

Pragmatism, Belief, and Reduction

Stereoformulas and Atomic Models in Early Stereochemistry

Peter J. Ramberg

Abstract: In this paper I explore the character and role of stereoformulas and models of the atom that appeared in the early history of stereochemistry, including those of Jacobus Henricus van't Hoff, Aemilius Wunderlich, Johannes Wislicenus, Victor Meyer, Arthur Hantzsch, Alfred Werner, and Hermann Sachse. I argue that stereochemists constructed and used stereoformulas in a pragmatic way that ignored the physical implications of the spatial distribution of valence, and that the models of the atom were created to reconcile the physically curious concept of valence with known physical laws. Although such models were explanatory at a deeper level, they had little impact on the theory and practice of chemistry, and were not serious attempts to reduce chemical theory to physical laws.

Keywords: *atomic models in 19th century chemistry, stereochemistry, affinity, pragmatism, reduction.*

1. Introduction

The construction and use of representational models is a central activity in the formation of chemical theory. Such models make visible the invisible world of the atom and molecule; they give them a graphic clarity, or *Anschaulichkeit*. The means of producing this *Anschaulichkeit* has taken two major forms – physical and symbolic. Physical hand-held models in chemistry are a unique mode of non-semiotic reasoning that is nevertheless highly sophisticated despite the lack of mathematics. Such models occupy a middle position between material epistemic objects (those things under investigation) and the written language of chemical formulas. Curiously, the use of such models has never been given prominence as a methodology within the chemical literature, and their construction and use is usually implicit rather than explicit.¹ Chemists generally have favored the other means of representing molecules: the two-dimensional symbolic language of formulas and imag-

es, in which the chemical and spatial relationships of atoms within molecules is implied.

Both of these ubiquitous forms of modeling – physical and symbolic – have their origins in the nineteenth century, when chemists carefully crafted a means of making atoms and molecules *anschaulich*. Techniques for modeling molecules and atoms date at least to John Dalton’s wooden spheres and graphic circles of the early nineteenth century, and by the 1850s and 1860s, chemists had created a vast array of physical lecture demonstration models and two-dimensional symbolic representations of molecules, particularly in organic chemistry. Curiously, these models were not originally meant to make molecules *anschaulich* in a physical sense, and all but ignored the structure of the atom itself.^{2,3} Beginning with van’t Hoff’s theory of the tetrahedral carbon atom in 1874, however, chemists began to give those same formulas and models a true physical *Anschaulichkeit*, and by the end of the nineteenth century, the transformation in meaning had largely been completed. In the words of the chemist-philosopher Roald Hoffmann, chemical models before and after 1874 were the same and yet not the same.⁴

Although the adoption of van’t Hoff’s principles was initially slow, by the late 1880s and 1890s, the chemical literature blossomed with a new symbolic language for the three-dimensional properties of molecules (hereafter called stereoformulas).⁵ As I will argue below, chemists employed stereoformulas to achieve the two traditional aims of nineteenth century chemistry – explaining the existence of isomers and predicting the existence of new compounds – even though these formulas were curious, or even absurd, from the standpoint of physical laws. It is not surprising then, that concurrent with the appearance of these stereoformulas was the publication by several stereochemists of unprecedented atomic models that attempted to provide a sound basis for the physical nature of valence, bonding and affinity. These atomic models served well as explanatory devices, but they were not serious attempts to reduce chemistry to physics, and equally did not further the aims of chemistry.

2. Stereoformulas

The first stereoformulas were given by one of the founders of stereochemistry, Jacobus Henricus van’t Hoff, in his now-famous Dutch pamphlet of 1874.⁶ In this pamphlet and in the two expanded French and German versions (appearing in 1875 and 1877), van’t Hoff argued that the explanation of certain cases of isomerism required considering the valences of the carbon atom as pointing towards the corners of a tetrahedron. A few illustrations in the 1877 edition did not include the lines of valence, but in most cases, he depict-

ed the ‘tetrahedral carbon atom’ literally as a tetrahedron in which the carbon atom occupied the center, and the vertices were the sites of affinities (Fig. 1). As historians of chemistry have noted previously, van’t Hoff’s conception of a tetrahedral arrangement was at least partially inspired by August Kekulé’s lecture demonstration models in which the valences, as metal rods, pointed towards the corners of a tetrahedron.⁷ In most of the stereoformulas introduced by van’t Hoff, the immediate parallel to Kekulé’s models is obvious: ‘bonding sites’ are at the corners of the tetrahedron, and the groups attached to the asymmetric carbon atom are attached at the vertices. Although in his drawings the valences were always placed at the corners of the tetrahedron, in some of his three-dimensional models, van’t Hoff colored the faces of the tetrahedron to represent the different groups attached to the carbon atom (Fig. 2).

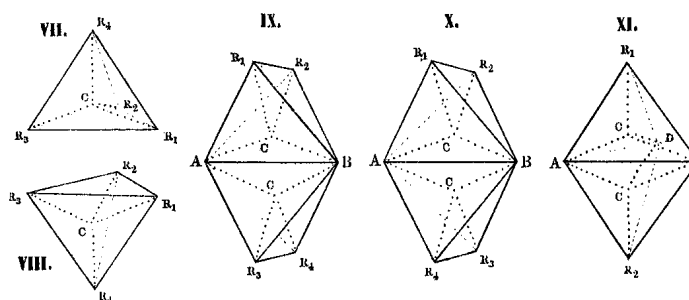


Figure 1: From left to right, van’t Hoff’s stereoformulas for individual carbon atoms, and for single, double and triple bonds. From van’t Hoff, *Proposal* (cf. Note 6).

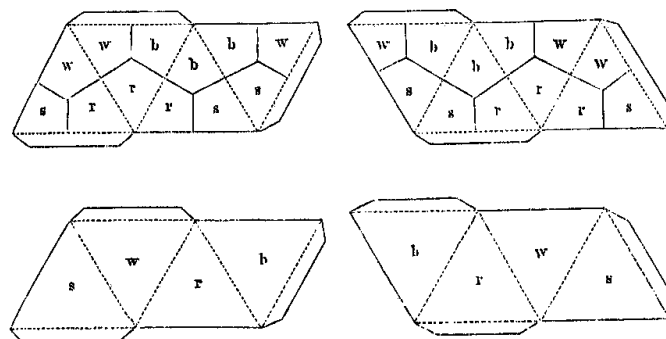


Figure 2: van’t Hoff’s template for constructing the two different types of cardboard tetrahedra with groups at either the faces or the corners of the tetrahedron. From the appendix to van’t Hoff, *Die Lagerung der Atome in Raume* (cf. Note 6).

The two types of models had their origins in two different phenomena that required modeling. The drawings, based on Kekulé's ball and stick models, illustrated the new cases of isomerism and showed bonding most clearly, while the face-centered models allowed easy construction of a physical model of a carbon-carbon single bond, and showed more easily the enantiomorphism or identity of two tetrahedra.⁸

Many subsequent stereoforulas drew on van't Hoff's explicit portrayal of the tetrahedron. In his influential 1887 theoretical essay on the unsaturated acids and supporting publications, Johannes Wislicenus depicted the tetrahedron literally, and removed the central carbon atom and valence lines (Fig. 3a).⁹ In Arthur Hantzsch and Alfred Werner's 1890 paper outlining the stereochemistry of nitrogen, the tetrahedron outwardly resembles van't Hoff's picture (Fig. 3b), yet the nitrogen occupies one vertex and the edges depict the lines of valence, and not the edges of an imaginary tetrahedron. Hantzsch would use the same form of representation in his later papers (Fig. 4a), although he often published papers with no drawings of the tetrahedron (Fig. 4b), in which the spatial relationships were implied. In his 'Beitrag zur Constitution anorganischer Verbindungen', Alfred Werner explained the isomerism of the cobalt ammines by an octahedral arrangement of groups around the central metal atom (Fig. 5). Because Werner ignored the individual valences and central atom of the octahedron, his drawings of the octahedron closely resemble Wislicenus' drawings.

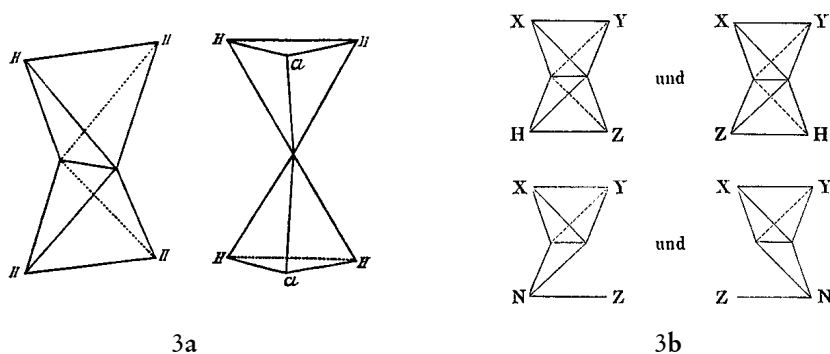


Figure 3: a) Wislicenus' stereoforulas for single (right) and double (left) bonds. From Wislicenus, 'räumliche Anordnung' (cf. Note 9). b) Hantzsch and Werner's stereoforulas for the stereoisomers of nitrogen, showing the analogy between the carbon-carbon and carbon-nitrogen double bonds. From Hantzsch and Werner, 'Ueber die räumliche Anordnung der Atome in stickstoffhaltigen Molekülen', *Berichte der deutschen chemischen Gesellschaft*, 23 (1890), 11–30.

