Joseph Loschmidt, Physicist and Chemist

When atoms and molecules were still quite hypothetical, Loschmidt used kinetic theory to get the first reasonable estimate of molecular size.

Alfred Bader and Leonard Parker

Josef Loschmidt, a pioneer of 19th-century physics and chemistry, deserves to be better known in the English-speaking world. Born 15 March 1821 in Putschirn (now Pocerny), a small village in what is now the Czech Republic, Loschmidt was the son of a poor Bohemian farmer. In his first publication, in 1861, Loschmidt proposed the first structural chemical formulae for many important molecules, introducing markings for double and triple carbon bonds.[1]

That prescient paper was ignored by the chemical establishment. But four years later, while he was still teaching in a secondary school at age 44, Loschmidt solved one of the most long-standing and difficult problems of the age: He became the first person to use the kinetic theory of gases to obtain a reasonably good value for the diameter of a molecule.[2] This was at a time when the kinetic theory and indeed the very existence of molecules were still quite hypothetical.

What we call "Avogadro's number" is, in German-speaking countries, called "Loschmidt's number." The molecular size determination quickly brought Loschmidt recognition. At the urging of Josef Stefan, he was given a faculty position at the University of Vienna in 1866. In 1870, Loschmidt published the most accurate measurements yet of the interdiffusion of two gases.[3] James Clerk Maxwell,[4] following Loschmidt's lead, used these data to calculate the molecular diameters of various gases. Loschmidt rose rapidly at the university, becoming a full professor in 1872. (See figures 1 and 2.)

Loschmidt and his younger university colleague Ludwig Boltzmann became good friends. (See figure 3.) His critique of Boltzmann's attempt to derive the second law of thermodynamics from kinetic theory became famous as the "reversibility paradox." It led Boltzmann to his statistical concept of entropy as a logarithmic tally of the number of microscopic states corresponding to a given thermodynamic state.

Mentors

Throughout his life, Loschmidt was fortunate in his encounters with others who appreciated his brilliance. The first was a Bohemian priest, Adalbert Czech, who persuaded Loschmidt's parents to send young Josef to high school in the Piarist monastery in Schlackenwerth and, in 1837, to advanced high-school classes in Prague, followed by two years of philosophy and mathematics at Prague's Charles University.

At the university, Loschmidt met his second important mentor, the philosophy professor Franz Exner. Because Exner's eyesight was failing, he asked Loschmidt to be his personal reader. Exner was known for his innovative school reforms, which included promotion of the teaching of mathematics and science as important subjects. He suggested to Loschmidt, who became a close personal friend, that he try to apply mathematics to psychological phenomena. Not surprisingly, Loschmidt failed. But in the process, he became a very able mathematician. Moving to Vienna at the age of 20, Loschmidt was attracted by the lectures in chemistry and physics at the Polytechnic Institute and the university. He supported himself by giving private lessons.

After graduating from the Polytechnic in 1846 with the equivalent of a bachelor's degree in physics and chemistry, Loschmidt failed to get an academic position. We know from his letters to Exner that he considered various alternatives, including becoming a settler in the new state of Texas. Instead, he went to work in a paper factory and then started a company near Vienna to produce potassium nitrate. The business eventually failed, essentially because the imperial government, with its gunpowder monopoly, set fixed prices that failed to take account of inflation during the war in Hungary.

In 1856, Loschmidt became a high-school teacher in Vienna, teaching chemistry, physics, arithmetic, and bookkeeping. But the school allowed him his own small laboratory. Five years later he published, at his own expense, a booklet, *Chemische Studien I*, containing his first two papers.[1] The first of these is a 47-page paper titled "Constitutions-Formeln der Organischen Chemie in Graphischer Darstellung [Diagrammatic Structural Formulae of Organic Chemistry]." These pioneering molecular images (see figure 4) ran afoul of the cautious doctrine then holding sway.[5] "One must keep in mind that the rational formulae are only reaction formulae and not formulae of constitution. . . . They do not in any way describe the positions of the atoms in the compounds. This should be clearly stressed because, oddly enough, some chemists still believe that by the study of chemical reactions one can . . . depict atomic positions," wrote August Kekulé in his famous 1861 textbook.[6] He summarily dismissed the work of this unknown high-school teacher without a doctoral degree.

