosure at θ_0 will be $A\alpha^{\theta_0} + B$ so that the rate of cooling will be:

$$f(\theta) - f(\theta_0) = A(\alpha^\theta - \alpha^{\theta_0}) \quad \dots (3)$$

or

$$\frac{d\theta}{dt} = -E(\alpha^\theta - \alpha^{\theta_0}) \quad \dots (4)$$

In the same memoir Dulong and Petit also investigated the rate of cooling under the simultaneous action of radiation and convection and represented it by a very complicated formula [Eq. (5)]. The term representing the loss of radiation was the same as given in, Eq. (4), while that which represented the loss by conduction and convection depended on the pressure of the gas, being jointly proportional to a power of the pressure varying with the nature of the gas and a power of the temperature excess, which was the same for all gases.

With great wisdom Dulong and Petit determined the role played by each of the variables that contributed to the final result: temperature and disposition of the source that emitted heat, temperature and nature of the receiving surrounding; and influence of the surrounding gas compared to an empty environment. They realized that it was necessary to separate the heat losses caused by the surrounding fluid (today, convection), from those caused by a heat sink not necessarily in contact with the hot body (radiation) and hence performed separate experiments in vacuum and in the presence of air.

Dulong and Petit reasoned that the simplest case of cooling was that represented by a body of sufficiently small dimensions to neglect its internal temperature gradient¹⁷. That is, at any instant the body could be considered to be isothermal. In a brilliant stroke they assumed that the bulb of a mercury thermometer could be used as an example of this situation and went onto measure the cooling rate of three bulbs having a diameter of 2, 4, and 7 cm, as a function of their excess temperature above that of the surrounding air. Analysis of their results led them to conclude that the excess temperature was *independent of the size of the bulb*. They were not able to determine qualitatively how the heat loss depended on the *area* of the bulb because of the technical difficulties in measuring the area of a bulb blown at the end of a tube. Nevertheless, their approximate measurements indicated that this loss was inversely proportional to the diameter of the bulb.

Additional experiments were performed to determine the influence of the liquid employed (concentrated sulfuric acid, water, and absolute alcohol), and the shape and material of the bulb (glass or iron). Their results indicated that neither the nature of the liquid nor the shape of the bulb did influence the rate, but that a bulb made out of iron cooled faster than a glass one.

Dulong and Petit measured then the rate of cooling in vacuum using a spherical bulb with a diameter of 3 cm of a mercury thermometer. The bulb was heated up to 300°C and put into a concentric spherical enclosure at a constant temperature of 0°C or 20°C and the cooling rate measured. In some experiments the spherical enclosure was evacuated down to pressures of 2 mm Hg. The measured rate of cooling decreased with decreasing pressure and finally the data were extrapolated to zero pressure. It was supposed that by doing this, convection and conduction were avoided and only the cooling by radiation was observed. A mathematical analysis led them to determine *for the first time* a law that described heat transfer by radiation. Their final expression had the form

$$V = -\frac{d\Delta t}{d\theta} = 2.037 a^{\theta} (a^{\Delta t} - 1) \quad \dots (5)$$

where, V , is the rate of cooling when the difference in temperature is Δt , θ is the temperature of the surroundings, and a is a parameter of the system. Dulong and Petit found that for their set-up a was equal to 1.0077 when both Δt and θ were expressed in °C. Since parameter a was *independent* of the nature of the surface Eq. (4) was a general expression for the rate of cooling in vacuum of all bodies¹⁷.

The next stage in their investigation was to determine the rate of cooling when the bulb of the thermometer was in contact with a gas (air, CO₂, ethylene, and hydrogen)¹⁸. Experiments performed with the bulb of the thermometer, silver plated or not, indicated that the rate of cooling: (i) was independent of the state of the surface, (ii) for a given excess temperature it was a function of the temperature and the density of the gas, (iii) the cooling power of a gas (P) varied exponentially with the pressure of the same (P) according to $P^n = \text{constant}$, where n was a constant typical of the gas ($n_{\text{air}} = 0.45$, $n_{\text{H}_2} = 0.38$, $n_{\text{CO}_2} = 0.517$, and $n_{\text{ethane}} = 0.501$), and that (4) the total rate of cooling for radiation and convection was given by:

$$V = -\frac{d\Delta t}{d\theta} = m(a^{\Delta t} - 1) + sP^n(\Delta t)^b \quad (6)$$

where $a = 1.0077$, $b = 1.233$, m was a coefficient that depended on the nature of the contact surface and the temperature of the surrounding medium, and n and s other coefficients that depended on the nature of the gas.

