LOSCHMIDT AND THE DISCOVERY OF THE SMALL

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In elementary chemistry courses in the United States it is traditional to begin the course by examining the foundations of stoichiometry, which involve combining weights that need not be related to the size of atoms. Indeed, texts are often careful to point out that Dalton's atomic hypothesis explained the laws of stoichiometry without actually requiring a good estimate of the size or mass of atoms. Even with Cannizzaro's brilliant demonstration in 1858 of the intellectual economy and elegance of Dalton's and Avogadro's hypotheses, so that formulas and atomic weights became firmly established, individual atomic masses and diameters remained completely undetermined. Cannizzaro himself made it clear in his publication that these true atomic quantities were unknown:

> "...to fix this well in the minds of my pupils, I have recourse to a very simple artifice: I say to them, namely, 'Suppose it to be shown that the half molecule of hydrogen weighs a millionth of a milligram, then all the numbers of the preceding table become concrete numbers, expressing in millionths of a milligram the concrete weights of the molecules and of their components: the same thing would follow if the common unit had any other concrete value,' and so I lead them to gain a clear conception of the comparability of these numbers [atomic weights], *whatever be the value of the common unit.*" [Emphasis added; from Leicester and Klickstein, *A Source Book in Chemistry, 1400-1900,* Harvard, 1952]

Although the concept of atoms is introduced quite early in essentially every text, and although the modern values for Avogadro's number and true atomic isotopic masses are used from a very early stage, it is not common for students to be taken through the earliest approaches to an experimental determination of atomic sizes. The determinations of internuclear distances and of Avogadro's number by X-ray diffraction are sometimes presented, but earlier determinations (such as that from Perrin's work on Brownian motion) are never given.

The earliest determination from experimental data of the size of an atom was made by Johann Josef Loschmidt, in 1865. (See a biographical article by Moritz Kohn in *J. Chem. Ed.*, **1945**, *22*, 381.) His value for the diameter of a N_2 molecule was 9.69×10^{-10} m, or about three times what we would currently take as the van der Waals diameter of N_2. Loschmidt made the calculation from the recently published papers on the kinetic theory of gases by Maxwell, Clausius, and Meyer. The calculation was published in the *Proceedings of the Academy of Science of Vienna,* or Sitzb. Akad. Wiss. Wien, which was not widely read. As a result, the result did not attract a great deal of attention, and indeed is still little known. It was, however, the original discovery of the size of an atom (and from the size, a value for the number density in a given volume), and there is a real sense in which Loschmidt may be said to have discovered the small.

Loschmidt's paper is not long, and it connects to the kinetic theory only slightly beyond the level reached by the higher level introductory chemistry texts. As a result, it seems appropriate to present a translation of the paper here for reference purposes, with some explanatory notes where his approach or his results are not couched in modern terms. For example, he considers a liquid's volume at high temperature if its container had been removed but it had not yet become a gas; this awkward formulation of critical volume comes about because the concept of a critical point had itself not yet been formulated. What follows is our translation of Loschmidt's paper, Sitzb. Akad. Wiss. Wien **1865**, *52*, 395-413:

ON THE SIZE OF THE AIR MOLECULES

By J. Loschmidt

It has been agreed that in gases the molecules are separated by distances that are large compared to their diameters. The molecules are in constant motion, and the velocity of this motion is governed by the temperature. On the nature of the motion two sharply different models have been proposed in recent years. The earlier one holds the gas molecules through opposing forces of attraction and repulsion in equidistant locations, about which they oscillate in a sort of stable equilibrium. These forces of attraction and repulsion are assumed to be intrinsic to the nature of the molecule, or, more probably, are a property of the ether environment or the molecule's own caloric content.

This model seems able to account for all general experimental observations, but in the end it appears able only to explain that which it has already initially assumed. Beyond that it cannot go.

> *It is interesting that, although we remain aware of the phlogiston model for oxidation reactions, and of the plum-pudding model for the electronic atom, this competing model for the structure of gases is never mentioned. Apparently it viewed gases as giant expanded crystals, with each gaseous atom or molecule occupying a symmetrical cell in which it was centered by long-range forces. We might call it the "static molecular theory of gases."*

Far better is the second model, developed by Herapath and Kronig from the studies of Clausius, Maxwell, Rankine, and others, which has been more successful.

