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PIERRE HUARD

MARIE JOSÉ IMBAULT-HUART

LOSCHMIDT, JOHANN JOSEPH (b. Putschirn, near Carlsbad, Bohemia [now Karlovy Vary, Czechoslovakia], 15 March 1821; d. Vienna, Austria, 8 July 1895), *physics, chemistry*.

Loschmidt was the oldest of four children of a poor peasant family. The young Loschmidt showed more aptitude for schoolwork than work in the fields and was enrolled in the parochial school in Schlackenwerth (near Carlsbad) in 1833 with the help of the village priest; in 1837, again with the assistance of the Catholic clergy, he entered Humanistic Gymnasium in Prague. From 1839 he studied classical philology

and philosophy at the German University in Prague.

Loschmidt became a lecturer under Franz Exner, who aided the impoverished young man and advised him to concentrate on mathematics. He commissioned Loschmidt to enlarge on Herbart's attempts at a mathematical treatment of psychology and to put it on a more solid basis. However, despite intense efforts, Loschmidt achieved only negative results, primarily because of difficulties encountered in the measurement of the intensities of psychological experiences.

In 1841 Loschmidt joined Exner in Vienna to study the natural sciences, though his favorite field remained the border area between physics and philosophy. Influences of Herbartian philosophy were evident in his thought throughout his life. Loschmidt was unsuccessful in obtaining a teaching post when he graduated in 1843 and he therefore turned to industry. He worked in Anton Schrötter's laboratory until the end of 1846. With his friend Benedikt Margulies, Loschmidt discovered a process for converting sodium nitrate into potassium nitrate, used for manufacturing gunpowder. They could not know, of course, that the same process had been discovered half a century earlier by Thaddäus Haenke, who had actually turned it to practical use in Peru.¹ From then until 1854 Loschmidt tried again and again to establish businesses but the drastic social, political, and financial upheavals of Europe in the mid-nineteenth century made it almost impossible for any businessman to succeed, and in 1854 he went into bankruptcy.

Discouraged by his many failures, Loschmidt decided to return to a career in science. Early in 1856 he passed, with excellent marks, his examinations to qualify as a teacher. In September of that year he obtained a post at a Vienna Realschule, where he taught chemistry, physics, and algebra and used his free time for scientific research. At that time Vienna had become the center of crystallography, and Loschmidt concentrated his studies on the chemistry of crystals.² During this period he met J. Stefan, the young director of the Institute of Physics of the University of Vienna, and they became close friends. Stefan soon recognized Loschmidt's talents and offered him the facilities of the institute's laboratory and library, and Loschmidt, who had had enough of practical work, turned to theoretical research.

Various attempts were being made in those days to represent symbolically and graphically molecular formulas in analogy to the efforts at a unified and internally consistent system of atomic weights for the chemical elements. In 1861, at the age of forty, Loschmidt published in Vienna, at his own expense, his first scientific work, *Chemische Studien*, I (there never was a part II). Loschmidt was the first to

represent graphically the double and triple bonds of polyvalent atoms by means of connecting lines. He also was probably the first who viewed cane sugar as an "ether-like compound," and he expressed the opinion that ozone consisted of three oxygen atoms. Above all, Loschmidt was the first to envision a ring-shaped chain formula of carbon atoms for benzene, but he expressly rejected the assumption of double bonds, preferring to hold such a decision in abeyance.

In his representation of benzene derivatives, for which he gave 121 graphical formulas, Loschmidt represented the benzene as a hexavalent nucleus by means of a circle, erroneously assuming that the carbon atoms and their valences were unevenly distributed about the circle. This model of the benzene nucleus impeded his understanding of the isomeric relationships in polysubstitution derivatives, whereas the strength of Kekulé's benzene model, by contrast, showed up at just this point. Nevertheless, Loschmidt correctly recognized toluene as methyl benzene, and thus accurately explained the isomerism of cresol with benzyl alcohol. He was the first to state that in alcohols with several OH groups each C atom can bind no more than one OH group.

