

rocks. If the rate of formation of an inactive decay product could be determined, the total amount found in a mineral would immediately yield its age. Both lead and helium (believed by most to be the alpha particle) were seen as suitable elements and, indeed, served in radioactive dating techniques. The helium method, pioneered in England by R. J. Strutt (later the fourth Baron Rayleigh), could not, however, give more than a minimum age because a variable portion of the gas would have escaped from the rock. But the lead method, developed by Boltwood in 1907, proved satisfactory and is still in use today. In effect, Boltwood reversed his procedure of confirming the accuracy of lead:uranium ratios by the accepted geological ages of the source rocks, and used these ratios to date the rocks. Because most geologists, under the influence of Lord Kelvin's nineteenth-century pronouncements, inclined toward an age of the earth measured in tens of millions of years, Boltwood's claim for a billion-year span was met with some skepticism. However, the subsequent work of Arthur Holmes, an understanding of isotopes, and the increasing accuracy of decay constants and analyses finally brought widespread acceptance of this method in the 1930's.

Boltwood's major contributions lay in the understanding of the uranium decay series. Still, he was able to suggest, with Rutherford in 1905, that actinium is genetically related to uranium, though not in the same chain as radium, while in the thorium series he almost beat Hahn to the discovery of mesothorium in 1907. His other significant service to the study of radioactivity was to bring greater precision and advanced techniques into the laboratory, as in his insistence that only by complete dissolution and boiling of the mineral could all the emanation be extracted from radioactive bodies.

Boltwood remained at Yale the rest of his life, except for the academic year 1909–1910, when he accepted an invitation to Rutherford's laboratory at the University of Manchester. Yale, fearing that he would remain in England indefinitely, offered Boltwood a full professorship in radiochemistry. This appointment brought him back to New Haven, but it also marked the end of his research career. Heavy academic duties, including supervision of construction of the new Sloane Physics Laboratory and unsuccessful efforts to obtain large quantities of radioactive minerals for research, seem to have taken all his time and energy. His stature as the foremost authority on radioactivity in the United States brought him membership in the National Academy of Sciences, the American Philosophical Society, and other organizations, but it also brought him numerous requests from

prospectors, mine owners, speculators, chemical refiners, and wholesalers to analyze samples, devise separation processes, and find financial backing (from wealthy Yale alumni) for various projects. These efforts probably helped stimulate the production of radium, in which the United States led the world by about 1915, although they did not appreciably aid the progress of science.

In 1918 Boltwood was appointed director of the Yale College chemical laboratory and presided over the consolidation of the Yale and Sheffield chemistry departments. To cement this union, the new Sterling Chemistry Laboratory was proposed, and Boltwood was placed in charge of its design. He completed it successfully, but the strain of this effort caused a breakdown in his health from which he never fully recovered. Periods of severe depression alternated with his more customary cheerful spirits, and resulted in his suicide during the summer of 1927.

Boltwood's influence in radioactivity was widespread—through his published papers, correspondence, and personal contacts, for he trained surprisingly few research students. Part of his success stemmed from his close association with Rutherford, but like Rutherford's other chemical collaborators, Soddy and Hahn, he was eminently capable of major contributions in his own right.

BIBLIOGRAPHY

I. ORIGINAL WORKS. A reasonably complete list of Boltwood's publications is in Alois F. Kovarik's sketch of him in *Biographical Memoirs of the National Academy of Sciences*, **14** (1930), 69–96. His unpublished correspondence, papers, and laboratory notebooks are preserved in the Manuscript Room, Yale University Library. His extensive correspondence with Rutherford is in the Rutherford Collection, Manuscript Room, Cambridge University Library.

II. SECONDARY LITERATURE. In addition to Kovarik's memoir (see above), the following obituary notices offer information about Boltwood: *Yale Alumni Weekly*, **37** (7 Oct. 1927), 65; Kovarik, in *Yale Scientific Magazine*, **2** (Nov. 1927), 25, 44, 46; Rutherford, in *Nature*, **121** (14 Jan. 1928), 64–65; Kovarik, in *American Journal of Science*, **15** (Mar. 1928), 188–198.

LAWRENCE BADASH

BOLTZMANN, LUDWIG (*b.* Vienna, Austria, 20 February 1844; *d.* Duino, near Trieste, 5 September 1906), *physics*.

Boltzmann's father, Ludwig, was a civil servant (*Kaiserlich-Königlich Cameral-Concipient*); his mother was Katherina Pauernfeind. He was educated at Linz and Vienna, receiving his doctorate in 1867 from the

University of Vienna, where he had studied with Josef Stefan. Boltzmann held professorships at the universities of Graz, Vienna, Munich, and Leipzig. In 1876 he married Henrietta von Aigentler, who bore him four children.

Distribution Law. The first stimulus for Boltzmann's researches came from teachers and colleagues at the University of Vienna, especially Stefan and Josef Loschmidt. In a lecture Stefan suggested the problem in electrical theory whose solution constituted Boltzmann's first published paper (1865);¹ he also published a few papers on kinetic theory and did important experimental work on gases and radiation that provided the basis for some of Boltzmann's theories. Loschmidt (also in 1865) accomplished the first reliable estimate of molecular sizes with the help of the Clausius-Maxwell kinetic theory. Although Loschmidt was later to dispute Boltzmann's interpretation of the second law of thermodynamics, the problem of finding quantitative relations between atomic magnitudes and observable physical quantities was a common interest of both men.