This model also assumes the great distances between gas molecules, but removes the binding which connects a molecule to its neighbors, keeping it in one location; proposing instead a translational motion. According to this the molecule moves in a straight line without interaction with the others, except at the moment of collision. At that moment a rebound occurs, just as in the collision of elastic spheres.

With the removal of the assumed binding between molecules, a severe difficulty was removed from the theory; it became possible to do a detailed calculation determining average values within the chaos of random interpenetrating motion of the molecules. Quantitative results could be obtained, through which one could hope (with the aid of ad hoc assumptions such as the general spherical shape of the molecules and the like) to achieve either confirmation or rejection of the model.

This suggests that the prospects for the new theory are favorable. The studies of the abovenamed workers have allowed, on the one hand, precise and lucid explanation of the principal properties of gases—such as the atmospheric pressure, heat conductivity, and the propagation of sound—and on the other hand, through a more insightful grasp of concepts, make possible numerical determination of important constants. We emphasize especially: the determination of the average velocity of the molecules for different gases at different temperatures, and the relationship of the total kinetic energy of a gas corresponding to that velocity—both concepts established by the work of Clausius, and further through the mean free path of air molecules according to Maxwell and O. E. Meyer.

It is the purpose of this communication to obtain with the help of this theory, a value for yet another constant—namely the magnitude of the diameter of the air molecules. This size has previously been assumed to be infinitesimally small—whether millionths of a millimeter, or billionths, or even smaller—and has never been discussed. The new theory is capable of giving us this information.

We apply for this purpose an equation due to Maxwell(1), as slightly modified by Clausius(2). The latter gives:

$$1 = 4/3\ N\pi \ell s^2$$

Here N is the number of air molecules contained in a unit volume, ℓ is the mean free path between collisions, and s is the molecular diameter.

We can give this equation a form expressing the relationship between molecular volumes:

$$1/N = 5\tfrac{1}{3}\cdot(\pi \ell s^2)/4$$

It is known that all gaseous phases contain equal numbers of molecules in a unit volume at equal temperatures and pressures. Since N is the number of molecules, $1/N$ is the portion of the unit volume occupied by each molecule if it is assumed that they are equally distributed. We call this quantity the *molecular volume* of the gas.

> *Loschmidt is here assuming the validity of Avogadro's hypothesis, which Cannizzarro had placed at the center of his article establishing atomic weights and formulas. In spite of this serene assumption, it had only been two years since Cannizzarro's article had been given wide circulation, and there were still many chemists who were unconvinced of the validity of Avogadro's hypothesis, even though Maxwell had included a proof in his 1860 paper (Loschmidt's reference 1). A century and a quarter later, we take the statement for granted.*

On the right side of the equation, we have the quantity $\pi \ell s^2/4$. This describes the volume of a cylinder whose base is the circular cross-section and whose height is the mean free path of the molecule. It represents therefore the total volume that the molecule successively occupies as it moves through an average path. We call it the *molecular path volume* accordingly, and our equation tells us that the molecular volume of the gas is 5⅓ times greater than the molecular path volume; this is equally true for all gases.

For our purposes it is necessary to give the equation still another form. Since $\pi s^3/6$ is the volume of a single molecule, and 1 the unit volume that N such molecules occupy, $N\pi s^3/6$ is the proportion of the unit volume that the N molecules themselves occupy when not in motion. We signify the ratio of $N\pi s^3/6$ to unity by ϵ, which we shall call the *condensation coefficient* of the gas. The equation finally becomes

$$s = 8\,\epsilon \ell$$

and tells us that the diameter of a gas molecule is equal to eight times the mean free path, multiplied by the gas's condensation coefficient.

> *Here Loschmidt is preparing for the calculation of the number of molecules in a given volume, as for example 1 cm^3. The "condensation coefficient" is in effect the excluded volume within 1 cm^3—the volume actually occupied by the number of molecules in 1 cm^3 under standard conditions. It is thus analogous to the van der Waals* b *molar parameter, divided by the 22414 cm^3 occupied by one mole at STP.*

For gases that can be condensed and form solid bodies, the molecules are so close together that their spheres of repulsion actually touch. Although in a liquid state molecules are in constant rotation and diffuse through each other relatively slowly, in the solid state the molecules are in fixed locations and fixed orientations. They can only oscillate about these fixed locations in a stable equilibrium.

