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CHAPTER NINE

Molecules and Croquet Balls

Christoph Meinel

For much of its history chemistry had an ambiguous attitude to visual representations. While a rich tradition depicted chemical laboratories and (al)chemists at work, the language of chemistry and its theoretical notions remained verbal and abstract (Crosland 1962; Knight 1993, 1997). Even John Dalton's highly figurative atomic theory of 1808 and his speculations about atoms as little spheres arranged in space were incorporated only in the non-figurative version of Berzelius' algebraic notation (Thackray 1970, 264–66; Rocke 1984).[1] During the 1860s, however, the dominant way chemists thought about matter changed from an abstract and verbal to a constructivist and pictorial approach. This gradual transition was closely related to the new interest in molecular constitution stimulated by the rise of organic chemistry during the first half of the nineteenth century, and intimately linked to the advent, from the late 1850s, of a new theory of chemical structure. As a result, molecules were considered to be composed of atoms, the relative positions of which were determined by their respective valency or binding force. Yet to what extent these structures represented the true arrangement of atoms within the molecule remained controversial. Most chemists preferred to use these formulae as mere aids to classification and were reluctant to take their spatial properties for physical reality.

As a consequence of a new vision of chemistry's future, proposed by a London-based group of chemists engaged in organic synthesis, this attitude changed and scientists began to realise that a 'chemistry in space' would not only allow them to relate chemical behaviour to physical, for example optical, properties, but could also be used as a blueprint for a new laboratory

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practice based upon the idea of a molecule as a truly spatial arrangement. This was indeed one of the great revolutions in nineteenth-century chemistry, as announced in Jacobus Hendricus van't Hoff's manifesto, *The Arrangement of Atoms in Space*, first published in Dutch in 1874 (van't Hoff 1874; Ramsay 1975).

Historians of chemistry have treated the emergence of stereochemistry as a sequence of arguments and discoveries within the development of chemical theory. Molecular models have been seen as merely illustrating theoretical concepts such as atom, valency, or space (Ramsay 1974, 1981; Spronsen 1974). In this chapter I argue that the change that eventually resulted in a three-dimensional representation of molecules was led, not by theory, but by modelling—a kind of modelling invented, not primarily to express chemical theory, but rather as a new way of communicating a variety of messages. By manipulating tin boxes or tinkering with little spheres and toothpicks, chemists not only visualised their abstract theoretical notions but also impressively testified to the claim that they would build a new world out of new materials. For this purpose molecular models supplied the elements of a new symbolic and gestic language by which chemists conquered new spaces: material space in the form of new substances, notional space in the new stereochemistry, and social space by expressing professional claims to power. Though the use of these models remained epistemologically problematic, their social and cultural message was much more easily understood, and this predisposed younger chemists to accept their implicitly constructivist and three-dimensional approach. The active construction of space was not peculiar to chemistry, but part of a more comprehensive change in perceiving the world and making it one's own, an attitude present in cultural domains from pedagogy to architecture.

SYNTHESIS AND CHEMICAL STRUCTURE

The notion of synthesis and the notion of structure mark the beginning of a reorientation in mid-nineteenth-century chemistry. Both concepts originated with a group of London chemists who, in the mid-1840s, proposed the idea that chemistry's foremost task was no longer analysis and understanding, but rather the making of compounds. 'Chemical synthesis' was the new slogan, introduced by Hermann Kolbe in 1845 and subsequently turned into a research programme by Edward Frankland and Kolbe at the Royal School of Mines in London. At a meeting of the Chemical Society of London in April 1845, August Wilhelm Hofmann, then head of the Royal College of Chemistry, proclaimed that the old-fashioned analytical approach dating from Lavoisier would soon give way to a new era of synthetic chemistry (Muspratt and Hofmann 1845; Russell 1987; Rocke 1993b). And by the late 1850s many chemists were convinced that even complicated natural compounds could be prepared in the laboratory, provided their molecular constitution was established. Finally, Marcellin Berthelot's *Organic Chemistry Based upon Synthesis*, published in French in 1860 (Berthelot 1860), became the manifesto of this new approach, the counterparts of which were the advent of chemical industrialisation and the success of artificial dyestuffs prepared according to the principle of chemical synthesis.

The original basis of chemistry's new self-image was the so-called substitution theory of chemical combination. This theory treated the molecule as a unit in which individual atoms or groups could be replaced by other elements without fundamentally changing the general character of a substance. Compounds that could be formally reduced to a common scheme belonged to the same 'chemical type'. Hydrochloric acid, water, ammonia, and marsh gas (methane) were believed to represent the four basic patterns, or types, out of which the entirety of chemical compounds could be derived. In the late 1850s, the type theory was supplemented by the theory of chemical structure developed by Frankland and Hofmann in London, and by August Kekulé, who had been a member of this London group before he moved to Heidelberg and, in 1858, to Ghent in Belgium. The interpretation favoured by this group of young chemists took the chemical type in a 'mechanical' sense, indicating how atoms or groups are linked together depending on the number of valencies or binding units peculiar to each sort of element.

In the beginning, however, neither type nor structural formulae were meant to represent the true intramolecular arrangement of the atoms. Rather, the formulae were regarded as a mere aid to classifying reactivities and searching for analogies—a taxonomic model with no correlation to a reality that was assumed to be fundamentally unintelligible (Brooke 1976). Nevertheless, the idea of a 'mechanical type' offered the tremendous advantage of permitting, for the first time, predictions regarding possible and still unknown compounds. As a consequence, type formulae became the most powerful tools of the new synthetic chemistry.

TYPE MOULDS AND ATOMIC CUBES

Hofmann's model substance was ammonia (NH_3), the three hydrogen atoms of which could be replaced, one after another, by other groups. In this way a whole array of homologous primary, secondary, and tertiary amines could be obtained, and the number of possible combinations was almost unlimited. In this combinatorial game, the chemical type provided an aid to construction, a template in the spaces of which atoms or atomic groups could be inserted like bricks in a wall—very much in the same way that Berzelian formulae had been used as paper tools for modelling chemical reactions since the 1830s (Klein 1999). To visualise this way of chemical reasoning Hofmann prepared three-dimensional frames, consisting of two, three, or four wire cubes made to receive solid painted cubes representing atoms or atomic groups. These "type moulds", first presented in a publication of 1862, were "mechanical types", transformed into pedagogical tools that could be used in chemistry lectures (Hofmann 1862).

Anschaulichkeit, the ability to appeal to the mind's eye by transforming abstract notions into vivid mental images was Hofmann's chief pedagogical method. Impressive demonstration rather than abstract reasoning was supposed to transmit scientific knowledge. In this way theoretical notions turned into mental images could be read as a language, "presented to the mind in neat pictures" (Hofmann 1871, 119). Hofmann wanted the student to acquire the kind of pictorial representation that would emerge "if we use these formulas as types, as blueprints for as many classes of chemical compounds. All members of each class are cast, so to speak, into the same mould, and thus they render the peculiarities of the models as in true imitation" (Hofmann 1871, 108).

The choice of the model and the language that came with it disclose a modeller's or an architect's approach, and it was indeed architecture where the notion of model originated. From Vitruvius through the eighteenth century a model meant a concrete exemplar or mould after which something else was prepared (Baker, this volume). Architectural templates teach us how to make something. Epistemology or ontology does not matter in this case;

Figure 9.1 Samuel M. Gaines' "chemical apparatus" as patented by U. S. patent no. 85299 of 29 December 1868. The box contains coloured wooden cubes in two sections marked "Metalloid" and "Metals". The cubes represent chemical weights from 1 to 39. Case size 225 × 225 × 85 mm. National Museums of Scotland, Edinburgh, acc. no. T.1985.112; copyright Trustees of the National Museums of Scotland.

moulds may prove useful in practice, but the notion of truth would be alien to them.

This was exactly the way Hofmann used his type moulds. Convinced as he was that symbolic notations in chemistry were purely formal tools that did not immediately correspond to reality, this approach explicitly avoided the question of truth. Consequently, Hofmann's type moulds and atomic cubes were not meant to represent the physical arrangement of the atoms.

They rather supplied a pattern according to which the chemical operations of elimination and substitution could be classified and analogies found.