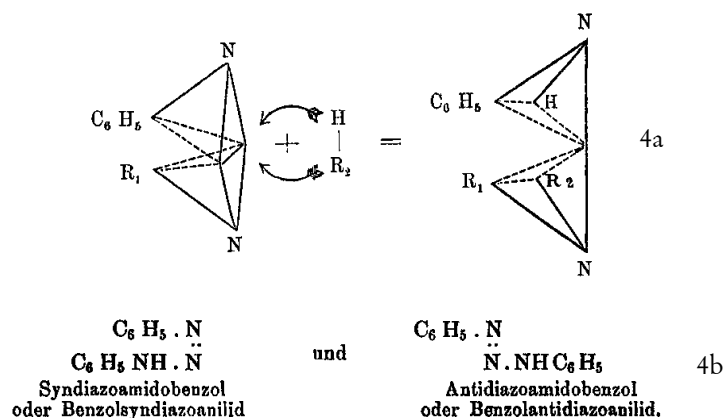


Figure 4: a) Hantzsch's use of stereof formulas. This diagram represents an addition reaction to the nitrogen-nitrogen double bond in a diazo compound. From 'Zur Statik und Dynamik der Stickstoffverbindungen', in: *Festschrift der Naturforschenden Gesellschaft in Zürich 1746-1896*, Zürcher and Furrer, Zürich, 1896, pp. 186-202. b) Hantzsch's depiction of isomeric diazo compounds without explicit stereof formulas. From Hantzsch, 'Über stereoisomere Diazoamidverbindungen', *Berichte der deutschen chemischen Gesellschaft*, 27 (1894), 1857-67.

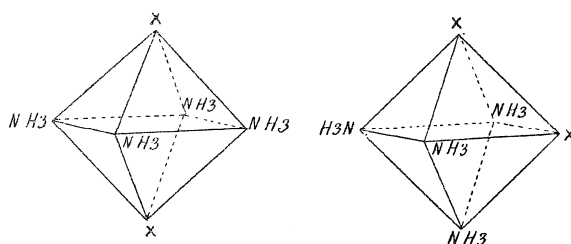


Figure 5: Werner's stereof formulas for the isomeric metal octahedral complexes. From Werner, 'Beitrag zur Konstitution anorganischer Verbindungen', *Zeitschrift für anorganische Chemie*, 3 (1893), 267-330.

These stereof formulas that literally depict a polyhedron are physically and chemically curious, because they de-emphasize the bonding relationships, and include edges of the polyhedra which have no physical or chemical significance. The model for nitrogen does emphasize bonding lines, but the affinities are depicted as an *uneven* distribution – all three valences point in a single

overall direction. The octahedral model is also curious in that, even though such compounds are said to have ‘octahedral geometry’, implying the importance of the faces of the octahedron, it is in fact the *vertices* that are important, and there are only six groups surrounding the central carbon atom.

Because of these curiosities, the stereoforulas using literal polyhedra were not universally adopted. Victor Meyer recognized the physical absurdity in these drawings of tetrahedra and chose instead to emphasize the lines of valence in his stereoforulas (Fig. 6). These drawings, Meyer said, “appear to me more convenient than the complicated drawings used by van’t Hoff and Wislicenus, in which the four valences of the carbon are not drawn at all, but instead six tetrahedral edges that of course have no importance.”¹⁰ In his investigation of the isomers of glucose, Emil Fischer did not employ the polyhedral stereoforulas, but for purely practical reasons. Because glucose and its isomers possessed four asymmetric carbon atoms, representing them by two-dimensional drawings of tetrahedra would be difficult to realize and visualize. In 1877, van’t Hoff had already proposed a convention for designating the configuration of compounds with multiple asymmetric carbon atoms (Fig. 7). Fischer initially adopted this scheme, but quickly abandoned it in favor of his new *Projektionen* (the famous Fischer projections), that showed the groups around each asymmetric carbon atom (Fig. 8).¹¹ Fischer’s stereoforulas did not depict tetrahedra at all; rather, he represented the three dimensionality of each asymmetric carbon atom by means of a two-dimensional convention.

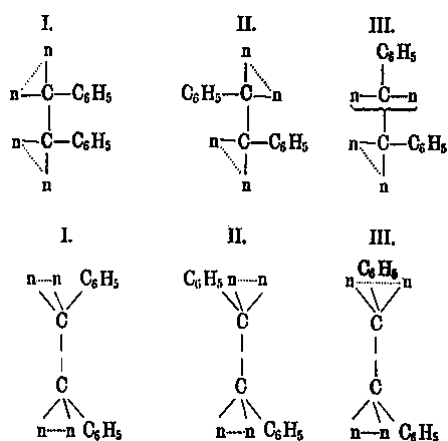


Figure 6: Meyer’s formulas for the isomeric benzildioximes that emphasize the lines of bonding. The top are simple planar drawings. The bottom set are meant to be drawn in perspective. From Meyer & Auwers, ‘Untersuchungen’ (cf. Note 10).

				11	12	13	14	15	16
+	+	-	-	+	+	+	+	+	-
+	-	+	-	+	+	+	-	-	+
+	-	+	-	+	-	-	+	-	-
+	+	-	-	-	+	-	-	-	-
+	+	-	-	+	-	-	+	-	-
+	+	-	-	+	+	+	-	-	+
+	+	-	-	+	+	+	+	+	-
1	2	3	4	5	6	7	8	9	10

Figure 7: van't Hoff's scheme for depicting the individual configurations of the isomers of glucose. Adapted by Emil Fischer in 'Über die Konfiguration des Traubenzuckers und seiner Isomeren. I' (*cf.* Note 11).

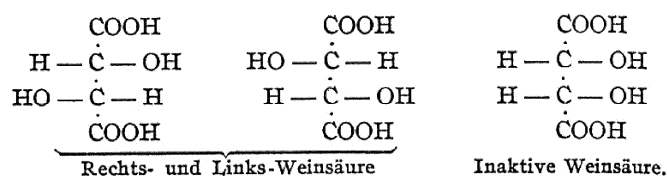


Figure 8: The first use of the 'Fischer projections', from Fischer, 'Über die Konfiguration des Traubenzuckers und seiner Isomeren. II' (*cf.* Note 11).

3. Atomic Models

When chemists introduced the concept of valence and multivalent atoms in the 1860s, they begged the physical question about how an atom's chemical affinity could be 'split' into different parts. As a concept developed to account for chemical transformations, valence was simply a number that possessed no physical significance. The concept of affinity itself had always remained an elusive, slippery idea, and chemists had used it, much like physicists had used the concept of force, as an entity whose existence is known (because of its effects), but whose exact origins were nearly totally unclear.¹² The traditional means of explaining chemical affinity had been to make analogies to the known physical attractive forces, such as electricity and gravitation, but these forces never displayed an ability to split into different parts, and therefore the concept of an 'affinity unit' was absurd in physical terms.¹³

Accepting van't Hoff's theory that the four valences of the carbon atom were directed towards the corners of the tetrahedron made the physical basis of valence more puzzling, because it not only assumed that affinity was split into parts, but that it was oriented in specific *directions*. In his 1890 *Habilitationschrift*, Karl Auwers recognized this physical problem most acutely: "The idea that such a force should not operate towards all directions in space, but in only very certain directions, contradicts the concept of an attractive force."¹⁴ The model of the double bond in van't Hoff's stereoforulas was especially curious, as the attractive force between atoms appeared to work around corners. Yet the assumption of the tetrahedral arrangement was very useful for explaining and predicting the existence of isomers. It was precisely this discord between the chemical usefulness of the tetrahedron and the properties of the known attractive forces that prompted chemists to offer physical models of the carbon atom and valence that would explain the tetrahedron and van't Hoff's model for bonding.

Chemists addressed this problem with varying degrees of sophistication. The easiest solution, adopted by van't Hoff, Hantzsch, and Fischer, was to ignore it. Van't Hoff implicitly raised the question of valence when he introduced the tetrahedron, but he was nearly silent about the exact nature of the carbon atom. His only suggestion about the physical location of the affinity unit was in a public letter to the Dutch physicist C.H.D. Buys-Ballot, in which he located the sites of bonding with the faces and not the corners of the tetrahedron.¹⁵ He also later confided to Wilhelm Ostwald that the carbon atom "must consist of tetrahedral symmetry". It seems clear, however, that what he meant by the "tetrahedral carbon atom" was not the atom itself, but the spatial distribution of valences *around* the atom.¹⁶ The arrangement was defined only in reference to the atoms bound to carbon, and not in the atom itself. That he used different models to emphasize different aspects of his theory illustrates a pragmatic use of stereoforulas without an explicit interest in the actual appearance of the carbon atom.