Equation (5) may be considered a good example of a "bad" influence. Dulong and Petit were aware that Newton had stated that the values of the rate of cooling taken at equal time intervals formed a geometric progression. Dulong and Petit had found that the rate was faster, but the idea of some kind a progression was probably behind the mathematical model they used in developing Eq. (4) (Inspection of the latter shows that it is closely related to the *sum* of an infinite geometric progression). Had Petit used his exceptional mathematical skills in another form he could have perhaps put the temperature *as the basis* of the power and arrived at the equation that Josef Stephan (1835-1895) would develop empirically in 1879 stating that the heat radiated was proportional to the difference of the fourth powers of the absolute temperatures^{19,20}.

Ferdinand Hervé de la Provostaye (1812-1863) and Paul Desains (1817-1885) carefully studied the range of applicability of Dulong and Petit's formula^{21,22}. De la Provostaye and Desains, found that when a body of small dimensions was put in a surroundings having all parts at a constant temperature and lower to the body, the temperature of the latter would decrease for two reasons: (i) radiation of the body to the surroundings, which was larger than that of the surroundings to the body; (ii) the different gases separating the body from its surrounding carried continuously heat to the bodies. This quantity of heat did not depend on the state of the surface but on the pressure of the gas and the difference in temperature between the body and its surroundings.

Dulong and Petit's Eq. (4) although very elegant, was not general enough. It did not show how it should be modified when the emissive power of the balloon ceased to be absolute, it assumed that the cooling rate was independent of the size of the environment and, finally, it had been established for the case where the temperature of the body was higher than that of the environment (cooling process).

De la Provostaye and Desains decided to extend the experiments of Dulong and Petit in order to determine the influence of the size and nature the environment on the rate of cooling on changing the size or the nature of the environment, and the laws describing a heating process in vacuum or in air at any particular pressure.

Their results indicated that:

- (a) Dulong and Petit's formula could be applied only within a limited range, like all other empirical formula, in the neighbourhood of the experiments

from which the various constants happened to be determined.

- (b) It described reasonably well the cooling of a glass or silvered thermometer, located in a blackened environment of large dimensions. When the surface of the thermometer was metallic, the coefficient m , that measured the radiation power, varied with the temperature, increasing when the latter decreased. Its value varied little with a naked-bulb thermometer, but with a silvered bulb it changed from 0.0087 at 150°C to 0.0109 at 63°C. In addition, the absolute value of the cooling action of air appeared slightly increased.
- (c) The constant s was also found to depend to some extent on the emissivity E , being greater for a metallic surface than for the naked glass.
- (d) Decreasing the size of the environment the law of cooling became more complicated and different.
- (e) A change in the emissive power of the surroundings did not change the form of the cooling law only the value of the m coefficient sometimes changed substantially. This led to the result that at a given temperature the rate of cooling in vacuum for a given thermometer coated of different substances changed with the emissive power of the surroundings.
- (e) The cooling power of the gas was found not to be proportional to a power of the pressure (P') when the pressure was low. The experiments appeared to show that as the pressure diminished from 760 mm Hg, the cooling power decreased at first, and then remained constant from a value P_1 to a value P_2 of the pressure, after which it augmented with reduction of the pressure. These limiting pressure P_1 and P_2 were further found to be more elevated and more widely separated the smaller the dimensions of the enclosure. This behaviour was attributed to the effect of the diminution of pressure and of the smallness of the chamber on the convection currents. Under these circumstances the cooling effect due to convection was almost entirely eliminated, and the cooling due to the gas took place entirely by molecular convection.