Loschmidt also assumed that an element could have multiple valences (he used the terms "pollency" and "capacity"). Sulfur, for example, could have a valence of 2, 4, or 6. Thus, Loschmidt arrived at the proper structural formula for sulfuric acid, giving sulfur a valence of 6. According to him, nitrogen had a valence of 3 or 5, carbon always had a valence of 4, oxygen always had a valence of 2, and hydrogen of 1. Exceptions were NO, NO₂, and CO.

Loschmidt's book apparently had little influence on other chemists, except perhaps on Kekulé, who published his textbook *Lehrbuch der organischen Chemie* (Stuttgart) in different volumes between 1859 and 1887, and Crum-Brown, also an organic chemist who was involved with the representation of chemical formulas. Priority disputes and mutual influences among the three men are still open to investigation, but resolving the problem would require the analysis and evaluation of much published and unpublished material. Loschmidt's book remained largely ignored for over fifty years until it was republished in Ostwald's *Klassiker* in 1913,³ with the subtitle *Constitutions-Formeln der organischen Chemie in graphischer Darstellung*.

Herbart's metaphysical speculations on the antinomies of the real continuum had led him to construct reality out of simple entities, which he considered spherical, and which attract and repel each other by partial penetration. Loschmidt, in *Zur Constitution des Aethers* (Vienna, 1862), extended this Herbartian

metaphysics of elementary quanta into the realm of physics in line with Lamé's elasticity and ether theory. He attempted to formulate a mathematical theory for luminiferous ether very similar to that of Lord Kelvin thirty years later. According to Loschmidt, every molecule is surrounded with an envelope of ether, the density of which falls off inversely with distance from the molecule's center. Matter and ether attract each other; the ether particles repel each other. Ether is the carrier of energy exchange in the universe; and the attracting and repelling forces of ether spheres summarized under the term "affinity" are, in a manner of speaking, the souls of the atoms. All natural phenomena were to be derived from the reciprocal action of the atoms by means of their energy spheres. He contrasted the prevalent atomic theory—which ascribed to each atom a sharply limited nucleus of impenetrable matter—with the concept of an energy sphere surrounding the atom, itself perhaps a conglomerate of the smallest ether particles.

Loschmidt's other scientific achievement was the first accurate estimations of the size of air molecules.⁴ This linked directly with the speculations of Clausius and Maxwell. Clausius assumed at the outset that all molecules of a gas are at rest and that a mass point moves through them.⁵ The probability that this mass point penetrates a layer of thickness x without colliding with the molecules = a^x , where a is the probability for thickness 1. Thereby a is a function of the radius ρ of the molecular energy spheres and of the mean distance λ of nearby molecules. With $a = e^{-\alpha}$ (e being the base of the natural logarithms), α has to be determined. For small layer thicknesses δ there results $W_\delta = e^{-\alpha\delta} = 1 - \alpha\delta$. Furthermore, the probability that the point penetrates the layer is equal to the relationship between the superficial area of the layer not covered by the molecular cross sections to the total surface. For a layer of thickness λ the fraction $\pi\rho^2/\lambda^2$ of the total surface is covered with molecular cross sections. For a layer of thickness δ this must be multiplied by δ/λ , that is, $(\pi\rho^2/\lambda^3)\delta$. Thus, the probability that the point penetrates a layer of thickness δ is $W_\delta = 1 - (\pi\rho^2/\lambda^3)\delta$. Equating the two expressions for W_δ , $\alpha = \pi\rho^2/\lambda^3$. For any layer thickness x with this value for α the following formula for the penetration possibility is obtained:

$$W = e^{-\frac{\pi\rho^2}{\lambda^3}x}$$

Accordingly, out of Z mass points the layer thickness $x + dx$ is penetrated by

$$Z \cdot e^{-\frac{\pi\rho^2}{\lambda^3}(x+dx)} = Z \cdot e^{-\frac{\pi\rho^2}{\lambda^3}x} \cdot \left(1 - \frac{\pi\rho^2}{\lambda^3}dx\right)$$