Boltzmann began his lifelong study of the atomic theory of matter by seeking to establish a direct connection between the second law of thermodynamics and the mechanical principle of least action (1866). Although Clausius, Szily, and others later worked along similar lines, and Boltzmann himself returned to the subject in his elaboration of Helmholtz' theory of monocyclic systems (1884), the analogy with purely mechanical principles seemed insufficient for a complete interpretation of the second law. The missing element was the statistical approach to atomic motion that had already been introduced by the British physicist James Clerk Maxwell.² Boltzmann's first acquaintance with Maxwell's writings on kinetic theory is indicated by his paper on thermal equilibrium (1868). In this paper, he extended Maxwell's theory of the distribution of energy among colliding gas molecules, treating the case when external forces are present. The result was a new exponential formula for molecular distribution, now known as the "Boltzmann factor" and basic to all modern calculations in statistical mechanics. To understand how Boltzmann arrived at this result, we must first review the work of Maxwell on which it is based.

Maxwell, in his first paper on kinetic theory (1859), had pointed out that the collisions of gas molecules would not simply tend to equalize all their speeds but, on the contrary, would produce a range of different speeds. Most of the observable properties of a gas could be calculated if one knew, instead of the positions and velocities of all the molecules at any

given time, only the average number of molecules having various positions and velocities. In many cases it seems reasonable to assume that the gas is spatially uniform, that is, the average number of molecules is the same at different places in the gas. The problem is then to determine the velocity distribution function $f(v)$, defined so that $f(v) dv$ is the average number of molecules having speeds between v and $v + dv$.

Maxwell argued that $f(v)$ should be a function that depends only on the magnitude of v , and that the velocity components resolved along the three coordinate axes should be statistically independent. Hence, he inferred that

$$f(v) = (N/\alpha^3\pi^{3/2})e^{-(v^2/\alpha^2)}, \quad (1)$$

where N is the total number of molecules, and α^2 is inversely proportional to the absolute temperature.

In his long memoir of 1866, Maxwell admitted that the assumptions used in his previous derivation of the distribution law "may appear precarious"; he offered another derivation in which the velocities of two colliding molecules, rather than the velocity components of a single molecule, were assumed to be statistically independent. This means that one can express the joint distribution function for the probability that molecule 1 has velocity v_1 , while at the same time molecule 2 has velocity v_2 , as the product of the probabilities of these two separate events:

$$F(v_1, v_2) = f(v_1)f(v_2). \quad (2)$$

To derive the distribution function itself, Maxwell argued that the equilibrium state would be reached when the number of collisions in which two molecules with initial velocities (v_1, v_2) rebound with final velocities (v_1', v_2') is equal to the number of collisions in which two molecules with initial velocities (v_1', v_2') rebound with final velocities (v_1, v_2) ; from this condition it follows that

$$F(v_1, v_2) = F(v_1', v_2'). \quad (3)$$

By combining this equation with that for the conservation of energy (in the case when no forces act),

$$\frac{1}{2} m_1 v_1^2 + \frac{1}{2} m_2 v_2^2 = \frac{1}{2} m_1 v_1'^2 + \frac{1}{2} m_2 v_2'^2, \quad (4)$$

Maxwell deduced (as before) that

$$f(v_1) = (N/\alpha^3\pi^{3/2})e^{-(v_1^2/\alpha^2)}. \quad (5)$$

This type of reasoning about velocity distribution functions was repeatedly used and generalized by Boltzmann in his own works on kinetic theory. He began, in his 1868 paper, by considering the case in which one of the particles of a system is acted on by a force with a corresponding potential function,

$V(x)$. The condition of conservation of energy would then be

$$\begin{aligned} \frac{1}{2}m_1v_1^2 + V(x_1) + \frac{1}{2}m_2v_2^2 \\ = \frac{1}{2}m_1v_1'^2 + V(x_1') + \frac{1}{2}m_2v_2'^2, \quad (6) \end{aligned}$$

and Boltzmann could then apply Maxwell's procedure to deduce the distribution function

$$f(v) = (\text{const.}) e^{-h(mv^2/2 + V[x])}. \quad (7)$$

The constant factor h could be related to the absolute temperature of the gas, as Maxwell and Clausius had done, by comparing the theoretical pressure of the gas with the experimental relation between pressure and temperature (Gay-Lussac's law). In modern notation, h is equivalent to $1/kT$, where k is a constant, now called Boltzmann's constant, and T is the absolute temperature on the Kelvin scale.

The physical meaning of the Maxwell-Boltzmann distribution law is that the energy ($E = mv^2/2 + V[x]$) of a molecule is most likely to be roughly equal to kT ; much larger or much smaller energies occur with small but finite probability.

In the same paper of 1868, Boltzmann presented another derivation of the Maxwell distribution law that was independent of any assumptions about collisions between molecules. He simply assumed that there is a fixed total amount of energy to be distributed among a finite number of molecules, in such a way that all combinations of energies are equally probable. (More precisely, he assumed uniform distribution in momentum space.) By regarding the total energy as being divided into small but finite quanta, he could treat this as a problem of combinatorial analysis. He obtained a rather complicated formula that reduced to the Maxwell velocity-distribution law in the limit of an infinite number of molecules and infinitesimal energy quanta.

