A Philosophical Essay on Molecular Structure

A Philosophical Essay on Molecular Structure

By

Ochiai Hirofumi

Cambridge
Scholars
Publishing

A Philosophical Essay on Molecular Structure

By Ochiai Hirofumi

This book first published 2021

Cambridge Scholars Publishing

Lady Stephenson Library, Newcastle upon Tyne, NE6 2PA, UK

British Library Cataloguing in Publication Data
A catalogue record for this book is available from the British Library

ISBN (10): 1-5275-6307-3
ISBN (13): 978-1-5275-6307-0

To everyone who loves chemistry

CONTENTS

LIST OF FIGURES

PREFACE

We can take an X-ray photograph of molecules. But we cannot take any photograph whatsoever of molecular structure. Why? What is molecular structure in the first place? The idea of writing this book arose from my own curiosity about molecular structure. I wanted to know whether or not what we assume to be molecular structure is relevant to the real structure of the molecule, if molecular structure exists at all.

It was not "skepticism" but "curiosity" that drove me to writing the book. As someone once kindly pointed out to me in personal communication, skepticism is of a social nature, if it means the doctrine that knowledge in a particular area is subject to being doubted. Skepticism can be personal as well, if it involves an attitude toward a particular object. This kind of skepticism can be shared, however, with people who regard an object in the same way. On the other hand, curiosity is quite personal by nature, for it is supported by emotions like comfort or discomfort, which originate from and belong to a particular individual. (Dogs are very curious but not skeptical—probably!) Accordingly, while skepticism can be either agreed or disagreed with, curiosity is seen with empathy. I hope this book receives your warm empathy.

As a practitioner of organic chemistry, I know that the concept of molecular structure is sufficient for many purposes. A moment's reflection is enough to realize this. Let us say we want to synthesize chemical compounds which have a certain physiological effect. Without knowledge of molecular structure, we have no way to proceed other than to rely upon trial and error. We would be back in the nineteenth century. In fact, present-day drug research is performed with great precision and in an amazingly efficient manner because it is based on structure-activity relationships. Our knowledge of molecular structure also enables logic-guided chemical synthesis.

Thus, there is no problem with assuming the existence of molecular structure for practical purposes. There is no skepticism of either type, at least among chemists. But, to me, the case I described above seems only to show that it is empirically adequate. Since the molecule is too small to see, visual evidence is not available. Everything we know about molecular structure is circumstantial. Reality may be different from what we assume it to be. Moreover, since submicroscopic entities are subject to the laws of quantum mechanics, the details of these entities may be hard to represent by analogy with things around us. For instance, we can find nothing parallel to the particle-wave duality of electrons in the world of possible experience.

My questions can be specified as follows: In what sense is our concept of molecular structure relevant to reality? Can we (or how can we) defend it from criticism of the kind that it cannot be derived from quantum mechanical calculations of the molecule? (It is customary to think that an ab initio method provides exact accounts of molecules because it is grounded on fundamental physical principles. It is more reliable than what is conceived of based on empirical data. In fact, “ab initio” does not mean starting from scratch.) Is it that “molecular structure” is an ingenious device to describe the chemical properties of molecules but that the true nature of molecules is otherwise? Structure is a concept that has a proper use within the bounds of the senses. Then, is it legitimate to talk about the structure of what exists beyond those bounds? I believe that these questions are fascinating, both for practical chemists and for philosophers of chemistry.

The arguments in this book lead us to consider the meaning of reality. In everyday life we take things we perceive as real. But the way of perceiving objects depends on the conditions under which perception occurs. (It depends on cognitive abilities as well: kestrels, which perceive UV rays, might be seeing a world quite different from ours.) Since we, unlike the Omnipotent, cannot enjoy a view from anywhere but a first-person perspective, what we perceive has to be conditional and provisional. We need to reconsider the idea of objective reality.

The majority of chemists may be too busy with their work to care about the questions described above. But not to take anything for granted, or at least to reconsider what is taken for granted, is needed for practitioners to deepen their understanding of what they are doing. Some people do not hesitate to equate what we assume to be molecular structure with reality, for example those who take orbitals to have physical significance. As Scerri pointed out, orbitals are none other than mathematical wave functions. (Scerri 2008, pp.200-213) Critical faculties are essential for scientists as well as for philosophers.