Accordingly, $Z \cdot e^{-(\pi\rho^2/\lambda^2)x} \cdot (\pi\rho^2/\lambda^2) dx$ points are retained in layer dx . Multiplication by x gives the total length of path of all these points together. Then, by integration from $x = 0$ to $x = \infty$ and division by Z , the mean free length of path to $l' = \lambda^3/\pi\rho^2$ is obtained for one point. In the case of molecules with radius ρ , instead of mass points, the value of this radius must be doubled—that is, replaced with diameter s . However, if there are no molecules at rest but all molecules move at the same mean speed, this expression must also be multiplied by 0.75, so that

$$l = \frac{3}{4} \frac{\lambda^3}{\pi s^2}.$$

The proof is as follows. If, according to Maxwell,⁶ v represents the speed of a molecule and $1/\lambda^3 = N$, the number of molecules per volume unit, then the number of collisions per minute for a moving molecule, with the remaining molecules at rest, is:

$$v/l' = v \cdot \pi s^2 N,$$

with $s = 2\rho$. But if the other molecules are also moving, then the v on the right side of the equation must be replaced by the mean speed r of the molecule under consideration relative to the others. In that case, one obtains for the number of collisions per minute of the molecule under consideration: $v/l = r \cdot \pi s^2 N$. Thus

$$v/l : v/l' = v : r, \quad l' : l = v : r.$$

Now, according to Clausius, the relative speed between one molecule moving at speed v and another at speed u is: $\sqrt{u^2 + v^2 - 2uv \cos \theta}$, if θ is the angle between the directions of movement of the two molecules.⁷ Since all angles occur with equal frequency, the number of those molecules whose lines of motion make angles between θ and $\theta + d\theta$ with the line in which the first molecule moves will have the same ratio to the whole number of molecules as the corresponding spherical zone to the total spherical surface—that is, as $2\pi \cdot \sin \theta \cdot d\theta : 4\pi$. Accordingly, the number of these molecules per volume unit is $N \cdot 1/2 \sin \theta \cdot d\theta$. Thus, the mean speed r of the particular molecule relative to the other molecules in motion is

$$r = \frac{1}{2} \int_0^\pi \sqrt{u^2 + v^2 - 2uv \cos \theta} \cdot \sin \theta d\theta.$$

On the average, $u = v$; and in this case the pertinent integral is $r = 4v/3$, *q.e.d.*

Thus $1/l = \frac{4}{3} \pi s^2 N$. As Loschmidt showed, estimates of the relative size of the gas molecules can be

obtained from this equation. He initially transformed it to some extent:

$$\frac{1}{N} = \frac{16}{3} \cdot \frac{\pi l s^2}{4}.$$

$1/N$ is that part of the volume unit assigned to one molecule, if the molecules are considered to be evenly distributed. Loschmidt termed it the "molecular gas volume."

Since, according to Avogadro's principle, N is equal for all gases, the same applies to $1/N$. On the right side of the equation, $\pi l s^2/4$ indicates the cylindrical path traveled by the molecule covering the distance l , that is, the "molecular distance volume." Accordingly, the equation states that the latter quantity also is the same for all gases. $\pi s^3/6$ is the volume of a molecule. Its N fold is that part of the unit of volume which is taken up by the molecules assumed at rest; its ratio to the unit is designated as the condensation coefficient ϵ of the gas. Consequently, the above equation results in $s = 8\epsilon l$. The mean free length of path l for air had already been calculated by Maxwell and O. E. Meyer. The condensation coefficient ϵ can be approximated from increases and decreases in volume due to evaporation and condensation, if the plausible assumption is made that in a liquefied state the action spheres of the molecules almost touch. The regularities indicated by Hermann Kopp also permit an estimation of the condensation coefficient of air from those of condensable gases. With these estimated values for l and ϵ , Loschmidt obtained from the last equation the molecule diameter $s = 8 \times 0.000866 \times 0.000140 = 0.000000970$ mm—that is, the correct size of somewhat less than 10^{-7} cm. He also stressed that this was to be considered only as a rough approximation, although this value certainly was not ten times too large or too small.

