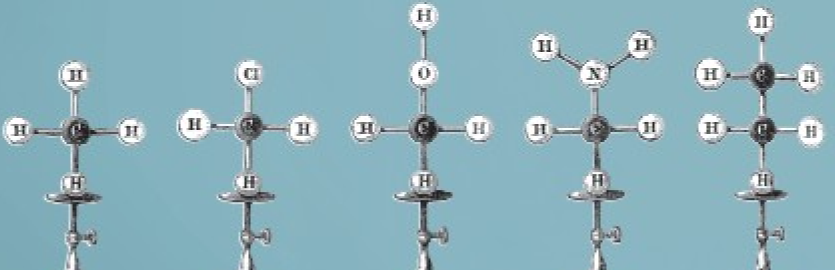
IMAGE & REALITY

KEKULÉ, KOPP, AND THE SCIENTIFIC IMAGINATION



ALAN J. ROCKE

Image and Reality

synthesis

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Image and Reality

Kekulé, Kopp, and the Scientific Imagination

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Dedicated to the memory of

AARON J. IHDE (1909–2000)

AND

FREDERIC L. HOLMES (1932–2003)

Contents

Preface

[P]hysical investigation, more than anything besides, helps to teach us the actual value and right use of the Imagination . . . which, properly controlled by experience and reflection, becomes the noblest attribute of man; the source of poetic genius [and] the instrument of discovery in Science . . .
B. C. BRODIE, SR.[1]

We chemists talk in our own special language . . . [I]n the final analysis we think in definite ideas [in bestimmten Vorstellungen], according to which we tell beforehand the course of the phenomena to be examined or confirmed by experiment. If we want to make ourselves understood, it is necessary that such associations of ideas [Ideenassociationen] be self-evident for both speaker and listener. THEODOR CURTIUS[2]

For the past several years, *Science* magazine and the National Science Foundation have jointly sponsored a "Science and Engineering Visualization Challenge," a program designed to celebrate and reward the creation of beautiful scientific imagery. The winning entry for 2006 was a computer-generated rendering of five famous mathematical surfaces. The images' creators, Richard Palais and Luc Bernard, pointed out that more than beauty is involved. They wrote, "Mathematicians have always needed to 'see' the complex concepts they work with in order to reason with them effectively. In the past, they conjured up mental images as best they could, but the wonders of computer graphics provide them with far more detailed pictures to think with."[3]

[1] Brodie, address by the president (1859), 165.
[2] Curtius, *Bunsen als Lehrer* (1906), 4.
[3] Nesbit and Bradford, "2006 Visualization Project" (2006), 1729.

Such historians as Martin Rudwick in the history of the earth sciences, Gerald Holton and Arthur Miller in Einstein studies, and Peter Galison in twentieth-century physics are representative of a movement of scholars who have been concerned to demonstrate the essential role of visual culture within the history of science. Many have rightly argued that images can serve not merely as discretionary illustration, but as constitutive elements of scientific argument. Norton Wise has urged historians to bridge the gulf between scientists' use of analogies and models on the one side, and their use of the visual and other senses (including visual mental images) on the other, by exploring what he calls a "materialized epistemology." And Ursula Klein has helped open our eyes to the transformations that "paper tools" have effected over the last two centuries.[4]

The present work has much in common with the contributions of these scholars, but offers a somewhat different orientation. For one thing, I want to focus not on material images or paper tools such as diagrams, pictures, or other physical representations, but on what these things suggest for understanding more broadly how scientists think through their work. I want to examine historically the role of the visual imagination in the pursuit of science. My sense is that human minds work far more visually, and less purely linguistically, than we realize. Jacob Bronowski once wrote, "Many people believe that reasoning, and therefore science, is a different activity from imagining. But this is a fallacy . . . Reasoning is constructed with movable images just as certainly as poetry is."[5] If this is true, then we need to focus far more than we have on the role that such "movable [mental] images" have played in the history of scientific thought.

The second way in which my approach differs from most past studies is my choice of field of application. I suggest that chemistry—nineteenth-century chemistry in particular—holds a special place in this story, since the primary objects of chemical investigation, atoms and molecules, were and are beyond the direct reach of our bodily senses. In fact, I argue that it was chemists who were the first to move

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[4] Wise, "Making Visible" (2006), 81–82. In coining this term, he is intending to generalize Pamela Smith's phrase "artisanal epistemology"; Smith, *Body of the Artisan* (2004), 59. See also Klein, *Experiments, Models, Paper Tools* (2003); and Klein, ed., *Tools and Modes of Representation* (2001).

[5] Bronowski, *Visionary Eye* (1978), 21. For examples of those who have explored this issue, see Nersessian, *Faraday* (1984); Nersessian, "Opening the Black Box" (1994); Miller, *Imagery in Scientific Thought* (1986); and Gooding, "Picturing Experimental Practice" (1998). A fuller discussion of this historiography is found in the last two chapters of this book.

beyond high-level philosophical speculation regarding the unseen microworld, pursued since antiquity, into the kind of productive, empirically founded, and heuristically powerful investigative programs that have since become routine.[6] The origin of this new phase dates to the years just after 1800, when such workers as John Dalton and Jacob Berzelius began aggressively to pursue the chemical atomic theory. From about 1850, a new generation of chemists found that they could go much further than even Dalton and Berzelius had, building reliable and productive theories of intricate molecular architecture, sight unseen. All of this was well under way when the community of physicists began to follow a similar path.