Most of the arguments in this book are based on Kant's *Critique of Pure Reason*. Kant is the figure in philosophy most comparable to Kekulé in chemistry. Just as Kekulé synthesized two seemingly conflicting claims about molecular constitution into the theory of molecular structure, Kant settled disputes between empiricists and rationalists and provided science with firm philosophical grounds. His theory of knowledge serves as a guiding principle for our arguments. Its significance is twofold: first, it shows us how our cognition of objects is possible and how concepts are legitimately or illegitimately applied to those objects; second, it warns us not to mistake a subjective conception for an objective one.

As you see from the description above, this book does not aim to be a textbook or a review article of a particular field of philosophy or chemistry. Rather, it will find its value in stimulating your mind by shaking your beliefs about chemistry. (Hence it is desirable for readers to have an undergraduate-level knowledge of chemistry. But, of course, those who are merely interested in chemistry or philosophy are welcome.) You may find several arguments in this book hard to agree with. If so, try to explain to yourself why. Understand clearly with what point or in what sense you cannot agree. In so doing, confirm your philosophical standpoint and make alternative—or your original—arguments. That is how we learn philosophy. I hope this book gives you a chance to learn about the philosophy of chemistry. Actually, I am not sure whether my intention will be successful. In the end, it is you who will decide. I would appreciate your honest opinions and advice.

I have another word about the composition of the book: The arguments in Chapter 2 and Chapters 5 through 8 are based on my original works. Some of them have been published in *Foundations of Chemistry* and *Hyle—International Journal for Philosophy of Chemistry*. The minimum knowledge necessary for reading these chapters is provided in Chapters 1, 3 and 4. Since there are potentially as many ways of choosing the necessary minimum as viewpoints, what I show you in these chapters is the contents of my tool-box, as it were. When I think, I always refer back to pieces of information collected in these chapters. So, I hope they are helpful for you, too. It is said that, if you have a look at a person's tool-box, you can see what he is thinking about. The arguments in Chapters 1 and 3 are based on secondary sources. Chapter 4 is an abstract of Kant's *Critique of Pure Reason*, which provides the basis for the chapters that follow.

You may find confusion or contradictions in the arguments. Such may be a sign that the writer is going astray. He is groping his way, which is neither straight nor easy to find. With a big heart, go along with him for a while, and you can enjoy this book as a memoir of a philosophical journey.

I thank the journals mentioned above for allowing me to reproduce the principal arguments of my articles. I also express my thanks to the reviewers of my articles published in these journals, who gave me valuable comments and advice to make my arguments coherent and convincing. I express my special thanks to Jeffrey I. Seeman. In our personal communication at the beginning of 2020 he reminded me of how important it is to be exact with words in philosophical arguments. Finally I express my cordial gratitude to Eric Scerri, who kindly opened the door for me to "The International Society for the Philosophy of Chemistry" where I have become acquainted with many fellow philosophers of chemistry. Without their support and intellectual stimulation this small book was not written.

CHAPTER 1

A HISTORICAL OVERVIEW OF THE THEORY OF MOLECULAR STRUCTURE

Significant developments in chemistry in the 19th century

1800	Volta invents the Voltaic pile, the first electric battery.
1803	Dalton presents his atomic theory in *A New System of Chemical Philosophy*.
	Berzelius develops the “theory of electrochemical dualism”.
1807	Davy isolates Na and K by electrolysis of molten alkaline salts.
1808	Gay-Lussac discovers the law of combining volumes.
1811	Avogadro presents the “equal volumes equal numbers hypothesis”.
1828	Wöhler succeeds in creating urea from inorganic materials.
1830-7	Liebig develops the elemental analysis of organic compounds.
1837	Laurent develops the non-electrochemical “nucleus theory”.
	Berzelius develops the “radical theory”.

1838	Dumas prepares trichloroacetic acid and develops the “type theory”.
1839	Gerhardt puts forward the “theory of residues”.
1839-41	Berzelius develops the “copula theory”.
1845-49	Hofmann prepares secondary and tertiary amines.
1848	Pasteur succeeds in the optical resolution of tartaric acid.
1848-49	Kolbe and Frankland try to isolate alkyl radicals.
1849	Wurtz prepares primary amines.
	Frankland stumbles on the first organometallic compounds.
1850	Williamson prepares various ethers.
1852	Gerhardt prepares various mixed acid anhydrides.
	Frankland puts forward the concept of saturation capacity.
1853	Gerhardt develops the “new type theory”.
1857	Kekulé presents the concept of the C-C bond.
1858	Canizzaro calculates atomic weights from vapor densities.
	Couper’s suggestion of the C-C bond is publicized.
1860	Cannizzaro’s system of atomic weights is accepted at the Karlsruhe Congress.
1864	Crum-Brown begins using a prototype of structural formulas.
1865	Hofmann first uses the croquet-ball model.
	Kekulé proposes the structure of the benzene ring.