The device of starting with finite energy quanta and then letting them become infinitesimal is not essential to such a derivation, but it reveals an interesting feature of Boltzmann's mathematical approach. Boltzmann asserted on several occasions that a derivation based on infinite or infinitesimal quantities is not really rigorous unless it can also be carried through with finite quantities. While this prejudice kept him from appreciating and using some of the developments in pure mathematics that appeared toward the end of the nineteenth century, it also had the curious effect of making some of his equations for energy distribution and transfer look similar to those of modern quantum theory. (This is perhaps not quite

accidental, since Planck and other early quantum theorists were familiar with Boltzmann's works and used many of his techniques.)

Transport Equation and H-theorem. Although Maxwell and Boltzmann had succeeded in finding the correct distribution laws by assuming that the gas is in an equilibrium state, they thought that the kinetic theory should also be able to show that a gas will actually tend toward an equilibrium state if it is not there already. Maxwell had made only fragmentary attempts to solve this problem; Boltzmann devoted several long papers to establishing a general solution.

Approach to equilibrium is a special case of a general phenomenon: dissipation of energy and increase of entropy. It was Boltzmann's achievement to show in detail how thermodynamic entropy is related to the statistical distribution of molecular configurations, and how increasing entropy corresponds to increasing randomness on the molecular level. This was a peculiar and unexpected relationship, for macroscopic irreversibility seemed to contradict the fundamental reversibility of Newtonian mechanics, which was still assumed to apply to molecular collisions. Boltzmann's attempts to resolve this contradiction formed part of the debate on the validity of the atomic theory in the 1890's. Seen in this context, the proof of the distribution law has even more significance than the law itself.

Boltzmann's major work on the approach to equilibrium (and on transport processes in gases in general) was published in 1872. This paper, like that of 1868, took Maxwell's theory as the starting point. Boltzmann first derived an equation for the rate of change in the number of molecules having a given energy, x , resulting from collisions between molecules. He considered a typical collision between two molecules with energies x and x' before the collision, and energies ξ and $x + x' - \xi$ after the collision. Such a collision reduces by one the number of molecules with energy x ; the number of such collisions is assumed to be proportional to the number of molecules with energy x , and also to the number of molecules with energy x' . Boltzmann used here, without any comment, Maxwell's assumption of statistical independence of the velocities of two colliding molecules (eq. 2); later it was recognized that there might be valid grounds for objecting to this assumption.³ With this assumption, the decrease in $f(x)$ will be equal to the product, $f(x)f(x')$, multiplied by an appropriate factor for the collision probability and integrated over all values of x' . Similarly, the increase in $f(x)$ may be attributed to inverse collisions in which the molecules have energies ξ and $x + x' - \xi$ before the collision, and x and x' after the collision. By such

arguments Boltzmann arrived at the equation

$$\frac{\partial f}{\partial t} = \int_0^\infty \int_0^{x+x'} \left[\frac{f(\xi, t) f(x+x'-\xi, t)}{\sqrt{\xi} \sqrt{x+x'-\xi}} - \frac{f(x, t) f(x', t)}{\sqrt{x} \sqrt{x'}} \right] \sqrt{xx'} \psi(x, x', \xi) dx' d\xi \quad (8)$$

(This is a special case of the general Boltzmann transport equation [eq. 9]; terms describing the effect of external forces and nonuniformities on the change of f are here omitted. The square root expressions in the denominators, which do not appear in the form of the equation generally used, result from the fact that energy rather than velocity is the variable.)

One additional assumption involved in this derivation should be mentioned: the collision probability function, $\psi(x, x', \xi)$, is the same for both the direct and inverse collisions; that is, the collision is perfectly reversible.

Following Maxwell's 1866 development of the transport equations, Boltzmann showed how the diffusion, viscosity, and heat conduction coefficients of a gas could be calculated by solving the general transport equation

$$\frac{\partial f}{\partial t} + \xi \frac{\partial f}{\partial x} + \eta \frac{\partial f}{\partial y} + \zeta \frac{\partial f}{\partial z} + X \frac{\partial f}{\partial \xi} + Y \frac{\partial f}{\partial \eta} + Z \frac{\partial f}{\partial \zeta} + \int d\omega_1 \int b db \int d\phi V (ff_1 - f'f'_1) = 0, \quad (9)$$

where (ξ, η, ζ) are components of the velocity of a particle and (X, Y, Z) are components of the force acting on it, and V, ϕ, b , and ω_1 are variables characterizing the relative motion of the two molecules during a collision. (Values of the function f for velocities of the two molecules before and after the collision are indicated by f, f_1, f' , and f'_1 .)

It is difficult to obtain exact solutions of Boltzmann's transport equation except when the molecules interact with inverse fifth-power forces, a case for which Maxwell had found an important simplification.⁴ Boltzmann made several attempts to develop accurate approximations for other force laws, but this problem was not satisfactorily solved until the work of S. Chapman and D. Enskog in 1916–1917. Boltzmann's equation is now frequently used in modern research on fluids, plasmas, and neutron transport.