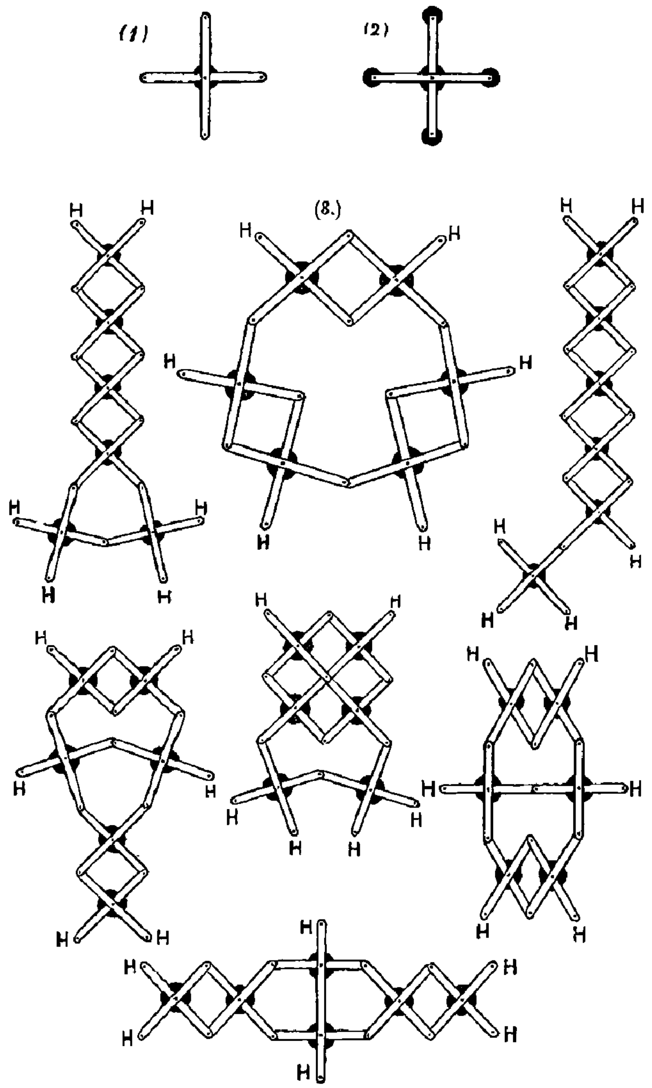
Shortly afterwards Hofmannian model kits were manufactured commercially. The 1866 sales catalogue of John Joseph Griffin's London instruments company advertised a kit of painted atomic cubes made from white biscuit ware and sold "in a neat black wood cabinet" for 31s 6d (Griffin 1866, nos. 194–95; Gee and Brock 1991).[2]

> Atomic Symbols for the illustration of Theoretical Subjects at Chemical Lectures: consisting of Coloured Cubes of Pottery, about two inches square, intended to represent chemical atoms or gaseous volumes. They can be easily grouped, so as to easily illustrate the atomic composition of compounds, the theory of combination in volumes, and the double decomposition of salts, and to illustrate various chemical doctrines by equations. The following series of sixty models is sufficient to explain the formulae of most frequent occurrence (Griffin 1866, no. 194).

No set of the Griffin models seems to have survived, but the National Museum of Scotland has an American derivative, a wooden box marked "Gaines' Chemical Apparatus" (Fig. 9.1). It contains numbered cubes of wood, coloured and of various sizes, representing atomic masses between 1 and 39. The item was patented for a certain Samuel M. Gaines of Glasgow, Kentucky, in 1868, and the patent claims a new "method of teaching the rudiments of chemistry by means of moveable material bodies" (U. S. Patent 85299 1868).[3]

CIRCLES AND LINES

The models discussed so far were used to illustrate chemical reactions by means of physical objects that could be manipulated according to certain rules. These objects represented relations rather than specific particulars of the natural world. Their meaning and iconography remained closely linked to the type-mould pattern and to the chemistry of elimination and substitution reactions. By marking the cubes with the respective atomic masses the model could even be used as a calculating device, as in Gaines' apparatus. However, it operated within the framework of the type theory; its units could be individual atoms or whole groups, such as phenyl, but it was not meant to convey the idea of structure or molecular constitution.



Formulæ of Benzol.

Figure 9.2 James Dewar's brass bar formulae of 1866, used to illustrate the tetravalent carbon (1, 2) and various C_6H_6 combinations, including Kekulé's benzene formula (3) and third row, right, what is now called Dewar benzene. Source: Dewar, *Proceedings of the Royal Society of Edinburgh* 6 (1866–67): 85.

In 1861 a new way of representing chemical formulae was introduced by the young Edinburgh medical graduate Alexander Crum Brown to be used with the new structural theory. Adopting an earlier proposal, made by Archibald Scott Couper while working at the chemistry laboratory in Edinburgh, to draw dotted lines between the atomic symbols to denote the valencies, Crum Brown suggested drawing circles around the atomic letters, a move John Dalton had already proposed. This first attempt at a graphic representation of molecular constitution was published in 1864 (Crum Brown 1864; Crosland 1962, chap. 3; Larder 1967; Russell 1971, 100–4).

Although Crum Brown's atomic design did not add anything new in terms of chemical theory, his 'graphic formulae' appealed more vividly to the imagination than the alphanumeric formulae of Berzelius' atomic symbols used so far, even though they were by no means meant to be more realistic. In fact Crum Brown stated that "by [this notation], it is scarcely necessary to remark, I do not mean to indicate the physical, but merely the chemical position of the atoms", alluding to the then familiar distinction between physical (i.e., real) and chemical (i.e., functional) atoms. As to the use of this notation for teaching purposes, he added that "while it is no doubt liable, when not explained, to be mistaken for a representation of the physical position of the atoms, this misunderstanding can easily be prevented" (Crum Brown 1864, 708)—namely by reminding the students of the purely formal nature of these formulae. Correspondingly, they were intended to be read in the plane of the paper and not to imply any spatial relationship.

Inspired by Crum Brown's graphic formulae, James Dewar, another student of Lyon Playfair, professor of chemistry in Edinburgh, prepared a model kit in 1866 (Dewar 1866–67) (Fig. 9.2). A series of narrow thin bars of brass of equal length were taken and clamped together in pairs by a central nut to form an X-shaped unit, the arms of which could be adjusted to different angles. This combination represented a single carbon atom with its four places of attachment. "In order to make the combination look like an atom" [!], Dewar even recommended placing a thin disc of blackened brass under the central nut. Little holes at the ends of the arms allowed one carbon atom to be connected with another. Hydrogen atoms were represented by white discs equipped with a screw to be fixed at the free carbon valencies; and oxygen was a red disc in the middle of a brass bar long enough to fit exactly between the free ends of two carbon valencies.[4] In this way mechanical structures could be assembled and disassembled, but besides being an assembly kit Dewar's model did not add anything new to the graphic notation on paper.

CROQUET BALLS AND MOLECULAR SCAFFOLDING

In 1865 Crum Brown's paper tools were developed into a much more elaborate device by Hofmann in London (Hofmann 1865; Torracca 1991). The context is well documented. On 9 January, Hofmann lectured at the Royal College of Chemistry on the determination of chemical equivalents, and he may have used his type mould models described above. After the lecture, he went to Herbert McLeod, at that time his assistant, and told him "about a new mechanical dodge of his for showing the atomic constitution of bodies" (James 1987, 9 January 1865). The wording in McLeod's diary suggests that no new chemical theory had come to his master's mind, but rather a pedagogical trick to improve his teaching. Six weeks later McLeod recorded attempts at trying "some dodges for colouring the spheres" which Hofmann wanted to show in the next day's lecture (James 1987, 14 February 1865). The test must have been a success, for when Hofmann began to prepare for one of the famous Friday Evening Discourses at the Royal Institution several weeks later, we find him again thinking about mechanical models. On 4th April, McLeod was sent "to the painter to see how he is getting on with the balls and cubes. Told him how some lines are to be painted on the cubes" (James 1987, 4 April 1865).