Ironically, it was only a few years later that Kekulé proposed the ring structure of the benzene molecule, a configuration that was adumbrated by Loschmidt's diagrams for more than a hundred aromatic hydrocarbons.

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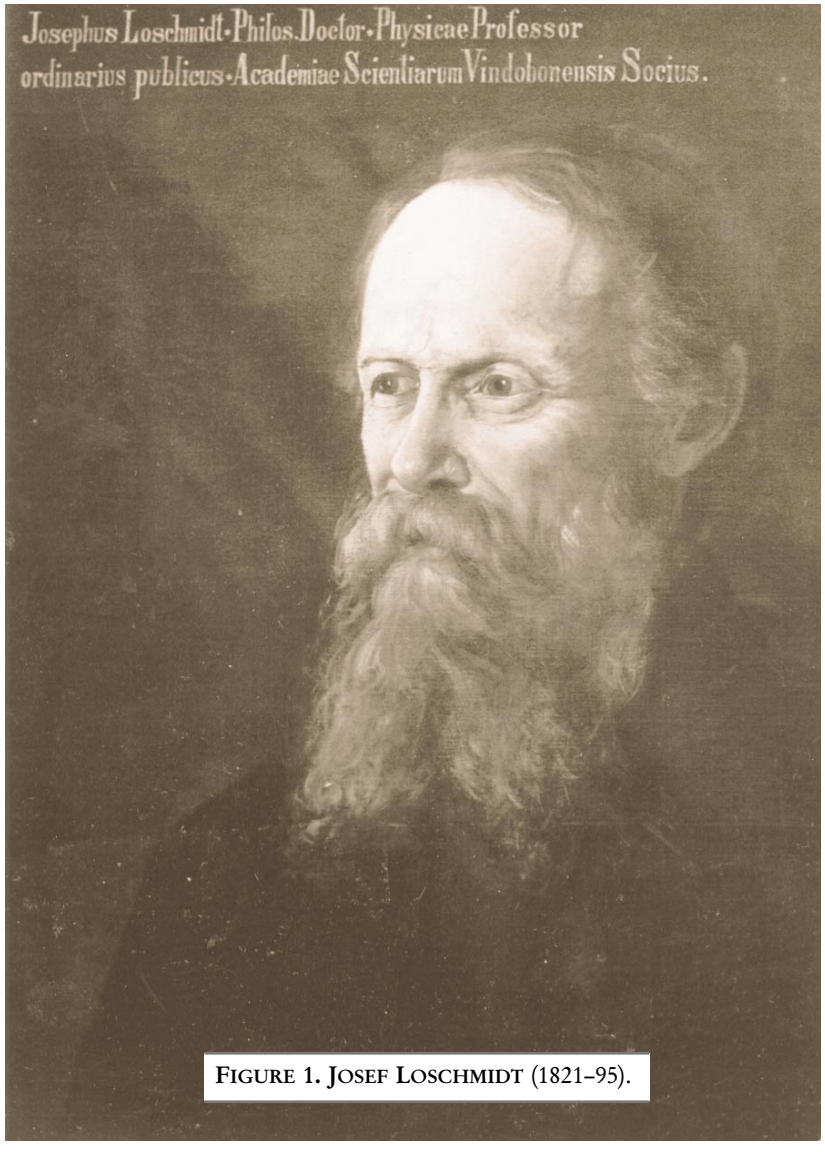

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FIGURE 1. JOSEF LOSCHMIDT (1821–95).

