Alfred Bader fonds

Writings

Josef Loschmidt
by Christian R. Noe, Alfred Bader, & William T. Wiswesser

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It happens seldom in the life of a historian that he comes across the work of a man who has really produced a great masterpiece and has then been practically forgotten.

This may be more common in art history that it is in the history of science.

To give you just one example, one of the greatest painters of the 17th century was Jan Vermeer who can truly be considered one of the first impressionists ever (fig. 1). He painted very little, only about 40 works, half of which were in the collection of one Delft collector whose estate was sold in 1696. In the 18th and early 19th centuries, Vermeer's work was little known, and his paintings were often attributed to other artists. We can well imagine how the great French art historian, Theophile Thoré Bürger, must have felt when he realized that these wonderful works attributed to others were really by one hand, that of Jan Vermeer.

In the history of science, this may be much rarer, and yet it does happen, and today we would like to discuss one specific example--that of Josef Loschmidt (fig. 2).

In each generation since Loschmidt's death in Vienna in 1895, someone has recognized his greatness and has written about it extensively, only to have Loschmidt's name forgotten again.

The first to recognize that greatness was Richard Anschütz, a student of Kekulé, who became his biographer and his successor as professor in Bonn. In 1913 he reprinted and annotated Loschmidt's work of 1861. Anschütz's comments speak for themselves. He wrote on page 101 of his

reprint, "Loschmidt presented his views of the constitution of aromatic compounds four years before Kekulé. If these views had been published in a well-known chemical journal, they would really have created a great deal of stir and would have added substantially to the development of chemistry. Besides that, Loschmidt developed his graphic formulae on the basis of ideas about molecules which even today (1913) deserve careful consideration."

On page 105 of his reprint, Anschütz poses the important question whether Kekulé had seen the original of Loschmidt's 1861 work, or whether he had only learned superficially about the graphic formulae through a third party. In a single one-line sentence on page 105, he denies that Kekulé had actually seen Loschmidt's book but asserts that he must have learned about the formulae, in all probability through a good friend, Hermann Kopp, who was not an organic chemist and who had written an abstract of Loschmidt's book in Liebig's Jahresbericht der Chemie, in 1861.

Anschütz may have been too kind to Kekulé. Perhaps Loschmidt's little book was better known than he realized. Why was it that just after its publication so many alternative benzene structures appeared?

And why would Kekulé himself comment on these structures in a personal letter of January 14, 1862 to Erlenmeyer (fig. 3) had he not seen the structures--"Loschmidt's Confusionsformeln" he calls them. Did he really find them confusing? Was this some snide comparison, a play on words, "Loschmidt's Constitutions-Formeln" are just Confusionsformeln? And why, if he had not seen the structures, would he again refer to them, this time publicly in his famous paper presented by Wurtz in Paris on January 27th and printed in the "Bulletin de la Société chemique."

What a bit of luck that Anschütz came across Loschmidt's name in

Kekulé's French paper (fig. 4). Note that Kekulé said that he preferred his structures to those of Loschmidt and Crum-Brown! Surely when a scientist says that he prefers one structure over another, he must know both. And now look carefully at Kekulé's paper, (also of 1865) in the Zeitschrift für Chemie. Notice that in the German paper footnote 2, referring to Loschmidt, is left out. Was that accidental or deliberate?

Anschütz's role is a most interesting one. Time and again he recognizes Loschmidt's greatness, for instance in acknowledging that he was the first to predict the existence of cyclopropane (p. 118), to formulate ozone (p. 130), and to depict toluene, benzyl alcohol, phenol and many other aromatics correctly. He also agrees that Loschmidt's presentation of simple molecules like acetic acid is preferable to Kekulé's sausage formula, which he actually illustrates on page 110! Yet as the student and successor of Kekulé, he could not bring himself to say what is so clear to us: Loschmidt's was a far greater mind than Kekulé's. Instead, Anschütz made an enormous effort to reformat Loschmidt's book and to add many footnotes which help greatly in the understanding of his work--truly a most singular act of atonement by a student for the omissions of his teacher!