Under the simplifying assumption of a spherical molecular shape, the volume that a specified number of these molecules occupy as a liquid must be much smaller than their volume as a gas, as the condensation coefficient indicates; the liquid molecules necessarily have small empty spaces between them, which in the estimation of the condensation coefficient has not been taken into account. These interstitial volumes can differ, depending on the symmetry of the layers of molecules. Our spherical molecules occupy, in a close-packed arrangement, a volume only slightly greater than the condensation coefficient suggests—about 1:1.17—whereas in the loosest possible stable constrained arrangement the difference becomes significant—1:1.91. One might imagine that this interval (from 1.17 to 1.91) might explain the expansion of liquids on warming—and if the minimum represents the point of greatest density the maximum represents the volume the liquid would occupy at high temperature if its container had been removed but it had not yet changed to the gaseous form. For nonspherical molecules a greater difference between maximum and minimum can obviously be expected. This discussion may make the use of observed condensation behavior quite misleading if the conditions of the approximations are not met; and if the fundamental assumption of sphericity of the molecule and the assumed sphere of repulsion, etc., are only barely adequate.

Here, however, where we are dealing only with the question of general magnitudes of the diameter of molecules, the observed condensation behavior is completely adequate.

> *Loschmidt is dealing with the geometric parameter we would call the "packing fraction", although we normally express it as fraction:1, rather than 1:1.fraction. Unfortunately, Loschmidt has the wrong packing fraction; in our formulation, his 1:1.17 becomes a packing fraction in a close-packed lattice of 0.855, when in fact the packing fraction for a close-packed lattice of identical spheres is 0.740. He should have used a ratio of 1:1.35. However, this does not seriously damage his subsequent derivation. Perhaps more interesting is his "loosest possible stable constrained arrangement", which should correspond to the critical volume of the liquid, expressed as a multiple of the individual sphere volume. For this packing, he quotes a ratio of 1:1.91. In fact, if spheres are removed from a close-packed arrangement until the average coordination number is down to 3 (the border for an unconstrained arrangement), the ratio of sphere volume to packing volume per sphere is 1:4.316, considerably larger than the number he puts forward but consistent with molar critical volumes. We should not be surprised by his awkward wording; the concept of a critical point for fluids had not yet been formulated.*

With respect to the assumption that when two molecules touch in the liquid phase their centers are separated by the same distance as in the moment of gaseous collision, this seems in all probability correct. The low compressibility of liquids, even under high pressures, is consistent with the assumption, and the kinetic energy that brings two gaseous molecules together, should not bring them closer than this. In the same way, observations of the density of solid forms are little different from those of liquid forms. Consequently, the diameter of a gas molecule cannot be significantly smaller than that of a molecule in a liquid. But it also cannot be significantly larger, because observations support the assumption that the interval between the onset of repulsion between two molecules and that point at which the repulsive forces become dominant appears to be vanishingly small. Finally, the differences in the density of a liquid arising from temperature changes are within the limits that a more dense or less dense arrangement of molecules could adopt.

> *Loschmidt correctly recognizes that intermolecular repulsion must occur as an extremely short-range force. It would be more than fifty years before Lennard-Jones proposed the* $1/r^{12}$ *potential for such repulsion.*

For a temperature basis of zero Celsius, observation leads to the following condensation coefficients: water, 0.00081; NO, 0.00154; NO_2, 0.00143, NH_3, 0.00102; CO_2, 0.00204.

> *These values are the molar volumes of the liquids at 0 °C divided by the molar gas volume, 22414* cm^3*. Some of the values are in error—virtually no cryogenic studies had been done—but most are close enough not to affect his final numerical result significantly. For instance, a modern result for* NH_3 *is 0.00111.*

For air, which is not condensable, condensation behavior cannot be directly observed, and this is the only substance for which the mean free path cannot be reliably determined. Fortunately, H. Kopp(3) has provided a method by which the density of a substance in a liquid state can be estimated from its chemical formula. In the spirit of the discussion above it follows that each atom in the liquid must occupy an unchanging spherical volume. The constancy in the space-filling property of atoms is altered by the form and symmetry of the interstitial spaces, and so to speak concealed.

