Josef Stefan. Radiation, conductivity, diffusion, and other phenomena

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RESUMEN. A Josef Stefan (1835-1893) le debemos el desarrollo de un método preciso para medir la conductividad de un gas, la determinación empírica de la ley que describe la radiación de un cuerpo negro (la ley de la cuarta potencia), el análisis del movimiento de la interfase en la fusión de la capa de hielo polar, un método para medir el coeficiente de difusividad y un análisis del tono de un sonido. Aun cuando la derivación de Stefan de la ley de radiación se basó en datos experimentales de otros que más tarde se probó que estaban errados, Boltzmann demostró posteriormente su validez usando argumentos termodinámicos.

ABSTRACT. To Josef Stefan (1835-1893) we owe the development of a precise method for measuring the heat conductivity of gases, the empirical determination of the law describing the radiation from a black body (fourth-power radiation law), analysis of the moving interface in the melting of the polar ice, a method for measuring the diffusivity coefficient, and analysis of the pitch of sound. Although Stefan’s derivation of the heat radiation law was based on experimental data of others, which were later proven to be wrong, Stefan’s equation was later proven to be correct by Boltzmann based on theoretical thermodynamic reasoning.

LIFE AND CAREER
Josef Stefan (Figures 1 and 2) is well known for his discovery of the fourth-power heat radiation law that carries his name. Most of the publications related to him describe this particular contribution, but almost none give personal details about his life or his seminal contributions to other physical and thermodynamic subjects.1,2 Only Strand’s pamphlet goes into some details and his work will be used here.

Josef Stefan was born on March 24, 1835, at St. Peter, now a part of Celovec (Klagenfurt). He was the illegitimate child of Marija Startinik who worked as a maid. Josef was eleven years old when his mother married his father and went to live with him. At that time his father had just opened a shop for selling milling and bakery products; the family was poor but could afford to provide the child with basic education, an important attitude considering that his parents are said to have been illiterate.

Josef attended primary school in his hometown where his teachers observed his talents and recommended further schooling. In 1845 he entered the Klagenfurt gymnasium and graduated eight years later. In school he showed a particular interest in learning the Slovenian language and literature. After graduation he moved to Vienna to study Mathematics and Physics at the Philosophical Faculty of the University of Vienna. In 1857, while in his fourth year of studies, he passed the teacher’s examination. At that time he was already giving physics lectures for pharmacy students. After passing the examination he also taught at a private secondary school (the oberrealeschule in the inner State) and even took part in administering the school as deputy school-master.3

On his own initiative he began research in theoretical physics, prepared two papers and sent the third to the Academy of Science. Its reading at the Academy was well received and attracted the interest of Carl Ludwig (1816-1895), a well-known professor of Physiology, who invited him to collaborate in experimental work at the Institute of Physiology. Stephan accepted his invitation and worked with Ludwig on the flow of water through tubes.

In 1858 Stefan passed his final examination at the university, the philosophical rigorosum, and was granted his doctorate. The following year he became Privatdozent in...
Mathematical Physics and as such he was officially entitled to lecture at the University. In 1860, thanks to the proposal of Ludwig and his colleague Ernst Wilhelm Brücke (1819-1892) he was elected a corresponding member of the Imperial Academy of Sciences. All these achievements did not advance Stefan’s chances for obtaining a position at the Institute of Physics, which would allow him to carry his own research. Nevertheless, the situation improved. Both professors of physiology persuaded a high official in the ministry of education to attend one of Stefan’s lectures. The official was so impressed by the lecture that when a new position of full professor (Professor Ordinarius) of mathematics and physics was opened it was offered to Stefan. Thus, in 1863, at the age of 28 he became the youngest full professor in the Austro-Hungarian Empire. A series of fortuitous events catapulted his scientific career ahead. First, Wilhelm Joseph Grailich (1829-?) was made a member of the faculty board, of which Stefan had become a member, and he was transferred to his apartment at the Institute, where he also lived. He did not travel and participate at scientific meetings that were organized in Europe already at that time.

According to Strnad Stefan could well have become a Slovenian poet if he had not chosen physics. While living in Carinthia, German was spoken in towns at that time but Slovenians populated the country. In 1848 the Slovenian language became an obligatory subject and also a subject at the general examination for Slovenians and a non-obligatory subject for the others. When this event took place Stefan was in the fifth class and from there on he began to write poems in Slovenian under the tutorship of Anton Janezic (1829-1869). In the same year (1849) he and his schoolfellows launched a manuscript literary journal called Slavija. Some of the poems written by Stefan were later published in Slovenian journals appearing in Austro-Hungary. Up to 1853 the poems were signed Stefan, late on either Stefan or with a pseudonym, mainly J. A. Spleteni, after the meaning of the Greek word stephanos (interlaced). In addition, he started publishing popular scientific articles in Slovenian magazines and thus contributed to the development of Slovenian language in natural science.