The model Hofmann presented at his Friday Evening Discourse on 7 April 1865 to a distinguished audience, including the Prince of Wales, the Duke d'Aumale, and the Prince de Condi, was borrowed from one of the most popular games in Victorian England: table croquet (Fig. 9.3). Croquet balls were Hofmann's atoms, painted in white for hydrogen, green for chlorine, red for the 'fiery oxygen', blue for nitrogen, and black for carbon—colour codes still in use today which seem to originate from that remarkable evening lecture. To exhibit the 'combining powers', i.e. the valencies, metallic tubes and pins were screwed into the balls "to join the balls and to rear in this manner a kind of mechanical structures in imitation of the atomic edifices to be illustrated" (Hofmann 1865, 416). Hydrogen and chlorine croquet balls received one single arm each, oxygen two, nitrogen three, and carbon four. In this way chemical formulae could be realised in a three-dimensional,

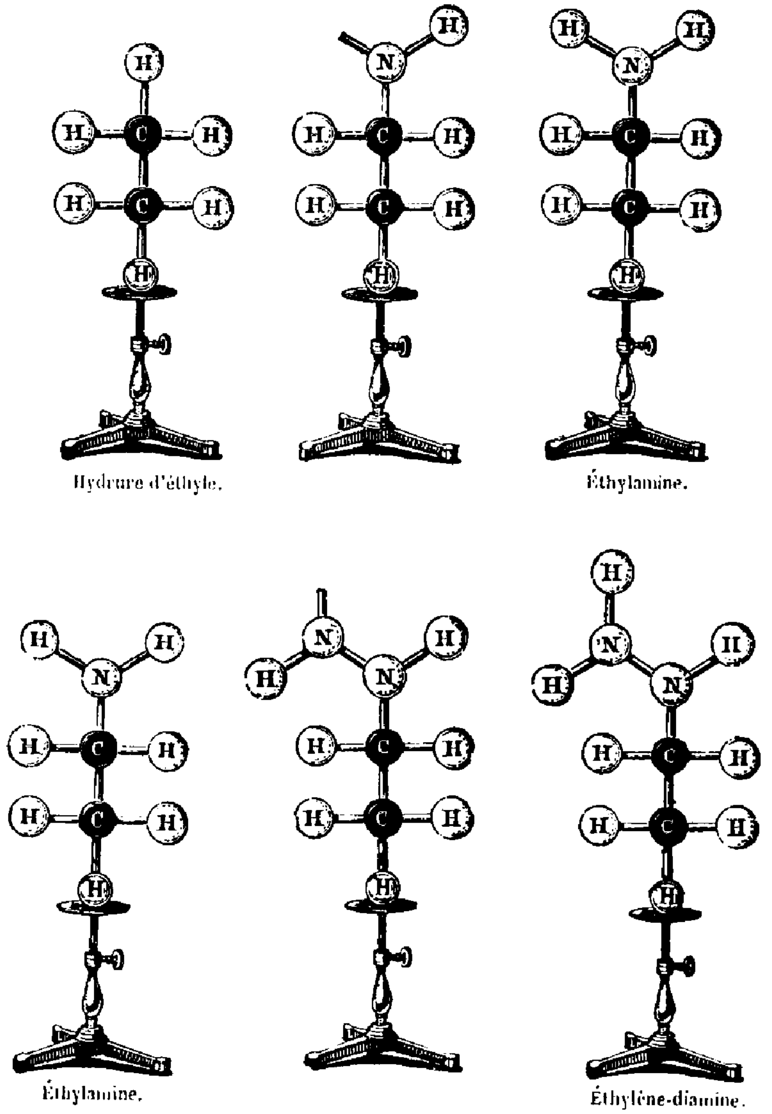


Figure 9.3 August Wilhelm Hofmann's glyptic formulae of 1865: amino derivatives of ethane. Source: Hofmann, *Proceedings of the Royal Institution of Great Britain* 4 (1865): 421.

spatial way. They were therefore called "glyptic [i.e., 'sculptured'] formulae" ("Glyptic formulae" 1867, 78).

Hofmann's new model was based on Crum Brown's 1864 publication, but went one important step further. The croquet balls translated a flat arrangement into a three-dimensional and visually more attractive device. Yet its spatial properties were clearly not a consequence of theoretical considerations, but a mere side effect of using croquet balls to turn lines on paper or a blackboard into a mechanical device to be put on the table of the lecture theatre. Consequently, Hofmann's ball-and-stick model maintained two features of its forerunner: the valencies retained the planar symmetrical orientation, and it was by no means meant to represent the physical arrangement of the atoms.

But the chemical theory did not really matter in this Friday Evening Discourse. What Hofmann delivered in front of the powerful and the leisured was not meant as an introduction to organic chemistry. Instead, it was a most carefully composed performance primarily meant to convey the idea of the chemist as someone who knows how to manipulate matter according to his will, and who will eventually be able to build a new world out of chemical building materials that could be assembled and disassembled *ad libitum*.

> The facility with which our newly-acquired building material may be handled, enables us to construct even some of the more complicated substances.... We are thus enabled, by availing ourselves exclusively of oxygen as building material, to convert the two-storied molecule of hydrochloric acid successively into a three-, four-, five-storied molecule, and ultimately even into the six-storied molecule of perchloric acid; and there is no reason why a happy experimentalist, by using additional and more complicated scaffolding, should not succeed in raising still loftier structures (Hofmann 1865, 418–19).

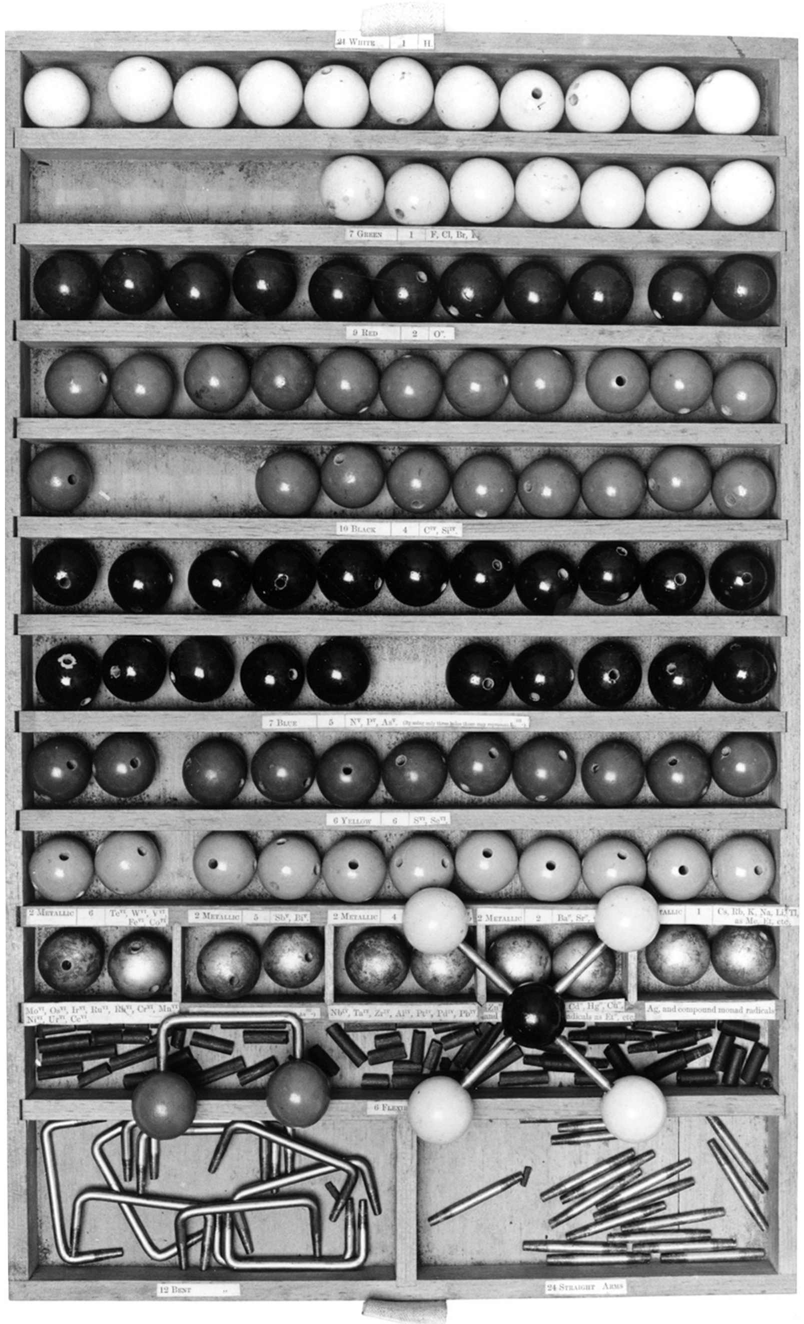
The chemist as the architect of a new world: this was the core of Hofmann's message. In this context the ball-and-stick models created a symbolic space, the conquest and control of which the chemist proved by the skilful use of his hands. The lofty and colourful structures of hydrocarbons that covered the desk at the end of the lecture may have conveyed to the audience the imaginary skyline of a world within the reach of man's constructive power: "It is scarcely necessary to expand on these illustrations, and if I venture to raise up a few more of these mechanico-chemical edifices, it is because I want to show you that our building stones are available for many purposes" (Hofmann 1865, 424). Appropriately, the lecture ended by referring to the "sense of mastery and power" associated with the "great movement of modern chemistry" and by invoking "the grandeur belonging to the conception of a world created out of chaos" (Hofmann 1865, 430).