> *Kopp's series of papers had established a series of more or less constant values for the volumes of atoms (on a molar basis) when combined into molecules, such that the densities of liquids could be predicted by adding the contributions for each atom in the formula. However, Kopp's additive constants could vary considerably for a single element depending on the functional group it was in—what he and Loschmidt called a "radical". Because Loschmidt wants to use mean-free-path values for air, which had not been liquefied, he needs to be able to estimate the "condensation coefficient" for air, which requires a density for liquid air. The ensuing several paragraphs are devoted to a demonstration that good density values can be estimated with truly constant atomic molar volumes that don't vary with functional group.*

Suppose now that the empty interstitial spaces among the constituent atoms are distributed so that one is able to estimate the observed density of selected compounds from atomic volume tables for the chemical elements. In the formula of a liquid substance, instead of the chemical symbols, we could substitute the atomic values—just as from tables of chemical equivalents we can calculate the equivalent weight for a compound. This assumes that the overall packing density of all liquids is approximately the same. This is, however, not to be expected—because the packing density obviously depends on the structure of the molecules, as well as the temperature, and therefore for different liquids in a different fashion.

We might expect, if only to a limited extent, that a substance's specific volume—calculated at a temperature only loosely defined—will agree with the observed value, and that for substances with similar chemical characteristics there is an analogy that may manifest itself at these temperatures. As H. Kopp has shown, we can only achieve such agreement if the temperature is chosen for all liquids so that they have the same vapor pressure—as is the case at the boiling point. It cannot be denied that for a series of liquids heated sufficiently to yield a vapor pressure sufficient to overcome atmospheric pressure, a similarity in molecular packing is to be expected, at least as long as their chemical constitution is not too different.

> *Loschmidt is here anticipating the law of corresponding states; as we use it, the law deals with reduced PVT values for gases, ratios to the critical-state values, but as we have seen the concept of*

a critical state had not yet been formulated. His table takes molar volumes at the boiling point, which is about $0.6T_c$ for substances in general and may thus be taken as reasonably proportional.

In the appended tables, specific volumes are quoted for almost all liquids for which observations are available, and which contain only oxygen, hydrogen, nitrogen, carbon, sulfur, chlorine, bromine, and iodine. With few exceptions, these are taken from the work of H. Kopp.

The first column contains the name of the substance; the second, the chemical formula; the third, the specific volume at 0; the fourth, the specific volume at the boiling point—both derived from observations. In the fifth column are specific volumes at the boiling point calculated according to Kopp; in the sixth, specific volumes calculated to the assumptions above. For the latter calculations we took O=11, H=3.5, N=13, C=14, S=26, Cl=22.8, Br=32.1, and I=43. The values in column seven will be discussed below.

The differences between observation and calculation in our sixth column are somewhat larger than in Kopp's case; his assumptions don't agree well with the approach proposed above to the constitution of liquids. His specific values are C=11, H=5.5, O in a radical 12.2, O outside a radical 7.8, S in a radical substituted on carbon 28.6, S outside a radical 22.6, N in volatile bases 2.3, N in NO_2=8.6, N in cyano compounds 17, and finally Cl=22.8, Br=27.8, and I=37.5.

The small specific volume of nitrogen in bases indicated above is surprising. Kopp himself mentions this; the value is similar to that for metals! This is usually not the case for nitrogen, though one might have expected such a low value for hydrogen. Furthermore, nitrogen has two other specific volumes: 8.6 and 17. Such an increase from 2.3 to 17 is inconsistent with our assumption of invariable atomic volumes, because packing differences cannot account for so great a change. Kopp attaches a special importance to the difference in specific volumes for atoms arranged differently within the molecule. He sees this as proof of the necessity of rational formulas, and at the same time as a touchstone for correct choice in ambiguous cases.