1866	Frankland proposes the concept of the chemical bond.
1869	Mendeleev presents the table of elements.
1874	van ’t Hoff proposes the concept of the tetrahedron carbon atom. Le Bel introduces the idea of the tetrahedron with regard to molecular types. Körner uses the word “molecular structure”.

1. The dawn of structural chemistry

Nineteenth-century chemistry developed around the following two poles: the invention of the Voltaic pile, Dalton’s chemical atomism. The impact of these historic events cannot be fully appreciated without understanding the philosophical and scientific contexts in which they took place. To put it simply, the dominant philosophical atmosphere in that era was characterized by a belief in dualism, and the dualistic philosophical framework fostered scientific ideas in which electricity played a central role. (Articles collected in Knight 1968 illustrate the philosophical atmosphere in the nineteenth century.)

The Voltaic pile was not only the first electrical battery but also a symbolic apparatus that revealed the dynamic nature of matter. Making use of the Voltaic pile Davy achieved the electrolysis of various molten salts, which resulted in the discovery of alkaline and alkaline earth elements such as sodium, potassium and calcium. These discoveries suggested that the essence of chemical affinity is electric attraction, and that when the attractive and repulsive forces exerted by electrodes were stronger than chemical affinity, electropositive and electronegative elements would be pulled apart and attracted to electrodes with an opposite charge. It is reasonable that Berzelius, who advocated electrochemical dualism, appreciated Davy's Bakerian Lecture in 1806 and wrote "that it must be placed among the finest memoirs with which chemical theory has been enriched." (Knight 1998, p.62) It was awarded the prize for the best work on electricity given by the Institute in Paris. This prize was offered on the instructions of Napoleon and was open to citizens of any nation.

If it is Davy who should be remembered for linking chemical action with electrolysis, it is Berzelius who gained historical fame by linking chemical atomism with dualism. He thought that chemical compounds consist of electropositive and electronegative elements or groups of elements, as is suggested by the composition of sodium chloride and sodium sulfate, for instance. His theory of the binary constitution of inorganic compounds was widely accepted in the 1810s and 20s. Then, he went one step further and claimed that organic compounds also consist of electropositive and electronegative components. Methyl sulfate may be a simple example which illustrates his idea. Such an electropositive organic component as the methyl in methyl sulfate he later named "radical."

The concept of the radical originated in 1787 with Guyton de Morveau who spoke of it as “the simple substance of an acid which modifies oxygen,” consistent with Lavoisier’s notion of the radical. (Russell 1971, p.23) Lavoisier considered organic acids to be oxides of radicals which contained carbon and hydrogen. During the 1830s “the concept of the radical developed in the arguments of electrochemical dualism and took on a number of epistemologically interesting characteristics.” (Ramberg 2003, p.17) The idea was simple: if radicals play the same role in organic molecules as chemical elements do in inorganic compounds, they could be isolated just as chemical elements can be isolated from inorganic compounds. Given electrochemical dualism, “determining the true nature of radicals would be the endpoint of chemical investigation.” (ibid. idem, p.18) It is not surprising that many chemists were absorbed in isolating radicals. Among others the studies on the benzoyl radical by Liebig and Wöhler, the cacodyl radical by Bunsen, etc., are famous examples. Actually, in spite of great efforts, all attempts to isolate organic radicals failed, though some of them bore unexpected fruit. For instance, Kolbe and Frankland pioneered electrochemistry and organometallic chemistry, respectively, in their joint research aimed at isolating alkyl radicals. The regularity found in the number of organic ligands would lead Frankland to the concept of saturation capacity, another name for valence of our day.

In addition to the failures to isolate radicals, another problem that was unfavorable to the radical theory arose. From the late twenties to the thirties it was discovered that the electropositive hydrogen of hydrocarbon radicals could be replaced by electronegative chlorine. In 1827 Dumas found that chlorine-based bleaching agents could chlorinate wax. This was incomprehensible to chemists who took the tenets of electrochemical dualism for granted. The sodium of sodium sulfate could not be replaced by chlorine, but the hydrogen of wax could! What difference was there between them? In the 1830s Laurent discovered that the hydrogen of naphthalene could be replaced by chlorine and Dumas chlorinated acetic acid to make trichloroacetic acid. Also, Dumas' assistant Louis Melsens found a method of reducing chlorinated compounds back to their starting materials. With this accumulation of facts, the radical theory—and the copula theory, which was the modified version of the former—became highly controversial.