In Hofmann's hands the structural theory of organic chemistry was translated into rules for construction and put into practice. It was a maker's vision of the future of chemistry. Whether his models were true representations of reality mattered little as long as they supplied precepts for chemical syntheses. For Hofmann chemistry was a "magical tree, reaching out in every direction with its branches and twigs and ramifications" (Hofmann 1890, 41; Brock, Benfey, and Stark 1991; Brock 1992; Meinel 1992, 1995) and his research programme followed this same agenda. In the laboratory the assembly-kit principle worked surprisingly well, and the systematic charting of whole classes of substances soon became the standard approach to the chemistry of synthetic dyestuffs and thus to the first major success of a science-based industry.

"ANYTHING BUT ABSTRACT CHEMICAL TRUTH"

Hofmann's Friday Evening Discourse appeared with plenty of illustrations in the 1865 volume of the *Proceedings of the Royal Institution* and was reprinted in the widely read *Chemical News* of 6 October 1865 (Hofmann 1865). In May 1867 the journal *The Laboratory* inserted a brief editorial note advertising a set of Hofmannian "glyptic formulae" for "those teachers who think, with Dr. Frankland and Dr. Crum Brown, that the fundamental facts of chemical combination may be advantageously symbolised by balls and wires, and those practical students who require tangible demonstrations of such facts" ("Glyptic formulae" 1867, 78). Made by a certain Mr. Blakeman of Gray's Inn Road, London, and supplied in a box of 70 balls with brass rods, straight or bent, and some rubber bands, the set was praised for the striking constructions that could be assembled from it, "more likely to rivet the attention of students than chalk symbols on a blackboard" ("Glyptic formulae" 1867, 78).

It is difficult to tell how much such model kits were used. The scarcity of examples in museum collections argues for their being used up in classroom teaching and thrown away afterwards: transient objects that could be made out of cheap materials by even the least skilled laboratory assistant. Accordingly, most surviving molecular model sets have no manufacturer's name, although size, design, and colour codes are very similar. An early boxed set, now kept in Oxford (Fig. 9.4), contains coloured wooden balls



of 30 mm diameter to represent hydrogen (white), halogen (green), oxygen (red), carbon or silicium (black), nitrogen or arsenic (green), sulphur or selenium (yellow), and the metals (silver). Holes drilled into the atom balls mark the respective number of binding units to be joined mechanically by means of the straight, bent, or flexible arms contained in the same box.[5]

Contemporary debates about the use of such models in chemistry courses are almost non-existent, and in general very little is known about the methods of classroom teaching at that time. Molecular models may have been popular for disseminating scientific education, but it is likely that their adoption met with scepticism from the beginning. Even the very first advertisement—most unusually for this genre—contains two warnings. The first makes clear that it might be dangerous to mix up serious science and children's toys: "At first sight, the collection of bright-coloured and silvered balls suggests anything but abstract chemical truth, and a very young philosopher might excusably convert them to purposes of exclusively recreative science." The second warning is even more interesting, for the unknown author writes somewhat cryptically: "Whether they [these models] are calculated to induce erroneous conceptions is a question about which much might be said" ("Glyptic formulae" 1867, 78).

Physical models were indeed looked upon with suspicion by many a scientist. In a meeting of London's Chemical Society on 6 June 1867, Benjamin Brodie, the most ardent critic of atomism in Britain, ridiculed the ball-and-stick model as a materialistic bit of joiner's work. Referring to Mr. Bateman's kit advertised in *The Laboratory*, he continued:

lak [[Blakeman]]

> [T]he promulgation of such ideas—even the partial reception of such views—indicates that the science must have got, somehow or another, upon a wrong track; that the science of chemistry must have got, in its modes of representation, altogether off the rules of philosophy, for it really could only be a long series of errors and of misconceptions which could have landed us in such a bathos as this (Brodie 1867, 296; Brock 1967).

Figure 9.4 Hofmann's glyptic formulae, circa 1870. The case (630 × 310 × 60 mm) contains 109 wooden atom balls (diameter 30 mm) plus 24 straight, 12 bent, and 6 flexible arms. Source: Museum of the History of Science, Oxford, inv. no. 42347 (for further pictures and descriptions, see Hill 1971, no. 395; Turner 1983, fig. xix; Turner 1991, 295).

Two years later William Crookes, a former assistant of Hofmann and at the time well known as an independent chemist and experimenter, advised an unknown correspondent of *Chemical News*:

> As you are a student of chemistry, take our advice, and leave atoms and molecules alone for the present. Nobody knows how the atoms are arranged in elements of different atomicities. Graphic formulae, diagrams, etc., are only artificial aids to fix certain properties of bodies on the memory; but no one intends them to represent the architectural plan and elevation of the body. Avoid theory: stick to experiment (Crookes 1869).

Edward Frankland on the other hand, Hofmann's successor at the Royal College of Chemistry, was one of the early converts to using models in teaching. His *Lecture Notes for Chemical Students*, written on the basis of lectures given in the winter of 1865–66, was the first textbook to use Crum Brown's graphic formulae systematically—despite the problems they created for the printer (Russell 1996, chap. 10). Frankland is also known to have used Hofmann's ball-and-stick models in the classroom, as he believed that their pedagogical advantages would outweigh their epistemological deficiencies.

> I am aware that graphic and glyptic formulae may be objected to, on the ground that students, even when specially warned against such an interpretation, will be liable to regard them as representations of the actual physical position of the atoms of compounds. In practice I have not found this evil to arise; and even if it did occasionally occur, I should deprecate it less than ignorance of all notion of atomic constitution (Frankland 1866, v–vi).

For similar reasons the cautious use of models was recommended "for lecture illustrations" by Carl Schorlemmer, the first professor of organic chemistry at Owen's College in Manchester. In this context Schorlemmer explicitly referred to the use of globes in geography; there was no danger that any student "should acquire curious notions about the brazen meridian, or the wooden horizon". Nevertheless he recalled that, due to the naïve use of atomic models in chemistry courses, "it happened indeed that a dunce, when asked to explain the atomic theory, said: 'Atoms are square blocks of wood invented by Dr. Dalton"' (Schorlemmer 1894, 117).

As a rule, these early molecular models appeared in the context of teaching, not research,and they seem to have been fairly popular—at least in Britain (Russell 1996, 284–303). On the European continent the situation was different. In France the atomic theory was a minority view vigorously opposed by the powerful Paris-based schools of Jean-Baptiste Dumas and Marcellin Berthelot. There was an early French translation of Hofmann's 1865 Royal Institution Discourse, issued by the prolific Jesuit populariser and physicist Abbé François Moigno (Hofmann 1866), but this favourable reception remained an exception. Even Adolphe Wurtz, one of the few defenders of chemical atomism in France, did not adopt the new visual aids—with one notable exception: At the 1876 meeting of the French Association for the Advancement of Science Wurtz used them in front of a general audience; but after the lecture he admitted in a somewhat sceptical tone, "I have constructed this formula [rosaniline] from black, white, green balls, which represent the atoms of carbon, of hydrogen, of nitrogen. They understood that, or they believed they understood, for they clapped. I am almost proud of this success for the theory".[6]

In Germany, too, the prevailing attitude required that science should stick to facts and data produced in the laboratory, and refrain from speculation which was still tainted by association with Romanticism. The usual distinction between chemical and physical atoms provided a common denominator for those who did not want to engage in metaphysical debates about the existence of atoms, but rather sought to pursue chemistry pragmatically (Nye 1989; Görs 1999). For the same reason most publications continued to use the old empirical formulae, which gave only the quantitative composition, or a modified type-theory notation. It is interesting to note that even Hofmann, when he returned from England in late 1865, turned to a facts-oriented, atheoretical way of teaching, and there are no hints that he ever used glyptic formulae in his Berlin lectures.