Our approach is also consistent with small changes in specific volume for atoms according to their position in the molecule. For example, the numbers for cyano compounds indicate that the molecular packing at the boiling point is not the normal value found for other nitrogen compounds; one must accept observations made at distinctly higher temperatures. One can say in the spirit of Kopp's approach: The nitrogen in cyano compounds effects more expansion of the molecule than a nitrogen in a different position, and one can consider this expanding force as an enlargement of the specific volume of cyano nitrogen atoms. If this approach is strictly followed, one will achieve greater agreement between observation and calculation for the boiling point. The numbers in column 7 of the table have been calculated in this way. Here we have used C=14 throughout, O=11 whether in a radical or not but O outside a radical though next to O in a radical =10, N in nitrogen oxides =12, N in cyano compounds =14.

A remarkable case for which the placement of the atoms in the molecule must be considered is the phenyl radical. The low atom count in C_6 in the radical, compared to the normal 14 in caproyl, makes it apparent that here the six carbon atoms are unusually compressed; and in fact a satisfactory result can only be obtained if in column 6 C_6H_6 = 72 instead of 84, and these numbers are used for all substances containing that radical.

Otherwise, greater deviations occur only for difficultly condensable substances such as carbon dioxide and hydrogen cyanide; that is, in cases for which approximate close packing cannot be expected.

At this point Loschmidt has made his case for constant atomic volumes. The major difficulty he enounters is seen for the benzene ring; although he was simultaneously in the process of proposing *some of the first structural formulas, he can hardly be blamed for failing to recognize aromaticity. In his table (following the text) he is also unable to distinguish structural isomers such as 1,1-dichloroethane and 1,2-dichloroethane, but this concept requires a relatively advanced awareness of structural formulas.*

Since experience has shown that with respect to specific volumes chemical compounds and simple mixtures behave the same, one can compare the observed density of nitrogen oxides with the density of hypothetical liquid air. Thus we find:

Nitric oxide	NO_2	N content 30.45%	O 69.55%	d=1.50
Nitrous oxide	N_2O	65.45%	34.15%	d=1.30
Air		77%	23%	d=1.224

so that with increasing nitrogen content we see decreasing density.

As we found above, the ideal condensation coefficient relates to the observed value at the temperature of greatest density as 1:1.17; here we should have taken 1.43 in place of 1.224. But the number 1.224 would apply at the boiling point of air, and if we take into account the differences in density for different temperatures we must consider the value 1.5 to be too small rather than too large. Because air in gaseous form is 770 times lighter than water we have, finally, the condensation coefficient of air:

$$1/(770 \times 1.5) = 1/1155 = 0.000866$$

Maxwell(1) has calculated the mean free path of air with the help of the coefficient of viscosity estimated by Stokes, and found 0.000062 millimeter.

Loschmidt's value of 1.43 for the condensation coefficient is just 1.17×1.224. We have noted, however, that a correct close-packing ratio should be 1.35, which would yield a condensation coefficient of 0.000787. Maxwell's value was expressed as a fraction of an inch; his metric value would be 0.0000576 mm. However, in Loschmidt's reference 2 Clausius had corrected a geometric error in Maxwell's paper. Loschmidt's version is the corrected value.

Most recently O. E. Meyer(4) has revised Maxwell's work, and as a result of several corrections has derived a substantially larger value. Experiments by Bessel also apply here, which have been done with extreme precision, as well as a series of his own observations done with extreme care. All this work gave consistent values, averaging 140 millionths of a millimeter.

Maxwell had used Stokes' experimental value for the viscosity of air, which in Maxwell's derivation is directly proportional to the mean free path. Unfortunately, that experimental value was in error. Meyer and Bessel had done more sophisticated measurements of the coefficient of viscosity, but were still in error. A modern value of the mean free path for N_2 at 300K (Hirschfelder, Curtiss, and Bird, Molecular Theory of Gases and Liquids, *Table 1.2-2) is 654 Å, or 0.0000654 mm. Using that value of the mean free path and the corrected condensation coefficient (above), the calculation that follows would yield a diameter for an "air molecule" of 4.12 Å. Inasmuch as Hirschfelder* et al. *also quote a collision diameter of 3.75 Å for N_2, it is clear that Loschmidt is on the right track.*

On this basis we have, finally:

$$s = 8 \times 0.000866 \times 0.000140 = 0.000000969 \text{ mm}$$

or in round numbers one millionth of a millimeter for the diameter of an air molecule.