All this casts some doubt on Kekulé's famous tale, many years later, that the benzene ring structure had come to him in a dream.

The second, shorter paper in the booklet foreshadows Loschmidt's calculation of "Avogadro's number" in 1865.

How big are molecules?

By 1808, Joseph Gay-Lussac had established that when different gases combine chemically, the combining volumes of the gases are in the ratio of simple integers. In 1811, Amedeo Avogadro took this observation to imply that the number of molecules in a liter of gas at a given temperature and pressure is the same for all gases. But Avogadro was never able to determine that number. Before it could be calculated, one would have to find the characteristic size and mass of a molecule.

In 1815, Thomas Young unsuccessfully attempted to estimate the size of a molecule by considering the surface tension and tensile strength of liquids. The problem remained unsolved until 1865, when Loschmidt found an ingenious way to determine molecular diameters from the densities of liquefied gases and the mean free paths of molecules in the gaseous state.[2]

An immediate consequence of Loschmidt's calculation of the diameter of a molecule was a reasonably good estimate of molecular mass and the number of molecules per unit volume of a gas at standard temperature and pressure (STP). The second essay in Loschmidt's *Chemische Studien I*, entitled "Spannkraft der Gase [Pressure of Gases]," was the first publication in which corrections to the ideal gas law due to both finite molecular size and delays during collision were calculated and compared with experiment.[7] The inclusion of the time delay allowed him to fit the experimental data. But Loschmidt's modified gas law was missing an important correction that was discovered 12 years later, when Johannes van der Waals postulated a weak attractive force between molecules.

The method that Loschmidt used[2] in 1865 to determine the diameter s of a molecule starts with the expression that Rudolph Clausius derived in 1859 for the mean free path l between collisions of a molecule in a gas, namely, $l = (3/16)/(na)$, where na is the product of molecular number density and cross-sectional area ($\pi s^2/4$). In 1860, Maxwell introduced his distribution of molecular velocities and derived the somewhat more accurate expression $l = 1/(4\sqrt{2}na)$

The mean free path of a molecule in air was known approximately. But there were no plausible estimates of n or s. To arrive at the molecular diameter s, Loschmidt considered the fraction ϵ of the total gas volume that is occupied by the molecules themselves. He argued that this fraction, which he called the coefficient of condensation, was related to the mean free path by

$$\epsilon = s/(8\,l). \qquad (1)$$

He was assuming that, when a gas is liquefied, the molecules in the liquid phase form a configuration of packed spheres occupying a volume that is only slightly larger than the volume occupied by the molecules themselves.

Thus one could estimate ϵ by comparing the volume V_l of a liquefied gas with its original, much larger gas volume V_g. The volume ratio $V_l/V_g = \epsilon f$, where f is a factor, somewhat larger than unity, that gives the ratio of the actual volume occupied by the liquid (at its boiling point, say) to the total volume of all the individual molecular spheres. Loschmidt was faced with an obstacle. As his experimental gas, he was forced to use air, the one gas for which mean-free-path measurements had been made. But air had not yet been liquefied!

Fortunately, Hermann Kopp[8] had introduced the notion of specific volumes, which Loschmidt could use to estimate the density of liquid air. Kopp defined the specific volume of a compound as its relative molecular weight divided by the density of the compound in the liquid state. From measured densities of liquids formed from compounds having the same constituent elements in different proportions, Kopp had found that specific volumes were approximately additive.

This additivity permitted Loschmidt to relate the not-yet measured density of liquid air to the measured densities of other liquids formed from nitrogen and oxygen. In

particular, the measured liquid density of NO_2 was 1.50 g/cm^3 and that of N_2O was 1.30 g/cm^3. Taking air to be about 77% nitrogen and 23% oxygen, Loschmidt deduced that the density ρ_l of liquid air (at its boiling point at 1 atm) should be about 1.22 g/cm^3. That turns out to be roughly 30% larger than the measured value.