For centuries, chemists and other natural philosophers had been pondering the invisible microworld. Only now, in the early and middle decades of the nineteenth century, were these conceptual forays transformed into an epistemically robust methodology that could be employed to confidently explore many of the intriguing details of that world. A habitual and recurrent (though nearly invisible) pillar of that methodology, I propose here, was the productive use of the visual imagination. I do not suggest that visual imagery was a new part of chemistry in the nineteenth century. Nor do I believe that that this was the only mental skill required of scientists; nor that the people I study here held a monopoly on this skill. Quite the contrary: I believe that mental visuality has been an important element of scientific thinking throughout history, though there has always been a wide range in the degree of visual skills and proclivities across the spectrum of scientific mentalities. What I do want to propose is that many nineteenth-century chemists learned to apply the technique with particularly pointed effect. They combined their mental images with complex chains of inference reaching from the sensual world right down to the microworld, also using heuristic symbolic tools of paper and of wood, successfully connecting macroscopic evidence to their imagined tableaux.

The magnitude of the chemists' achievement is insufficiently appreciated. Then as now, most chemists live in a world of beakers and flasks, boiling liquids, distillations, recrystallizations, titrations, and so on. Their encounters with matter are all in the world of sensed experience—actual solids, liquids, and gases transforming themselves

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[6] This historical claim is elaborated and defended here passim, but most pointedly in the last chapter of this book. I use the word "microworld" to signify not that which is visible through microscopes, but rather atoms and molecules, which are orders of magnitude smaller than Robert Hooke's fleas or Antonie van Leeuwenhoek's animalcules.

from one physical state to another and from one set of sensual properties to another. From the evidence derived solely from such macroscopic “wet-chemical” manipulations, chemists learned how to explore fine details of the unseen world of atoms and molecules vicariously, and to do so with considerable epistemological confidence. That was a truly heroic intellectual accomplishment—and one that conferred extraordinary new technological power. The spectacular rise of the fine-chemicals industry in the second half of the nineteenth century was made possible largely by this new scientific understanding.

Considering how completely this knowledge has transformed our world, the history of its development is still little explored, by comparison (for instance) to nineteenth-century biology, geology, or physics. Much of the history of nineteenth-century chemistry has been written with a trajectory from John Dalton to Stanislao Cannizzaro to Dmitrii Mendeleev, then to J. J. Thomson, Ernest Rutherford, and Marie Curie. Considering the subsequent history of chemistry and physics, this approach to the nineteenth century appears eminently reasonable. But in the present work I propose a different and arguably more historicist trajectory, one that moves in a synthetic rather than analytic direction, from Dalton and Berzelius to August Kekulé, Archibald Couper, Emil Erlenmeyer, Aleksandr Butlerov, Hermann Kolbe, Adolphe Wurtz, Edward Frankland, J. H. van’t Hoff, Adolf Baeyer, and Emil Fischer. Beyond question, for those who actually lived through the period, the dominating story in chemistry of the 1860s, 1870s, and 1880s was neither the periodic law, nor the search for new elements, nor the early stages of the study of atoms and molecules as physical entities. It was the maturation, and demonstration of extraordinary scientific and technological power, of the “theory of chemical structure”—loosely defined, a set of ideas that enabled one to succeed in tracing and portraying the exact way in which atoms are connected up with each other to form molecules.

This book has three interconnected strands. First, I wish to show how nineteenth-century chemists created a version of “transdiction” or distant inference to the microworld, one that was more powerful than any hitherto deployed. A second objective is to explore some of the mental and material techniques that enabled them to do this. It is obvious that one cannot convincingly achieve either of these historical goals without putting a good deal of scientific flesh on the skeleton, following many of the details in the story of how these chains of inference were gradually constructed and tested. So the present work also pursues a third end, a careful study of the development of structure theory. A spectacular historical instance that I will be using in later chapters as an emblem of the whole is the claimed discovery that one particularly important organic substance, benzene, consists of invisibly tiny molecules, each possessing six carbon atoms arrayed in a symmetrical hexagonal "ring," with each carbon atom bearing a single hydrogen atom on the outside of the circle. I propose that the success that chemists achieved in exploring and manipulating such shadowy objects was materially promoted by their ability routinely to use the visually imagined microworld in scientifically productive ways.

Two of the best-known and most dramatic instances of the use of the scientific imagination are the famous autobiographical anecdotes told by the German organic chemist August Kekulé (1829–96). In a speech given in the last decade of his life, Kekulé recounted how two reveries had led him first to the discovery of the theory of chemical structure, then to the theory of the benzene ring a few years later. These stories have been retold innumerable times, both credulously and incredulously, but they have often been manhandled out of recognition in the act of retelling. Certainly, they have never been investigated with a full understanding of the historical and cognitive context into which they must be fit—a prerequisite that must first be met before using them (along with much other evidence) to draw conclusions about the nature of scientific creativity.

Frederic L. Holmes has justly remarked, "it is from finely detailed case studies of the investigations of highly creative scientists that we are most likely to reach eventually a clearer understanding of the general nature of creative imagination in science."[7] So an essential aspect of my study of the rise of structure theory is to place Kekulé's work in such a more finely detailed context, for I believe that Kekulé was the most supremely successful practitioner of the creative intellectual skills that lie at the heart of the transition I want to study. In the process, I will also closely examine several of Kekulé's mentors, students, associates, rivals, and enemies, from ca. 1840 to ca. 1890, as well as the particularly instructive case of one of Kekulé's most eminent senior contemporaries, Hermann Kopp (1817–92).

My ambition here is not just to write a good history of these events (though I do indeed aspire to that goal), but also to explore why it is

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[7] Holmes, *Lavoisier* (1985), xvii. See also Holton, *Scientific Imagination* (1978); and Gruber and Bödecker, *Creativity* (2005).

that so many members of the chemical community were approaching this set of ideas, from slightly different directions and with slightly different conceptions, at about the same time. The answer to that riddle is not just a matter of the massive development of the empirical content of the science (though this surely played a role), nor is it simply the intensive communications and common sharing of tools, both physical and intellectual, among our cast of characters (which interaction is densely instantiated in the following chapters). It also involves the increasing ability of many leading figures in this scientific community to "see" with their mind's eye, in ways that earlier had not been as possible, or had not become customary to the same degree.