Measurement of radiation absorption

Until 1861 no experimenter had been able to detect any absorption of radiant heat by gaseous matter, and it was generally supposed that matter in the gaseous state transmitted perfectly all kinds of radiation. In 1861 and 1863 Tyndall conducted the first convincing

experiments on the transmission of radiant heat and the radiative properties of gases demonstrating that "perfectly colourless and invisible gases and vapours" were able to absorb and emit radiant heat. The elementary gases were almost transparent to radiant heat while others were opaque²²⁻²⁴. Tyndall's results indicated that air, oxygen, and nitrogen showed no absorption at all, but compound gases especially ammonia and ethylene, exhibited a very marked effect. The absorption increased with pressure, but not according to any simple law. For very small pressures, however, the absorption was found, as expected, to be very approximately proportional to pressure. The influence of the temperature of the source on the transmission of radiant heat by vapours was very marked. In addition, it appeared that in the main the molecules maintained their characteristics as absorbers of radiant heat, although the state of aggregation changed. Humid air was also tested at various pressures, and the results verified the anticipation that the absorption varied directly as the quantity of vapour present.

Tyndall's measurements indicated that water vapour absorbed eighty times thermal radiation than pure air and concluded that this property must exercise the most important influence on climate. According to Tyndall, every variation of water vapour content must produce a change in climate and similar remarks would apply to CO₂: "It is not necessary to assume alterations in the density and height of the atmosphere to account for different amounts of heat being preserved to the earth at different times; a slight change in its variable constituents would suffice for this. Such changes in fact may have produced all the mutations of climate, which the researches of geologists reveal"²³. Tyndall was apparently the first to make an important additional deduction, namely that glacial periods may have been caused by a decrease in atmospheric carbon dioxide.

The experimental procedure used by Tyndall consisted of heating a platinum wire with an electric current and leading the radiation through a rock salt lens and a prism. He was investigating *obscure radiation*, i.e., infrared light. In the part of the spectrum beyond red he put a thermopile and measured the deflection of a galvanometer connected to it. He did not measure the temperature of the wire but only gave the colour of its appearance.

Adolph Wüllner (1835-1908) came across the 1865 German translation of Tyndall's paper and included the quoted data into the new edition of his book²⁵. In

pages 214-215 he remarked that Tyndall's experiments indicated that "the quantity of heat emitted increases considerably more quickly than does the temperature, especially at higher temperatures". Moreover, he supplemented Tyndall's results by assigning somewhat arbitrary numerical quantities to the observed temperatures: 525°C to faint red and 1200°C to full white red. Thus, from the weak red glow up to the full white glow the intensity of the radiation increased almost twelve-fold, from 10.4 to 122 (exactly 11.7-fold). Wüllner could not guess that some 25 years later his arbitrary quantities would open the stage to the development of the exact relation between temperature and rate of radiation.

In the middle of the nineteenth century John William Draper (1811-1882) contributed additional important work on the properties of radiative heat²⁶. He claimed that although the phenomenon of the production of light by all solid bodies, when their temperature was raised to a certain degree, was very familiar, no one had attempted a critical investigation of it because of the inherent experimental difficulties. Many distinguished scientists had tried to determine the temperature at which bodies became self-luminous and achieved very different results. For example, Newton fixed the temperature at which bodies become self-luminous as 635°; not only that, he wrote "Is not Fire a Body heated so hot as to emit Light copiously"?³. Davy fixed the shining temperature at 812°, Josiah Wedgwood (1730-1795) at 947° and John Frederic Daniell (1790-1845) at 980°. Wedgwood, a China maker, was the first to notice that all objects when heated (regardless of chemical constitution or physical proportions) turned red at the same temperature. There were also similar contradictions regarding the nature of the light emitted. Some said that when a solid began to shine it first emitted red and then white rays; others claimed that a mixture of blue and red light was the first to appear.

By the middle of the nineteenth century the science of spectroscopy had developed enough to prove that all glowing solids emitted continuous spectra when heated unlike heated gases which emitted bands or lines. Eventually, Gustav Robert Kirchhoff (1824-1887) would discover that the power emitted was proportional to the power absorbed, that the proportionality constant was some function of the temperature and frequency, and the definition of a perfectly black body as that one which absorbs all the radiations which fall upon it, of whatever wavelength

they may be. For a black body the power absorbed was one so that the power emitted was a function of the temperature and frequency alone²⁷.

Draper set out to (a) determine the point of incandescence of platinum, and to "prove" that different bodies become incandescent at the same temperature, (b) to determine the colour of the rays emitted by self-luminous bodies at different temperature, and (c) to determine the relation between the brilliancy of the light emitted by a shining body and its temperature.