This value is, to be sure, only a rough approximation, but it is certainly neither too large nor too small by more than one power of ten; if no errors are found in the basic premises, then even with the corrections that may occur in the mean free path and condensation coefficient of air the proposition stands: in the domain of atoms and molecules, an appropriate diameter is a millionth of a millimeter.

This is roughly one seven-hundredth the wavelength of red light, and just as the kilometer is a suitable unit of measure for the longest distances on the planet, the millionth-millimeter is for the smallest. The number of these molecules contained in a cubic millimeter would form a continuous layer covering an area of a square meter.

Faraday has shown in an ingenious study that gold foil can be shown to be continuous under a microscope even when its thickness has been reduced to 1/100 the wavelength of light. This was shown with white in place of green light, which transmitted through greater thicknesses shows that a well collimated beam of light can pass through the interstitial spaces between molecules. By our calculation such a layer (in view of the larger size of gold atoms) would correspond to a thickness of no more than 3-5 molecules. Incidentally, the calculation suggests for the "atomic weight" of chemists a suitable unit of a trillionth of a milligram.

> *This quantity is the* amu, *for which our current value is* 1.66×10^{-21} *mg. Loschmidt's value seems far too large, until we realize that he used "billion" to mean a million million, or* 10^{12}, *and "trillion" to mean a million billion, or* 10^{18}. *His value is thus* 10^{-21} *mg, just what it should be.*

An imposing string of numbers such as our calculation yields, especially when taken into three dimensions, means that it is not too much to say that they are the true residue of the expectations created when microscopists have stood at the edge of the bottomless precipice and described them as "infinitesimally small". It even raises the concern that the whole theory, at least in its present form, might wreck on the reef that the infinitesimally small cannot be confined by experiment.

Nobert(5) sees a resolution of 4000 lines per millimeter; those most excellent instruments make possible the examination of the most delicate detail at this size in biological structures. This distance is still 250 times greater than the diameter of the air molecules. Because we accept the principle that a molecule of a simple gas is diatomic, the number is about 400 times the number of atoms of oxygen or nitrogen that would fit between two of Nobert's lines. A cube with this edge length would accommodate about 64 million such atoms, or—if close-packed—about 100 million atoms. The great bulk of biological molecules, however, are fairly complex molecules such as albumin, chitin, etc., which would have a cross-section of more than 50 atoms of C, N, H, and O. Our cube would contain only about 2 million molecules of such biological molecules.

> *In fact, the optical microscope he is describing had resolution adequate to see the smallest organisms, which have a diameter of about 0.001 mm. The microbiologists of the time assumed that organisms might be smaller and smaller, beyond the resolution of their microscopes in a more or less infinite regression.*

Since in living organisms fully half the weight is liquids whose molecules can fill the crevices between biomolecules, we estimate that in round numbers a million molecules are present in the smallest organism we can see with today's best instruments. But the biomolecules are indivisible building blocks, and a simple comparison suggests to us that a million building-block units would be needed for a not very complex cell membrane, let alone for a cell organism with all its organelles.

With respect to the very smallest, then, one can set the world of biological creatures in a descending order of size from our cells. But here, if the new theories of the gaseous and liquid states extend to solids, we can set a definitive barrier to descending sizes.

> *His "definitive barrier" was correct. It is in fact true that a cell requires very roughly a million biomolecules to form all its organelles. Viruses are, of course, smaller—but they are not considered to be organisms.*

We might be able to move this barrier farther if we could explain gas "molecules" as aggregates of simpler chemical molecules. We would need only to add (to the law that in similar volumes under similar conditions all gases contain the same number of molecules) the secondary assumption that for the simplest as well as for the most complex gases and vapors the same large number of chemical molecules are united in a single gas "molecule". But what physical necessity, if 1000 H_2 are bound into a single hydrogen gas molecule, also requires 1000 molecules of valeric acid, or amyl or benzoyl chloride, in their vapor molecular units? To accept this violates all probability if we pursue it farther.