Why and how could electronegative chlorine replace electropositive hydrogen? In order to understand the meaning of this question we need to consider the notion of atoms in the whole picture of nineteenth-century chemistry. We also need to understand the relation between the notions of elements, atoms and radicals. The questions we have to address are as follows: What was chemical atomism? What role did Dalton's theory play in the development of chemistry in the nineteenth century and thereafter?

Simply put, Dalton made atoms objects to be measured on a chemical balance. That is to say, the historical as well as the scientific significance of Dalton's theory consists in that it converted atoms from the metaphysical objects of antiquity into the material constituents of chemical compounds. The essence of the chemical atomic theory becomes clear when it is stated in relation to certain regularities observed in the weight proportions of elements that combine to form chemical compounds. The chemical atomic theory states the following: "*there exists for each element a unique atomic weight, a chemically indivisible unit that enters into combination with similar units of other elements in small integral multiples*." (Rocke 1984, p.12) In this sense chemical atoms served as a sound basis for the concept of elements defined by Lavoisier. He describes in *Elements of Chemistry* (1789) that "those things that have not been broken down into simpler substances should be considered elemental." (Ede 2006, p. 61)

The easiest way of understanding the chemical atomic theory might be to take a look at the situation which existed before its appearance. Before Dalton, it was the corpuscular theory that was most widely accepted among those who were interested in natural philosophy. "The atoms of the seventeenth- and eighteenth-century corpuscular philosophy were all composed of the same stuff and differed only in shape and size. Various arrangements of these particles formed larger units which, in their turn, composed the various substances we encounter.” (Knight 1968, p.xv) Boyle and Newton maintained that things were made up of different arrangements of a few kinds of prime matter. Such being the case, the corpuscular philosophy led to no detailed predictions or explanations of phenomena and it was regarded by most chemists to be of little value in chemistry. By ascribing an atomic weight to each element Dalton’s theory made it possible to say something meaningful about things happening beyond the bounds of the senses in relation to things observed within those bounds. In other words, it enabled “transdiction” in chemical reasoning, which we shall discuss in Chapter 5.

The radical theory was the first structure theory in the history of chemistry. Chemists of the Berzelian school sought a true and absolute picture of the microscopic world based on empirical knowledge of chemical reactions. In other words, they made a kind of inference (a projective inference in the vertical direction to the empirical horizon) and tried to make a link between what was within and what was outside the bounds of the senses. This is the key to understanding the reason why the isolation of radicals did not succeed. The concept of the radical derived from the dualistic view of chemical compounds. “The concept of the radical was not related to the study of the microscopic world but only to the manipulation of chemical formulas.” (Ramberg 2003, p.17) In the four-volume formulation of the day acetic acid was believed to consist of an electropositive C_2H_6 radical and an electronegative $C_2O_3 \cdot H_2O$

part—oxalic acid in their formulation—because the chemical property of acetic acid was explicable by their combination. "Radicals were discovered simply by manipulating formulas on paper." (idem)

2. The composition and the type of chemical compounds

Is acetic acid a copulated compound represented as $C_2H_6 \cdot C_2O_3 \cdot H_2O$? The term "copula" was originally used by Gerhardt to indicate the organic part of a molecule. (Russell 1971, p.28) Berzelius used this concept to defend his dualistic view of the molecule. He claimed that the hydrogen of an organic copula could be replaced by chlorine because this reaction "occurred only in the passive, chemically unimportant copula." If so, it would "not be a surprise that the fundamental chemical property of the compound did not change" due to the introduction of chlorine. (Rocke 1993, p.56) But does acetic acid really consist of a hydrocarbon copula and oxalic acid? Does it have a water molecule in it? No. Neither radicals nor copulas can be isolated after all. Another point to be considered is the system of chemical stoichiometry: Does acetic acid consist of four carbons, eight hydrogens and four oxygens? In other words, is the four-volume formulation correct? All these questions were to be solved together because they derived from one and the same historical fact.