To arrive at a value for the ratio f, Loschmidt assumed that, in the liquid state, the molecules would be fairly tightly packed. He had investigated crystal structures, and had evidently estimated f for molecules arranged in various lattice structures. He noted that $f = 1.91$ for spherical molecules in a simple cubic lattice and that, empirically, the tightest packing of molecules (not necessarily impenetrable spheres) gave an f of about 1.17. For liquid air at its boiling point, Loschmidt assumed that the molecules were about 5% less tightly packed than this empirical maximum, giving a density of 1.5 g/cm^3 = $f\rho_l$ if the molecules were crushed together so tightly that all the intermolecular space was squeezed out. Finally, he used the measured STP density ρ_a of air, (1/770) g/cm^3, to obtain the condensation coefficient

$$\epsilon = \rho_a/(f\rho_l) = 1/(770 \times 1.5) = 8.66 \times 10^{-4}.$$

The mean free path of a molecule in air had been estimated from measurements of the air's viscosity by Maxwell and by Oskar Emil Meyer. From Meyer's more recent (but less accurate) value of $l = 140$ nm, Loschmidt used equation 1 to calculate that $s = 0.97$ nm (see figure 5). Loschmidt's estimate of about 1 nm for the typical diameter of an air molecule was too high, but only by a factor of 3. If he had used Maxwell's smaller (62 nm) estimate of l, his calculation of s would have been only about 40% higher[9] than the modern value of 0.3 nm.

Nowadays, the "Loschmidt number" has come to mean simply Avogadro's number N_A, the number of molecules in a mole. But Boltzmann coined it originally to mean the number of molecules per cubic centimeter for an ideal gas at STP. That number n equals $6\epsilon/\pi s^3$, and the mass m of a molecule is simply the density of the gas divided by n. The modern value of n is about 2.7×10^{19} cm^{-3}. (That's essentially N_A divided by 22.4 liters, the STP molar volume.) Because n depends on the *cube* of the molecular diameter, Loschmidt's error in estimating s was magnified by a second factor of three in the estimates of n and m that he deduced in 1865.[9]

FIGURE 2. AMEDEO AVOGADRO (1776–1856).

Gas diffusion experiments

The main sources of error in Loschmidt's estimate of the molecular diameter were errors in the measurements of the mean free path and in the estimate of the density of liquid air. These uncertainties may have been on Loschmidt's mind when he devised a very accurate experimental method for measuring another quantity that is closely related to molecular size, namely, the coefficient D governing the rate of interdiffusion of one gas into another. His experimental diffusion results were published in two 1870 papers.[3]

In Loschmidt's experiments, two gases were initially separated by a horizontal partition in a vertical cylindrical container, with the lighter gas on top. The partition was removed and the two gases were permitted to diffuse into each other for a certain time, after which the fraction of mixing was carefully measured. By comparing his experimental results with Maxwell's mathematical solution for the time dependence of interdiffusion in such a setup, Loschmidt was able to determine diffusion coefficients with greater accuracy than any previous measurements had achieved.

Maxwell used Loschmidt's data to calculate the diameters of the molecules of several gases.[4] The interdiffusion coefficient appears in the diffusion equation

$$dp/dt = D d^2p/dx^2,$$

where p is the partial pressure, at height x and time t, of either one of the two gases that are interdiffusing within the cylinder.

Among Loschmidt's measurements were interdiffusion coefficients for the six pairings possible with four gases: O_2, H_2, CO, and CO_2. The measured results for those six interdiffusion coefficients gave Maxwell six equations with four unknowns, namely $s_i\sqrt{n}$, where s_i is the diameter of the ith molecular species under consideration. For this overdetermined set of equations, he was able to find values for the four unknowns that satisfied all six equations to good approximation. To quote Maxwell, "The numerical results . . . agree in a very remarkable manner with the formula derived from the kinetic theory." From these results he calculated mean free paths for each of the four gases. They ranged from 96.5 nm for H_2 to 43.0 nm for CO_2.