Hantzsch also practiced stereochemistry without any model of the atom beyond the simple tetrahedral arrangement of atoms. In his 1893 monograph on stereochemistry, *Grundriß der Stereochemie*, Hantzsch explicitly denied that any kind of theory of valence was necessary for, or followed from, the practice of stereochemistry:

at least in its present stage of development, [stereochemistry] requires no specific idea about the type and cause of intramolecular cohesion of atoms, (the nature of chemical affinity), or about the type and cause of the ratios in which different atoms combine (the nature of valence); at present it requires only the idea, proved by the existence of isomerism itself, that the atoms are not situated within the molecule in a chaotic state, but in a stable equilibrium position within certain limits.¹⁷

Hantzsch and Werner commented that their new theory of the benzildioximes “can be developed [...] quite independent of the uncertain conception of valence and the still uncertain ideas concerning the ‘direction’, ‘deviation’, and ‘bonding’ of valence [...]”.¹⁸ There was no need to postulate atomic models or address the issue of valence, for such speculation was unnecessary for the success of stereochemistry. Fischer’s use of van’t Hoff’s theory in his study of glucose was equally pragmatic; throughout his work on the configuration of glucose, he never mentioned the issue.

While van’t Hoff, Hantzsch, and Fischer ignored the physical problem of valence, other stereochemists attempted, with varying degrees of sophistication to reconcile it with known physical laws. We can recount here the models offered by Wislicenus, Meyer, Aemilius Wunderlich, Werner, and Hermann Sachse. In 1888, Wislicenus went slightly beyond the pragmatism of van’t Hoff, Hantzsch, and Fischer, and speculated on the nature of the carbon atom in a short reply to a critique of van’t Hoff’s theory by Wilhelm Lossen.¹⁹ Lossen clearly recognized the physical problems with van’t Hoff’s model for the double bond, noting that it was physically impossible because the lines of bonding did not lie on a straight line between carbon atoms. It implied that multivalent atoms were three-dimensional objects with distinct parts, and Lossen doubted the ability of chemists to know anything about these parts. Wislicenus answered Lossen quite directly – it was impossible, he said, *not* to conceive of atoms as “spatial objects” with their affinities located in different areas of those objects.

I do not consider it impossible that a carbon atom may be an object whose form more or less (perhaps quite closely) resembles a regular tetrahedron; further, it is not impossible that the causes of every effect that actually manifests itself in the affinity unit concentrate themselves in the corners of this tetrahedral object, and for analogous reasons, would possibly be similar to the electrical effect of an electrically charged metal tetrahedron. The actual carrier of this energy would ultimately be the primitive elementary atoms [*Uratome*], exactly like the chemical energy of compound radicals is undoubtedly a product of the inherent energy of the elementary atoms within them.²⁰

Wislicenus’ model was intentionally vague, and did not possess the “value of a scientific conviction” (*Werth einer wissenschaftlicher Überzeugung*) but he clearly identified the sites of bonding as the corners and not the faces of the tetrahedron. He did not offer a physical explanation for the free rotation of single bonds or the restricted rotation of double bonds. Wislicenus’ stereoformulas did not therefore imply much more than van’t Hoff’s original drawings.

Significantly, Wislicenus considered van’t Hoff’s theory as an important milestone in the development of the atomic theory. In his response to Lossen, he remarked that the study of chemical reactions had largely demon-

strated the existence of atoms and that the same process would yield information about the *parts* of those atoms. Because van't Hoff's theory provided a model for the structure of the atom, *i.e.* the direction of valences and possibly the atomic form, it was precisely this theory that *would* give information about the parts of the atoms. The establishment of configurational formulas led precisely to a deeper understanding of atoms and furthermore, to subatomic structure.²¹ In his various public lectures and addresses, Wislicenus made it clear that he regarded the atomic theory as the foundation of chemistry. Without atomism, he said, "the individual pieces of chemical knowledge would be a desolate pile of unrelated and incomprehensible observations, indeed, it would be less than that: to a great extent, it would not exist at all."²²

While atomism was also important to Meyer, the principles of stereochemistry were more significant for an understanding of valence. In a short theoretical article entitled 'On Carbon's Valence and its Bonding Ability' that appeared in 1876, Meyer had remarked that despite the dazzling success of the structure theory in ordering organic compounds and explaining isomerism, "[...] at the moment, the nature of that what we call a valence or affinity is still completely unclear." The more the theory of valence proved its value, said Meyer, the more one needed a "certain, physically permissible conception" of valence (*bestimmte, physikalisch zulässige Vorstellung*).²³ Meyer attempted to form a vague idea of the nature of valence by studying the limitations on the carbon atom's bonding ability. For example, he pointed out that all reactions in which he expected cyclopropanes (three membered rings) as the product gave only products with other structures. The fact that these compounds did not exist – coupled with the non-existence of C₂ (carbon with a 'quadruple' bond), despite the fact that these compounds were "easily expressible by our usual formulas" – indicated specific limits on the nature of valence.

Meyer became reinterested in the nature of valence in 1887 when he read Wislicenus' extensive essay on the stereoisomerism of the unsaturated acids, and was inspired to reinvestigate the chemistry of isomeric benzildioximes discovered in his laboratory some years earlier. In 1888, Meyer and his assistant Karl von Auwers published a lengthy article in which they established the stereoisomerism of the benzildioximes and explained this isomerism by proposing that carbon-carbon single bonds, like double bonds, could also have restricted rotation. By an analysis using conventional chemical formulas, Meyer and Auwers predicted the existence of a third isomer of benzildioxime that they isolated in 1889. Meyer and Auwers' theory of the benzildioximes was clearly inspired and shaped by Wislicenus' study of the unsaturated acids, but Meyer distanced himself from the physical implications of van't Hoff's and Wislicenus' stereoformulas. In a paper that appeared shortly before the paper on the benzildioximes, Meyer noted that van't Hoff's theory of double

and triple bonds explicitly raised the question about the physical nature of valence:

As soon as one assumes van't Hoff's [theory of free rotation] – an hypothesis whose fundamental meaning Wislicenus recognized first and which he has taken as the basis of his doctrine and has executed with admirable consequences – certain conceptions about the form of atoms and the nature of valence must be introduced, if these speculations are not to have an inexact foundation.

Meyer's criticism was not about van't Hoff's theory, but the specific means of representation:

The assumption of valences meeting in certain places of empty space, free of atoms, cannot as such be made, and is only possible on paper or with a model, where lines and wires figure instead of forces (valences). It is now necessary – and I believe also possible – that positive and physically durable hypotheses about the nature of valence can be made and consequently implemented.²⁴

Meyer therefore sympathized completely with Lossen's theoretical critique. It was impossible to reconcile the picture of multiple bonding with the idea that atoms consisted of material points, since the valences appeared to meet in a "space free of atoms".

Meyer wrote to his brother Richard in early 1888 about his theory of the benzildioximes, expressing excitement about the opportunity this chemistry offered for a more detailed picture of atoms and valence.

I am quite splendidly excited about all these things, dreaming of them and wander around during the day as if in a dream. For I have the feeling that a great step is being made into the knowledge of nature, we are grabbing concepts of atom and valence!²⁵

The chemistry of the benzildioximes and Meyer's interest in valence led to a collaboration with his colleague of the Göttingen University physics faculty, Eduard Riecke, whom Meyer met after his 1885 move to Göttingen.²⁶ In 1886 and 1887, Riecke had published two articles on the pyroelectricity of tourmaline (a brittle crystalline mineral used for gems), in which he described the properties of its surface conductivity. In a series of experiments, Riecke found that the molecular unit in crystalline tourmaline possessed a permanent polarity, and concluded that "each valence was caused by a certain combination of two opposed electrical components".²⁷ In a lecture to the Göttingen Chemical Society on the benzildioximes, Meyer had supposed that carbon atoms were composed of spheres surrounded by an ether shell [*Aetherhülle*] that formed the seat of valence. Each valence he conceived as an "electricle", composed of a positive and negative piece arranged in a straight line. Each electricle underwent isochronous oscillation, and would therefore attract other valences with different oscillations and repel valences with the same oscillation. The four valences of the carbon atom must therefore repel

each other to form a tetrahedron, and when in the presence of other atoms the valences would arrange in an irregular tetrahedron, determined by the atoms joined to it.²⁸ Riecke was present at Meyer's lecture, and remarked in the discussion that the ether shell of pentavalent elements such as nitrogen or phosphorous could be ellipsoid; three valences occupied the corners of an equilateral triangle, and two occupied the poles.