The value of 0.000140 mm for l is that given by Meyer. Loschmidt felt that this value was preferable to the older value of 0.000062 given by Maxwell. But had Loschmidt preferred Maxwell's value, he would have obtained for the molecular diameter the more accurate value of $s = 0.0000004295$ mm, that is, approximately 0.5×10^{-7} cm. Thus he could have calculated directly from his first formula a likewise accurate value of $2 \cdot 10^{19}$ molecules per cubic centimeter of gas. But Loschmidt calculated the number of molecules in living organisms, as $13 \cdot 10^{19}$. For the number of gas molecules, in his lecture "Die Weltanschauung der modernen Naturwissenschaft" (1867)^{8a}, he indicated—generally without basis, although referring to his work of 1865—the figure of 866 billion molecules per cubic millimeter, which is about thirty

times too small. He recommends 10^{-18} of a milligram as a suitable unit for atomic weights, which is about 100 or 1,000 times too large. (According to modern measurements, a hydrogen atom weighs 1.67×10^{-24} g.) In conclusion, Loschmidt mentioned the hypothesis that atoms consist of even smaller particles and raised the question of whether his hypothetical ether envelopes could be used to explain the life processes.

Three years after Loschmidt, G. Johnstone Stoney attempted to compute the number of molecules per unit volume on the basis of Clausius' rough estimates. Thereby he obtained a value 100 times too large.⁸ In 1870, William Thomson (Lord Kelvin), unaware of Loschmidt's work, published in *Nature* (issue of 31 March, pp. 551 ff.) a fundamental work in which he calculated the sizes of atoms by various methods. Initially he stated that as early as thirty years previously Cauchy had frightened natural scientists with the daring statement that the well-known prism colors indicated that the sphere of molecular action was comparable with the wavelength of light. Eight years previously he himself had published notes on experiments with electrically charged, mutually attractive thin copper and zinc membranes, which enabled him—through a method also outlined there in principle—to estimate a magnitude of $3.3 \cdot 10^{-9}$ cm for atoms.⁹ He also obtained from experiments with liquid lamellae a molecular diameter of $\geq 5 \cdot 10^{-9}$ cm. From the kinetic theory of gases he calculated, in principle by the same method as Loschmidt, a molecular size not below $2 \cdot 10^{-9}$ cm and, for the number of molecules per cubic centimeter, $\leq 6 \cdot 10^{21}$. Thus the values obtained by Thomson were ten times too small for the molecular diameters and 100 times too large for the number of molecules.

Later, Thomson himself acknowledged Loschmidt's priority. In 1890, Lord Rayleigh directed attention to a forgotten work by Thomas Young, printed half a century before Loschmidt's, in the *Supplement* to the fourth edition (1810) of the *Encyclopaedia Britannica*.¹⁰ In it Young had estimated the range of molecular attraction from the surface tension of water, thus obtaining a value between 10^{-10} and $5 \cdot 10^{-10}$ inch for the size of water molecules. Furthermore, from the ratio between water density and steam density he obtained the value 10^{-8} cm for the distance between steam particles. These figures are about 100 times too small.

To date, many methods have been invented for determining these figures. With each method, roughly the same values are obtained: about $0.5 \cdot 10^{-7}$ cm for the molecular diameter. For the distance between molecules the figure was about $3 \cdot 10^{-7}$ cm and, for the number of molecules per cubic centimeter of gas

at 0° C. and 760 mm mercury, $2.7 \cdot 10^{19}$. Thus, one mole of any gas—22.414 liters—contains $6.03 \cdot 10^{23}$ molecules. This figure is called Loschmidt's figure or, sometimes, Avogadro's constant, although Avogadro never performed any pertinent numerical calculations.