Our good friend, the late Dr. William Wiswesser, was first attracted to Loschmidt's work by a review article written by Moritz Kohn in The Journal of Chemical Education of 1945. Dr. Wiswesser recognized that Loschmidt's formulae could be regarded as the first line formula notations, "rational formulae" so close to his heart--his Wiswesser line notation. Before his death last December, he prepared a great deal of material, collating Loschmidt's work with WLN notations, and Aldrich has now copies of this collation on computer disks available to interested historians of chemistry.

Dr. Wiswesser's article on Loschmidt which appeared in the Aldrichimica Acta, and the republication of Loschmidt's book and Anschütz's revision have sparked renewed interest in this almost forgotten chemist. We asked ourselves how Loschmidt arrived at his organic formulae. If he is known for anything it is the Loschmidt number, but that is something quite different. Was he an outsider who simply had a lucky break? The answer to that can be found in an important paper of 1878 entitled "The Scientific Goals and Accomplishments of Chemistry."

Beginning with Dalton's theory, the author describes the historical development of the understanding of the molecular construction of organic molecules. He names Avogadro's hypothesis of 1811 as an important step which was further developed until it was understood that gas particles are identical with chemical molecules. We all know that the development of Avogadro's hypothesis led to the Loschmidt number, and so it is clear that Loschmidt's studies in gas theory were the source and basis for his extraordinary work in chemistry.

Fig. 5 shows pages 17 and 18 of this 1878 paper, and we would like to draw your attention specifically to the sentences underlined. Note particularly the last paragraph which states, "The chemical aspect of atomic theory was substantially broadened approximately 20 years ago through the hypothesis developed by chemists (emphasis supplied) which can be called the theory of the chemical valence of atoms."

Now, which chemist was it who developed this hypothesis? It was, in fact, Josef Loschmidt. And of course, you will ask who made this important statement in 1878 describing Loschmidt's work, without naming him. It was none other than August Kekulé in his Rektoratsantrittsrede in Bonn (fig. 6). would he have forgotten the chemist's name? It is well-known that Kekulé had a marvellous memory, a photographic memory.

He must have known a great deal about Loschmidt's work and deliberately omitted his name in the very passage where only Loschmidt's name really fits. Here Kekulé talked of the relationship between physics and chemistry which Loschmidt understood so clearly.

Not only did he understand, he was able also to depict on paper representations of molecules which come remarkably close to our present day molecular modelling. No chemist before him, and very few in the 100 years that followed, have depicted molecules as realistically as he.

The title (fig. 7) of his book is important. He called it Constitutions-Formeln der organischen Chemie in geographischer Darstellung. The title of Richard Anschütz's reprint of 1913 is KONSTITUTIONS-FORMELN der Organischen Chemie in Graphischer Darstellung, that is "in graphic representation." The difference between geographic and graphic representation is significant. Here again, Loschmidt shows himself to be not only a superb chemist, but one of the great physicists of his time, and in fact, he became the world's first professor of physical chemistry. Loschmidt's models were the very first which considered atomic sizes and their relationships in molecules. He would have been advanced even in the 1940's, not to speak of 1861 or 1865 when Kekulé came out with his sausage-like representations. The following slides show a comparison between the way in which we depict molecules today, Loschmidt's representations of 1861, Kekulé's from 1865 on, and these same molecules in molecular modelling. You will come to the inevitable conclusion that Loschmidt was far closer to our molecular modelling than anyone in the 19th century.

Let us begin with a simple molecule, acetic acid (fig. 8). Compare Loschmidt's representation, first with our molecular modelling of

today and with the then accepted sausage formula. Note that the latter has the carbon atom of the carbonyl in direct contact with two hydrogen atoms! That formula was Kekulé's (fig. 9), and Anschütz points out on page 110 of his reprint how superior Loschmidt's formula is (fig. 10). Fig. 11 shows the situation in 1867. By that time, Kekulé, who in 1865 had preferred his own structures to Loschmidt's and Crum Brown's, had abandoned his sausage formula of acetic acid.

Acetone (fig. 12) is another clear example. Note that in Kekulé's textbooks published five and six years later, the oxygen atom is in contact with three carbon atoms!

Cyclopropane (fig. 13) was first made by Freund in 1882. Loschmidt predicted its existence 21 years earlier.

Anschütz (p. 110) pointed out that Loschmidt was the first to show double and triple bonds, with the overlaps, as shown with ethylene and acetylene (fig. 14).

Loschmidt, the physical chemist, thought about the sizes of atoms. Note how close he came to reality (fig. 15).