If the velocity distribution function is Maxwellian, then the integral on the right-hand side of eq. 8 vanishes identically for all values of the variables, and we find $\partial f / \partial t = 0$. In other words, once the Maxwellian state has been reached, no further change in the velocity distribution function can occur.

So far this is simply an elaboration of the previous arguments of Maxwell and of Boltzmann himself, but

now, with an explicit formula for $\partial f / \partial t$, Boltzmann was able to go further and show that $f(x)$ probably tends toward the Maxwell form. He did this by introducing a function, E , depending on $f(x)$

$$E = \int_0^\infty f(x, t) \left\{ \log \left[\frac{f(x, t)}{\sqrt{x}} \right] - 1 \right\} dx \quad (10)$$

and showing that E always decreases unless f has the Maxwellian form:

$$\begin{aligned} \frac{dE}{dt} &< 0 \text{ if } f \neq (\text{const.}) \sqrt{x} e^{-hx}, \\ \frac{dE}{dt} &= 0 \text{ if } f = (\text{const.}) \sqrt{x} e^{-hx}. \end{aligned} \quad (11)$$

(The proof is straightforward and relies simply on the fact that the quantity $(a - b) \log b/a$ is always negative if a and b are real positive numbers.) Boltzmann also noted that in the Maxwellian state E is essentially the same as the thermodynamic entropy (aside from a constant factor). Thus Boltzmann's " H -function" (the notation was changed from E to H in the 1890's) provides an extension of the definition of entropy to nonequilibrium states not covered by the thermodynamic definition.

The theorem that H always decreases for nonequilibrium systems was called "Boltzmann's minimum theorem" in the nineteenth century, and now goes by the name "Boltzmann's H -theorem." (It has not yet been proved rigorously except with certain specializing assumptions.)

Reversibility and Recurrence Paradoxes. The H -theorem raised some difficult questions about the nature of irreversibility in physical systems, in particular the so-called "reversibility paradox" and "recurrence paradox." (The modern terminology goes back only to the Ehrenfests' 1911 article, in which the words *Umkehrinwand* and *Wiederkehrinwand* were introduced.) The reversibility paradox, first discussed by Lord Kelvin (1874) and brought to Boltzmann's attention by Loschmidt, is based on the apparent contradiction between one of the basic premises of Boltzmann's derivation—the reversibility of individual collisions—and the irreversibility predicted by the theorem itself for a system of many molecules. Of course there must be such a contradiction between any molecular theory based on Newtonian mechanics and the general principle of dissipation of energy, but Boltzmann's work was the first to reveal this inconsistency explicitly.

Boltzmann's initial response (1877) to the reversibility paradox was the suggestion that the irreversibility of processes in the real world is not a consequence of the equations of motion and the form of

the intermolecular force law but, rather, seems to be a result of the initial conditions. For some unusual initial conditions the system might in fact decrease its entropy (increase the value of H) as time progresses; such initial conditions could be constructed simply by reversing all the velocities of the molecules in an equilibrium state known to have evolved from a nonequilibrium state. But, Boltzmann asserts, there are infinitely many more initial states that evolve with increasing entropy, simply because the great majority of all possible states are equilibrium states. Moreover, the entropy would also be almost certain to increase if one picked an initial state at random and followed it backward in time instead of forward.

The recurrence paradox arises from a theorem in mechanics first published by Poincaré in 1890. According to this theorem, any mechanical system constrained to move in a finite volume with fixed total energy must eventually return to any specified initial configuration. If a certain value of the entropy is associated with every configuration of the system (a disputable assumption), then the entropy cannot continually increase with time, but must eventually decrease in order to return to its initial value. Therefore the H -theorem cannot always be valid.

Poincaré, and later Zermelo (1896), argued that the recurrence theorem makes any mechanical model, such as the kinetic theory, incompatible with the second law of thermodynamics; and since, it was asserted, the second law is a strictly valid induction from experience, one must reject the mechanistic viewpoint.

Boltzmann replied that the recurrence theorem does not contradict the H -theorem, but is completely in harmony with it. The equilibrium state is not a single configuration but, rather, a collection of the overwhelming majority of possible configurations, characterized by the Maxwell-Boltzmann distribution. From the statistical viewpoint, the recurrence of some particular initial state is a fluctuation that is almost certain to occur if one waits long enough; the point is that the probability of such a fluctuation is so small that one would have to wait an immensely long time before observing a recurrence of the initial state. Thus the mechanical viewpoint does not lead to any consequences that are actually in disagreement with experience. For those who are concerned about the cosmological consequences of the second law—the so-called “heat death” corresponding to the final attainment of a state of maximum disorder when all irreversible processes have run their course—Boltzmann suggested the following idea. The universe as a whole is in a state of thermal equilibrium, and there is no distinction between forward and

backward directions of time. However, within small regions, such as individual galaxies, there will be noticeable fluctuations that include ordered states corresponding to the existence of life. A living being in such a galaxy will distinguish the direction of time for which entropy increases (processes going from ordered to disordered states) from the opposite direction; in other words, the concept of “direction of time” is statistical or even subjective, and is determined by the direction in which entropy happens to be increasing. Thus, the statement “Entropy increases with time” is a tautology, and yet the subjective time directions in different parts of the universe may be different. In this way local irreversible processes would be compatible with cosmic reversibility and recurrence. (Boltzmann’s concept of alternating time directions has recently been revived in connection with theories of oscillating universes.)