"We may now proceed for a few steps on a more hazardous ground," wrote Maxwell, "and inquire into the actual size of molecules. Prof. Loschmidt himself in his [1866] paper 'Zur Grösse der Luftmolecüle [On the Sizes of Air Molecules],' was the first to make this attempt. Independently of him and of each other, Mr. G. J. Stoney [1868] and Sir W. Thomson [1870] have made similar calculations. We shall now follow the track of Prof. Loschmidt." Setting the molecular diameter $s = 6\sqrt{2}\epsilon l$, which follows from Maxwell's expression for the mean free path, he calculated the diameters of the four molecules under consideration. His results ranged from 0.58 nm for H_2 to 0.93 nm for CO_2. He also obtained a value of 1.9×10^{19} for the Loschmidt number n. That's about 70% of the modern value.

The reversibility paradox

In 1866, a year after the publication of Loschmidt's work on molecular sizes, Boltzmann began what proved to be a

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FIGURE 3. LUDWIG BOLTZMANN (1844–1906) at age 31.

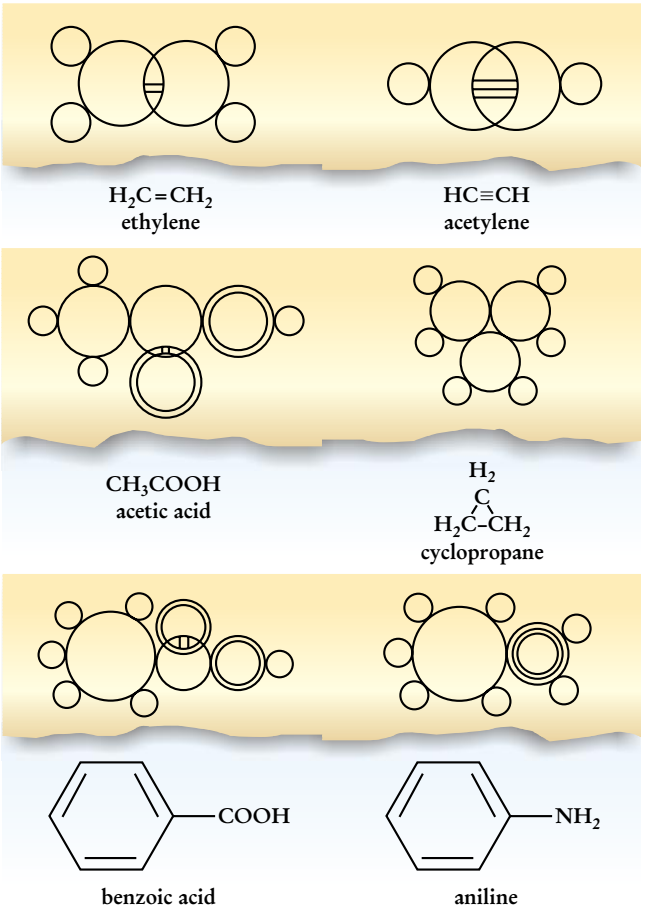


FIGURE 4. MOLECULAR STRUCTURAL FORMULAE, a few of the many appearing for the first time in Loschmidt's 1861 booklet,[1] *Chemische Studien I*. Among its innovations are the depictions of double and triple carbon bonds for ethylene and acetylene; the structure of acetic acid; a correct prediction for cyclopropane 21 years before it was made; and the structures of benzoic acid and aniline, two aromatic molecules with benzene-like rings. Loschmidt's role in the later discovery that benzene itself is a monocyclic six-carbon structure is still being debated by historians.

long and difficult undertaking: deriving the second law of thermodynamics from the mechanical laws governing aggregates of molecules. (See figure 4.) By 1872, he had made significant progress. Considering two-particle molecular collisions in a gas in the absence of external forces, he derived the Boltzmann equation governing the time-development of the velocity distribution $F(\mathbf{v}, t)$. He then introduced the quantity