Stefan was known as a cheerful youth who loved singing, took part in choirs, and was even involved in organizing them. In 1891, two years before his death, he married the widow Marija Neumann. By the end of 1892 he had an apoplectic stroke when he was visiting a friend. For a couple of weeks he lay unconscious and could not be moved back home. Then his health improved somewhat and he was transferred to his apartment at the Institute where he died on January 7, 1893, at the age of fifty-eight.

Josef Stefan may be considered the best-known Slovenian physicists; as one of the leading physicists of the Austro-Hungarian Empire he took advantage of the possibilities a prosperous capital could offer. His increased work in physics separated him little by little from taking part in Slovenian affairs and contributed to his alienation from Ljubljana. He was extremely active, as a provisional list of his duties around 1883 shows: member of the faculty board, Director of the Institute of Physics, a member of the International Committee on Explosions of Mining.
Gases, chairman of the scientific committee of the World Electro-
technical Exhibition in Vienna (1883) and the first chairman of the
Austrian Society of Electrical Engi-
neering and editor-in-chief of its
publications. In 1885 he was ap-
pointed chairman of the Interna-
tional Committee on Music Pitch in
Vienna. He was a member of several
foreign scientific academies, held
numerous Austrian and foreign hon-
rors, and was both royal and privy
Imperial councillor. As a “councilor at
court” he would be entitled to use
“von” with his name if only he would
apply for this. He did not.8

SCIENTIFIC CONTRIBUTION

Stefan did research in all
branches of physics: mechanics, op-
tics, thermodynamics, and electro-
dynamics.4-20 His contributions to
thermodynamics, particularly in
heat transfer, heat conduction, radia-
tion, and gas absorption, are prob-
ably the best known. He was the first
to measure correctly the heat con-
ductivity of gases,11 to determine the
correct relationship between ther-
mal radiation and temperature,14 and
to study the formation of ice in the
Polar seas, giving a special solution
to this non-linear conduction prob-
lem with phase change.16,18 He was
interested in fluid flow and in oscil-
lations and this led him to acoustics.
In his first paper in 1857 he consid-
ered general oscillatory equations 4
and problems related to the transver-
sal and longitudinal oscillations of
rods and on the velocity of sound.5
In optics he studied the polarization
of light,4 double refraction, interfer-
ence of light, especially Newton’s
rings, and measurement of the wave-
length.7 Afterwards, he put most of
his efforts on the experimental and
theoretical aspects of thermodyna-
mics and electrodynamics. In a well-
known work on the diffusion of
gases,10-12 Stefan measured the
evaporation of liquids in thin long
tubes and calculated the theoretical
coefficients of diffusion and of fric-
tion and their dependence on the ab-
solute temperature, showing that
the calculated values were in agree-
ment with the experimental results
obtained by James Clerk Maxwell’s
(1831-1879), Thomas Graham (1805-
1869), and Joseph Loschmidt (1821-
1895). Another well-known work
related to the relation between sur-
face tension and evaporation, which
included Stefan’s number and
Stefan’s law. He also demonstrated
that the apparent adhesion of two
glass plates is a hydrodynamic phe-
nomenon.

Although all his contributions,
made at the University of Vienna,
contain important work the most
important belong to thermodynam-
is. The results of his many activi-
ties resulted in the publication of
52 papers, almost without exception,
in the proceedings of the Vienna
Academy of Sciences. Twelve of
them dealt with mechanics and hy-
drodynamics, seven with acoustics,
twenty-five with thermodynamics
and the kinetic theory of gases,
twelve with optics, and twenty-six
with electricity and magnetism. He
began his research activities in the
field of mechanics.

Heat and mass transfer

As mentioned above, the two
main Stefan’s achievements in ther-
modynamics are related to heat con-
duction in gases and to the radiation
law. Stefan was the first to measure
the thermal conductivity of gases
and was led to the fourth-power ra-
diation law by considering measure-
ments of others. These and other
related subjects will be now de-
scribed in more detail.