Statistical Mechanics and Ergodic Hypothesis. Having followed Boltzmann’s work on irreversible processes into some of the controversies of the 1890’s, let us now return to his contributions to the theory of systems in thermal equilibrium (for which the term “statistical mechanics” was introduced by J. Willard Gibbs).

It would be possible (as is in fact done in many modern texts) to take the Maxwell-Boltzmann distribution function (eq. 7) as the basic postulate for calculating all the equilibrium properties of a system. Boltzmann, however, preferred another approach that seemed to rest on more general grounds than the dynamics of bimolecular collisions in low-density gases. The new method was in part a by-product of his discussion of the reversibility paradox, and is first hinted at in connection with the relative frequency of equilibrium, as opposed to nonequilibrium, configurations of molecules: “One could even calculate, from the relative numbers of the different distributions, their probabilities, which might lead to an interesting method for the calculation of thermal equilibrium.”⁵ This remark was quickly followed up in the same year (1877) in a paper in which the famous relation between entropy and probability,

$$S = k \log W,$$

was developed and applied. In this equation, W is the number of possible molecular configurations (“microstates,” in modern terminology) corresponding to a given macroscopic state of the system.⁶ (To make this expression meaningful, microstates have to be defined with respect to finite cells in phase space; the size of these cells introduces an arbitrary additive constant in S which can be determined from quantum theory.)

The new formula for entropy—from which formulas for all other thermodynamic quantities could be deduced—was based on the assumption of equal a priori probability of all microstates of the system (that is, all microstates that have the same total energy). As noted above, Boltzmann had already proved in 1868 that such an assumption implies the Maxwell velocity distribution for an ideal gas of noninteracting particles; it also implies the Maxwell-Boltzmann distribution for certain special cases in which external forces are present. But the assumption itself demanded some justification beyond its inherent plausibility. For this purpose, Boltzmann and Maxwell introduced what is now called the “ergodic hypothesis,” the assumption that a single system will eventually pass through all possible microstates.

There has been considerable confusion about what Maxwell and Boltzmann really meant by ergodic systems. It appears that they did not have in mind completely deterministic mechanical systems following a single trajectory unaffected by external conditions; the ergodic property was to be attributed to some random element, or at least to collisions with a boundary. In fact, when Boltzmann first introduced the words *Ergoden* and *ergodische*, he used them not for single systems but for collections of similar systems with the same energy but different initial conditions. In these papers of 1884 and 1887, Boltzmann was continuing his earlier analysis of mechanical analogies for the second law of thermodynamics and also developing what is now (since Gibbs) known as ensemble theory. Here again, Boltzmann was following a trail blazed by Maxwell, who had introduced the ensemble concept in his 1879 paper. But while Maxwell never got past the restriction that all systems in the ensemble must have the same energy, Boltzmann suggested more general possibilities and Gibbs ultimately showed that it is most useful to consider ensembles in which not only the energy but also the number of particles can have any value, with a specified probability.

The Maxwell-Boltzmann ergodic hypothesis led to considerable controversy on the mathematical question of the possible existence of dynamical systems that pass through all possible configurations. The controversy came to a head with the publication of the Ehrenfests’ article in 1911, in which it was suggested that while ergodic systems are probably nonexistent, “quasi-ergodic” systems that pass “as close as one likes” to every possible state might still be found. Shortly after this, two mathematicians, Rosenthal and Plancherel, used some recent results of Cantor and Brouwer on the dimensionality of sets of points to prove that strictly ergodic systems are

indeed impossible. Since then, there have been many attempts to discover whether physical systems can be ergodic; “ergodic theory” has become a lively branch of modern mathematics, although it now seems to be of little interest to physicists.

After expending a large amount of effort in the 1880’s on elaborate but mostly fruitless attempts to determine transport properties of gases, Boltzmann returned to the calculation of equilibrium properties in the 1890’s. He was encouraged by the progress made by Dutch researchers—J. D. van der Waals, H. A. Lorentz, J. H. van’t Hoff, and others—in applying kinetic methods to dense gases and osmotic solutions. He felt obliged to correct and extend their calculations, as in the case of virial coefficients of gases composed of elastic spheres. The success of these applications of kinetic theory also gave him more ammunition for his battle with the energeticians (see below).

Other Scientific Work. Although Boltzmann’s contributions to kinetic theory were the fruits of an effort sustained over a period of forty years, and are mainly responsible for his reputation as a theoretical physicist, they account, numerically, for only about half of his publications. The rest are so diverse in nature—ranging over the fields of physics, chemistry, mathematics, and philosophy—that it would be useless to try to describe or even list them here. Only one common characteristic seems evident: most of what Boltzmann wrote in science represents some kind of interaction with other scientists or with his students. All of his books originated as lecture notes; in attempting to explain a subject on the elementary level, Boltzmann frequently developed valuable new insights, although he often succumbed to unnecessary verbosity. He scrutinized the major physics journals and frequently found articles that inspired him to dash off a correction, design a new experiment, or rework a theoretical calculation to account for new data.