This work elevates scientific *thought* to center stage. Like other mortals, scientists influence—and are powerfully influenced by—the economic, social, cultural, and political currents of their day. Yet from the perspective of the working scientist, the cognitive details of their work form a vibrant foreground for their life, and the internal dynamic of the details of that foreground are "as fresh and new, as underdeveloped, as urgently in need of more concentrated, penetrating analysis as is the study of the social dimension" of scientific work. These again are the words of Larry Holmes, written a generation ago, but the assertion is just as true today.[8] It is equally relevant to suggest that issues of personality often become central for historical understanding; we cannot hope to recapture major pieces of a person's idea-world without understanding something of his psychology and character. As historical sociologists and social historians have rightly emphasized, science is manufactured by whole personalities in rich social contexts, not by free-floating automatons. Robert Richards has remarked, "[W]e catch ideas in the making only when we understand rather intimately the character—the attitudes, the intellectual beliefs, the emotional reactions—of the thinkers in question. Without an initial plunge into personality, logical analysis of the connections of their ideas will be blind, and social construction of their theories empty."[9] In line with these suggestions, in this book I aspire to establish robust interconnections between empirical evidence, personality and psychology, historical context, and the mental images that I believe often materially assist the scientist in the course of fruitful investigation.

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[8] Holmes, "Fine Structure" (1981), 60.

[9] Richards, *Romantic Conception* (2002), 5. Note the allusion to the famous Kantian aphorism: "thoughts without content are empty, intuitions without concepts are blind."

The first chapter of the book turns on a pivot named Alexander Williamson (1824–1904), the English chemist whose landmark paper of 1850 provided more than one new impulse in the science of chemistry. We follow his intellectual formation and set the broader context of what the field looked like on the eve of his entry into the profession. We will see that in Williamson's and other chemists' work there appears a curious tension between two opposing visions of how the microworld might appear if it were of a size susceptible to sensual observation; we will continue to encounter this same tension through the rest of our study. The first of these imagined ontologies takes its cue from parts of Newtonian physics and presents a scene of whirling atomic-molecular particles. At first glance this may seem to be the same as that hypothesized by certain obscure early-nineteenth-century physical theorists interested in mathematically reproducing the known empirical laws governing the behavior of gases. However, the chemists' dynamic microworld, represented in the imaginations of Williamson and others, was distinct from that of early kinetic-molecular theorists. Instead of positing inertial motion and elastic billiard-ball transfers of momentum as some physicists did, these chemical theorists rather vaguely invoked a more direct analogy to the solar system and the operation, in a manner never fully specified, of the force of universal gravitation.

The second vision that we find in Williamson and in many of our other protagonists has some commonality with that of the caloric theory of gases, as well as with the sorts of micromodels that had previously been invoked to understand the science of crystals: more or less stationary fundamental particles held in determinate geometric arrays. In the first third of the century this vision had proven particularly attractive to certain chemists who incorporated it into coulombic (polar electrostatic) theories of chemical composition, but then in the 1840s these electrochemical theories were strongly opposed by the important French theorists Auguste Laurent and Charles Gerhardt. As a young man, Williamson spent three years in Paris under the influence of Laurent and Gerhardt, and this probably formed one reason why Williamson was so powerfully attracted to the alternative dynamic chemical model. But the irony is that from Williamson on, new experiments by these reformers appeared to lead inexorably toward a molecular world in which atoms were viewed to hold roughly stationary positions within the molecule, after all—though not, it would seem, in any sort of electrochemical fashion. Williamson and Kekulé, as well as a number of other chemists of their day, appeared to live (in their mind's eye) in *both* of these imagined worlds, and none was ever fully able to resolve the obvious contradictions between them.

Kekulé and his work until 1864 is the focus of chapters 2, 3, and 4. Williamson was the most important influence in Kekulé's coming of age; in his five semesters as a lecturer at the University of Heidelberg Kekulé both synthesized and fruitfully extended the ideas he had absorbed from Williamson and others. These chapters portray Kekulé as having particularly well-developed powers of mental visualization, probably aided by his early training in arts, crafts, and architecture. Particular attention is paid to his printed sausage-shaped "graphic formulas" (by which was meant fully resolved structural formulas, explicitly mapping all the connections of every atom in the molecule), and to the wooden models of molecules that he used in his teaching. I argue that, like his mentor Williamson, Kekulé was committed to a realist-mechanist orientation toward the molecular world, rather than to the more abstract, conventionalist, or positivist style of Gerhardt, who in many other respects was so influential for both Williamson and Kekulé. The case for this viewpoint is laid out in some detail, both because in the existing secondary literature Kekulé has so often incorrectly been portrayed as an acolyte of Gerhardt's chemical epistemology and because the point is important for the broader argument made in this book. Kekulé's statements were occasionally ambiguous, sometimes deliberately so. We will see that arriving at any consistent understanding of Kekulé's molecular epistemology is challenging under all circumstances and impossible without a broad understanding of both text and context.

Kekulé was not the only important protagonist in the rise of the set of ideas that was ultimately consolidated under the rubric "structure theory"; for example, in addition to Williamson, Adolphe Wurtz, Emil Erlenmeyer, Hermann Kolbe, and Edward Frankland also played vital roles. At the time of the birth of the theory all of these men occupied respected positions in their field. Chapter 5 looks at four *outsiders*—Archibald Couper, Joseph Loschmidt, Aleksandr Butlerov, and Alexander Crum Brown—who at this time were relatively new to the science, but who made their marks in sometimes transformative ways during the years 1858–64. All four had definite ideas on how molecules should be conceived by the scientist and best represented for heuristic purposes. A tour of these figures provides a fuller understanding of the range of responses, opportunities, and creative options that were available during these tumultuous years in the science, and suggests partial reasons why priority disputes, then and now, have raged with such vigor (and occasionally vitriol).