Berzelius combined Dalton's theory and Davy's idea to postulate electrochemical dualism and, during that process, by his determination of atomic weights, transformed chemistry into a science based on exact data. He assumed that all atoms are spherical and of equal size—and so, he thought, the volumes of gases were proportional to the number of atoms—and determined chemical formulas for non-metallic compounds systematically, based on data of vapor densities. The most important thing from a historical point of view is that he determined the formulas of organic acids based on silver acetate and took silver and lead acetates as $[Ag]O \cdot C_4H_6O_3$ and $[Pb]O \cdot C_4H_6O_3$, respectively. Because of this mistake the molecular weights of organic acids became double the present values. (Summarized and quoted from Rocke 1984, pp.75-78; 2001, p.91) On the other hand, since the molecular weights of simple inorganic molecules such as water and carbon dioxide were determined by a different method and had correct values, the dehydration condensation reactions of acids produced H_4O_2 instead of H_2O. It was Gerhardt who addressed head-on the inconsistency in molecular weight between the organic and inorganic domains. He proposed either to halve the molecular weights of organic compounds or double those of inorganic compounds. In view of the Avogadro-Ampere hypothesis he pointed out that the former was the proper option to take. It is easy to imagine that his proposal annoyed many chemists of the day. Liebig and Wöhler rightly feared his adjustment would destroy all the relationships between compounds that had been painstakingly built up since the early work of Berzelius.

Gerhardt was “accused of doing algebra and not chemistry.” (Buckingham 2004, p.167) In fact, by virtue of his adjustment, the molecular formula of acetic acid became $C_2H_4O_2$ and, consequently, there was no room for radicals or copulas appearing in molecules. Thus, the unitary view of acetic acid, and of other organic compounds as well, was established.

Gerhardt was a former student of Liebig and spent many years in Paris, where he collaborated with Laurent, an assistant of Dumas. Paris in the mid-nineteenth century was under the influence of Auguste Comte (1798-1857), the founder of positivism. He taught that science progresses from a theological interpretation of nature to a metaphysical one and from there to a “positive” view where final causes are no longer sought and outward phenomena are all that matter. “It is more than a coincidence that its chief expositor was the friend and teacher of some of the leading chemists of Paris.” (Russell 1971, p.48)

Another feature common in nineteenth-century science was the use of analogy. This trend reached its highest around the mid-nineteenth century. Darwin thought that, just as massive crustal movements and deformations over a geological time had made the present landscape, every living creature had evolved over many generations. The idea of biological evolution must have been natural for him, since he had happened to witness crust uplifting from the Beagle. Chemistry was no exception. Comparison of all organic compounds with a limited number of types of simple inorganic compounds was quite in keeping with the general scientific outlook.

When Gerhardt came to Paris in 1838, Dumas was just fashioning his theory of types. Dumas prepared trichloroacetic acid from acetic acid and discovered that both compounds had almost the same chemical properties. He thought that something like chemical type was retained in substitution reactions. In fact, “Dumas based his theory not only on his experimental work on substitution reactions but also on the ideas of Laurent.” (Rocke 1984, p.201) As early as 1831 Laurent had studied the chlorination of naphthalene and put forward the nucleus theory. He regarded naphthalene as the fundamental radical that could be altered to form various derived radicals. Although he called it a radical, it was actually what we refer to as a hydrocarbon group. Laurent thought that the chemical properties of compounds were not directly connected to the properties of chemical elements, but rather to the positions of atoms in molecules. Both hydrogen and chlorine in a “nucleus”—a molecular skeleton consisting of hydrogen and carbon—could be electrically neutral. Laurent’s theory pioneered the structure theory not only through its unitary view of the molecule but also through the classificatory principle based on the types of compounds. In view of the later development made by Kekulé—the point of his claim was that each atom in the molecule was ontologically equivalent—"Laurent’s classificatory principle was far more fruitful than that of Dumas.” Dumas defined types as "bodies which are shown to be formed from the same number of chemical equivalents united in the same manner." (ibd. idem, p.198) Those types were conserved in substitution reactions, and so fundamental chemical properties were retained in all compounds of a given type. But since there existed many groups of compounds, as was the case with dimethyl ether and ethanol, that satisfied this definition and had different properties, Dumas asserted that "such compounds were not to be thought of as belonging to the same chemical type though they did belong to the same mechanical type." It is easy to see the influence of "nucleus" on "mechanical type." (ibid. idem, p.199)

Gerhardt put forward his theory of residues in 1839, in which he assumed that "double decomposition reactions involve the rearrangement of residues which were atomic complexes left over through those reactions." (Russell 1971, p.47) To apply his idea to esterification, the hydrogen of alcohol combines with the hydroxide of acid, and the residues—alkoxide and acyl—unite to give the ester. Although his residues retained a similarity to radicals, residues had no independent existence. Gerhardt claimed that they were merely the expressions of the mode of reactions. Gerhardt's theory served as a link between Dumas' and Laurent's unitary view and the radical theory.