And now consider some of Loschmidt's 121 aromatic structures, one of which, benzene, we see here.

Compare his structure of benzenesulfonic acid (fig. 16) with Kekulé's. In Kekulé's formula of five years later, the sulfur atom is in contact with three carbon and two oxygen atoms! And Kekulé considered his formulae superior to Loschmidt's. Today this sounds like an joke. Kekulé's are the Confusionsformeln!

Loschmidt used an odd representation for chlorine, as in chlorobenzene (fig. 17), but surely it is preferable to Kekulé's, where the

chlorine is in contact with three carbon atoms!

Now you will ask in astonishment: surely Kekulé presented his hexagonal structure of benzene in 1865--as is stated in most textbooks on chemisty. But look at his textbook of 1867 (figs. 18, 19, 20), all with these sausage formulae. What has been overlooked is that Kekulé considered the possibility that benzene might be a hexagon with corners of hydrogen atoms, not carbon atoms (fig. 21). Now you can understand why Kekulé presented aniline--for instance--as he did (fig. 22). The nitrogen atom has taken the place of a hydrogen--and the benzene ring is broken. Note to what other absurdities this leads (fig. 23). Only in the 1870's did Kekulé adopt the hexagonal formula with carbon atoms in the corners--long after other chemists had done so.

In contrast, look at other aromatic structures depicted by Loschmidt (figs 24, 25). Note that with cinnamic acid, aldehyde and alcohol the double bond is trans--in 1861!

Benzidine (fig. 26) is particularly instructive--Kekulé's formula is still based on the idea that the corners of the hexagon are hydrogen atoms! And look at the clarity of triphenylamine (fig. 27). The next (fig. 28) shows a part of one of Loschmidt's plates handcolored by Dr. Wiswesser. Note how very much information Loschmidt crammed into these plates--structures 185, 186 and 187 are those of benzene, phenol and anisole.

A great deal has been written about Kekulé's dream about a snake biting its tail. Did he have this dream? What difference does it make? Loschmidt's correct formulations preceded Kekulé by years. Kekulé certainly knew something--and probably a good deal--about Loschmidt's work, but only a psychiatric examination of Kekulé could have determined whether his silence

about Loschmidt was due to ambition or his anti-Austrian feelings. Today we celebrate 100 years of the Benzolfest, a Fest that was in fact four years late and honored the wrong chemist..

In recent years, fraud in science has been much discussed. Fraud can take many forms--with acts of commission and omission. Consider fig. 29, the article on Kekulé by Richard Lepsius, Kekulé's academic grandson, published in 1965. You have seen that Kekulé did not look on benzene in 1865 as Lepsius alleges. But Loschmidt did not look on benzene as is depicted here either, and to misspell Loschmidt's name is just adding a minor insult to a major injury. Loschmidt said that one might be tempted to think of benzene as Lepsius showed, but that he preferred structure 185 (fig. 30). Were Kekulé's and Lepsius' acts of commission or omission? We cannot be certain--but we can be certain of the results. Loschmidt must have known of Kekulé's derogatory remarks. Was he discouraged by such a summary dismissal of his work by this greatest of German chemists? Is this why his later work was mainly in physics where he was appreciated? Other chemists must also have known Kekulé's opinion, but they, like Kekulé, helped themselves freely to Loschmidt's ideas. However, if Kekulé had publicly recognized the importance of Loschmidt's work, molecular modelling as we now know it would have come much earlier. Scientists--we--have been the losers.

Loschmidt's work on the structure of molecules was published privately. We don't even know how many copies were printed, but it was reviewed by Kopp in Liebig's Jahresbericht of 1861, and we know that one example found its way to the British Library and there has a date stamp of 1862. When Boltzmann wrote in Loschmidt's obituary that Loschmidt's "work forms a mighty cornerstone which will be visible as long as science exists,"

he understated the facts. Boltzmann clearly did not know Loschmidt's *Chemische Studien*, and should have said that Loschmidt's work forms two important cornerstones, one in physics and one in chemistry.

Loschmidt published relatively little and never outside of Austria, nor did he ever go to international meetings to present his views. His works include the one small book of 1861, a few essays, and 17 scientific papers, mostly in physics, presented in the *Sitzungsberichte der Akademie der Wissenschaften* in Vienna between 1865 and 1890. His most famous paper in physics, "Zur Grösse der Luftmoleküle" (*Sitzungsberichte*, 52, Abt. II, pp. 396-443 (1866)), describes his calculation of the number of molecules in one milliliter of an ideal gas--the Loschmidt number.