Chapter 6 takes a closer look at the interesting case of Hermann Kolbe, who energetically denied that one should ever use one's imaginative or visualizing faculty in the pursuit of science; certainly, he affirmed, *he* would never commit such a blunder. He thus forms a contrary instance with which my various positive instances can usefully be compared and contrasted. (Kolbe was a fine chemist; whether he possessed sufficient psychological insight for accurate self-reflection is a separate question.) The crucial case of aromatic compounds, centered on the substance benzene, forms the central focus of chapter 7. Chapter 8 explores the rise of explicitly three-dimensional thinking in chemistry, in the development of the subfield known since about 1890 as stereochemistry. We revisit in this chapter the two alternative (dynamic versus static) chemical ontologies outlined above, and make some comparisons to the rise of kinetic-molecular theory among the physicists just at this time. Chapter 9 looks at the case of Hermann Kopp, whose fanciful 1882 exploration of the idea-world of atoms and molecules contains much humor, but also much solid content worth pondering. The chapter concludes with a look at a humorous chemical lampoon issued in 1886, in the same year as the important third edition of Kopp's fantasy.

In chapter 10 we return to the famous stories that Kekulé told as the guest of honor at the elaborate "Benzolfest" of 1890 and explore what these anecdotes, if taken as sincerely told, might suggest concerning the nature of scientific thought. The final section of this chapter examines "eureka experiences" more broadly and suggests that unconscious cognition, as arguably in the Kekulé case, can sometimes form a vital element of scientific thought. I also affirm that such episodes must be seen in the context of all the other more familiar aspects of scientific work. Chapter 11 provides a final summation and analysis. The first two sections of this chapter examine mental imagery both theoretically and phenomenally and explore some of the methodological challenges that intrude when the historian attempts to incorporate them into his view of the past. In the last section I summarize and further refine the argument for a special role for chemistry in the history of the exploration of the unseen microworld.

* * *

Much of the scientific subject matter of this book is drawn from organic chemistry. Readers who are familiar with this science will find the scientific material smooth sailing, but they might stumble over some of the historical terminology. In facing the problem of using historical actors' terms or contemporary terms, I have tried to steer a middle course, in order to capture much of the historicity of the language without unnecessarily impeding understanding for those to whom modern terminology is second nature.[10]

I hope equally to engage readers for whom modern chemical language and ideas are *not* second nature. As is portrayed especially in chapters 2 and 5, the basic rudiments of structural chemistry are as readily accessible as are the beloved (and visually rich) Tinkertoy constructions from our youth. Let me address chemically untutored readers for a moment. Imagine a special set of Tinkertoys in which the wooden centers come in four different varieties rather than the single one normally found. One kind of wooden center is painted white and possesses a single hole in which a stick may be inserted. A second type is painted red and has two holes in it; a third is painted blue and possesses three holes; and a fourth kind is painted black, each one of which has four holes in it. The first kind represents atoms of hydrogen or chlorine (H or Cl), the second kind, atoms of oxygen or sulfur (O or S); the third, nitrogen or phosphorus (N or P); and the fourth, carbon (C). The centers of any and all colors can now be connected together at will, using the single-color, single-length wooden sticks that come with this special Tinkertoy set.

This then represents a simple version of the theory of valence. Atoms of each element can form only certain numbers of bonds to other atoms—each atom of hydrogen typically to only one other atom of any other element, oxygen to two, nitrogen to three, and carbon to four. Hydrogen is thus monovalent, oxygen divalent, nitrogen trivalent, and carbon tetravalent. However, in this book we will generally employ the mid-nineteenth-century words for these denotations: hydrogen is "monoatomic," oxygen "diatomic," nitrogen "triatomic," and carbon "tetratomic."

Once chemists conceived of atomic valence—or "atomicity," as they called it until about 1870—they could explore the possibility of constructing molecules, in thought, following those valence rules. That is the essence of the "theory of chemical structure." Give a child a formula such as that for alcohol, C_2H_6O, along with our special Tinkertoy

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[10] These readers will need to keep in mind the special (now archaic) senses in which such terms as "atomicity," "diatomic," "equivalent," "rational formula," and "graphic formula" were used in the middle of the nineteenth century. These historical senses are explained in the text.

set to connect the model atoms together—that is, let the child be given two black centers, six white centers, and one red center, along with a bunch of sticks—and he or she can merrily build several different detailed possibilities for the fully resolved "graphic" or "glyptic" or "rational" (theoretical or structural) formula. This conception of structure theory is almost parodic in its naïveté, and one can easily understand why there was real resistance in the professional community to such oversimplification. When the theory first began to be formulated just after midcentury, the simple gamelike character of structure theory constituted one of the most telling objections against it. Nature could not possibly be that juvenile, many protested, and besides, what kind of force of nature can be imagined to constitute a Tinkertoy-like "stick"? We will see both of these tendencies, heuristic simplification and determined resistance to the same, well represented in our story.

I have attempted to maintain a certain narrative structure to that story, but at times I have considered it useful to expand upon technical and historical-chemical details, occasionally perhaps beyond what some readers may wish to pursue. These excursus build a more complete picture of the issues faced by my protagonists, but they are not indispensable to the book's main thematic lines of development, and can be skimmed or even skipped without fatal disadvantage.

As everyone must, I draw certain boundaries on my material. Although I treat many personalities and events in Britain, France, and elsewhere, the principal scene of action is the German-speaking sphere. This limitation was drawn for both substantive and pragmatic reasons. Substantively, it happens that the majority of the leading actors in the development of the theory and practice of investigating molecular "constitutions" (from, say, Liebig and Kolbe to Baeyer and Fischer) were either German themselves or operated primarily in a German-speaking context. Pragmatically, it is my experience that the manuscript resources available to the historian, especially collections of surviving correspondence, are more voluminous for nineteenth-century German chemists than for French or British. This is partly due to the highly decentralized character of nineteenth-century German academia, which required scholars residing in widely separated and otherwise undistinguished small towns such as Giessen, Marburg, and Heidelberg to rely heavily on correspondence rather than direct personal contact for scientific communication.