Soon after he started to follow Maxwell’s work on kinetic theory, Boltzmann began to study the electromagnetic theory of his Scottish colleague. In 1872, he published the first report of a comprehensive experimental study of dielectrics, conducted in the laboratories of Helmholtz in Berlin and of Töpler in Graz. A primary aim of this research was to test Maxwell’s prediction that the index of refraction of a substance should be the geometric mean of its dielectric constant and its magnetic permeability ($i = \sqrt{\epsilon\mu}$). Boltzmann confirmed this prediction for solid insulators and (more accurately) for gases. He also confirmed the further prediction that if the speed of light (and hence the index of refraction) varies with direction in an

anisotropic crystal, then the dielectric constant must also vary with direction.

During the next few years, Boltzmann began experimental work in diamagnetism while continuing his theoretical research in kinetic theory. He proposed a new theory of elastic aftereffects, in which the stress on a material at a given time depends on its previous deformation history.

In 1883, as a result of preparing an abstract of H. T. Eddy's paper (on radiant heat as a possible exception to the second law of thermodynamics) for Wiedemann's *Beiblätter*, Boltzmann learned of a work by the Italian physicist Adolfo Bartoli on radiation pressure. Bartoli's reasoning stimulated Boltzmann to work out a theoretical derivation, based on the second law of thermodynamics and Maxwell's electromagnetic theory, of the fourth-power law previously found experimentally by Stefan:

$$(\text{radiation energy}) \propto (\text{absolute temperature})^4.$$

Although at the time the "Stefan-Boltzmann law" for radiation seemed to be an isolated result with no further consequences, it did at least show a possible connection between thermodynamics and electromagnetism that was exploited in the later quantum theory. In the 1920's it was applied by Eddington and others in explaining the equilibrium of stellar atmospheres.

In the 1890's Boltzmann again revived his interest in electromagnetic theory, perhaps as a result of Hertz's experiments, which he repeated before a large audience in Graz. He published his *Vorlesungen über Maxwells Theorie . . .* in 1891 and 1893, along with some papers in which he suggested new mechanical models to illustrate the field equations. In 1895 he published an annotated German edition of Maxwell's paper "On Faraday's Lines of Force" in Ostwald's *Klassiker der exakten Wissenschaften*. Boltzmann was partly responsible for the eventual acceptance of Maxwell's theory on the Continent, although he did not advance the theory itself as much as did Lorentz, nor did he grapple with the difficult problems that ultimately led to Einstein's theory of relativity.

Defense of the Atomic Viewpoint. Throughout his career, even in his works on subjects other than kinetic theory, Boltzmann was concerned with the mathematical problems arising from the atomic nature of matter. Thus, an early paper with the title "Über die Integrale linearer Differentialgleichungen mit periodischen Koeffizienten" (1868) turned out to be an investigation of the validity of Cauchy's theorem on this subject, which is needed to justify the application of the equations for an elastic continuum to a crystalline solid in which the local properties vary

periodically from one atom to the next. Every time someone published new data on the specific heats of gases, Boltzmann felt obliged to worry again about the distribution of energy among the internal motions of polyatomic molecules.

Until the 1890's, it seemed to be generally agreed among physicists that matter *is* composed of atoms, and Boltzmann's concern about the consistency of atomic theories may have seemed excessive. But toward the end of the century, the various paradoxes—specific heats, reversibility, and recurrence—were taken more seriously as defects of atomism, and Boltzmann found himself cast in the role of principal defender of the kinetic theory and of the atomistic-mechanical viewpoint in general. Previously he had not been much involved in controversy—with the exception of a short dispute with O. E. Meyer, who, ironically, had accused Boltzmann of proposing a theory of elasticity that was inconsistent with the atomic nature of matter. But now Boltzmann found himself almost completely deserted by Continental scientists; his principal supporters were in England.

In retrospect it seems that the criticisms of kinetic theory in this period were motivated not primarily by technical problems, such as specific heats of polyatomic molecules but, rather, by a general philosophical reaction against mechanistic or "materialistic" science and a preference for empirical or phenomenological theories, as opposed to atomic models. The leaders of this reaction, in the physical sciences, were Ernst Mach, Wilhelm Ostwald, Pierre Duhem, and Georg Helm. Mach recognized that atomic hypotheses could be useful in science but insisted, even as late as 1912, that atoms must not be considered to have a real existence. Ostwald, Duhem, and Helm, on the other hand, wanted to replace atomic theories by "energetics" (a generalized thermodynamics); they denied that kinetic theories had any value at all, even as hypotheses.

In the first volume of his *Vorlesungen über Gastheorie* (1896), Boltzmann presented a vigorous argument for the kinetic theory:

Experience teaches that one will be led to new discoveries almost exclusively by means of special mechanical models. . . . Indeed, since the history of science shows how often epistemological generalizations have turned out to be false, may it not turn out that the present "modern" distaste for special representations, as well as the distinction between qualitatively different forms of energy, will have been a retrogression? Who sees the future? Let us have free scope for all directions of research; away with all dogmatism, either atomistic or anti-atomistic! In describing the theory of gases as a mechanical *analogy*, we have already indicated, by

the choice of this word, how far removed we are from that viewpoint which would see in visible matter the true properties of the smallest particles of the body [Brush trans., p. 26].