He found that the point of incandescence of platinum was 977°F and to his conviction, this was the temperature at which *all* solids begin to shine. In addition, he concluded that as the temperature of an incandescent body raised, it emitted rays of light of an increasing refrangibility, and that the apparent departure from this law was due to the special action of the eye in performing the function of vision. The luminous effects were due to a vibratory movement executed by the molecules of platinum and the frequency of these vibrations increased with temperature. In addition, if the quantity of heat radiated by platinum at 980°F was taken as unity, it will have increased at 1440° to 2.5, at 1900° to 7.8, and at 2360° to about 17.8.

Stefan's contribution

Stefan did research in all branches of physics: mechanics, optics, thermodynamics, and electrodynamics. His contributions to thermodynamics, particularly in heat transfer, heat conduction, and gas absorption, are probably the best known. He was the first to measure correctly the heat conductivity of gases²⁸, to determine the correct relationship between thermal radiation and temperature²⁰, and to study the formation of ice in the Polar seas, giving a special solution to this non-linear conduction problem with phase change²⁹.

Before him, many scientists had tried to measure the conduction of heat in gases but were unable to achieve what they thought was an indispensable condition: that the gas remain at rest under a temperature gradient. In all the experimental arrangements devised the gas was heated near the hot body so that its density diminished and started to move upwards. That is, conductivity was always accompanied by convection making the results highly unreliable. To overcome these difficulties Stefan devised a different experimental strategy, which involved a non-stationary situation and determining

the temperature by way of the pressure of the gas, which he measured by means of a manometer. His final results indicated that the heat conductivity of gases was independent of density or pressure, as Maxwell had predicted in the framework of the kinetic theory. His measurements agreed fairly well with those calculated on the basis of the kinetic theory of gases, especially in the cases of air and hydrogen. Stefan explained the deviations from theory as resulting from the movements of atoms against each other within the molecules.

During the following years Stefan continued to do research on heat transfer phenomena, including radiation. Apparently, Stefan's attention was directed to this issue by the low surface temperature of the sun calculated according to the Dulong-Petit equation by Claude Pouillet's (1790-1868) and Jules Violle's (1841-1923) and by Jonathan Homer Lane (1819-1880)³⁰. His previous work on the conductivity of gases made him aware that heat conduction in a gas did not depend on pressure and understood that the experimental procedure used by Dulong and Petit had eliminated convection but not conduction. Therefore, he decided to find a better empirical equation for the heat transferred by radiation. Dulong and Petit had used the Celsius scale in their equation and Stefan, experienced in the kinetic theory, chose the absolute temperature.

In 1879 Stefan used Wüllner's report of Tyndall's data²⁵, transforming them to absolute temperature. He realized that by raising the ratio of the absolute temperatures $(273+1200)/(273+525) = (1473/798) = 1.846$ to the fourth power, he got 11.6, almost the same reported by Wüllner for the increase of the intensity of radiation the weak red glow up to the full white glow. From this result he made the bold statement that the heat radiated was proportional to the fourth power of the absolute temperature. "This observation", Stefan said, "caused me at first to take the heat radiation as proportional to the fourth power of the absolute temperature"¹⁹:

$$j = \sigma T^4 \quad (7)$$

where, j , is the emitted energy flux density and σ a proportionality constant, which Stefan estimated to be $4.5 \times 10^{-8} \text{ W/m}^2 \cdot \text{K}^4$. The present value of Stefan's constant is $5.6703 \times 10^{-8} \text{ W/m}^2 \cdot \text{K}^4$. Equation (6) constitutes the well-known *Stefan radiation law*.

When comparing the complexity of Eq. (6) with the simplicity of Eq. (7) one cannot but recall Ockham's

Razor Principle: The simplest solution is usually the correct one.

Stefan then proceeded to discuss the experiments of Dulong and Petit¹⁶⁻¹⁸, de la Provostaye and Desains²¹, Draper²⁶, Tyndall²²⁻²⁴, Ericsson³¹, and others. Stefan showed that his formula agreed with their results in all temperature ranges, if allowance was made for conduction through the gas. He suggested that Dulong and Petit had described their data incorrectly because their extrapolation procedure to eliminate the influence of air on the net heat flow could not have eliminated the effect of the thermal conductivity of the gas. Stefan estimated the thermal conductivity through air at all pressures contributed between 10 to 15% of the rates of cooling reported by Dulong and Petit for a bare thermometer, and up to 50% for a silver-coated thermometer (because of its low emissivity).