Footnotes employ a variety of abbreviated references; a list of these follows. Short-title citations are given in full form in the bibliography. All translations are my own, except where otherwise noted. Original foreign-language texts from translated manuscript materials (but not from translated *printed* materials) are provided in the notes verbatim et literatim, including archaic spellings and punctuation. Emphasis in the original (i.e., underlining) is silently reproduced in italics, as are original printed passages that appeared in German letterspacing (gesperrter Text). As was usual for German printed scientific texts during the nineteenth century, esszett is normally written out (ß = ss), but all umlauts are retained. Russian words, including names, are given in standard Anglo-American transliteration, except in citations from foreign-language journals.

This book has had a long gestation, and many colleagues have made such essential contributions to it that I cannot hope even fully to acknowledge, much less to repay that debt. The research was supported by Scholar's Award no. SES-0618093 from the National Science Foundation, by the Henry Eldridge Bourne endowment in history at Case Western Reserve University, and by a special supplemental grant from the dean of the College of Arts and Sciences, CWRU. I remember here with filial gratitude those Wisconsinites who first engendered my love for chemistry: William Brown, Bernard Saxe, and Harlan Goering; and for the history of science: David Lindberg, Daniel Siegel, and Erwin Hiebert. For their vital assistance, I am deeply grateful to archivists and colleagues at local and foreign institutions, including Norma S. Hanson and the hardworking interlibrary loan and OhioLINK specialists at Kelvin Smith Library, CWRU; James Edmonson and Laura Travis at the Dittrick Medical History Center; Christoph Meinel and Christine Nawa, Universität Regensburg; Elisabeth Vaupel, Deutsches Museum, Munich; Hans-Werner Schütt, Technische Universität Berlin; Ursula Klein, Max-Planck-Insitut für Wissenschaftsgeschichte, Berlin; Colin Russell; William Brock; O. Bertrand Ramsay; and the helpful staffs at the Archive of the Berlin-Brandenburgische Akademie der Wissenschaften (Berlin), the Deutsches Museum Archive and the Handschriftenabteilung of the Bayerische Staatsbibliothek (Munich), the Hugo-Dingler-Stiftung (Aschaffenburg), the Universitätsarchiv and Universitätsbibliothek in Heidelberg, the Universitätsarchiv in Leipzig, the archive of Vieweg Verlag (Braunschweig), the Chemical Heritage Foundation (Philadelphia), and the D. M. S. Watson Library of University College and the Library of the Royal Society of Chemistry (London).

Professors Klaus Hafner and Frieder Lichtenthaler generously gave me unfettered access to the extraordinary August-Kekulé-Sammlung in the Institut für Organische Chemie of the Technische Universität Darmstadt. The Museum Boerhaave in Leiden, the Museum voor de Geschiedenis van de Wetenschappen of the University of Ghent, and the Deutsches Museum Porträtsammlung kindly supplied illustrations; Li Feng assisted me in converting my scrawls into camera-ready structural diagrams; and Laura Travis of the Dittrick Medical History Center expertly photographed the illustrations that were taken from nineteenth-century books and periodicals. I am also deeply grateful for the fine work of Karen Merikangas Darling, Kate Frentzel, Natalie Smith, and the superb staff at University of Chicago Press.

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Abbreviations

ADM	Archiv des Deutschen Museums, Munich (with record number)
AKS	August-Kekulé-Sammlung, Institut für Organische Chemie, Technische Universität Darmstadt
AMW	H[ermann] K[opp], *Aus der Molecular-Welt* (Heidelberg: Winter, 1882)
Anschütz	Richard Anschütz, *August Kekulé,* vol. 1, *Leben und Wirken,* and vol. 2, *Abhandlungen, Berichte, Kritiken, Artikel, Reden* (Berlin: Verlag Chemie, 1929)
Annalen	*(Liebigs) Annalen der Chemie und Pharmacie*
Berichte	*Berichte der Deutschen Chemischen Gesellschaft*
BBAW	Archiv, Berlin-Brandenburgische Akademie der Wissenschaften, Berlin
BLB	Justus Carrière, ed., *Berzelius und Liebig: Ihre Briefe von 1831–1845,* 2nd ed. (Munich: Lehmann, 1898)
BSB	Sammlung Liebigiana, Bayerische Staatsbibliothek, Munich
BWB	Otto Wallach, ed., *Briefwechsel zwischen J. Berzelius und F. Wöhler,* 2 vols. (Leipzig: Engelmann, 1901)
CA	A. J. Rocke, *Chemical Atomism in the Nineteenth Century: From Dalton to Cannizzaro* (Columbus: Ohio State University Press, 1984)
DMSWL	Archives, D.M.S. Watson Library, University College London
DSB	*Dictionary of Scientific Biography*
EFA	Edward Frankland Archive, Open University, Milton Keynes
HDN	Hugo-Dingler-Nachlass, Emil Erlenmeyer Nachlass, Hofbibliothek, Aschaffenburg
HERC	H. E. Roscoe Collection, Royal Society of Chemistry, London.