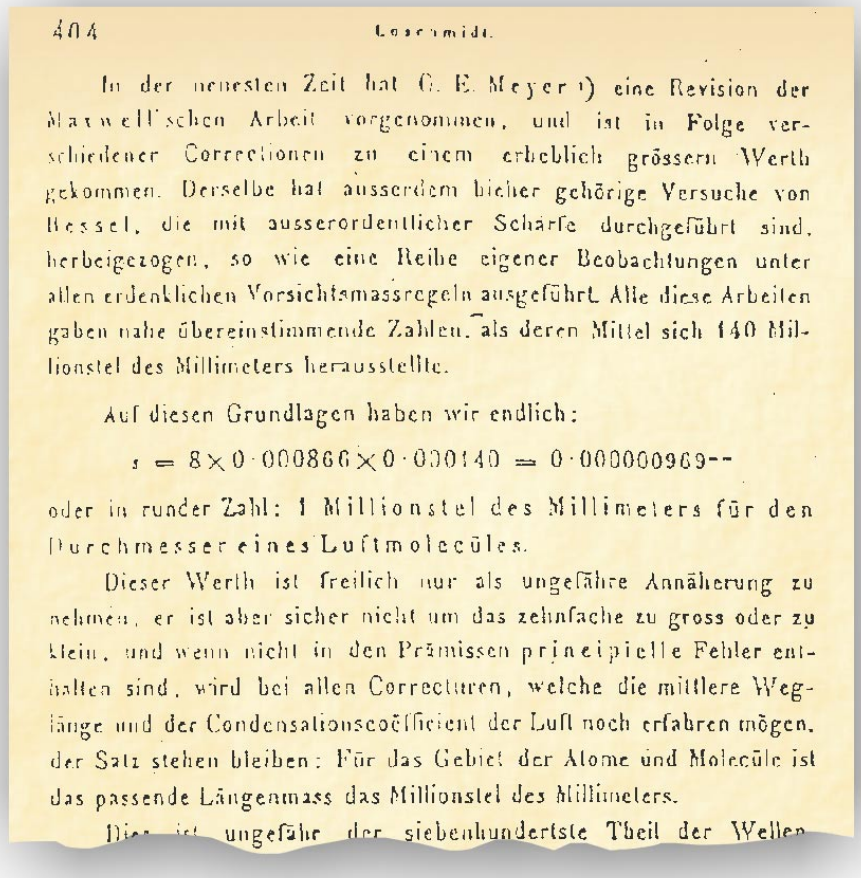
$$H(t) = \int F \ln F \, d^3v,$$

which is proportional to the negative of the equilibrium expression for the entropy S. Boltzmann showed that, if the molecular distribution function F is not the Maxwell distribution at a time t, the gas will evolve in such a way that $H(t)$ must decrease toward a time-independent minimum that is reached only when F takes the form of the Maxwell distribution. And so it appeared that $-H$, increasing monotonically as the system approaches equilibrium, was an acceptable entropy function.

Partly motivated by his distaste for the eventual heat death of the universe that appeared to follow from the second law, Loschmidt searched for flaws in Boltzmann's proof. In 1876 papers taking gravity into account,[10] Loschmidt argued that temperature would depend on height in a gas in vertical equilibrium in a uniform gravitational field. In that regard, he disagreed with Maxwell and Boltzmann. They contended that, even though the molecular velocity distribution function would depend on height in the cylinder, the equilibrium distribution of the gas would nonetheless be characterized by a single uniform temperature. This was not a simple problem. Maxwell himself describes the difficulties he had in proving the uniformity of temperature with height in a dilute gas, and how an error in his calculation had misled him for a while into believing that temperature increased with height in a gas at equilibrium. (See figure 6.)