In 1948, Hubert de Martin submitted a well-written Ph.D. thesis on Loschmidt to the University of Vienna. His discussion of Loschmidt's book recapitulates Anschütz's comments. He refers (p. 68) to Loschmidt's greatest work in physics: "Loschmidt's paper 'The Size of Air Molecules' presents in a few pages the solution to a problem which had engaged the world's best minds for millenia--since Democritus and Epicurius...."--his cornerstone in physics.

We believe that the few pages, 47 in all, of his 1861 book, where he dealt with organic structures as no one had before, constitute his cornerstone in chemistry.

Loschmidt must have been a truly shy and self-effacing man. It is interesting to know a little about his background. He was born in a small village near Karlsbad in Bohemia in 1821, his parish priest recognized some of his potential and urged him to go to high school and then to university in Prague, where he studied first philosophy and mathematics and then the natural sciences, physics and chemistry. He then studied at the Polytechnic Institute

in Vienna, now the Technische Universität, and then worked with a number of industrial companies in Lower Austria, Styria, Bohemia and Moravia. Unfortunately, most of the industrial enterprises failed, and Loschmidt returned to Vienna in the early 1850's penniless, and accepted a job as a ~~concièrge in an apartment house~~, giving private lessons to high school students.

He then qualified as a high school teacher in chemistry and physics. He must have been very much of a loner but his keen interest in theoretical questions, coupled with his practical knowledge in all sorts of commercial chemical enterprises, led to his studying some of the most fundamental questions in physics and chemistry of his time. He became the good personal friend of two very able younger Viennese physicists, Josef Stefan and Ludwig Boltzmann, who appreciated his competence and ingenuity, and helped him become Privatdozent at the University of Vienna in 1866. A man without a Ph.D. hardly ever reached the position of Privatdozent, about the equivalent of the American assistant professor. Two years later, in 1868, he became associate professor after his election to the Royal Academy of Sciences in Vienna the year before. Also in 1868, he founded the Chemisch-Physikalische Gesellschaft, a society of chemists and physicists in Vienna which still exists today. In 1869, he received the well deserved honorary degree of Doctor of Philosophy. In 1875 he became the chairman of the Physical Chemistry Institute and the first professor of physical chemistry in the world. Two years later he became dean of the Faculty of Philosophy, and finally in 1885 was elected to the Senate of that faculty.

We venture to say that this meteoric advance from a penniless Hausbesorger, a concièrge, to highschool teacher, professor, dean and senator,

is unique in the annals of science. However, it is clear that this recognition, and the personal respect and admiration of his good friends, was based almost entirely upon his important work in physics.

On a personal level, we know of only one woman in his life, Karoline Mayr, with whom he lived for many years. Only when he was 66 and she was expecting his child were they married. Sadly, their one son, Josef Karl, died of scarlet fever just three years after his father's death in 1895. Karoline Loschmidt survived her husband for many years, and died of cancer in Vienna in 1930.

31 Why are we making such an effort with Loschmidt (fig. 31)? One of the greatest achievements in the history of western culture is the development of this concept, that matter is constructed of molecules. Only in the last years have we been able to prove, e.g., through Xrays and NMR methods, that organic molecules really look as the models show--models which have been developed in the last 200 years by many brilliant minds. When we deal with molecular modelling as a matter of course, then, for the sake of truth and justice, the father of the correct molecular depictions in organic chemistry, Loschmidt, must be honored.

We hope that not only Austrian and Czech chemists, but chemists around the world, will have the good sense to remember Loschmidt in 1995, the 100th anniversary of his death, and that our grandchildren will have another Benzolfest in 2061, the 200th anniversary of the correct formulation of benzene. And of course it will be important to ascertain that authors and editors of text books of chemistry acknowledge Loschmidt not just as the first to depict benzene correctly, but as the true father of molecular modelling.

Reverse to 32

Reverse to

32

As Dr. Wiswesser wrote (Aldrichimica Acta, 22, (1989)), "...that tiny book of 1861 was really the masterpiece of the century in organic chemistry." (fig. 32)