Before we accept this, thinking of the atom itself as having greater complexity, and taking the oxygen or hydrogen atom as a conglomeration of many smaller particles, we must distinguish between pure substances and those of a mixed nature. We choose rather, along with other recognized researchers, to pursue another way out, which, even in case experimental fact should press us, opens a limitless perspective that does not deviate too severely from the accepted atomic hypothesis that has been so conducive to the progress of understanding. We mean the comparison of the ether envelope to the explanation of the ultimate ramifications of life processes. Since its existence is always unavoidable in the theory of light and electricity, it should not be expected that it would not play an important role in the ultimate structure of organized matter. From this viewpoint, biological molecules themselves would appear as proper elementary organisms, experimentally accessible materials are made out to be only frameworks through which the ether envelope passes as an immeasurably more subtle material, affording space for an inexhaustible variety of elementary life forms. As to the necessity or the value of such a broadening of the atomic theory, future work must decide.

> *Loschmidt is trying hard not to upset every applecart. In the 1860's, the existence of an insubstantial ether in which light waves moved through the universe was assumed as necessary in the physics of the time. Although he has no idea how to do it, he supposes that the immeasurably fine ether might allow even smaller living systems, or even finer subdivision of matter. But "future work must decide", and the Michelson-Morley interferometric studies that were to destroy the concept of an ether envelope lay two decades in the future.*

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(4) Meyer, O. E., Ann. der Phys. und Ch. v Pogg. **1865,** *125*, 2

(5) Nobert, *Special Catalog of the Customs Union Exhibition, London 1862,* p. 83, and Harting, *The Microscope*, (trans. Theile), p. 881

The table that follows has been abridged. Loschmidt's original table included 109 compounds, nearly all organic, in order to demonstrate the adequacy of his constant-atomic-volume model. We here show a sampling of compounds with most of the atoms or functional groups he mentions, but it is interesting to note that he had the correct molecular formula for every compound except sulfur monochloride (SCl to Loschmidt) and elemental bromine (Br).

Specific Volume

		observed		calculated		
		at 0 point	at boiling pt.	Kopp	Loschmidt	
Water	H_2O	18	18.8	18.8	18	18.6
Hexane	C_6H_{14}	122.6	137	143	133	137.2
Heptane	C_7H_{16}	141.4	162	165	154	158.8
Octane	C_8H_{18}	159.7	184.5—186.8	187	175	180.4
Methanol	CH_4O	39.12	41.9—42.2	40.8	39	40.2
Ethanol	C_2H_6O	56.8	61.8—62.5	62.8	60	61.8
Amyl alcohol	$C_5H_{12}O$	106.6	123.6—124.4	128.8	123	126.6
Ethyl ether	$C_4H_{10}O$	100.5	105.6—106.4	106.8	102	105
Ethylene oxide	C_2H_4O	49.1	52	51.8	53	54.2
Acetaldehyde	C_2H_4O	54.5	56—56.9	56.2	53	54.2
Valeraldehyde	$C_5H_{10}O$	104.75	117.3—120.3	122.2	116	119
Benzene	C_6H_6	86.8	96.0—99.7	99	93	
Cymene	$C_{10}H_{14}$	152.5	183.5—185.2	187	177	
Phenol	C_6H_6O	86.96	103.6—104	106.8	104	
Benzyl alcohol	C_7H_8O	101.6	123.7	128.8	125	
Benzaldehyde	C_7H_6O	99.5	118.4	122.2	118	
Nitrous oxide	N_2O	45.6(-6°)	36.1		37	35

Nitrogen dioxide	NO_2		31.7—32.4 15° below BP	33	35	34
Nitromethane	CH_3NO_2		61.6 (27° above BP)	60.5	59.5	59.3
Nitroethane	$C_2H_5NO_2$		79—84	82.5	80.5	80
Amyl nitrite	$C_5H_{11}NO_2$	133.4(15°)	148.4	148.5	143.5	144.8
Ammonia	NH_3	22.4(10°)		18.8	23.5	
Ethylamine	C_2H_7N	64.6(8°)	65.3	62.8	65.5	
Amyl amine	$C_5H_{13}N$	116(18°)	125	128.8	128.5	
Octyl amine	$C_8H_{19}N$	164(15°)	190	194.8	191.5	
Aniline	C_6H_7N	90	107.35	106.8	109.5	
Hydrogen cyanide	CHN	38.5		33.5	30.5	31.8
Methyl cyanide	C_2H_3N	49.1	54.5	55.5	51.5	53.4