In 1868 Loschmidt was appointed to the new position of associate professor of physical chemistry at the University of Vienna, and he received an honorary Ph.D. several months later. He then received modest grants for experimentation and investigated the diffusion of gas in the absence of a porous membrane.¹¹ This involved the experimental confirmation of certain conformities (diffusion speeds) already theoretically derived by Maxwell from the kinetic gas theory, and a more accurate determination of the mean length of path from diffusion instead of from interior friction, as done previously.

Loschmidt also worked on the electromagnetic wave theory and even attempted to demonstrate experimentally the Kerr and Hall effects, although without success, because of the inadequate equipment. Also, as Hertz did later, he worked on the production of electrical resonances and came close to inventing the dynamo. Jokingly, he proposed the founding of a Viennese journal for unsuccessful experiments.

Loschmidt also continued his theoretical work. In the course of a controversy with Boltzmann, he sought a way to escape the heat death resulting from the kinetic theory ("reverse argument"), although without success.¹² These speculations, however, resulted in Loschmidt's first application of the second law of thermodynamics to the theory of solutions and chemical compounds.¹³ Thus he became a forerunner of Horstmann and Gibbs. This also led to a modification of Maxwell's homogeneous-distribution axiom in the case of perceptible gravity effect.

Loschmidt let gases escape into a vacuum in order to observe the effects on their temperature (in accordance with the kinetic theory, the temperature must not change for ideal gases). He also speculated on the manner of propagation of sound in air: "Deduktion der Schallgeschwindigkeit aus der kinetischen Gastheorie."¹⁴ He gave a simpler derivation of the equation of a point system.¹⁵ He attempted to derive the Weber-Ampère law from that of Coulomb, and, in accordance with Kirchhoff, to derive Ohm's law from hydrodynamic flow laws, analogous to Poiseuille's law.¹⁶ Finally, he attempted to calculate, on the basis of Lamé's elasticity theory and his own atomistic concept, the existence of spectral lines from the vibrations of ether spheres surrounding the atoms.¹⁷

In 1867 Loschmidt was named corresponding member of the Imperial Academy of Sciences in

Vienna, and in 1870 a full member. In 1869 he and Josef Stefan founded the Chemical-Physical Society. Loschmidt became the first director of the Physical-Chemical Laboratory (today the Second Institute of Physics). He was dean of the Philosophical Faculty in 1877–1878 and acting dean in 1878–1879. In 1887 he married his housekeeper; they had a son who died of scarlet fever at the age of ten. Loschmidt retired in 1890 and was decorated with the Order of the Iron Crown, third class. He turned over his institute to his pupil Franz Serafin Exner, the son of his professor. Other important pupils were Gustav Jäger and Ludwig Boltzmann.