Loschmidt also had another objection to Boltzmann's proof of the increase of entropy. He pointed out the "reversibility paradox." Let us assume that an isolated system does indeed evolve from an initial state to a final state of lower H (higher entropy). But, Loschmidt argued, the microscopic laws of mechanics are invariant under time reversal. Therefore there must also exist an entropy-decreasing evolution for which $H(t)$ increases with time. That evolution, is, of course, set in motion simply by taking the final state of the previous evolution as the new initial state and then reversing all the individual molecular velocities. This time-reversed evolution would seem to violate the second law of thermodynamics.

In an 1874 paper, William Thomson (the future Lord



404 Loschmidt.

In der neuesten Zeit hat O. E. Meyer[1]) eine Revision der Maxwell'schen Arbeit vorgenommen, und ist in Folge verschiedener Correctionen zu einem erheblich grössern Werth gekommen. Derselbe hat ausserdem hieher gehörige Versuche von Bessel, die mit ausserordentlicher Schärfe durchgeführt sind, herbeigezogen, so wie eine Reihe eigener Beobachtungen unter allen erdenklichen Vorsichtsmassregeln ausgeführt. Alle diese Arbeiten gaben nahe übereinstimmende Zahlen, als deren Mittel sich 140 Millionstel des Millimeters herausstellte.

Auf diesen Grundlagen haben wir endlich:

$$s = 8 \times 0{\cdot}000866 \times 0{\cdot}000140 = 0{\cdot}000000969\text{--}$$

oder in runder Zahl: 1 Millionstel des Millimeters für den Durchmesser eines Luftmolecüles.

Dieser Werth ist freilich nur als ungefähre Annäherung zu nehmen, er ist aber sicher nicht um das zehnfache zu gross oder zu klein, und wenn nicht in den Prämissen principielle Fehler enthalten sind, wird bei allen Correcturen, welche die mittlere Weglänge und der Condensationscoëfficient der Luft noch erfahren mögen, der Satz stehen bleiben: Für das Gebiet der Atome und Molecüle ist das passende Längenmass das Millionstel des Millimeters.

Dies ist ungefähr der siebenhundertste Theil der Wellen-

FIGURE 5. A PAGE FROM LOSCHMIDT'S 1866 paper, "Zur Grösse der Luftmolecüle [On the Sizes of Air Molecules],"[2] shows his calculation of s, the mean diameter of air molecules (0.969 nm) from his "condensation coefficient" for the liquefaction of air (8.66×10^{-4}) and Oskar Meyer's somewhat excessive measurement (140 nm) of the mean free path of air molecules. "For the regime of atoms and molecules," says the last sentence shown here, "the appropriate unit of length is a millionth of a millimeter."

Kelvin) had raised much the same question. He pointed out that, if one were to reverse the velocities of all particles at a given time, then processes in which kinetic energy was dissipated as heat would be reversed, so that heat energy would be returned to the body and raise its kinetic energy. It appears likely, however, that Loschmidt raised this paradox earlier, in private discussions with Boltzmann[11] about the evolution of $H(t)$.

Boltzmann considered Loschmidt's reversibility objection to be of great importance in arriving at a proper understanding of the second law. His response to Loschmidt's paradox led Boltzmann to the realization that a statistical interpretation of the second law was essential. Ultimately it led Boltzmann to the famous expression for entropy

$$S = k \log W$$

that adorns his grave in Vienna's Central Cemetery. W is the number of microstates compatible with the values of the thermodynamic variables characterizing a system's macroscopic state, and k has come to be known as Boltzmann's constant.

Loschmidt's objection also led Boltzmann to a better understanding of the role of statistical fluctuations. Just as Loschmidt said, there must be motions in which H will increase. But, Boltzmann showed, the probability of any such excursion that would take H far from its minimum is exceedingly small. The requisite initial conditions occupy a negligible fraction of the system's phase space. Boltzmann conceded that $H(t)$ would indeed experience spontaneous fluctuations in which it temporarily increased, even when it was near its minimum. But large fluctuations, he argued, taking $H(t)$ far from its minimum, would be extremely infrequent.