LB	August Kekulé, *Lehrbuch der organischen Chemie,* 2 vols. (Erlangen: Enke, fascicles published in 1859, 1860, 1861, 1863, 1864, and 1866)
LWB	August Wilhelm Hofmann, ed., *Aus Justus Liebig's und Friedrich Wöhler's Briefwechsel in den Jahren 1829–1873,* 2 vols. (Braunschweig: Vieweg, 1888)
NDSB	*New Dictionary of Scientific Biography*
NS:	A. J. Rocke, *Nationalizing Science: Adolphe Wurtz and the Battle for French Chemistry* (Cambridge, MA: MIT Press, 2001)
QR	A. J. Rocke, *The Quiet Revolution: Hermann Kolbe and the Science of Organic Chemistry* (Berkeley: University of California Press, 1993)
VA	Kolbe file, archive, Vieweg Verlag, Braunschweig (with letter number)

ONE

Ether/Or

But a state of rest as well? O! to believe that everything in the liquid is arranged lock-step and in repose—that is an outdated concept, which became untenable when, in the March-days of the science, springtime broke out for chemical theory too (according to the calendar followed by a portion of the human world, it was in the late summer of 1850), on the broader basis of the motion of the smallest parts of the components of compounds. HERMANN KOPP[1]

Who does not remember the revolution brought about, when Wurtz discovered the compound ammonias and Williamson introduced the type HHO?! CARL SCHORLEMMER[2]

Springtime for Chemistry?

In 1882, the eminent chemist and historian of chemistry Hermann Kopp published an imaginative 105-page expedition into the world of molecules, *Aus der Molecular-Welt,* in which he exercised his (and his reader's) "mind's eye" to describe anthropomorphized spectacles that are forever hidden from the bodily eye. In addition to its wry humor, the work is filled with obscure topical and literary allusions, including the epigraph just cited, and hardly any real scientists' names can be found anywhere in the book—not even Kopp's own name on the title page.[3] In the epigraph above, Kopp's evocation of springtime and the month

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[1] *AMW,* 102.

[2] Schorlemmer to Roscoe, 5 November 1881, HERC.

[3] Published initially anonymously, the title page of the third edition (1886) finally contained the name of the author, as well as that of the dedicatee, Robert Bunsen.

of March suggests an intertwining of two metaphors: broadly, the start of the season of blissful warmth, freedom, and growth; and more specifically, the "März-Tage" that for Germans uniquely call to mind the ebullient start of the (ultimately failed) liberal democratic revolution in March 1848—German historians ever after having adopting the terms "Vormärz" and "Nachmärz" to denote the eras adjoining that watershed month. But to what beneficent revolution for chemical theory in "the late summer of 1850" was Kopp pointing?

Kopp was almost certainly referring to a paper by Alexander W. Williamson, then just twenty-six years old, read at the annual meeting of the British Association for the Advancement of Science in Edinburgh on 3 August 1850. One piece of evidence for this is Kopp's explicit reuse of a turn of phrase found in Williamson's concluding sentence: "In using the atomic theory, chemists have added to it of late years an unsafe, and, as I think, an unwarrantable hypothesis, namely, that the atoms are in a state of rest. This hypothesis I discard, and reason upon the broader basis of atomic motion."[4] In addition to matching the "late-summer" timing and the parallel phrasing of words, in an earlier explicitly historical account Kopp had already made clear to his readers how very revolutionary he regarded the work of the English chemist to have been.[5]

Though few chemists took immediate notice of it, Williamson's 1850 paper was indeed groundbreaking in more than one respect. As the first of an important series of papers on the formation of ethers, the constitutions of molecules, and reaction dynamics, we will see in this chapter how this work would lead to dramatic changes in chemical theory. Though these changes can be expressed in conventional terms, the real key to the revolutionary character of Williamson's contributions, I suggest, lay in his then-unfashionable eagerness to take seriously the reality of the molecular world, even though direct sensual or instrumental access to that level was not possible.

Whether consciously or only instinctively, Williamson understood that molecular reality could best be grasped and explored scientifically using vivid mental images, the very sort that Kopp would later por-

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[4] Williamson, "Theory of Aetherification" (1850), 356; German translation in *Annalen* 77 (1850): 31–49, citing the 3 August presentation date. Kopp's source was presumably the latter.

[5] Kopp, *Entwickelung* (1873), 736–40, 750–53, 802–8. Kopp wrote that Williamson's work, in addition to exploring molecular motion, settled the difficult problem of inconsistent molecular magnitudes, set a pattern for others to pursue the same sorts of molecular arguments, and prepared the way for the discovery of valence. In doing all this, Kopp averred, Williamson helped establish the very distinction between atoms and molecules (740, 803).

tray so engagingly in *Molecular-Welt,* with the additional assistance of "paper tools" such as molecular formulas and chemical equations. Because Williamson provides a particularly striking example of a lively chemical imagination, because of his early and fundamental role in the "quiet revolution" in chemistry, and because of his powerful influence on Kekulé and on Kopp, whose work will loom large in these pages, we need to examine this interesting figure with care.

The Education of Alexander Williamson

Born in London of Scottish parents, Williamson's childhood was comfortable, due to his parents' substantial means.[6] His father, also named Alexander, was an official in the East India House who moved in an elevated cultural circle that included James and John Stuart Mill. About 1840 the family relocated to the Continent, and young Alexander benefited from education in Paris, Dijon, and Wiesbaden. He learned to speak and to write nearly perfect French and German. In 1841 Williamson matriculated at the University of Heidelberg with the intent to study medicine, but the lectures of Leopold Gmelin soon decided him for chemistry. After three years of intensive study he transferred to the University of Giessen to earn his doctorate with the great master Justus Liebig, whose famous laboratory in those years had become the destination of pilgrimages by would-be chemists from around the world.

En route to his doctoral degree Williamson published three small but excellent pieces of research in inorganic chemistry, while devoting most of his attention to a new theory (of which we know no details) concerning the controverted phenomenon of electrolysis. William Brock justly writes of a "peculiar trait in his character" according to which a series of obsessive secondary interests outside of chemistry nearly always ran parallel to the research that would ultimately bring him renown. These secondary interests, Brock notes, "sometimes show amazing fertility of invention [but] could not fail to have dissipated his energies."[7] Williamson had an extraordinary power of imagination combined with remarkable discipline and self-criticism. In a letter to his father (probably from 1845) Williamson wrote, "I often find [a solitary] walk of as much real service to me in my progress as a whole week's la-

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[6] The important biographical sources are Foster, "Williamson" (1905); Divers, "Williamson" (1907); Harris and Brock, "From Giessen to Gower Street" (1974); Paul, "Williamson" (1978); and Brock, "Williamson" (2004).