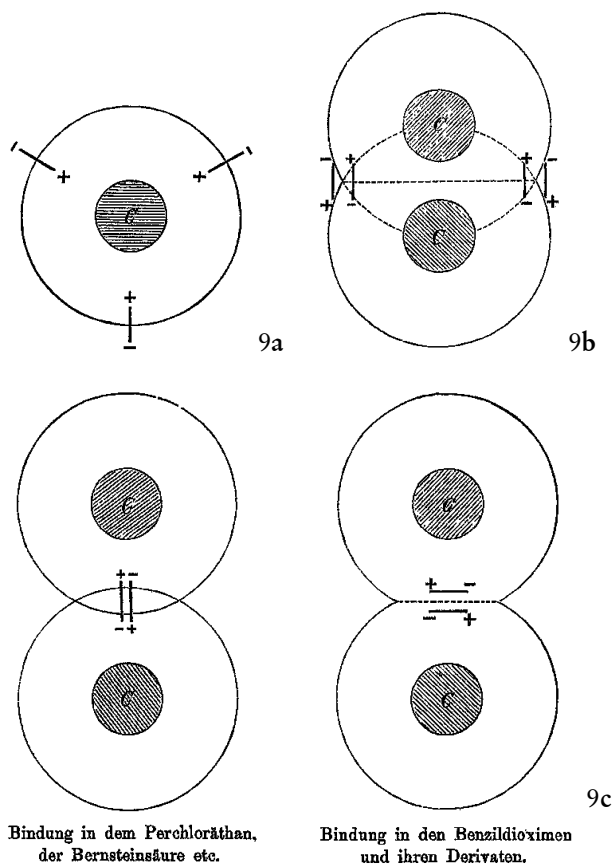


Figure 9: Meyer and Riecke's models: **a)** the carbon atom (one valence is behind the atom pointing away from the viewer); **b)** the carbon-carbon double bond; and **c)** the two forms of carbon-carbon single bonds. From Meyer and Riecke, 'Einige Bemerkungen' (*cf.* Note 27).

Meyer and Riecke subsequently collaborated and co-authored a paper containing "A Few Remarks on the Carbon Atom and Valence", that proposed

an ingenious account of carbon-carbon bonding that explained both the nature of multiple bonding and Meyer's theory of free and restricted rotation of single bonds. The carbon atom was surrounded by a spherical ether shell that possessed a number of dipoles corresponding to the valence number. The dipoles arranged themselves pointing towards the atom such that the outer ends would repel each other and point towards the corners of a tetrahedron (Fig. 9a).²⁹ In a 'normal' single bond (Fig. 9c, left), two dipoles aligned by means of electrical attraction along the carbon-carbon axis. The two atoms remained free to rotate about the carbon-carbon axis. The dipoles could also align in a second way (Fig. 9c, right) in which rotation was not possible, and the nature of the radicals bound to carbon would determine how the dipoles would arrange.³⁰ In double bonds, two pairs of dipoles aligned themselves, and in a triple bond three pairs (Fig. 9b). These models also precluded the possibility of rotation about the carbon-carbon axis.

This model presented a strikingly different and more detailed view of the carbon atom than Wislicenus had offered to Lossen one month earlier. Unlike Wislicenus, Meyer and Riecke offered a specific depiction of the parts of the atom and how they worked together to produce the chemical effects that Meyer and Auwers had found. It offered a higher level explanation for the conclusions of stereochemical theory. Why did some atoms combine to allow free rotation and others not? Why were the valences arranged in a tetrahedron? The plastic nature of the dipoles offered a clear picture of how the carbon atom could distort when it was attached to different radicals. An anonymous writer for *Nature* commented that the theory offered a "strikingly natural explanation [...] of the nature of single, double, and triple linking of carbon atoms".³¹

In 1886, Aemilius Wunderlich, a recently promoted organic chemist at the University of Würzburg, published a novel theory about the form of the carbon atom in a 32 page pamphlet entitled *Configuration organischer Moleküle*.³² In a somewhat complicated argument without diagrams, Wunderlich proposed that each atom possessed "binding points" (*Bindestellen*) that contain a center of bonding, a *Bindeschwerpunkt*. By chemical and geometrical reasoning, Wunderlich suggested that the carbon atom had a tetrahedral arrangement of *Bindestellen* (Fig. 10). A single bond would result if the *Bindestellen* from two carbon atoms joined, but in multiple bonds, it was physically impossible for more than one *Bindestelle* to join completely. A double or triple bond would therefore occur when two or three *Bindestellen* got as close as physically possible to each other. The resulting double and triple bonds would then, as was well known, not simply be two or three times as strong as a single bond. Wunderlich's model for bonding was comprehensive, providing physical models not only for the tetrahedron, but also for the process of addition and elimination reactions, Baeyer's strain theory, and Kekulé's oscil-

lation hypothesis for the benzene molecule. Like the model of Meyer and Riecke, the atomic model given in *Configuration* accounted for the known characteristics of the chemical bond, and was compatible with known physical forces; that is, all attractive forces between atoms were in straight lines. Although it is now obscure, Wunderlich's model was cited frequently in the chemical literature throughout the 1890s as a physically pleasing conception of valence and bonding.

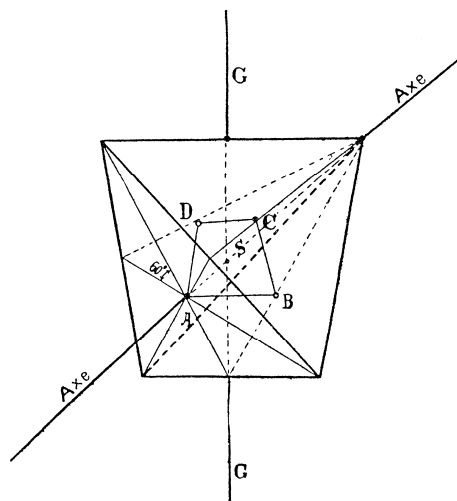


Figure 10: Wunderlich's model of the carbon atom, as illustrated in Carl Bischoff and Paul Walden, *Handbuch der Stereochemie*, H. Bechold Verlag, Frankfurt, 1894, p. 54.

In his 1891 *Habilitationschrift*, Werner proposed a non-mechanical conception of the atom in which he assumed that valence was simply a number and that chemical affinity was not divided at all. Instead, it was an “attractive force acting equally from the center of the atom toward all parts of its spherical surface”, much like light from the sun.³³ The four radicals attached to the carbon atom “arrange themselves in the mutual position of the corners of a regular tetrahedron, because in this way the greatest exchange of affinity between them and the carbon atom, *i.e.*, the greatest bonding ability occurs.”³⁴ In the analogy to sunlight, they each receive the greatest amount of light. In other words, the affinity of the carbon atom was distributed equally when the radicals occupied a symmetrical position. The net result was an apparent division of chemical affinity; valence was not divisible, but simply shared between the different radicals. Werner's model was more comprehensive than Wunderlich's, providing explanations not only for the tetrahedron, but also

for the process of racemization, the interconversion of unsaturated molecules, benzene theory and the stereochemistry of nitrogen.

The last model we will consider was presented by Hermann Sachse in four articles that appeared between 1888 and 1892. In an 1888 article on the configuration of benzene, Sachse attempted to create a stereochemical model of the benzene molecule that was compatible with Kekulé's cyclohexatriene structure. Sachse agreed with Wislicenus that the carbon atom had a tetrahedral shape and was explicit that the sites of affinity were at the corners:

However the remainder of the carbon atom may be formed, it possesses four points at greatest equivalent distance from the center, that lie at the corners of a regular tetrahedron, and towards which the four forces of affinity [*Affinitätskräfte*] are directed. These points may be designated as points of affinity [*Affinitätspunkte*]. [...] The atoms of the remaining elements also have certain fundamental geometric ideals, determined by the number and position of the points of affinity.³⁵

In an 1890 article on cyclohexane, now the most famous of Sachse's publications, he used the same model of the carbon atom to argue against Adolph von Baeyer's planar model for cyclohexane and proposed the two non-planar models now known as the chair and boat forms.³⁶

Except for their novel stereochemical models of benzene and cyclohexane, these two articles would not strike the reader as out of the ordinary, but in two later articles, both published in the *Zeitschrift für physikalische Chemie*, Sachse provided a deep geometrical and physical explanation for his earlier qualitative statements about the tetrahedral carbon atom. The first article was an expansion of the 1890 article on the configuration of cyclohexane that contained a lengthy, intense mathematical argument for the two configurations of cyclohexane.³⁷ In the second, which appeared in 1892 shortly before his premature death at the age of 31, Sachse offered "An Interpretation of Affinity". In this 35 page article, Sachse expanded on his earlier brief statements about the form of the carbon atom, and offered a model for bonding that employed two fundamental properties of matter. First, all matter was to a certain extent magnetic and consisted of a "system of smallest particles, around which or in which solenoids stream in circular paths."³⁸ Second, when the distance between two bodies becomes sufficiently small, attractive forces generally turn into repulsive forces, an "idea that, to my knowledge, molecular physics can scarcely do without". These two principles were then combined with the "fact" of the tetrahedron:

Let us consider a regular tetrahedron in which a great number of fixed points are divided according to a specific law. These points may be surrounded by circularly flowing electrical currents [*Ströme*] of the kind that form the middle point of these circles. While the middle point of this central point of the ring is invariable, the position of the plane of the circle and the direction of the

current shall be variable. Both will be determined under the mutual influence of the currents on one another, that is, only by the law governing the arrangement [*Anordnung*] of each fixed point. But as soon as one such system is brought close to an electromagnet, each current will be redirected in a certain way. We can always naturally consider the solenoids, in the interests of promoting visual clarity, as linear magnets whose direction is perpendicular to each circular surface.