An earlier argument by Boltzmann, purporting to show that H is a nonincreasing function, had implicitly contained a plausible assumption concerning the randomness of initial molecular collision velocities. But that assumption was incompatible with time-reversal invariance.

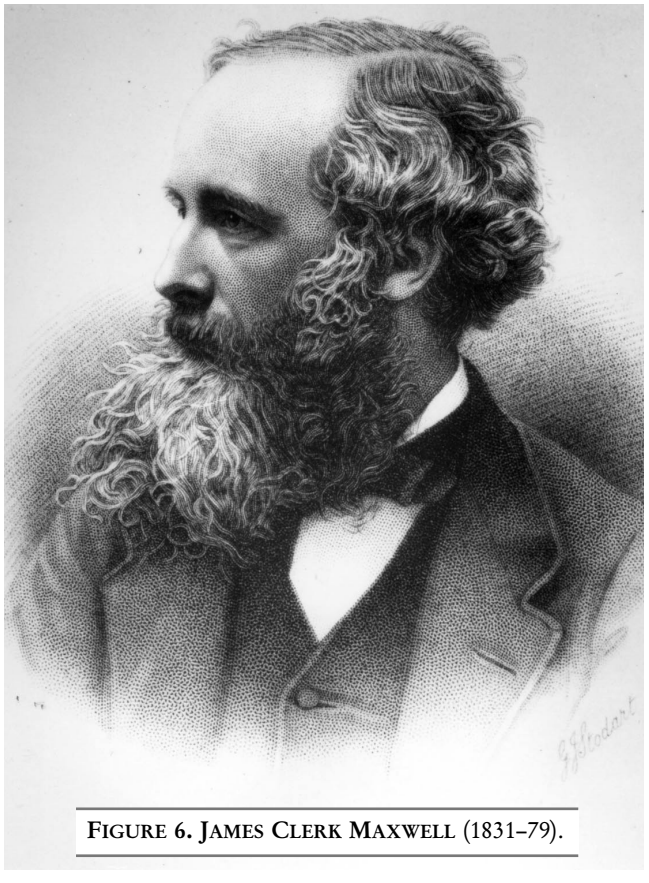


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FIGURE 6. JAMES CLERK MAXWELL (1831–79).

A journal for failed experiments

Loschmidt's experimental investigations in electromagnetism figure in the prehistory of the work of Edwin Hall,

John Kerr, and Heinrich Hertz. Loschmidt's work underlines the difficulty of the experiments those pioneers performed. It is clear from Loschmidt's diffusion experiments that he was a skilled experimenter. He undertook experiments to detect the Hall and Kerr effects, and to discover the induction of sparks by electromagnetic waves transmitted from other sparks.

These attempts preceded the successful experiments that enshrined the names of Hall, Kerr, and Hertz in the annals of 19th-century electromagnetic discovery. But alas, Loschmidt's experimental setups were insufficient to detect the electromagnetic effects he sought. He once joked to Boltzmann that he would like to start a negative scientific journal to publish nothing but failed experiments. Boltzmann repeated that sardonic remark in his eulogy[12] on the occasion of Loschmidt's death in 1895.

The prominent chemists of his day rejected or ignored Loschmidt's pioneering work on chemical structures. By contrast, Stefan, Maxwell, Boltzmann, and other leading physicists were very receptive to Loschmidt's determinations of molecular size and mass, and to his later work in physics. In his eulogy, Boltzmann said of his good friend, "His work forms a mighty cornerstone that will be visible as long as science exists . . . Loschmidt's excessive modesty prevented his being appreciated as much as he could and should have been."

We thank Thomas Schönfeld and Robert Rosner for their many suggestions, and Alpan Raval for his helpful comments

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