[7] Harris and Brock, "From Giessen to Gower Street," 103.

bour [in the laboratory]. The great difficulty in a research such as that I am now pursuing consists not so much in performing the experiments once fixed upon, as in inventing and choosing from those most calculated to attain the desired object."[8] In all of his scientific work, a prominent characteristic of his style was the meticulous and unusually clever rational design of his experiments. "If you know clearly what you want to do," he wrote in another letter, "there is always a way of doing it."[9]

At some point Williamson encountered difficulties that Liebig attributed to his deficient mathematical training. Williamson therefore resolved to make himself "a complete mathematician, or failing in that to turn shoemaker."[10] For this purpose, and with the aid of a letter of introduction from John Stuart Mill, Williamson moved to Paris to study with Auguste Comte. With the help of his parents' money, and probably residing with them, he devoted himself for two years to intensive study, and then spent a third year pursuing experiments in organic chemistry. Williamson's enthusiastic though temporary embrace of Comte's "philosophie positive" could only have reinforced those elements of critical, empirical, and skeptical approaches inculcated by his previous education, influenced as it was by utilitarianism and the "philosophical radicalism" of his father, Jeremy Bentham, and the Mills. One may reasonably presume that Williamson also read in philosophical works of the day, including John Herschel, William Whewell, and the Scottish Common-Sense philosophy of Thomas Reid and Dugald Stewart.[11]

Comtean positivism was distinct from the late nineteenth-century positivism of Ernst Mach or that of the Vienna Circle logical positivists, for in Comte's work there were distinct realist impulses superadded to the dominating desire to extirpate metaphysics. Moreover, Comte actually had a healthy respect for the beneficial role of hypotheses in

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[8] Quoted in ibid., 106. Williamson did not say, nor can it be inferred, to which research project he was referring.

[9] Quoted in Foster, "Williamson," 611. Foster had access to letters written by Williamson and since destroyed; his quotations from them fail to cite dates or addressees.

[10] Williamson to [Liebig], 4 August 1847, Sammlung Wachs 628, BBAW.

[11] In *Scottish Philosophy and British Physics,* Richard Olson offers a vigorous argument for the importance of Common-Sense philosophy on the course of British physical science, including on John Herschel's influential *Preliminary Discourse on the Study of Natural Philosophy* (London, 1830). One can see much in Williamson's language and method that derives from Herschel's book, including a respect for the power of the method of hypothesis, a search for *verae causae,* and the belief that crucial experiments could provide definitive choices between rival theories. In concert with Herschel, both Reid and Stewart, and the Common-Sense philosophers more broadly, opposed the radical skepticism of David Hume and reaffirmed the legitimacy of a search for *verae causae*. Stewart also became a proponent of a major methodological theme in Williamson's work, what later became known as hypothetico-deductive method.

science—even, under certain conditions, hypothetical entities that were in principle unobservable.[12] But Williamson's friend John Stuart Mill, for a time a positivist fellow-traveler, ended by criticizing (and severely disappointing) Comte, and Williamson soon was to follow a similar path.[13]

Interpreting Chemical Atoms

When Williamson and his contemporaries thought about the symbols that appeared in the chemical formulas they bandied about, just what did they have "in mind"? To provide even a provisional answer to this question, we need briefly to review the early history of the atomic theory in chemistry.[14]

In 1803 John Dalton developed a method to derive relative weights for the presumed smallest portions (chemical atoms) of each of the known elements, and molecular formulas for all the compounds that they form. For Dalton and other early chemical atomists, it was necessary first to *assume* molecular formulas for certain simple substances in order to calculate relative atomic weights from analytical data. For instance, Dalton posited that each molecule of water was composed of one atom of hydrogen and one of oxygen, and he represented this molecule by drawing two contiguous dissimilar circular symbols. With such a presumed molecular formula, and considering the measured proportions of the elements that form water, Dalton's atom of oxygen had to weigh 8 relative to the weight of his hydrogen atom (conventionally considered as 1, to provide a fiducial standard).[15] Once one decided upon a set of relative elemental atomic weights, any pure compound could in principle be represented atomistically. Soon after Dalton had shown the way, other early chemical atomists offered slightly differing choices for assumed formulas and atomic-molecular representations.

In 1814 the London physician-chemist William Wollaston proclaimed that "practical convenience" rather than deep theory really ought to be the only guide to the determination of relative atomic

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[12] Laudan, "Reassessment" (1971).

[13] For which see Harris and Brock, "From Giessen to Gower Street," 107, 109, and Divers, "Williamson," xxviii–xxix.

[14] Much of what follows summarizes material in *CA* and in Klein, *Experiments, Models, Paper Tools* (2003).

[15] Dalton's atomic weight of oxygen in 1808 was actually 7, relying on Gay-Lussac's prior determination that water is 87.4 percent oxygen and 12.6 percent hydrogen, since 87.4 ÷ 12.6 ≈ 7. Soon thereafter, Berzelius determined that the first number was closer to 89 percent, hence O = 8 or 16, depending on whether one assumed HO or H_2O as the molecular formula for water.

weights, and proposed what he called “equivalents” for the elements that nearly (but not quite) matched Dalton’s “atomic weights.” Wollaston’s putatively pragmatic “equivalents” proved popular in competition with the more obviously theoretically derived atomic weights that were developed by the influential Swedish chemist Jacob Berzelius between 1813 and 1826. British chemists tended to prefer Wollaston’s system, whereas German chemists, such as Liebig, Friedrich Wöhler, and Robert Bunsen, preferred Berzelius’s. French chemists mostly used a third variant, developed by Joseph-Louis Gay-Lussac and Jean-Baptiste Dumas. Yet a fourth variant was proposed in 1842, which will be discussed below.