In the foreword to the second volume of this book (1898), Boltzmann seemed rather more conscious of his failure to convert other scientists to acceptance of the kinetic theory. He noted that attacks on the theory had been increasing, but added:

I am convinced that these attacks are merely based on a misunderstanding, and that the role of gas theory in science has not yet been played out. The abundance of results agreeing with experiment which van der Waals has derived from it purely deductively, I have tried to make clear in this book. More recently, gas theory has also provided suggestions that one could not obtain in any other way. From the theory of the ratio of specific heats, Ramsay inferred the atomic weight of argon and thereby its place in the system of chemical elements—which he subsequently proved, by the discovery of neon, was in fact correct. . . .

In my opinion it would be a great tragedy for science if the theory of gases were temporarily thrown into oblivion because of a momentary hostile attitude toward it, as was for example the wave theory because of Newton's authority.

I am conscious of being only an individual struggling weakly against the stream of time. But it still remains in my power to contribute in such a way that, when the theory of gases is again revived, not too much will have to be rediscovered. . . . [Ibid., pp. 215–216].

Boltzmann and Ostwald, although on good personal terms, engaged in bitter scientific debates during this period; at one point even Mach thought the argument was becoming too violent, and proposed a reconciliation of mechanistic and phenomenological physics.⁷ While teaching at Leipzig with Ostwald during the period 1900–1902, Boltzmann was undergoing periods of mental depression and made one attempt at suicide. He returned to Vienna in 1902, where he succeeded himself as professor of theoretical physics and also lectured on the philosophy of science, replacing Ernst Mach, who had to retire for reasons of health. In 1904 he went to the United States to attend the World's Fair at St. Louis, where he lectured on applied mathematics, and also visited Berkeley and Stanford. He later described his experiences on this trip in a satirical article, "Reise eines deutschen Professors ins Eldorado." But despite his travels and discussions with scientific colleagues, he somehow failed to realize that the new discoveries in radiation and atomic physics occurring at the turn of the century were going to vindicate his own theories, even if in somewhat altered form. The real cause of Boltzmann's

suicide in 1906 will never be known; but insofar as despair over the rejection of his lifework by the scientific community may have been a contributing factor (as has sometimes been suggested without much evidence), it is certainly one of the most tragic ironies in the history of science that Boltzmann ended his life just before the existence of atoms was finally established (to the satisfaction of most scientists) by experiments on Brownian motion guided by a kinetic-statistical theory of molecular motion.

NOTES

1. All of Boltzmann's publications for which only the year is given may be found in his *Wissenschaftliche Abhandlungen*.
2. See *The Scientific Papers of James Clerk Maxwell* (Cambridge, 1890). The 1859 and 1866 papers of Maxwell, together with other papers by Clausius, Boltzmann, Kelvin, Poincaré, and Zermelo (cited by year in this article) may be found in S. G. Brush, ed., *Kinetic Theory*, 2 vols. (Oxford, 1965–1966).
3. See Boltzmann, *Vorlesungen über Gastheorie*, I, §3; P. and T. Ehrenfest, "Begriffliche Grundlagen der statistischen Auffassung in der Mechanik."
4. It was in reference to this result of Maxwell's that Boltzmann wrote his oft-quoted comparison of styles in theoretical physics and styles in music, dramatizing the almost magical disappearance of V from the integrand of eq. 9 when the words "let $n = 5$ " were pronounced (*Populäre Schriften*, p. 51).
5. Brush, *Kinetic Theory*, II, 192.
6. This formula for S is clearly related to Boltzmann's earlier expression for the H -function (eq. 9). If we know that the system has probability W_i of being in macrostate i , with given values of W_i for all i , then the expectation value of the entropy can be calculated from

$$S = k \sum W \log W$$

with an appropriate interpretation of the summation or integration.

7. *Die Principien der Wärmelehre, historisch-kritisch entwickelt* (Leipzig, 1896), pp. 362 ff.

BIBLIOGRAPHY

I. ORIGINAL WORKS. The technical papers that originally appeared in various periodicals have been reprinted in Boltzmann's *Wissenschaftliche Abhandlungen*, F. Hasenöhl, ed., 3 vols. (Leipzig, 1909). Lectures and articles of general interest are collected in *Populäre Schriften* (Leipzig, 1905). A review article written with J. Nabl, "Kinetische Theorie der Materie," was published in *Encyklopädie der mathematischen Wissenschaften*, V, pt. 1 (Leipzig, 1905), art. V8. Other works are *Vorlesungen über Maxwells Theorie der Elektrizität und des Lichtes*, 2 vols. (Leipzig, 1891–1893); his ed. of Maxwell's "On Faraday's Lines of Force," *Ueber Faradays Kraftlinien* (Leipzig, 1895), with 31 pages of notes by Boltzmann; *Vorlesungen über Gastheorie*, 2 vols. (Leipzig, 1896–1898), trans. by S. G. Brush, with introduction, notes, and bibliography, as *Lectures on Gas Theory* (Berkeley, 1964); *Vorlesungen über die Principe der Mechanik*, 3 vols. (Leipzig, 1897–1920); and

Über die Prinzipien der Mechanik, Zwei akademische Antrittsreden (Leipzig, 1903). Books based on Boltzmann's lectures are Charles Emerson Curry, *Theory of Electricity and Magnetism* (London, 1897), with a preface by Boltzmann; and Hugo Buchholz, *Das mechanische Potential*, published with *Die Theorie der Figur der Erde* (Leipzig, 1908).