Now if we think of this tetrahedral system as somehow filled with matter, according to the description above it would receive the capacity [*Eigenschaft*] for exerting a repulsion on other similar systems that find themselves, within certain limits, in its vicinity.³⁹

According to Sachse, two atoms formed a bond when they approached one another with either a point, line, or plane in common, and a bond formed when an equilibrium between attractive and repulsive forces was reached, resulting in a relative energy minimum. The goal of stereochemistry was to determine these stable equilibrium arrangements. Like his earlier article on the configuration of hexamethylene rings, his 'Interpretation' was a mathematically and geometrically rigorous argument that most chemists would have found extremely difficult to follow.

4. Pragmatism, Belief, and Reduction

As stereochemists pointed out, stereoformulas were closely related to, and even a natural extension of, traditional structural formulas. Van't Hoff's initial pamphlet was a modest request to extend the traditional concept of arrangement to mean spatial arrangement. As representations of molecular form, they served to explain the appearance of optical activity and the existence of isomers that had previously been puzzling. Importantly, they also served as predictive tools that would indicate if a particular compound would be optically active or have stereoisomers. The greatest success of stereochemical theory was in this domain of 'chemical statics', or 'isomer counting' – for making the theoretical number of compounds agree with the number of known compounds.⁴⁰ The accomplishment of this agreement demonstrated the usefulness of considering the molecule as a spatial object, from the explanation of optical activity, to the chemistry of the unsaturated acids, oximes, diazo compounds, sugars, and cobalt ammine complexes. Any physical or chemical problems raised by the means of representing those formulas were therefore subordinated to their usefulness in meeting these traditional aims of chemical theory.

The use of stereoformulas illustrates a general tendency of chemists to be pragmatic, in the simple sense of being practical, in adopting the tools and

concepts necessary to reach their goals. That is, chemists will adopt useful concepts and tools even if those tools and concepts raised significant physical or philosophical questions. For example, chemists adopted the principle of valence almost without question, even though it raised crucial physical questions about its nature, because it helped to explain chemical behavior of substances and the appearance of isomers. Chemists had a similar pragmatic attitude towards the use of the atomic theory, by excluding questions about the actual reality of atoms from their discussion, and simply proceeding to use them *as if* they existed.⁴¹ Chemists constructed and used stereoformulas in a similar pragmatic way. Stereoformulas were devised to make *anschaulich* the explanation of isomers by the tetrahedral carbon atom or octahedral metal atom, and were tools for portraying visually what could not be described verbally. Stereochemists used stereoformulas *as if* the tetrahedron were real, despite the fact that it forced questions about the nature of affinity and valence – questions that could be answered, but did not require an answer. We must also keep in mind that because these representations were meant to differentiate isomers by showing spatial differences in molecules, stereoformulas did not represent the three-dimensional characteristics of the *atom*. Therefore, a specific model for the carbon atom was unnecessary, as Fischer and Hantzsch (and to a large extent, Wislicenus) carried out highly successful research programs without addressing the nature of valence.

If atomic models were unnecessary for the success of stereochemistry, then what role did they play in the thought of nineteenth century chemists? In simple terms, they served to explain the phenomena of valence, bonding, and the tetrahedron at a higher level. But while they were explanatory (with varying degrees of success), they were not at all *predictive* for chemical theory. The models they presented were ‘stories’ meant simply to account for the physical characteristics of the carbon atom demanded by stereochemical theories. They were independent of chemical theory and irrelevant to the ‘progress’ of stereochemistry, that is, its capability of predicting isomers or postulating reaction mechanisms. Even the most influential of the models, those by Wunderlich and Werner, remained purely explanatory and had no predictive character. The concept of affinity in both was still rather vague physically, as it remained an *undefined* attractive force. Sachse’s model had the physically most sophisticated conception of valence and affinity, but his model was also an attempt to explain in more fundamental terms what stereochemists had already accepted: that the carbon atom was tetrahedral, that in carbon-carbon single bonds there was free rotation, and that in carbon-carbon double bonds there was no free rotation.

The pragmatic use of stereoformulas and the independence of atomic models from chemical theory are also reinforced by doubts that chemists ex-

pressed about ever understanding the ultimate nature of matter. In a letter to Arrhenius, van't Hoff noted the provisional nature of the tetrahedron:

the representations themselves, atom, molecule, their dimensions, and perhaps their shapes, are after all something doubtful, as is the tetrahedron itself. But as long as something good come *from* it, one can console oneself and believe that there is also something good *in* it.⁴²

Two years after the appearance of his paper with Riecke, Meyer remarked that their theory of valence had little relevance to his actual work on the benzildioximes, and none of the papers on the chemistry of the benzildioximes mentioned the Meyer/Riecke theory. It was not necessary to rely on the theory of valence to explain this isomerism, because the hypothesis

originated simply from the necessity that Riecke and I simultaneously felt to posit a comprehensible idea in place of the previously entirely uncertain concept of valence. That our hypothesis harmonizes certain pyroelectric phenomena as well as the observations on the benzildioximes, can serve in certain senses as support of it; the inverse alone is incorrect, that any hypothesis of valence may be necessary for my explanation of the benzildioximes.⁴³

In the original paper, Meyer and Riecke themselves hesitated to display too much confidence in their model, and pointed out that this model did not adequately address the "essence" of chemical affinity:

No one feels clearer than ourselves how far away the view presented here still is from the path to a comprehensive physical theory of chemical phenomena. May our investigation be viewed only as a modest advance on this still so dark path that initiates a clearer understanding of a few phenomena and presently is certain to prompt greater penetration into areas of the valence problem.⁴⁴

Four years later Meyer would emphasize in his *Lehrbuch der organische Chemie* that

We still do not possess a clear idea of the essence of valence – on the cause by which the different saturation capacities of the elements is determined. For the moment we can only derive from the observations that a carbon atom possesses four times greater an atomic binding power than a hydrogen atom, since it is just in the position to express its affinity to four other atoms.⁴⁵

Even Wislicenus, the strongest proponent of physical atomism among the stereochemists, did not offer any concrete suggestions about the ultimate nature of matter. Convinced of the basic premise of atomism, he still offered many suggestions about an atom's composition:

How does chemistry imagine the last principle of matter is constituted? Can it be the luminiferous ether, which physics requires to explain certain groups of phenomena, above all the propagation of transverse waves? Is it perhaps beings of entirely different magnitude than the elementary atoms, perhaps exten-

sionless, turbulent centers of force that act on one another, through which only their spatial aggregations form the simplest corpuscular units? Isn't matter a concept actually formed of experience, like all our external experience, only a product of the effects of the unchanging quantity of energy in space?⁴⁶

Chemistry, Wislicenus claimed, "has no specific answer for these kind of questions, since all these ideas – like also the materially conceived luminiferous ether – are of a purely hypothetical nature." They were objects of speculative, mathematical thought.

Yet in describing the use of stereoformulas and atoms as 'pragmatic' or 'practical', we must be careful not to equate this pragmatism with pure instrumentalism. 'Pragmatism' in the sense described here does not mean, for example, that chemists considered stereoformulas as merely instruments that did not depict reality independent of human experience. Stereochemists believed that the groups around the carbon atom were arranged in a tetrahedron, and that stereoformulas represented in some fashion the molecule as a physical object. In short, they believed they had access to the physical appearance of the molecule, and had not simply invented instruments for prediction. Furthermore, as Wislicenus made evident, considering molecules as physical objects – and thereby implying a three-dimensional distribution of valences of the atoms in the molecule – necessitated considering the *atom's* properties as a physical object, specifically how the valences could be directed in space. Stereochemists therefore created the first plausible epistemological foundation for a true physical atomism in organic chemistry, threatened by the quasi-mechanical formulas of the structure theory.⁴⁷ Describing chemists' use of stereoformulas as pragmatic therefore does not preclude their belief in the reality of the spatial arrangement of valences, nor the related conviction that they could address – as some did – and eventually solve the theoretical problems entailed by the spatial division of affinity.

The pragmatic use of stereoformulas and the simultaneous appearance of reductionist models of the atom also beautifully illustrate the tension in nineteenth century chemistry between chemical and physical explanations. During much of the nineteenth century, chemists created a largely autonomous and non-mathematical discipline with unique ontological, epistemological, and methodological characteristics. Yet chemists always had the lurking conviction that chemistry would only become a 'true' science when it had been reduced to physical laws described by mathematics, and chemists therefore felt compelled to suggest a physical basis for chemical theories.⁴⁸ In his 'Deutung der Affinität', Sachse employed extensively "the language of mechanics, in which ultimately shall just dissolve (*sich auflösen*) the language of our science."⁴⁹

Meyer exemplified this tension between autonomy and reduction when he recognized a need for a physical conception of valence, but was reluctant to

endorse fully his own theory of the atom that met this need. He also revealed this tension in his 1889 lecture 'Contemporary Chemical Problems', given in a general session of the Heidelberg meeting of the *Gesellschaft deutscher Naturforscher und Ärzte*. Meyer placed chemical theory in a peculiar, almost schizophrenic, position. He appeared to oscillate between two poles, at first advocating the reduction of chemical theory to mathematical physics and then advocating its theoretical autonomy. The final goal of chemical theory, according to Meyer, was a complete reduction of chemical reactions to mathematical mechanics, because "nature is not understood until we are able to reduce its phenomena to simple movements, mathematically traceable".⁵⁰ He was certain that all chemical explanations would one day be completely understood in mathematical terms.