Heat conductivity of gases

Before Stefan, many physicists
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
stay at rest under a temperature gra-
dient. In all the experimental ar-
rangements devised the gas was
heated near the hot body so that its
density diminished and started to
move upwards, that is, conductivity
density diminished and started to
cannot develop. Conduction of
heat through the gas gap cooled the
air in the inner cylinder and reduced
its pressure. The rate of change of
pressure allowed calculating the
heat conductivity of the gas in the
gap. The values obtained with appar-
ratus built of different materials
agreed very well with one another;
the conductivity of air was found to
be 0.000 056 cm/s, which was nearly
20 000 times smaller than that of cop-
per and 3 400 times less than that of
iron. The calculated value compared
very well with the one calculated by
Maxwell from the dynamical theory
of gases: 0.000 055.21 Stefan noted
that “the conductivity of air...about
3 400 times smaller than of iron.
Maxwell states that air must conduct
about 3 500 times worse than that of
iron”.

Stefan also measured the
conductivity of other gases and
found, for example, that the conduc-
tivity of hydrogen was seven times
greater than that of air. An important

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outcome of Stefan’s experiments was that it supported Maxwell’s prediction that the conductivity of air should not depend on pressure. Decreasing the pressure in the air gap to one half its normal value did not alter the rate of cooling. Stefan wrote “Also another law, which is given by the law of collisions, namely the independence of the conductivity from density, has proved correct in a completely indisputable way by this experiment.” Stefan explained the deviations from theory as resulting from the movements of atoms against each other within the molecules.

**Heat radiation**

Stefan’s most important work dealt with heat radiation. At his time experimental information about the phenomenon and its characteristics was accumulating very fast, but still there was no equation that described it accurately.

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. He found that 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. 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.

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), John Leslie (1726-1832), 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 increases more rapidly than what Newton’s law predicted. Richmann restated Newton’s in the form: the speed of cooling is proportional to the difference in temperature between the heated body and the surrounding atmosphere.

Fourier in his famous book *Analytical Theory of Heat* stated that “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.”

François Marcet Delaroche (1803-1883) 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.

In the period 1800-1835, experiments on radiant heat by William Herschel (1738-1822), Leslie, Macedonio Melloni (1798-1854), and others showed that radiant heat increases more rapidly than 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.

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 colorless and invisible gases and vapors” were able to absorb and emit radiant heat. The elementary gases were almost transparent to radiant heat while others were opaque. 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. The influence of the temperature of the source on the transmission of radiant heat by vapors was very marked.

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 color of its appearance.

Adolph Wüllner (1855-1908) came across the 1865 German translation of Tyndall’s paper and included the quoted data into the new edition of his book. 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: 552 °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.

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 to define a perfectly black body as the one that 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 alone.

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 color of the rays emitted by self-luminous bodies at different temperatures, 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. The luminous effects were due to a vibratory move-
ment 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 1 440 °F to 2.5, at 1 900 °F to 7.6, and at 2 360 °F to about 17.8. During the last quarter of the nineteenth century 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).23 His previous work on the conductivity of gases had made him aware that heat conduction in a gas did not depend on pressure and to realize 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 Wülliner’s report of Tyndall’s data,24 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 value reported by Wülliner for the increase of the intensity of radiation of 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:”

\[ j = \sigma T^4 \]  

where \( j \) is the emitted energy flux density and \( \sigma \) proportionality constant, which Stefan estimated to be 4.5 \( \times 10^4 \) W/(m²·K⁴) [the present value of Stefan’s constant is 5.670 \( \times 10^4 \) W/(m²·K⁴)]. Equation (1) constitutes the well-known Stefan radiation law.

Stefan then proceeded to discuss the experiments of Dulong and Petit,25-27 Ferdinand Hervé de la Provostaye (1812-1883) and Paul Desains (1817-1885),28 Draper,29 Tyndall,26-28 Ericsson,30 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 6 000 °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 1 450 °C for the minimum value (Pouillet) and 2 025 °C for the maximum value (for an emissivity of 0.025). With the fourth-power formula the corresponding range was from 5 600 to 11 000 °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 it 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) Wülliner’s temperatures, as remarked already, were chosen somewhat arbitrarily.

The theoretical deduction of Stefan’s relationship was first achieved in 1884 by Ludwig Boltzmann40 (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 Maxwell’s result for the pressure of light.23 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 Max Planck (1858-1947) in 1901, which covers the entire frequency range

\[ P_\lambda = \frac{8 \pi \hbar c \lambda^5}{e^{\hbar c / \lambda k T} - 1} \]  

where \( P_\lambda \) is the energy of radiation per unit volume per unit wavelength (\( \lambda \)), and \( h \) and \( k \) are Boltzmann’s and Planck’s constants respectively. Planck’s law signals the beginning of quantum physics and modern physics.