However, the issue was never discussed publicly. In a private letter only Hermann Kolbe, professor of chemistry in Leipzig and one of the most ardent opponents of structural chemistry, having received Frankland's *Lecture Notes* from the author, replied by appealing to the most weighty metaphysical argument, the biblical "thou shalt not make unto thee any graven image":

> Frankly, I believe that all of these graphic representations are out-of-date and even dangerous: dangerous because they leave too much scope for the imagination, as for example happened with Kekulé: his imagination bolted with his understanding long ago. It is impossible, and will ever remain so, to arrive at a clear notion of the spatial arrangement of the atoms. We must

therefore take care not to think of it in a pictorial way, just as the Bible warns us against making a sensual image of the Godhead.[7]

BREAD ROLLS AND SAUSAGES

To what extent such protestations were but part of a widespread rhetoric without being necessarily characteristic of the way chemists thought and practised their science in private, is a difficult question to answer. There was clearly much pressure within the discipline to disclaim realism and to pay lip-service to a stick-to-the-facts attitude. The most notable exception was the group of young chemists who gathered in Kekulé's laboratory at the University of Ghent in Belgium.

By this time Kekulé had established the doctrine of constant valency and the tetravalent carbon atom, and made major contributions to the theory of molecular structure, and was struggling with the benzene problem (Gillis 1967, 1996; Russell 1971, 61–71, 100–7). For it was one of the challenges to the new structural chemistry that it account for the peculiarities of non-saturated and aromatic hydrocarbons. Kekulé's 'bread rolls' or 'sausage formulae', first introduced in his Heidelberg lectures of 1857/58, represent the number of affinity units of the individual atoms by the length of the sausage. Multiple bonds—and this was the advantage of this notation—could now be symbolised by the lateral contact of several valency units. Through Kekulé's *Textbook of Organic Chemistry*, which began to appear in German in 1859, these formulae reached a wider audience. They were adopted in a modified form by Wurtz (Wurtz 1864, 132–38), reappeared in 1865 in Kekulé's sausage formula of benzene (Kekulé 1865, 1866) and were used systematically the same year in Alfred Naquet's *Principles of Chemistry based on the Modern Theories* as a kind of graphic algorithm or "'algebraic scheme" to map the number of possible molecules from a given number of atoms (Naquet 1865).

In Kekulé's view aromatic compounds contain a nucleus of six carbon atoms that form a closed chain of alternating single and double bonds. In print this was rendered as a linear chain of a length corresponding to the number of valencies, with markers on the two unsaturated positions at each end to indicate that they link to make a closed ring. It goes almost without saying, however, that the odd sausage-shaped form of the carbon was not meant to represent the true form of the atom, as this would have clearly offended the traditional iconography of the atom as a little sphere (Lüthy 2000).

It is likely, therefore, that Kekulé favoured the more abstract, linear representation in order to avoid a too-realist reading of his sausage formulae (Kekulé 1861–66, 1: 159 n).The original version, however, was more tangible. Already in the 1857 Heidelberg lectures Kekulé had used 3-D models assembled from well-turned wooden balls; he used the same type of device when he discussed the benzene hexagon in 1865 (*Tussen kunst* 1992, 93) (Fig. 9.5).

Thus between 1860 and 1865 a number of chemists were engaged in the search for a new visual language that would give mental images to the new structural chemistry. Paul Havrez's curious speculations about molecular symmetry that took Kekulé's benzene model as their point of departure (Havrez 1865; Kekulé 1861–66, 2: 515 n; Heilbronner and Jacques 1998a and b), and Joseph Loschmidt's *Constitutional Formulae in Graphic Representation*, designed after a quasi-cosmological idea of atomic interaction with different 'spheres of action' (Loschmidt 1861; Wotiz 1993; Schiemenz 1994; Eliel 1997; Heilbronner and Hafner 1998) belong to the same context. Though clearly not meant to represent physical reality, these were attempts to overcome the merely stoichiometric and a-visual tradition of chemistry and tentatively to inscribe the new notions of valency and molecule into a form that would give them, in Loschmidt's words, "immediate figurative quality" (*unmittelbare Anschaulichkeit*) (Loschmidt 1861, 4).

In 1865 Kekulé adopted Crum Brown's graphic formulae and their didactic counterpart, namely Hofmann's ball-and-stick models. The latter may have been brought from London by Kekulé's assistant Wilhelm Körner, who went there to buy laboratory equipment for his master. From the practical point of view, however, Hofmann's model was deficient in one regard: multiple bonds, a key problem for the doctrine of valency in explaining the structure of non-saturated and aromatic compounds, were difficult to realise with the stiff metal joints. Commercial Hofmann/Bateman model kits provided U-shaped bridges or rubber joints for this purpose, but the resulting structures were not easy to assemble. In addition, the use of two different sorts of bonds, namely the short straight line between the two atomic centres and the much longer curved bond that bridged them, added another question mark to an already questionable model. Furthermore, Hofmann's glyptic formulae did not really provide what Kekulé was looking for at the time: representations

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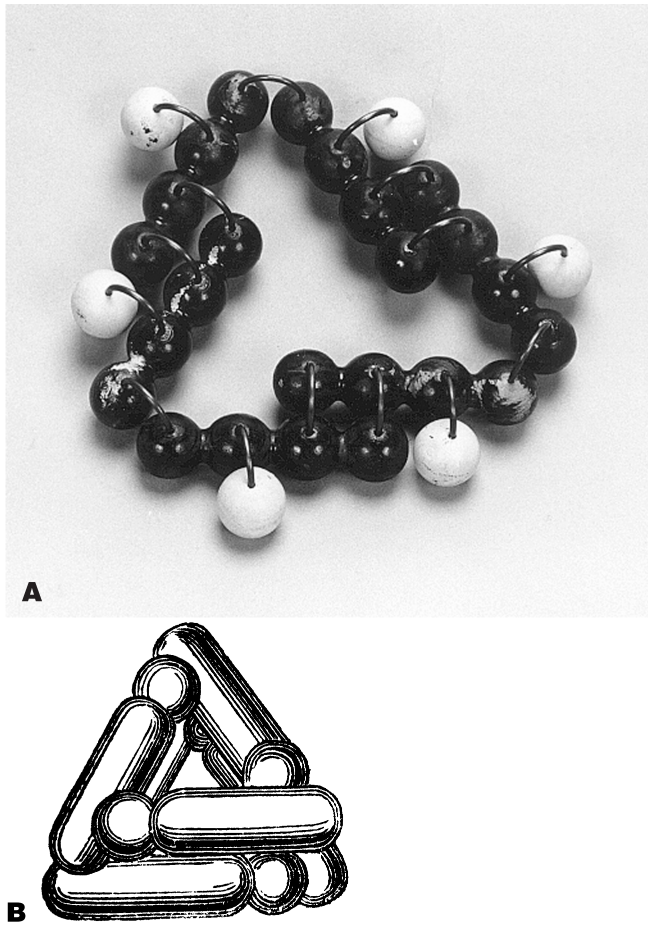

Figure 9.5 August Kekulé's benzene model of 1865 and Paul Havrez's graphic representation in Kekulé's textbook. The four-membered C-'sausages' are made from one piece of wood, the connecting tubes are of metal; total dimensions of the benzene ring circa 15 × 15 × 2 cm. Sources: Museum Wetenschap en Techniek, Ghent, inv. no. MW95/118; Kekulé, *Lehrbuch der Organischen Chemie*, vol. 2 (Erlangen, 1866), 515.

of molecular structure that would show spatial arrangements—if not necessarily in a realist sense. The English ball-and-stick models were three-dimensional in the restricted sense that they translated drawings on paper into a bigger, and hence more visible and more attractive, lecture-hall device.

But with their planar valencies Hofmann's glyptic formulae only appeared to be spatial, whereas, if taken seriously, everything remained in the plane and the model offered no real advantage compared to the drawing (Kekulé 1867, 218).