The time will come, even for chemistry, when this highest kind of treatment will prevail. The epoch in which the foremost impulse of its research was a serenely creative phantasy will then have passed; the joys, but also the pangs and struggles, peculiar to youth, will have been overcome. Reunited to physics, her sister science, from which her ways at present are separated, Chemistry will run her course with firm and unfaltering steps.⁵¹

If this were truly the goal of all science, declared Meyer, "a science, which is so far distant from this aim as to look merely for the *path* that shall someday lead to it, must be considered in its infancy."⁵²

According to Meyer, the "infancy" of chemistry was not a "blemish", nor did it detract from the "immense achievements [it had] registered on its own."⁵³ The lack of rigorous mathematical principles, Meyer claimed, gave chemical thought a plasticity that the logical, mathematical sciences lacked. Chemists had a greater tendency for imaginative thought or speculation (*Phantasie*) that brought a creative enjoyment similar to that experienced by artists.

He, however, who only knows chemistry as a tradition of perfectly clear facts, or who thinks to see the real soul of chemical study in measuring the *physical* phenomena which accompany chemical transformations feels no breath of this enjoyment.⁵⁴

Furthermore, chemical research was aided by what Meyer termed "chemical feeling" or intuition that would disappear "as soon as the progressive approach of chemistry to the mathematical physical basis shall have disclosed its meaning".⁵⁵

This reluctance towards complete reduction and the pragmatic use of chemical formulas has never really disappeared. The concepts of hybridization and molecular orbitals, like their nineteenth century counterparts, offer a deeper physical explanation for the appearance of valence, bonding, and their three-dimensional arrangement. They are much more sophisticated in

that they allow predictions about spectroscopic properties (and to a limited extent chemical reactivity), but they are no more predictive than their nineteenth century equivalents about the number of possible isomers than non-mathematical structural and stereoformulas. The uniquely chemical concept of isomerism, developed to explain the existence of and differences between specific kinds of substances, is therefore not necessarily reducible to mathematics. As any first year student in organic chemistry learns, there is no mathematical formula for deriving all possible structures and stereoisomers for all possible isomers from a given compositional formula.⁵⁶ It often amazes students of modern chemistry that the tetrahedral carbon atom predates electronic theories of bonding by fifty years, and even the electron itself by twenty five years. Like its nineteenth century counterparts, Linus Pauling's mathematical model of orbital hybridization was created to explain what was already well known at a scientifically 'lower' level for over fifty years: that the carbon atom was tetrahedral.⁵⁷

Notes

- ¹ E. Francoeur, 'The Forgotten Tool: the Design and Use of Molecular Models', *Social Studies of Science*, 27 (1997), 7-40, and 'Beyond Dematerialization and Inscription: Does the Materiality of Molecular Models Really Matter?', this issue of *HYLE*. I thank Francoeur for making the unpublished manuscript available to me.
- ² Those models that did imply an atomic structure, such as Kekulé's famous 'sausage formulas', were used heuristically, and not meant to be a literal snapshot of the atom.
- ³ A.J. Roche, *Chemical Atomism in the Nineteenth Century: From Dalton to Cannizzaro*, Ohio State University Press, Columbus, 1984; Ch. Meinel, 'Modeling a Visual Language for Chemistry, 1860 – 1875', unpublished manuscript. I thank Dr. Meinel for making his manuscript available to me.
- ⁴ R. Hoffmann, *The Same and Not the Same*, Columbia Univ. Pr., New York, 1995.
- ⁵ The term 'stereoformulas' was not used until after 1889, after Victor Meyer introduced the word 'stereochemistry'. The prefix 'stereo-' subsequently was employed frequently to distinguish structural features (connectivity) from spatial features of molecules. Describing chemical formulas published before 1889 as 'stereoformulas' is therefore somewhat anachronistic, but for the purposes of this article, I have chosen to use it for the sake of clarity and consistency, rather than historical accuracy.
- ⁶ The other co-founder of stereochemistry, Joseph Achille Le Bel, did not portray graphically the tetrahedron, and did not use stereoformulas. J.H. van't Hoff, *Voorstel tot Uitbreiding der tegenwoordig in de scheikunde gebruikte Structuur-Formules in de ruimte; benevens een daarmee samenhangende opmerking omtrent het verband tusschen optisch actief Vermogen en Chemische Constitutie van Organische Verbindingen*, Greven, Utrecht, 1874; *La chimie dans l'espace*, Bazendijk,

- Rotterdam, 1875; and *Die Lagerung der Atome in Raume*, Vieweg, Braunschweig, 1877.
- ⁷ Kekulé developed these models to illustrate multiple bonds, but like most chemists who developed such models, he did not give the arrangement of valences any physical significance. Meinel, 'Visual Language' (Note 3); O.B. Ramsay, 'Molecular Models in the Early Development of Stereochemistry: I. The van't Hoff Model' & 'II. The Kekulé Models and the Baeyer Strain Theory', in: O.B. Ramsey (ed.), *Van't Hoff Le Bel Centennial*, American Chemical Society, Washington, DC, 1974, pp. 74-96.
 - ⁸ Van't Hoff, *Die Lagerung* (Note 6), p. 47; O.B. Ramsay, 'Molecular Models' (Note 7).
 - ⁹ J. Wislicenus, 'Ueber die räumliche Anordnung der Atome in organischen Molekülen und ihre Bestimmung in geometrisch-isomeren ungesättigten Verbindungen', *Abhandlungen der mathematischen-physikalischen Classe der königlichen sächsischen Gesellschaft der Wissenschaften*, **14** (1887), p. 1.
 - ¹⁰ "Diese Bezeichnungweise scheint mir zweckmässiger als die von van't Hoff und Wislicenus gebrauchten complicirten Zeichnungen, bei welchen die vier Valenzen des Kohlenstoffs, auf welche es gerade ankommt, gar nicht gezeichnet sind, statt ihrer aber sechs Tetraëder-Kanten, welche doch für die Betrachtung ohne jeden Belang sind." (V. Meyer & K. von Auwers, 'Untersuchungen über die zweite van't Hoff'sche Hypothese', *Berichte der deutschen chemischen Gesellschaft*, **21** (1888), pp. 790-817 [786]). Unless noted, all translations are mine.
 - ¹¹ Fischer describes the invention of these projections from *Gummimodellen*, physical molecular models developed by Friedländer, at the *Karlsruhe Technische Hochschule*. The flat drawings were derived by literally squashing these flexible three-dimensional models into two dimensions. E. Fischer, 'Über die Konfiguration des Traubenzuckers und seiner Isomeren', I & II, *Berichte der deutschen chemischen Gesellschaft*, **24** (1891), 1836ff., 2683ff. (repr. in: Emil Fischer, *Gesammelte Werke*, ed. by M. Bergmann, Springer, Berlin, 1906-1923, vol. 5, pp. 417-27, 427-31).
 - ¹² M.J. Nye, 'Explanation and Convention in Nineteenth-Century Chemistry', in: R.P.W. Visser (ed.), *New Trends in the History of Science*, Editions Rodopi, Amsterdam, 1989, pp. 171-86.
 - ¹³ A.J. Roche, 'Convention Versus Ontology in Nineteenth-Century Organic Chemistry', in: J.G. Traynham (ed.), *Essays on the History of Organic Chemistry*, Louisiana State University Press, Baton Rouge, 1987, pp. 1-20 (14).
 - ¹⁴ "Daß aber eine solche Kraft sich nicht nach allen Richtungen des Raumes bethätigen soll, sondern nur nach ganz bestimmten, widerspricht dem Begriff einer Anziehungskraft." (K. von Auwers, *Die Entwicklung der Stereochemie*, Carl Winter's Universitätsbuchhandlung, Heidelberg, 1890, p. 25).
 - ¹⁵ J.H. van't Hoff, 'Isomerie en atoomligging. Antwoord op den openbaren brief van Dr. C.H.D. Buys Ballot', *Mandblad vor Natuurwetenschappen*, **6** (1875), pp. 37ff.; German translation by E. Cohen in: *Jacobus Henricus van't Hoff: Sein Leben und Wirken*, Akademische Verlagsgesellschaft, Leipzig, 1912, pp. 104-113.
 - ¹⁶ Van't Hoff to Wilhelm Ostwald, January 20, 1888, in: H.-G. Körber (ed.), *Aus dem wissenschaftlicher Briefwechsel Wilhelm Ostwalds*, 2 vols., Akademie-Verlag, Berlin, 1969, vol 2, p. 213.
 - ¹⁷ "[die Chemie bedarf] wenigstens in ihrem gegenwärtigen Entwicklungsstadium, keiner bestimmten Vorstellung über Art und Ursache des intramolekularen Zu-

sammenhaltes der Atome, also über die Natur der chemischen Affinität, oder über Art und Ursache des Zahlenverhältnisses, in welchem sich verschiedene Atome verbinden, also über die Natur der Valenz; sie bedarf zur Zeit nur der durch die Existenz der Isomerie überhaupt bewiesenen Vorstellung, daß sich die Atome innerhalb des Molekel nicht in einem chaotischen Zustande, sondern in einer innerhalb gewisser Grenzen stabilen Gleichgewichtslage befinden.” (A. Hantzsch, *Grundriss der Stereochemie*, Trewendt, Breslau, 1893, p. 1).