**Evaporation and diffusion**

In 1866, within the development of his molecular theory of gases, Maxwell derived an equation describing the movement of a component by diffusion caused by a concentration gradient in a mixture. Stefan clearly recognized that diffusion could give rise to a convective movement in the mixture and did a series of experiments to determine the characteristics of the phenomenon on a macro scale.16,17 His apparatus consisted of long and narrow open tubes, filled partially with a liquid and held at constant temperature. The tubes were narrow to avoid a great lowering of temperature at the evaporating surface.

The following results were obtained: (a) the velocity of evaporation of a liquid from a tube is inversely proportional to the distance of the level of the liquid from the open end of the tube. This law is very exact when the distance is larger than 10 mm, (b) the velocity of evaporation is independent of the diameter of the tube (for tubes between 0.3 to 8 mm) and, (c) velocity
increases with the temperature because of the increase in vapor pressure of the liquid. If \( P^0 \) is the maximum vapor pressure at the temperature of experimentation and \( P \) the atmospheric pressure then the rate of evaporation is proportional to \( \log[P/(P - P^0)] \).

Some Serious observations were made when the open end of the tube was immersed in ether: bubbles were seen to form and disengage continually from the tube and, in the beginning, the times in which successively equal numbers of bubbles formed were proportional to the odd numbers. The upper part of the immersed tube was filled with hydrogen instead of air; the same number of bubbles formed in one-fourth the time. In other words, evaporation in hydrogen proceeded four times as rapidly as in air. If now the tube was provided with a cock on its open end, and submerged in ether, the level of the liquid within the tube sank below that of outside and, at first, the depths to which the interior level sunk below the exterior in an infinite time was as the square-roots of those times.

The Stefan diffusion tube has been widely used for the determination of vapor phase diffusion coefficients. The liquid to be vaporized is placed in the bottom of a vertical tube, which is maintained at a constant temperature. A gas is passed over the top of the tube at a rate sufficient to keep the partial pressure of the vapor there essentially corresponding to the initial composition of the gas but low enough to prevent turbulence. The mass flux is determined by weighing the tube during the quasi steady state evaporation period. The vapor phase diffusion coefficients are readily calculated from the mass flux and the concentration gradient over the diffusion tube with the assumption of plug flow in the tube. Lee and Wilke have presented a critical review of the experimental technique.

In the steady state the rate of vaporization \( N_A \) is given by the well-known equation

\[
N_A = \frac{D_x P^0 \Delta P}{R T P X} \quad (3)
\]

where \( D_x \) is the diffusion coefficient of component \( A \), \( P \) the total pressure, \( P^0 \) the saturation pressure corresponding to the surface temperature \( T \) of the liquid, \( P^0 \) the vapor pressure of the inlet gas, \( x \) the axial distance, and

\[
\frac{P - P^0}{P - P^0} = \ln \left[ \frac{P - P^0}{P - P^0} \right] \quad (4)
\]

Stefan also derived an equation for the calculation of the total transport rate of a component caused by diffusion in a mixture with a concentration gradient. This problem is nowadays known under the name the Stefan Diffusion Problem.

**Change of state**

A very important problem of theoretical and practical significance is that of the change of phase, in which a substance (pure or mixed) changes from one phase to another, with release or absorption of heat. This phenomenon arises in many contexts in which the most important are melting and solidification. The problem of ground freezing and ice formation is of great importance both in geophysics and in ice manufacture. A great deal of attention has been paid to the solidification of castings.

The essential feature of phase change phenomena is the existence of a moving surface of separation between the two phases. The way in which this surface moves has to be determined. Heat is liberated or absorbed on it, and the thermal properties of the two phases on different sides of it may be different, so that the problem is one of considerable difficulty.

Apparently the first work of interest in this area was the paper\(^6\) of Gabriel Lamé (1795-1870) and Be-noit-Pierre-Emile Clapeyron (1799-1864) published in 1831. In this work the problem was posed of determining the thickness of the solid crust generated by the cooling of a liquid filling the half space \( x > 0 \) under the influence of a constant temperature at the plane \( x = 0 \). The temperature of the liquid was initially everywhere equal to the crystallization temperature. Lamé and Clapeyron found that the thickness of the crust is proportional to the square root of the time, but did not determine the coefficient of proportionality. The first published general discussion seems to be that by Stefan\(^9\) in a study of the thickness of polar ice and for this reason the problem of freezing is frequently referred to as the problem of Stefan.