ARMS, SOCKETS, EYES, AND THE CONSTRUCTION OF THREE-DIMENSIONALITY

In late 1866 Kekulé received a set of Dewar's brass-bar models from Playfair in Edinburgh, and arranged for the young author to spend the next summer in his Ghent laboratory. In the same year the university hired Theodor Schubart as a new mechanic to work for Kekulé. During the spring of 1867 Kekulé, Körner, and Schubart were busily experimenting with molecular models intended for teaching purposes. In April 1867 Körner wrote to Kekulé: "Your benzene models are all painted, and Schubart has finished the stand.... The little spheres are as colourful as Easter eggs, and I am waiting for your order to send them. They can easily be packed in a small cigar box".[8] These new models took Hofmann's glyptic formulae as their point of departure. But the latter were modified such that the valency arms of the black carbon balls were no longer in a planar orientation but pointed to the edges of a tetrahedron. When their lengths were appropriately chosen so that the free ends were at equal distances, double and even triple bonds could be realised without bending (and possibly breaking) the thin brass tubes. The touching arms were joined by a straight slit-tube fastener or, in the case of angular bonds, by small brass sockets that could be joined by a ring looped through little eyes drilled through their ends. The white hydrogen and green chlorine atoms received brass tubes of an appropriate size so that the valency arms of the carbon could be plugged into them. In order to put the entire molecule on the lecture-hall desk some of the carbon atoms had little sockets to fix them on a firm stand (Anschütz 1929, 1: 356).

It seems as if in the beginning the introduction of the tetrahedral carbon atom was merely a technical trick to improve the joining of their valency sticks and to give the model a spatial appearance. There were of course ideas about molecular symmetry in the background, and Kekulé may also have recalled that Alexander Butlerov, a colleague from his years in Heidelberg, had tentatively suggested a tetrahedral carbon five years earlier. Despite this, Kekulé's new model was not introduced in order to solve any theoretical problems. Rather, it offered a solution to a mechanical problem and to the quest for *Anschaulichkeit*. And it was to a partly non-chemical audience that Kekulé presented his model for the first time at the assembly of German naturalists and doctors in 1867 in Frankfurt am Main (*Tageblatt* 1867, 95, 114).

FROM TEACHING AID TO RESEARCH TOOL

Designed as didactic devices, Kekulé's molecular models soon turned into research tools that could be used to interpret and guide chemical reactions. The first application in a research context was Kekulé's own paper on trimethyl benzene, the formation of which from three acetone units could thus be demonstrated convincingly (Kekulé 1867, 218). This same paper presented Kekulé's new model for the first time in print (Fig. 9.6A), and one also learns that the formulae in the article were drawn after a physical model (Fig. 9.6B).

Once chemists had become used to this form of representation and learned to read spatial meaning, the new model could be applied to understanding unknown mechanisms and predicting possible reactions by giving them visual plausibility. As a consequence, we find these models being used by students and pupils of Kekulé who had been accustomed to looking at, and to thinking of, molecules in this new spatial manner.

As early as November 1867 Körner wrote to his master enthusiastically that, according to the model, there should be five isomers in a given compound instead of three as had been previously believed.[9] Two years later, he applied the model to a major deficiency of Kekulé's benzene formula. A hexagon with alternating double and single bonds would have yielded two different bisubstituted derivatives, depending on whether the substituents had a single or a double bond between them. Such isomers, however, do not exist and the formula needed to be reinterpreted. Körner solved the problem by altering the spatial configuration of the benzene nucleus. He abandoned the flat ring and linked each carbon atom with three others to yield a space-filling structure. The crucial innovation was the way he made use of the model. In order to test the steric possibility of the resulting structure, Körner demonstrated its feasibility by assembling his 3-D benzene from a ball-and-stick model (Koerner 1869; Schütt 1975; Paoloni 1992) (Fig. 9.7).

The step from interpretation to prediction by means of the model was achieved in the same journal in a paper by Emmanuele Paternò, Körner's friend and a fellow assistant in Stanislao Cannizzaro's chemical laboratory

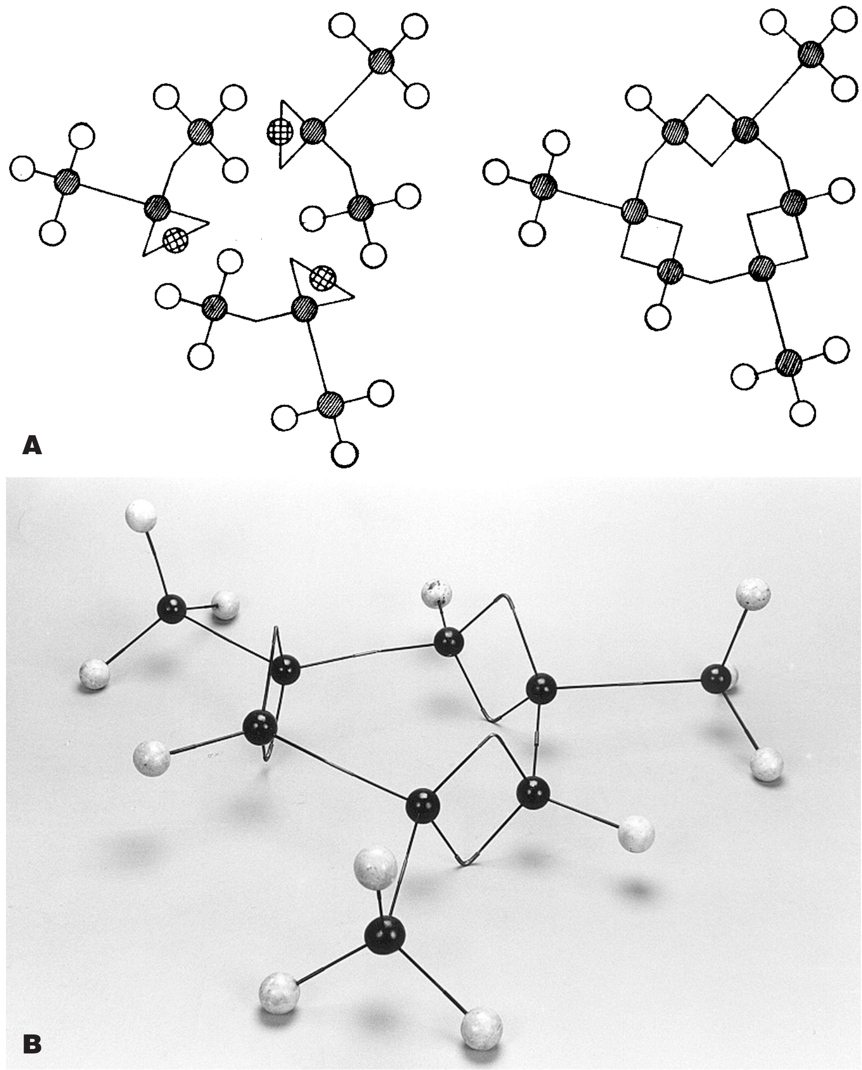

Figure 9.6 Mesitylene (1,3,5-trimethyl benzene), which is made of three molecules of acetone, as illustrated by August Kekulé using a tetrahedral carbon model. (A) Kekulé's figure, from "Über die Constitution des Mesitylens", *Zeitschrift für Chemie*, new ser., 3 (1867): 218. (B) An assembled mesitylene model, measuring circa 60 × 60 × 15 cm. Source: Museum Wetenschap en Techniek, Ghent, inv. no. MW95/116.