In 1853, Gerhardt proposed to classify every organic compound based on four types of simple inorganic compounds, that is, ammonia, water, hydrochloric acid and hydrogen. Later, the last one was replaced by the methane type; hydrochloric acid, water, ammonia and methane were regarded by Odling, Frankland and Williamson as the typical compounds representing valences I through IV. This is the reason why H, O, N and C are now called typical elements. Anyway, it was Gerhardt who systematized the existing speculation on types.

It was as early as 1840 that Liebig suggested that "ammonia could be considered as the prototype of all organic bases and predicted the possibility of ethyl-substituted ammonia." (Rocke 1984, p.223) This prediction was achieved by his former student Adolphe Wurtz in 1849. Another of Liebig's former students, A.W. Hofmann, prepared a variety of secondary and tertiary amines and regarded them as the results of the substitution of hydrocarbon radicals for hydrogen in ammonia. He established the ammonia type.

As Hofmann is associated with the ammonia type, A.W. Williamson is strongly associated with the water type. When Williamson became interested in the theory of etherification, there existed two different views: Dumas, who held the unitary view of the molecule, claimed that ethyl alcohol $C_2H_4 \cdot 2H_2O$ was dehydrated to give ethyl ether $C_2H_4 \cdot H_2O$; on the other hand Liebig claimed, from a radical theoretical point of view, that alcohol $C_4H_{10} \cdot H_2O$ was dehydrated to ether $C_4H_{10}O$. Williamson began his research with the intention of producing homologous alcohols through the action of potassium ethoxide on ethyl iodide. If Dumas' and Liebig's formulas were correct, the product would contain two oxygen atoms. The new substance he obtained, however, contained only a single oxygen atom. He also obtained a certain mixed ether by the action of potassium ethoxide on methyl iodide. These results suggested that ethyl alcohol was C_2H_5OH, and that potassium salt and ether were C_2H_5OK and $C_2H_5OC_2H_5$, respectively. In 1851 he read his third and the final paper of a series on ether synthesis at the annual meeting of the British Association. "I believe that throughout inorganic chemistry, and for the best-known organic compounds, one single type will be found sufficient; it is that of water, represented as containing 2 atoms of hydrogen to 1 of oxygen," thus publicizing his water type. (This paragraph is partially modified and quoted from Rocke 1984, p.220)

In contrast to Hofmann, who was careful to limit his idea of types to a small number of volatile organic bases, Williamson viewed the vast majority of chemical reactions as analogous to the formation of salts by means of double decomposition reactions between acids and bases. It led him to predict that acid anhydrides could be prepared by the dehydration of monobasic organic acids just as ethers were prepared from alcohols. Williamson thought that acid anhydrides were nothing but the ethers of organic acids. This was proved correct in 1852 by Gerhardt who prepared benzoic acid anhydride through the reaction of sodium benzoate with benzoyl chloride. Gerhardt also prepared a variety of acid anhydrides through the reactions of benzoic, cinnamic, salicylic and acetic acids. He stated that "water could serve as the type of all organic acids as ammonia does for the organic bases." In addition, Williamson developed concepts such as "monobasic" and "bibasic" moieties, from which the theory of valence is derived. These are the reasons why it is Williamson, and not Hofmann, who deserves most of the credit for the development of the mature theory of types. (Summarized and quoted from Rocke 1984, p.221)

3. From valence to structure

Why does the element of nitrogen combine with three equivalents of hydrogen, whereas oxygen combines with only two equivalents of hydrogen? Is it not because elements themselves have saturation capacities? In the 1850s it became apparent that an atom of a given element could combine with only a limited number of atoms of other elements. But ever since the days of Dalton, "the existence of indivisible atomic particles had been in dispute among chemists." Many chemists used the term "atom" purely as a convention without commitment to its etymological meaning. The term "atom" was what Nye calls "a perfect instance of polysemy in metaphor," because "it combined the property of concrete objects with the opposite property of infinitesimal points." (Nye 1993, p.80)

Wurtz, whose name is remembered for the so-called Wurtz coupling, was engaged in an attempt to isolate alkyl radicals through the action of metallic sodium on alkyl halides. With the same intention he investigated the reactions of glycerin and