In 1889, Stefan in his work on the freezing of the ground\(^9\) posed and solved the following problems: (a) A material existing in two phases (liquid and solid) and transmitting heat only by conduction, fills the half space \( x > 0 \). At the initial time it is at a constant temperature \( T_2 > 0 \). At the surface \( x = 0 \) it is maintained at constant temperature \( T_1 > 0 \), under the effect of which there arises crystallization, occurring isothermally for temperature \( T = 0 \), without supercooling, for which the small variable effects are neglected; (b) the heating material occupies the space \(-\infty < X < \infty \). At the initial time the liquid fills the domain \( 0 < X < \infty \) at temperature \( T_2 > 0 \), while the solid occupies the domain \(-\infty < X < 0 \) at temperature \( T_1 < 0 \). The remaining conditions are the same as in the first problem. It is then required to determine the temperature \( U_1(x,t) \) and \( U_2(x,t) \) of the solid and liquid phases and the position \( x = y(t) \) of the boundary between them. Calculation of the thermal balance yields, as shown by Stefan, the condition

\[
\lambda \frac{d^2 y}{dt^2} = \left[ k_1 \frac{\partial U_1}{\partial x} - k_2 \frac{\partial U_2}{\partial x} \right]_{x = y(t)} \quad (5)
\]

where \( \lambda \) is the latent heat of crystallization per unit mass, \( \rho \) the density, and \( k_1 \) and \( k_2 \) the coefficients of conductivity of the solid and liquid phases, respectively. Both problems examined by Stefan admit similarity solutions.

In the same work of 1889, Stefan gave an analogous description of process of neutralization for diffusion transport of material in a reaction zone\(^5\) and evaporation and condensation.\(^4\) Finally, in the same year Stefan published his fourth work related to the problem\(^17\) where he examined the problem of melting of a layer of ice with initial temperature equal to zero, subject to the influence of the temperature \( f(t) \) at the boundary \( x = 0 \).

The work of Stefan attracted the attention of geophysicists and caused led to several unsuccessful attempts to solve the more general problems.

**Miscellaneous**

**Acoustics**

Stefan also devoted part of his time to acoustical problems and published seven papers on the subject. Here we summarize his most important findings.

In a paper published in 1866 he reported on the effects of internal friction in the air on the motion of sound.\(^4\) His results indicated that friction increased the velocity of sound and that the increase was larger the higher the tone. Neverthe-
Standing vibrations are possible only if the length of the wave exceeds a certain value. Yet this is very small, equal to four times the mean molecular path, which, according to the kinetic theory of gases, a molecule makes from one impact to the other.

In standing waves also the amplitude decreases with the time in geometrical progression, with an exponent proportional to the square of the number of vibrations. The amplitudes of the tones of 1,000, 10,000, and 30,000 vibrations dropped to one-half before the lapse of 100.1, and 0.1 s, respectively.

Stefan was aware that the method introduced by Ernst Florens Friedrich Chladini (1756-1827) for determining the speed of sounds from the longitudinal tones of bars, was not applicable to bars, which were not long enough to be made to sound by friction [1]. For this reason he built an experimental device that overcame these limitations.

The body to be investigated was constructed in the shape of a small bar and fastened to a longer bar made of wood or glass, which could thus be readily made to sound. The compound bar was now made to sound by friction and the number of vibrations of the fundamental note or of a higher tone determined. Stefan deduced a rather complicated mathematical expression, which knowing the velocity of sound in the larger bar, allowed calculating the same in the smaller bar. His results indicated that, for example, the velocity of sound in wax at 20 °C was 730 m/s, that is, about twice as great as in air. Increasing the temperature led to a decrease in velocity: an increase in 1° reflected in a decrease of 40 m. At 30 °C the velocity of sound in wax and air are the same. For grease at 20 °C the velocity of sound was about one-half that in wax. Increasing the temperature the velocity decreased more rapidly than in air. In caoutchouc (natural rubber) the velocity of sound varied between 30 to 60 m/s; the softer the rubber the smaller the velocity. Stefan made the observation that his results recalled those of Hermann Ludwig von Helmholtz (1821-1894) for the velocity of nervous excitation, which is within the same limits as the velocity of soft rubber.