NOTES

1. Compare Gicklhorn, in *Sudhoffs Archiv für Geschichte der Medizin und der Naturwissenschaften*, 32 (1939–1940), 337–370; and Donald, in *Annals of Science*, 1 (1936), 29–47.
2. See *Sitzungsberichte der Akademie der Wissenschaften in Wien*, Math.-natwiss. Kl., 51, Abt. II (1865), and 52, Abt. II (1866).
3. The problem is treated in detail by the organic chemist and textbook ed. and reviser, R. Anschütz, in *August Kekulé*, 2 vols. (Berlin, 1929), especially pp. 271–306. Also see his "Anmerkungen" in *Ostwalds Klassikern der exakten Wissenschaften* no. 190 (Leipzig, 1913); and *Chemische Studien* in the same ed. for Loschmidt's formulas.
4. "Zur Grosse der Luftmoleküle," in *Sitzungsberichte der Akademie der Wissenschaften zu Wien*, Math.-natwiss. Kl., 52, Abt. II (1866), 395–413.
5. *Philosophical Magazine*, 4th ser., 17 (1859), 81–91.
6. *Ibid.*, 19 (1860), 19–32.
7. *Ibid.*, pp. 434–436.
8. *Ibid.*, 36 (1868), 132–141.
- 8a. In *Schriften des Vereins zur Verbreitung naturwissenschaftlicher Kenntnisse in Wien*, 8 (1867–1868), 41–106, esp. 53.
9. William Thomson (Lord Kelvin), *Reprint of Papers on Electrostatics and Magnetism* (London, 1972), 400.
10. *Philosophical Magazine*, 5th ser., 30 (1890), 474.
11. "Diffusion von Gasen ohne poröse Scheidewände," in *Sitzungsberichte der Akademie der Wissenschaften in Wien*, Math.-natwiss. Kl., 61, Abt. II (1870), 367–380; 62, Abt. II (1870), 468–478.
12. *Sitzungsberichte der Akademie der Wissenschaften in Wien*, Math.-natwiss. Kl., 73, Abt. II (1876), 128–142, 366–372; 75, Abt. II (1877), 287–288; 76, Abt. II (1877), 209–225.
13. *Ibid.*, 59, Abt. II (1869), 395–418.
14. *Ibid.*, 54, Abt. II (1866), 646–666.
15. *Ibid.*, 55, Abt. II (1867), 523–538.
16. *Ibid.*, 58, Abt. II (1868), 7–14.
17. *Ibid.*, 93, Abt. II (1886), 434–446.

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WALTER BÖHM

LOSSEN, KARL AUGUST (*b.* Kreuznach, Germany, 5 January 1841; *d.* Berlin, Germany, 24 February 1893), *geology, petrology*.

Lossen was the son of a doctor and his wife Charlotte Mayer. He was educated at the high school and Gymnasium in Kreuznach. He married his cousin Therese Lossen and had two daughters and one son. Lossen began work as a mining engineer in the siderite deposits of the Siegerland in Westphalia and in the coal mines of Saarbrücken. He broadened his studies in geology, mineralogy, and microscopic petrography, which was then just developing, under the guidance of Beyrich, Girard, Rammelsberg, G. Rose, and J. Roth. In 1866, after graduating from the University of Halle, he was introduced by Dechen at the Geological Survey of Prussia, and started working under the direction of Hauchecorne and Beyrich.

Lossen's main work was the mapping and description of the very complicated geology of the Harz Mountains, which were then still rather unknown, but which have since, because of Lossen's work, become one of the classic regions for geological study. He worked there part of every year from 1866 to 1892 and completed a geological map of the area in the scale of 1:100,000, and, incidentally, maps of smaller areas in the scale of 1:25,000 as by-products. He produced significant papers on the Devonian period, especially the Lower Devonian, and the early Carboniferous period in that region, which had previously been mistaken for Silurian.

Lossen also did essential work in microscopical petrology, and with this, along with geological observations in the field, became one of the first to report the influence of tectonic movements on metamorphism (dynamometamorphism).

By 1866 Lossen could show that gneissic and phyllitic rocks of the Hunsrück Mountains were Lower Devonian sediments. He discovered similar things in the Osthartz, where he also observed transitions between contact metamorphic and dynamometamorphic rocks. For metamorphic tuffs he coined the name "porphyroid."

In 1870 Lossen became a lecturer at the University of Berlin. He was appointed an associate professor in 1882 and full professor of petrology in 1886. While in Berlin, he redefined the old name "Hercynian," which he then used only for the lower part of the Lower Devonian.

Many of Lossen's works concern the magmatic rocks of the Saar-Nahe basin. From these were drawn numerous definitions, in part now completely misused, especially of rocks of the melaphyre-porphyrite-tholeite family.

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