- ¹⁸ “Die Hypothese selbst lässt sich [...] ganz unabhängig von dem schwankenden Begriffe der Valenz und den noch mehr schwankenden Vorstellungen über ‘Richtung’, ‘Ablenkung’, und ‘Bindung’ der Valenz entwickeln.” (A. Hantzsch & A. Werner, ‘Bermerkungen über stereochemisch isomere Stickstoffverbindungen’, *Berichte der deutschen chemischen Gesellschaft*, **23** (1890), 2764-9 [2769]).
- ¹⁹ W. Lossen, ‘Ueber die Lage der Atome in Raume’, *Berichte der deutschen chemischen Gesellschaft*, **20** (1887), 3306–10.
- ²⁰ J. Wislicenus, ‘Über die Lage der Atome in Raum. Antwort auf Lossen’s Frage’, *Berichte der deutschen chemischen Gesellschaft*, **21** (1888), 581-5 (584). A closer analysis of Lossen’s critique and a full translation of Wislicenus’ response is given in P.J. Ramberg, “Johannes Wislicenus, Atomism, and the Philosophy of Chemistry: A Translation and Commentary”, *Bulletin for the History of Chemistry*, **15/16** (1994), 45-53.
- ²¹ Wislicenus, ‘Lage der Atome’ (Note 20), p. 582.
- ²² “[dann] wäre das chemische Einzelwissen ein wüster Haufen unzusammenhängender und daher unverständlicher Beobachtungen, ja es wäre weniger als das: es wäre zum größten Theile überhaupt nicht vorhanden. [...] Für die heutige Chemie, auch wenn sie sich der hypothetischen Natur der atomistischen Anschauung durchaus bewusst bleibt, sind die Elementaratome Realitäten. Obgleich niemand sie sinnlich wahrgenommen hat, noch je wahrnehmen wird, so kennen wir von ihnen gewisse, zum Theil genau gemessene Eigenschaften, [...]” (J. Wislicenus, *Die Chemie und das Problem von der Materie*, Alexander Edelmann Verlag, Leipzig, 1893, pp. 20-1).
- ²³ “[daß wir uns über] die Natur dessen, was wir eine Valenz oder Verwandtschaft nennen, vorläufig noch unvollkommen im Unklaren sind.” V. Meyer, ‘Zur Valenz und Verbindungsfähigkeit des Kohlenstoffs’, *Justus Liebig’s Annalen der Chemie*, **180** (1876), 192-206 (192).
- ²⁴ “Sobald man aber die zweite van’t Hoff’sche Hypothese annimmt, [...] eine Hypothese, deren fundamentale Bedeutung zuerst Wislicenus erkannt und welche er zur Basis seines Lehrgebäudes genommen und mit bewunderungswürdiger Consequenz durchgeführt hat – müssen bestimmte Vorstellungen über die Form der Atome und die Natur der Valenzen eingeführt werden, wenn die Speculationen nicht der exacten Grundlagen entbehren sollen. Die Annahme an bestimmten Stellen des leeren, von Atomen freien Raum sich treffender Valenzen kann als solche nicht gemacht werden und ist nur auf dem Papier oder am Modell möglich, wo statt der Kräfte (Valenzen) Striche und Drähte figuriren. Jetzt ist es nothwendig – und, wie ich glaube, auch möglich – dass positive und physikalisch haltbare Hypothesen über die Natur der Valenz gemacht und consequent durchgeführt werden.” (V. Meyer & R. Demuth, ‘Zur Kenntniss der Isodibrombernsteinsäuren’, *Berichte der deutschen chemischen Gesellschaft*, **21** (1888), 264-270 [265]).
- ²⁵ “Ich bin ganz fabelhaft erregt über all diese Sachen, träume davon und gehe manchmal bei Tage wie im Traume herum. Denn ich habe das Gefühl, daß ein großer Schritt in der Erkenntnis der Natur weiter gemacht wird, wir kriegen doch

schon eher Begriffe von Atom und Valenz. Vor allem arbeiten wir nun mit Eifer daran, wirkliche Isomere zu machen, was leider sehr viel technische Schwierigkeiten bietet und nicht so rasch geht. Es ist, wie Hofmann seinerzeit sagte, als er die Phosphoniumbasen voraus ahnte: ‘Doch genug der Theorie! Langsam und nur von ferne folgt der schleppfüßige Versuch dem Fluge leicht beschwingter Phantasie!’” (Victor Meyer to Richard Meyer, 25 Januar 1888, in: R. Meyer, *Victor Meyer: Leben und Wirken eines deutschen Chemikers und Naturforschers 1848–1897*, Akademische Verlagsgesellschaft, Leipzig, 1917, p. 216.)

- ²⁶ W. Voigt, ‘Eduard Riecke als Physiker’, *Physikalische Zeitschrift*, **16** (1915), 219–21. Pyroelectricity is the ability of some minerals to develop electrical poles when heated.
- ²⁷ “[...] jede Valenz als bedingt [...] durch eine gewisse Combination zweier entgegengesetzt elektrischer Theilchen” (V. Meyer & E. Riecke, “Einige Bemerkungen über das Kohlenstoffatom und die Valenz,” *Berichte der deutschen chemischen Gesellschaft*, **21** (1888), 946–56 (946).
- ²⁸ Anonymous reviews of Meyer’s lecture to the Göttingen Chemical Society in *Nature*, **37** (1888), 327; and *Chemiker-Zeitung*, **12** (1888), 140.
- ²⁹ “[daß das Atom] umgeben ist von einer Aetherhülle, welche bei einem isolirten Atome, wie diese selbst, kugelförmige Gestalt besitzt; das Atom selbst betrachten wir als den Träger der spec[ifischen] Affinitäten, die Oberfläche der Hülle als den Sitz der Valenzen. Jede Valenz denken wir uns bedingt durch das Vorhandensein zweier entgegengesetzter elektrischer Pole, welche in den Endpunkten im Vergleich zum Durchmesser der Aetherhülle an kleinen geraden Linie befestigt sind.” (V. Meyer & E. Riecke, ‘Einige Bemerkungen’ [Note 27], p. 951).
- ³⁰ “[Sind] die an den beiden verschiedenen Kohlenstoffatomen haftenden Gruppen sehr verschiedenartiger Natur – üben also die specifischen Affinitäten derselben ihren orientirenden Einfluß in hohem Maasse – so wird ein stabiles Verharren in der weniger begünstigten Lage schwer oder unmöglich sein, und die zweite, freie Rotation ausschließende Form der Bindung wird in der unbegünstigte Lage nicht zu Stande kommen können. Stehen die Gruppe aber in ihren chemischen Functionen, bezw. dem Grade ihrer Negativität (Acidität), einander nahe, so daß die Affinitäten nur schwach orientirend wirken, so wird die Fixirung in beiden Lagen, der begünstigten wie der weniger begünstigten – die sich in diesem Falle in Bezug auf Stabilität nicht allzu sehr von einander unterschieden – möglich sein.” (*ibid*, p. 953–5).
- ³¹ Anonymous, *Nature*, **37** (1888), 327.
- ³² Ae. Wunderlich, *Configuration organischer Moleküle*, Leitholdt, Würzburg, 1886, p. 1.
- ³³ A. Werner, ‘Beiträge zur Theorie der Affinität und Valenz’, *Vierteljahrsschrift der Züricher Naturforschenden Gesellschaft*, **36** (1891), 129–69; trans. by G.B. Kauffman, ‘Alfred Werner’s Habilitationsschrift’, *Chymia*, **12** (1967), 183–216 (191).
- ³⁴ Kauffman, ‘Habilitationsschrift’ (Note 33).
- ³⁵ “Das Kohlenstoffatom besitzt, gleichviel wie es im übrigen gestaltet sein mag, vier Punkte von grösster gleicher Entfernung vom Mittelpunkte, die in den Ecken eines regulären Tetraeders liegen, und nach denen die vier Affinitätskräfte gerichtet sind. Diese Punkte mögen daher als Affinitätspunkte bezeichnet werden. [...] [Es] liegen auch den Atomen der übrigen Elemente gewisse durch Zahl und Lage der Affinitätspunkte bestimmte geometrische Ideale zu Grunde.” (H. Sachse,