At the International Conference on Musical Pitch, held at Vienna in 1885, the proposals of the Austrian commission of experts were generally adopted in central and eastern Europe; the standard pitch was established at 435 cycles per second, as had already been done in France in 1859 and in Austria in 1862. For the production of this tone the conference prescribed, according to Stefan's account, the standard tuning fork constructed to replicate the tuning forks of Karl Rudolf König (1832-1901).

**Optics**

In optics, Stefan's interests centered on the polarization of light, double refraction, interference of light, especially Newton's rings, and measurement of the wavelength.

In a paper about the dispersion of light owing to the rotation of the plane of polarization, Stefan explained that there are only two possible forms of dispersion; each color in white light has either a particular velocity of propagation or a particular direction of vibration. The first kind of color dispersion occurs in refraction and diffraction; the second when light passes through a substance, which turns its plane of polarization inasmuch as the rotation has a different magnitude for each color. The occurrence of dispersion through refraction or through alteration of the plane of polarization means that in the one case the refractive index and in the other the angle of rotation is a function of the wavelength of a color. Each color is determined by its wavelength, also by the refractive index, or by the angle or rotation in a given substance. Hence these two quantities must be related and the corresponding relation may be disclosed by a prismatic analysis of the light as it leaves the polarizing apparatus.

The rotation of the place of polarization is proportional to the thickness of the plate of quartz. When the latter is considerable the amount of rotation for the different colors is equal to several complete revolutions. When the polarizer and analyzer are placed parallel, the latter removes from the light those colored rays coming through the quartz that have undergone rotations. The latter are odd multiples of 90°. In the places of these colors, dark bands appear in the spectrum. The number of bands is found multiplying the thickness of the plate in millimetres by 1/6 and 5/9; the number of odd integers between the two products is the number of bands.

When the analyzer is rotated the bands move from the red towards the violet end, or the reverse, according as the analyzer moves in the sense of rotation of the plane of polarization or the contrary. Thereby the number of bands may be altered by a difference of one. In addition, the relative position of the bands is dependent upon the nature of the substance forming the prism and upon the thickness of the rotating plate. For a prism made of crown glass or flint glass the following propositions may be deduced from the experiments: (a) the dark bands of the spectrum are equidistant, (b) the distance between two contiguous bands is inversely proportional to the thickness of the quartz plate employed and, (c) the bands move regularly and correspondingly on turning the analyzer. In addition, since the dark bands correspond to colors for which their angles of rotation differ by a constant quantity, then the distances of the colors in the spectrum are proportional to the differences in their angles of rotation.

Calculation of the refractive indices of the individual dark bands indicates that equal differences of refractive index correspond to equal differences of rotation. In other words, there is a linear relation be-

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Note 1. Ernst Florens Friedrich Chladini (1756-1827) was an 18th century physicist who found that playing a violin near a sand covered disk caused the sand to form geometric shapes.
between angle of rotation and the re-fractive index, that is, both are similar
functions of the wavelengths.

In a following publication Stefan
described a new method he had de-
veloped for measuring the lengths
of light waves. The basis for his pro-
posal was the fact that when light falls on a column of vapours, and on the
finished faces parallel to the optical
axis, each ray is resolved into the or-
dinary and the extraordinary ray, if
the faces of entrance and of emer-
gence are parallel. Bringing both
rays into a common direction of vib-
ration results in the extinction of
those rays having a difference of op-
tical path equal to an uneven num-
ber of semi-wavelengths. For the
complete spectrum the extinction
appears as dark interference bands
that are more numerous and thinner
the thicker the quartz. The differ-
ence of phase between two rays may
be calculated very accurately from
the thickness of the quartz and from
the quotients of refraction since only
the differences and not the absolute
value of the latter are required.
Twice the difference of phase di-
vided by the wavelength is an un-
even number for each dark band,
and for each succeeding one towards
violet it is two units greater. Know-
ing the wavelength and number of
bands in one Fraunhofer line allows
calculating the wavelength of the
following Fraunhofer line.

A wavelength may be deter-
mained directly by successively in-
creasing or decreasing the differ-
ence of phase for the place of the
spectrum in question. This leads to
a removal of the interference band.
The pertinent wavelength is then
calculated from the number of bands,
which have passed through the
cross wires and the change of the
difference of phase thus produced.

Stefan illustrated his procedure
by giving the calculated wave-
lengths of Fraunhofer’s lines B, C, D,
E, F, G, and H, as 687.3, 657.8, 527.1,
486.9, and 395.9 nm, respectively.
These values agreed very accurately
with those deduced from the diffraction
phenomena of fine gratings.

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