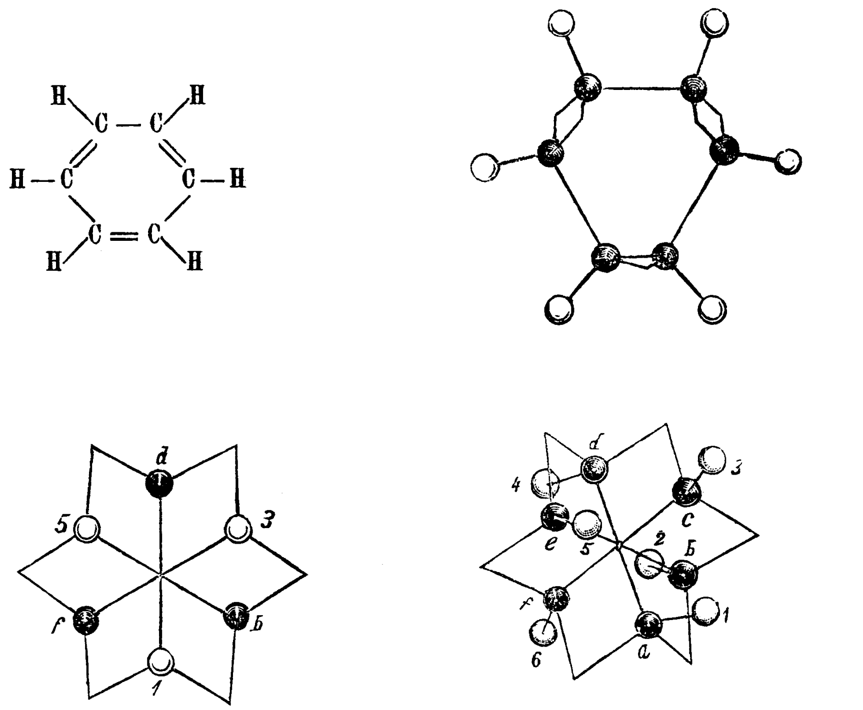

Figure 9.7 Wilhelm Körner's benzene model. Top: Kekulé's benzene formula realised by his tetrahedral carbon model. Bottom: Körner's proposal with the carbon atoms (dark spheres) roughly in what would today be a 'chair' conformation, three hydrogen atoms above and three below the C_6H_6 nucleus. Source: Körner, *Giornale di Scienze Naturali ed Economiche di Palermo* 5 (1869): 237, 241.

in Palermo. Working on halogenated ethanes Paternò predicted that there should be two isomers of the general formula $XH_2C–CH_2X$, depending on whether the halogen atoms point to the same or different directions of the tetrahedral carbon. If this were true the isomers could, at least in principle, be isolated by appropriate measures (Paternò 1869). In this argument, however, the use of the model was pushed much further than had been originally intended. The original ball-and-stick models were meant to represent only the atoms, their valencies, and their arrangement. They were essentially ball models, and the sticks just mere auxiliary means of denoting the number of valencies and joining balls that would otherwise have fallen apart. Paternò took the sticks seriously, so to speak, and imagined from their stiffness that the C–C bond would likewise be stiff. For his two isomeric 1,2-dibromoethanes would exist only if rotation about the carbon–carbon bond was restricted.

At a time, however, when the realist interpretation of a molecular model was still extremely controversial, no other chemist would have gone so far as to speculate about the rotation of bonds, which were, after all, not yet generally considered as physical entities. One should also bear in mind that the very publication of such speculations, done under Cannizzaro's patronage at the periphery of Europe, would have been much more difficult in the centres of nineteenth-century chemical orthodoxy such as Germany or France.

When Jacobus Henricus van't Hoff, who had been working with Kekulé in 1872–73, published his *Arrangement of Atoms in Space* in 1874 and thereby established stereochemistry, he could not only build upon an existing tradition of using 3-D models as didactic devices in chemical teaching, but may also have known about the first attempts to derive stereochemical consequences from them. We have no trace of an immediate influence, but it is evident that the problems van't Hoff was about to solve belong to the common context of understanding molecular complexity by introducing a new visual language to deal with the spatial properties of molecules. The solution he offered was different from the one Kekulé had proposed seven years earlier, but it is not unreasonable to assume that the model kits used in that group prepared him to think of chemical molecules in a visual way and in terms of three-dimensional structures.

New views do not emerge at once, nor do they spring from a single discovery. The chemists prepared 3-D models for teaching purposes, and in using them they learned to link the mind's eye with theoretical notions, with the manipulating hand, and with laboratory practice. Still, it took almost a decade before this gave birth to the new steric conception of matter. As there was surprisingly little discussion of epistemological questions and theoretical consequences of this approach, our story cannot be subsumed under the common nineteenth-century predilection for mechanical models in physical explanations; though these were a matter of vivid debate. The introduction of 3-D molecular models was not exclusively, nor even predominantly, part of a theoretical discourse, as is often assumed in the literature. Instead, the models were primarily used as tools for the creation of new types of *Anschauung* not only in the audiences taught, but also in the minds of those who developed these tools in struggling with the growing complexity of chemical constitution. And this approach was not peculiar to chemistry, but part of a more comprehensive change in perceiving the world and in dealing with it in a purposeful manner.

CONSTRUCTION THINKING AND THE CONQUEST OF SPACE

Reducing complexity to the simplicity of hidden structures, and using structural thinking in a constructivist way was not restricted to science. The nineteenth century was a culture of construction (Ferguson 1992; Peters 1996; König 1997). Modes of thinking peculiar to engineers and architects established their primacy over traditional scientific or humanistic thought. Builders' thinking deals primarily with how to make; it mediates between concepts of form, methods of science, and practical ways of dealing with materials. Space is one of its main concerns, as the spectacular iron constructions of the time so impressively testify.

Beginning in the late 1860s a discussion began among British engineers and architects about the primacy of an 'aesthetics of construction' over an 'aesthetics of decoration'. London's new St. Pancras Station, built in 1869 by George Gilbert Scott and W. H. Barlow for the Midland Railway Company with the widest span of any roof then in existence, was the primary example of a new type of structural and constructivist building by means of mouldings and standardised parts. At the same time the pages of the London weekly *The Building News and Engineering Journal* testify that, interspersed in between articles on gothic and neo-Palladian architecture, suddenly a new type of mostly anonymous articles appeared, devoted to topics such as the primacy of construction, the use of moulds, or the visibility of natural laws in the structures of buildings as first and foremost exemplified by iron bridges and railway stations. In one of the rare programmatic contributions of this kind, Britain's prevailing architectural taste was criticised as lacking true creativity and beauty. This could only be based upon the principles of science and construction, and if their devotees

> were to begin by an experimental study of stones, and bricks, and timber, investigating their qualities, and making tentative efforts of combination, or exercising their minds with at least the simpler ideas of form and construction, investigating the properties of geometrical solids, cones and cylinders, . . . and other mechanical forms of construction, we should have a race of intellectual architects, whose minds, trained practically in the school of thought and

invention, would outrival in their efforts all existing art by the very strength and vigour of their competitors ("Theory of the Arts" 1871, 209).

The builders' approach was by no means confined to architecture. A few years after the spectacular opening of Joseph Paxton's famous Crystal Palace, built for the Great Exhibition of 1851, and more than a decade before Hofmann invented his ball-and-stick model, toy boxes were sold in London and elsewhere, that enabled children to create a variety of polygonal forms by connecting peas or balls of wax by means of toothpicks (Brosterman 1997, 84) (Fig. 9.8).

Construction kits of this type originated with *Kindergarten* pedagogy. They were particularly designed to enable children to acquire a first notion of space (Brosterman 1997, 84; Ronge and Ronge 1855). According to Friedrich Fröbel's developmental psychology young children acquire their knowledge about the external world empirically by actively manipulating its particulars. Trained as an architect and later a student of physics, chemistry, and mineralogy, Fröbel was an assistant to Christian Samuel Weiss, the founder of modern crystallography, before he abandoned science and turned to pedagogy. In 1837 he opened the first *Kindergarten* for early childhood education. The *Kindergarten* movement spread rapidly through most of Protestant Germany, and after the failed revolution of 1848, liberal emigrée women brought it to Britain and the United States.

The foremost educational aids of the *Kindergarten* were geometric toys, meant to support the child's self-activity in exploring the world. Fröbel's typical *Kindergarten* 'gifts' (*Gaben*) were geometrical bodies, such as spheres, cylinders, and cubes, that would enable the child to apprehend and represent the external world and thus to train the mind's eye. By actively handling physical objects the invisible was thus to be grasped in a visible form, and an inner vision (*Anschauungsform)* of the world and the self would emerge (Fröbel 1974, 129).