Moreover, with the aid of his new formula Stefan could calculate, on the basis of Pouillet's and Violle's actinometric observations, that the surface temperature of the sun was approximately 6000°C. To do so he had to use data about the rate of emission of radiant energy from the sun and the emissivity of its surface, data that at that time were highly untrustworthy. Pouillet had used the value of 84,888 cal/cm²/min for the rate of emission and Violle a value 44% higher. Stefan found that the temperature of the sun was also strongly dependent of the value selected for the emissivity; Dulong and Petit's equation yielded 1450°C for the minimum value (Pouillet) and 2025°C for the maximum value (for an emissivity of 0.025). With the fourth-power formula the corresponding range was from 5600° to 11000°C.

Stefan's findings may be considered a good example of serendipity: his initial purpose was to find an empirical equation that would be better at high temperatures than that of Dulong and Petit. He achieved this goal but at the same time he discovered a universal law of nature that is valid, however, for a special body only, the black body which absorbs all incidental radiation and at a given temperature of all bodies is the optimal radiator. Not only that, he discovered the law using data which were later proved to be wrong: (a) Tyndall's measurements referred to infrared light and not to the radiation of all wavelengths, which is contained in Stefan's law; (b) for a platinum wire the fourth-power law does not apply. Platinum remains shiny and its emissivity increases with temperature, the radiated energy being approximately proportional to the fifth power of the

absolute temperature, and (c) Wüllner's temperatures, as remarked already, were chosen somewhat arbitrarily.

The theoretical deduction of Stefan's relationship was first achieved in 1884 by Ludwig Boltzmann (1844-1906), Stefan's most distinguished student, within the context of thermodynamics by studying an ideal thermal engine using radiation instead of a gas and taking into account James Clerk Maxwell's (1831-1879) result for the pressure of light³². The most important of Boltzmann's results was that the relation derived by Stefan was exact only for completely black bodies. So the law nowadays is known as the *Stefan-Boltzmann law*.

Today, both Stefan's law and Stefan's constant may be derived from the radiation law proposed by Planck in 1901, which covers the entire frequency range:

$$\rho_{\lambda} = \frac{8\pi hc}{\lambda^5 (e^{hc/\lambda kT} - 1)} \quad \dots (8)$$

where, ρ_{λ} , is the energy of radiation per unit volume per unit wavelength (λ), and h and k are Boltzmann's and Planck's constants respectively. Planck's law signals the beginning of quantum physics and modern physics.

Boltzmann's proof of Stefan's law

According to the electromagnetic theory of light, when light is incident perpendicularly on a plane surface, which is perfectly reflecting, it exerts a pressure on the surface equal to the density of the energy of the radiation, U/V , where U is the energy of the radiation contained in volume. Energy U is independent of the materials comprising the walls and depends on the temperature and the volume. If instead of a parallel beam, the light is incident in all directions, then the pressure exerted by the black body radiation in an enclosure is equal to one-third of the density of the energy, $P = u/3$. Black body radiation is therefore, completely specified by the pressure and volume of the radiation, and the temperature of the walls with which the radiation is in equilibrium.

Since the coordinates P , U , and T describe the black body, it may be treated as a chemical system and Maxwell relations used to derive Stefan's law as follows:

$$dU = TdS - PdV \quad \dots (9)$$

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial S}{\partial V}\right)_T - P \quad \dots (10)$$

but $(\partial S/\partial V)_T = (\partial P/\partial T)_V$ so that

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P \quad \dots (11)$$

Since $U = Vu$ and $P = u/3$, where u is a function of T only, Eq. (10) becomes

$$u = \frac{T}{3} \frac{du}{dT} - \frac{u}{3} \quad \dots (12)$$

$$\frac{du}{u} = 4 \frac{dT}{T} \quad \dots (13)$$

which integrates to

$$u = bT^4 \quad \dots (14)$$

where, b , is a constant.

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