- 'Über die Configuration des Benzolmoleküls', *Berichte der deutschen chemischen Gesellschaft*, **21** (1888), 2530-8 [2530]).
- ³⁶ H. Sachse, 'Ueber die geometrischen Isomerien der Hexamethylenederivate', *Berichte der deutschen Chemische Gesellschaft*, **23** (1890), 1365-6. This paper is analyzed in C.A. Russell, 'The Origins of Conformational Analysis', in: Ramsey, *Van't Hoff Le Bel Centennial* (Note 7), pp. 159-178; and O.B. Ramsay, 'The Early History and Development of Conformational Analysis', in: Traynham, *Essays*, (Note 13), pp. 54-77.
- ³⁷ H. Sachse, 'Über die Konfigurationen der Polymethylenringe', *Zeitschrift für physikalische Chemie*, **10** (1892), 203-41.
- ³⁸ "[...] ein System kleinster Teilchen, um welche oder in welchen Solenoidströme kreisen. [...] eine Vorstellung, die die Molekularphysik meines Erachtens kaum entbehren kann. [...] Denken wir uns ein reguläres Tetraëder, in welchem eine grosse Anzahl von festen Punkten nach einem bestimmten Gesetz verteilt ist. Diese Punkte seien von kreisförmigen elektrischen Strömen umflossen, derart, dass sie die Mittelpunkte dieser Kreise bilden. Während also der Ort dieser Kreismittelpunkte unveränderlich ist, soll die Lage der Kreisebene und die Richtung des Stromes veränderlich sein. Beide werden nur durch den gegenseitigen Einfluss der Ströme aufeinander bestimmt, d. h. nur durch das Gesetz der Anordnung jener festen Punkte. Sobald aber einem solchen System ein Elektromagnet genähert wird, so werden dadurch jene Ströme in bestimmter Weise neu gerichtet. Die Solenoide können wir natürlich, wenn es das Interesse der Anschaulichkeit erfordert, stets durch geradelinige Magneten ersetzt denken, deren Richtung senkrecht auf jener Kreisfläche steht. [...] Wenn wir nun dieses tetraëdrische System uns irgendwie mit Materie erfüllt denken, so erhält es gemäss dem oben gesagten die Eigenschaft, auf andere ähnliche Systeme, die sich in seiner Umgebung innerhalb gewisser Grenzen befinden, eine Abstossung auszuüben." (H. Sachse, 'Eine Deutung der Affinität', *Zeitschrift für Physikalische Chemie*, **11** (1893), 185-219 [186-7]).
- ³⁹ *Ibid.*, p. 187.
- ⁴⁰ The idea of 'isomer counting' was introduced by G.B. Kauffman, 'The Discovery of Optically Active Coordination Compounds: A Milestone in Stereochemistry', *Isis*, **65** (1973), 38-62.
- ⁴¹ For the example of atomism, see B. Görs, *Chemischer Atomismus: Anwendung, Veränderung, Alternativen im deutschsprachigen Raum in der zweiten Hälfte des 19. Jahrhunderts*, ERS Verlag, Berlin, 1999.
- ⁴² Van't Hoff to Svante Arrhenius, undated, quoted by A.G. van Melsen, *From Atoms to Atom: A History of the Concept Atom*, Harper, New York, 1960.
- ⁴³ "[Dies] entsprang lediglich dem Bedürfniss, welches Riecke und ich gleichzeitig empfanden, an Stelle des bisher gänzlich unbestimmten Begriffes der Valenz eine greifbare Vorstellung zu setzen. Dass unsere Hypothese mit gewissen pyroelektrischen Erscheinungen sowie mit den Beobachtungen über die Benzildioxime harmonirt, kann derselben in gewissem Sinne als Stütze dienen; allein unrichtig ist die Umkehrung, dass für meine Erklärung der Isomerie der Benzildioxime jene Hypothese über die Valenz nothwendig sei. [...] Gegen den Ausspruch von Hantzsch und Werner, dass unsere Auffassung der isomeren Benzildioxime 'ein neues Princip über das Wesen der Valenz erfordere', muss ich sonach Verwahrung einlegen." (V. Meyer, 'Die Ergebnisse und Ziele der Stereochemischen Forschung', *Berichte der deutschen chemischen Gesellschaft*, **23** (1890), 567-619 [601]).

- ⁴⁴ “Wie sehr weit der Weg von diesem, heut dargelegten Standpunkte bis zu einer umfassenden physikalischen Theorie der chemischen Erscheinungen noch ist, das empfindet niemand klarer als wir selbst. Möge unsere Untersuchung nur als ein bescheidener Fortschritt auf diesem noch so dunklen Pfade angesehen werden, welcher für einige Erscheinungen ein klareres Verständniß anzubahnen und zunächst zu weiterem Vordringen im Gebiete des Valenzproblems anzuregen bestimmt ist.” (Meyer & Riecke, ‘Einige Bemerkungen’ [Note 29], p. 956).
- ⁴⁵ “Über das Wesen der Valenz – über die Ursache, durch welche die verschiedene Sättigungscapazität der Elemente bedingt ist – besitzen wir noch keine klare Vorstellung. Aus den Beobachtungen können wir zunächst nur ableiten, daß ein Kohlenstoffatom eine viermal grössere Atombindkraft als ein Wasserstoffatom besitzt, weil es eben im Stande ist, seine Affinität vier anderen Atomen gegenüber zu äussern.” (V. Meyer & P. Jacobsen, *Lehrbuch der organische Chemie*, 3 vols., Leipzig 1893, vol 1, p. 58).
- ⁴⁶ “[...] wie denkt sich die Chemie das letzte Princip der Materie beschaffen? Kann es der Lichtäther sein, dessen die Physik bedarf um gewisse Gruppen von Erscheinungen, vor allem diejenigen strahlenförmiger Fortpflanzung transversaler Schwingungen zu erklären? Sind es vielleicht Wesenheiten ganz anderer Ordnung als die chemischen Elementaratome, etwa ausdehnungslose, bewegte und auf einander wirkende Kraftcentren, durch deren räumliche Aggregation erst die einfachsten Corpusculareinheiten entstehen? Ist nicht die Materie, der thatsächlich von der Erfahrung geschaffene Begriff, wie alle unsere äussere Erfahrung nur eine Produkt der Wirkungen der im All in unveränderlicher Quantität enthaltenen Energie? Die Chemie als solche hat auf derartige Fragen keine bestimmte Antwort, da alle diese Vorstellungen – wie auch der stofflich gedachte Lichtäther – rein hypothetischer Natur sind.” (Wislicenus, *Materie*, [Note 22], p. 26-27).
- ⁴⁷ Many chemists before the emergence of stereochemistry were physical atomists, but any belief in physical atoms was usually not reflected in the meaning they gave to structural formulas and molecular models. Chemists placed strict ontological and epistemological constraints on the meaning of structural formulas and physical models, interpreting them as ‘reaction formulas’ that did not represent physical objects. Stereochemists, on the other hand, saw structural formulas as representing the physical molecule, and had developed specific ways of justifying this meaning. Cf. P.J. Ramberg, *Theory and Methodology in the Early History of Stereochemistry*, (PhD: Indiana University, 1993); Rocke, *Chemical Atomism* (Note 3); Meinel, ‘Visual Language’ (Note 3); U. Klein, *Experimente, Modelle, Paper-Tools: Kulturen der organischen Chemie im 19. Jahrhundert*, Habilitationsschrift, University of Konstanz, 1999.
- ⁴⁸ The relationship between nineteenth century chemistry and physics is given in M.J. Nye, ‘Physics and Chemistry: Commensurate or Incommensurate Sciences?’, in: M.J. Nye, J.L. Richards, R.H. Stuewer (eds.), *The Invention of Physical Science: Intersections of Mathematics, Theology and Natural Philosophy Since the Seventeenth Century*, Kluwer, Dordrecht, 1992, pp. 205-224; and in *From Chemical Philosophy to Theoretical Chemistry: Dynamics of Matter and Dynamics of Disciplines, 1800-1950*, University of California Press, Berkeley, 1993.
- ⁴⁹ “[...] wenn wir uns der Sprache der Mechanik bedienen, in die sich ja die Sprache unserer Wissenschaft schliesslich auflösen soll.” (H. Sachse, ‘Affinität’ (Note 38), p. 185).
- ⁵⁰ V. Meyer, *Chemische Probleme der Gegenwart*; Heidelberg, Carl Winter, 1890. L.H. Friedburg translated the address in 1889, ‘The Chemical Problems of Today’,

Journal of the American Chemical Society, **11** (1889), 101-120. I have retranslated the title, but all subsequent translations are Friedburg's.

- ⁵¹ *Ibid.*, p. 120.
- ⁵² *Ibid.*, p. 103. Meyer's emphasis.
- ⁵³ *Ibid.*, p. 102.
- ⁵⁴ *Ibid.*, p. 103. Meyer's emphasis.
- ⁵⁵ *Ibid.*, p. 104.
- ⁵⁶ There is the rule, introduced by van't Hoff in 1875, that predicts that a compound with n stereocenters, will have a maximum of 2^n possible stereoisomers. This maximum number is easily reduced, however, by the presence of *meso* stereoisomers, making the prediction more difficult. In any case, this formula applies only to stereoisomers. There is no formula for generating the maximum number of structural isomers from a given empirical formula.
- ⁵⁷ B.S. Park, 'Graphs, Pictures and Diagrams: Visual Representations in the Making of Quantum Chemistry', paper presented at the Workshop on Types of Paper Tools and Traditions of Representation in the History of Chemistry, Max-Planck-Institute for the History of Science, December 1999.

Peter J. Ramberg
Max-Planck-Institut für Wissenschaftsgeschichte, Wilhelmstraße 44,
D-10117 Berlin, Germany; ramberg@mpiwg-berlin.mpg.de