Brick boxes made of little wooden cubes were particularly successful. From the 1840s Fröbel kits were commercially produced and became part and parcel of the *Kindergarten* movement.In the 1850s major international firms such as Myers & Co. in London and Milton, Bradley & Co. in Springfield, Massachusetts, started to produce them for a growing international market. Even more successful were Gustav Lilienthal and his brother Otto, the aeroplane pioneer, who, in 1875, invented a process for making artificially coloured stones for brick boxes that were mass produced and sold

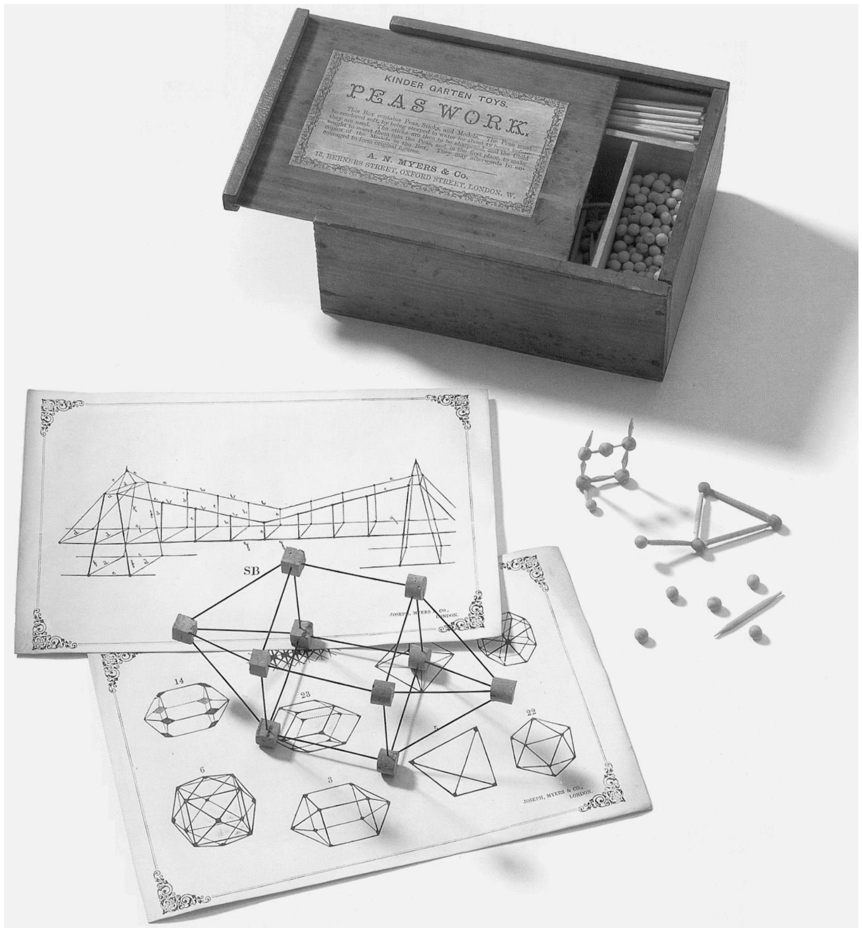

Figure 9.8 In the early 1850s the 'Peas Work' was added to the Fröbel Gifts in order to build three-dimensional structures. Top: a box of peas and toothpicks made by A. N. Myers & Co. in London. Bottom: a more elegant version with little cubes of cork manufactured by Joseph, Myers & Co. in London ca. 1855. Source: Norman Brosterman, *Inventing Kindergarten* (New York, 1997), 84.

worldwide by F. A. Richter & Co. in Rudolstadt, Thuringia, under the trade mark *Anker-Steinbaukasten*—a precursor of today's *Lego* (Noschka and Knerr 1986; Leinweber 1999).

As far as appearance, use, and implicit philosophy are concerned, the correspondences between Hofmann's type moulds, his ball-and-stick models, and the Fröbel gifts are striking. Both were symbolic tools for exploring abstract structures and training the mind's eye by manipulating physical objects. Both had their own syntax built into their mechanical joints, and both carried an implicit message that went beyond epistemology: the bourgeois ideal of taking possession of space by constructing it.

Of course we do not need to assume that Hofmann and his fellow chemists took *Kindergarten* toys as their source of inspiration. Yet at the time it would have been almost impossible not to be familiar with their existence and meaning. The sheer explosion of assembly kits during the second half of the nineteenth century testifies to the spread of construction thinking through Europe. The Fröbel gifts and the molecular models were part of this same movement.

CONCLUSION

Models have various messages and can be put to various uses. Richard Buckminster Fuller, the architect who invented the geodesic dome and whose name is commemorated in the football-shaped $C_{60}H_{60}$ fullerene structure first identified in 1985, recalled having used Fröbel's 'Peas Work' haptically to discover structures and construction principles he had been unable to grasp otherwise because of his bad eyesight (Brosterman 1997, 84). Hofmann, the chemist who initially wanted to become an architect before he was drawn into chemistry by Justus Liebig, used painted croquet balls instead of vulgar peas to present Victorian gentlemen with the vision of he chemist as the builder of a new world out of man-made materials ~~when he addressed~~. Kekulé, he too a would-be architect in his early years, converted the planar ball-and-stick models into truly space-filling constructions, but the tetrahedral carbon atom, by which this was achieved, was initially a mere trick to improve both the appearance and the joining of the model. In all of these cases the models have a life of their own. They are neither mere representations of scientific theories or data, nor are they purely practical tools. This partial autonomy, which is partly embedded in their physical structure, is a tricky thing, for it may give birth to developments not intended by those who made these models. At the same time—and this seems to be peculiar to chemistry—they provide a material link between theoretical notions, chemical reactions, and the body and gestures of the chemist.

Throughout the period considered in this chapter, the meaning of these models remained liable to more than one interpretation and more than problematic from an epistemological point of view. Yet it seems plausible that this very ambiguity explains their success. For models mediate between audiences without dividing them as theoretical or ideological language would do. They mediate between the mind and the hand; they symbolically connect what the chemist thinks with the substances in his flasks and the operations he performs with them. But models also mediate between teacher and pupil, and between expert and general public. In doing so, they transmit a variety of messages, both explicit and hidden (Hoffmann and Laszlo 1991; Laszlo 1993; Schummer 1999–2000). And as their language was in accordance with the constructivist thinking prevailing at the time, these messages were easily understood even without being publicly discussed. In this way the molecular models invented by chemists in the 1860s created a symbolic and gestic space into which theoretical notions, bodily actions, cultural values, and even professional claims could be convincingly inscribed. The models could then be used to conquer new spaces of possibility by those second-generation students of chemistry who had become accustomed to thinking and working in three dimensions.

NOTES

1. The Science Museum, London, has ball-shaped atomic models said to have been made for Dalton, at his suggestion, around 1810 (inv. no. 1949-21; depicted in Thackray 1970, 266, fig. XII). There is another set of wooden balls of various sizes, believed to have been used by Dalton, with holes drilled to allow them to be joined by pins (Museum of Science and Industry, Manchester, acc. no. 1997.6.53).

2. No. 195 lists the items individually: carbon (black), hydrogen (pale blue), oxygen (scarlet), nitrogen (white), chlorine (pale green), sulphur (yellow), phosphorus (pink), light metals (gold bronze), heavy metals (copper bronze), organic radicals (blue and black), and neutral gases (brown).

3. For similar items, see Hill 1971, 62–63; and Ramsay 1974, fig. 4 and note 24.

4. A set given to Kekulé by Lyon Playfair in 1866 is said to have survived in Bonn until 1925 (Anschütz 1929, 1: 357), but none seems to be extant.

5. There is another surviving kit of circa 1870 from the laboratory of Thomas McLachlan, a London consultant. The black carbon balls are drilled with four holes giving four planar bonds; but one of the black balls has extra holes drilled into it to create a tetrahedral carbon atom (Science Museum, London, acc. no. 1964-495). The Science Museum also has a hybrid form of Hofmannian glyptic formulae with tetrahedral carbon atoms in a beautiful mahogany case made in Spain. The maker's plate inside the lid reads "Coleccion para demonstrar las Combinaciones Quimicas

según A. W. Hofmann, constructor Gonzalez Verdiguier, Madrid" (Science Museum, London, acc. no 1977-126; reproduced in Knight 1997, 385).

6. Wurtz to Auguste Scheurer-Kestner, 29 August 1876, Bibliothèque Nationale et Universitaire de Strasbourg, ms. 5983, Correspondance d'Auguste Scheurer-Kestner, fol. 466. Alan Rocke kindly pointed me to this source.

7. Kolbe to Frankland, 23 July 1866, as translated in Rocke 1993a, 314; see also Kolbe to Frankland, 9 July 1867, quoted in Russell 1996, 285.

8. Körner to Kekulé, 25 April 1867, Kekulé-Archiv, Technische Universität Darmstadt.

9. Körner to Kekulé, 4 November 1867, ibid.; see also Klooster 1953.

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