II. SECONDARY LITERATURE. Works on Boltzmann are Engelbert Broda, *Ludwig Boltzmann: Mensch, Physiker, Philosoph* (Berlin, 1955); S. G. Brush, "Foundations of Statistical Mechanics 1845–1915," in *Archive for History of Exact Sciences*, 4 (1967), 145–183; René Dugas, *La théorie physique au sens de Boltzmann et ses prolongements modernes* (Neuchâtel, 1959); P. and T. Ehrenfest, "Begriffliche Grundlagen der statistischen Auffassung in der Mechanik," in *Encyklopädie der mathematischen Wissenschaften*, IV, pt. 32 (Leipzig, 1911), trans. by M. J. Moravcsik as *The Conceptual Foundations of the Statistical Approach in Mechanics* (Ithaca, N.Y., 1959); and G. Jaeger, "Ludwig Boltzmann," in *Neue Österreichische Biographie 1815–1918*, pt. 1, *Biographien*, II (Vienna, 1925), 117–137. Other articles on Boltzmann are listed in the bibliography of the Brush trans. of *Lectures on Gas Theory*.

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BOLYAI, FARKAS (WOLFGANG) (b. 9 February 1775, Bolya [German, Bell], near Nagyszeven [German, Hermannstadt], Transylvania, Hungary [now Sibiu, Rumania]; d. 20 November 1856, Marosvásárhely, Transylvania, Hungary [now Târgu-Mureș, Rumania]), *mathematics*.

Farkas Bolyai was the son of Gáspár (Kasper) Bolyai and Christina Vajna (von Páva) Bolyai. Bolya was the hereditary estate of the noble family of Bolyai de Bolya, which was mentioned as early as the thirteenth and fourteenth centuries. By the time of Gáspár it had been reduced to a small holding, but Gáspár added another holding (which belonged to his wife's family) in Domáld, near Marosvásárhely. He enjoyed a reputation as an industrious and intelligent landholder of strong character.

Young Farkas received an education at the Evangelical-Reformed College in Nagyszeven, where he stayed from 1781 to 1796. He excelled in many fields, especially in mathematics, and showed interest in theology, painting, and the stage. In 1796, he traveled to Germany, going first to Jena and then, with a fellow student at Nagyszeven, Baron Simon Kemény, entered the University of Göttingen, where he studied until 1799. Among his teachers were the astronomer Felix Seyffer and the mathematician Abraham Gotthelf Kästner. It was at this time that Bolyai began his lifelong friendship with Carl Friedrich Gauss, also a student at Göttingen, who already was intensely engaged in mathematical research. From this period dates Bolyai's interest in the foundations of geometry,

especially in the so-called Euclidean or parallel axiom, to which Kästner and Seyffer, as well as Gauss, were devoting attention. Bolyai maintained a correspondence with Gauss that, with interruptions, lasted all their lives.

After his return to Transylvania, Bolyai became a superintendent in the house of the Keménys in Kolozsvár (German, Klausenburg; now Cluj, Rumania). In 1801 he married Susanna von Árkos, the daughter of a surgeon. His wife was talented but sickly and nervous, and the marriage was not a happy one. The couple settled in Domáld, where Bolyai farmed from 1801 to 1804. In 1802 their son, János, was born, at the von Árkos home in Kolozsvár.

In 1804, Farkas accepted the position of professor of mathematics, physics, and chemistry at the Evangelical-Reformed College at Marosvásárhely, where he taught until his retirement in 1853. During this half century he was known as a patient and kind teacher, but one who lacked the faculty of easily transmitting to others his own scientific enthusiasm, despite the emphasis he placed on correct mathematical education. Meanwhile, he continued his research, concentrating on the theory of parallels. He sent a manuscript on this subject, *Theoria parallelarum*, with an attempt to prove the Euclidean axiom, to Gauss in 1804. The reasoning, however, satisfied neither Gauss nor himself; and Bolyai continued to work on it and on the foundations of mathematics in general.

The Euclidean axiom, which appears as the fifth postulate in Book I of Euclid's *Elements*, is equivalent to the statement that through a given point outside a given line only one parallel can be drawn to the line. It is also equivalent to the statement that there exists a triangle in which the sum of the three angles is equal to two right angles and, hence, that all triangles have this property. Attempts to prove this axiom—that is, to deduce it from other, more obvious, assumptions—began in antiquity. These attempts were always unsatisfactory, however, and the nature of the axiom had remained a challenge to mathematicians. Bolyai, working in almost total scientific isolation, often despaired while trying to understand it.

During such moments of discouragement, he sought consolation in poetry, music, and writing for the stage. In 1817, his *Ot Szomorujátek, Irtá egy Hazafi* ("Five Tragedies, Written by a Patriot") was entered in a contest. The following year, another play, *A Párisi Par* ("The Paris Process"), appeared. Bolyai's wife died in 1821, and in 1824 he married Theresia Nagy, the daughter of an iron merchant in Marosvásárhely. They had one son, Gregor.

Farkas began to interest himself in mathematics