In short, during the first half of the nineteenth century European chemists simply could not agree (e.g.) on whether the true relative atomic weight of the oxygen atom was 8 or 16, or whether carbon was 6 or 12. These varying atomic weights consequently required varying numbers of oxygen and carbon atoms in the formulas of their compounds, since those who thought (e.g.) that oxygen was 8 required twice as many oxygen atoms in their formulas as the $O = 16$ advocates did. All of this worked against interpreting *any one* of these systems as an actual portrayal of molecular reality.

How, indeed, should one interpret the symbols in a molecular formula? Dalton thought that each of the symbols in his formulas must signify an actual “atom,” in the sense of an absolutely unsplittable entity, much like an invisibly small but very real billiard ball—which is why he chose to represent his atoms by distinctive iconic circles, or spherical wooden models. Few chemists thereafter took such an unreflectively realist position. At the other extreme, some regarded chemical formulas purely conventionally, as a mere aid to memory in representing the empirical facts of chemical analysis and having no real referent in the microworld at all.

There were, of course, middle positions between ontological realism and extreme conventionalism or positivism. Berzelius devised the alphanumeric system which, in slightly modified form, chemists still use today in order to designate the presumed atomistic compositions of molecular formulas rather than to make any detailed statement about the nature of the atoms themselves. Each of Berzelius’s letters, such as the three entities in his preferred water formula, H_2O, might reasonably be taken to refer to a quantity of matter, the real micro-characteristics of which were deliberately elided. A Berzelian *chemical* (as opposed to *physical*) atom, by this more cautious interpretation, was simply a packet of elemental matter of a certain relative weight, a packet that might possibly, for all we know, have internal parts or structure, but that seemed to operate integrally across known chemical transformations. Berzelius's approach was no less theoretical than Dalton's, but appeared to set epistemological limits on what was knowable about the microworld.

As Klein has convincingly argued, a major reason for the popularity of the Berzelian formula system was surely its semiotic ambiguity—or flexibility. A Berzelian formula could be easily taken to occupy any of these philosophical positions, from the extreme ontological to the purely numerical. Independent of any particular philosophical interpretation, by about 1830 these formulas began to be used by workers such as Dumas and Liebig in a generative fashion, much as mathematicians use their equations on paper or biologists use physical tools such as microscopes, to understand the course of chemical reactions and to provide heuristic guidance for further investigation. This marked a major transition for the culture of organic chemistry, from what had exhibited a predominantly natural-historical character to what now became a highly experimental approach, with the preparation of new artificial substances placed in the foreground. The use of Berzelian "paper tools" was a sine qua non for this metamorphosis.[16]

In the 1840s, the prominent French theorists Auguste Laurent (1808–53) and Charles Gerhardt (1816–56) exemplified some of the new possibilities. Laurent was inclined toward realism (though not of the naïve Daltonian type); Gerhardt was more of a conventionalist or even phenomenalist. Both of these chemists had been exiled by the powerful elite in their field from Paris to provincial professorships, in Bordeaux and Montpellier, respectively, partly due to their unwillingness to adopt the sort of politics—of both the academic and the literal kind—that were so necessary for career advancement in Orleanist Paris. Each migrated back to the capital, essentially unemployed, in 1845 and 1848, respectively. Despite their continuing philosophical disagreements, Laurent and Gerhardt joined forces in 1843, and this partnership resulted in some of the first significant steps toward understanding an even more profound problem, how atoms (interpreted however one will) might be arranged within the molecules that they form.

The question of discerning the arrangements of atoms within a molecule was a thorny one at best. Even for those inclined toward molecular realism, the practical and epistemological challenges were evident. These challenges became even greater as the focus of the chemical

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[16] Klein, *Experiments, Models, Paper Tools.*

community gradually shifted from inorganic substances, most of whose molecules were rather simple, to organic compounds, whose formulas were often dismayingly large and complicated. How could one ever know how these atoms are internally arrayed and what those arrangements might signify chemically? Or to pose the question in a more operational manner: How could one possibly apply macroscopic chemical data, which is all that chemists had to work with, to make warrantable detailed inferences about the microworld?

Feasible initial approaches to this seemingly insoluble problem began to come into focus after the dominant chemical theory of the 1810s and 1820s, electrochemical dualism, was weakened by four developments: the substitution of chlorine for hydrogen in organic substances; the theory of chemical and physical "types"; a hydrogen theory of acidity; and a revised theory of chemical "radicals." Laurent and Gerhardt were involved with all of these events.

The principal architect of electrochemical-dualist theory had been Berzelius. Following the discovery of electrolysis—dismembering compounds by running a current through them—Berzelius suggested that chemical combination must be traceable to the electrical attractions of oppositely charged molecular components. From electrolytic experiments one could array elements and "radicals" (groups of atoms that behaved integrally, like elements) along an electrochemical scale, from highly negative to highly positive. For instance (and for the sake of clarity, employing modern atomic weights), sulfuric acid and potassium sulfate were formulated as $SO_3 \cdot H_2O$ and $SO_3 \cdot K_2O$, where the moieties on either side of the dot were thought to cohere electrically. Acids in general were thought to contain preformed water, and salts to contain preformed oxides. Compounds were schematically created by *addition* of moieties one to another, and everything was analyzed *dualistically.*

The system worked well for inorganic compounds, salts, and minerals, but problems emerged in the organic-chemical realm. The principal anomaly was the amazing discovery that chlorine could substitute for hydrogen in organic compounds with minimal alteration of chemical or physical properties. This was a surprise, because chlorine and hydrogen were known to lie at opposite ends of the electrochemical scale, hydrogen being highly positive and chlorine highly negative. Once the phenomenon was established beyond doubt, Berzelius proposed an adjustment to the theory that could resolve the anomaly. Perhaps, he suggested, certain portions of organic molecules were, in effect, insulated from electrochemical effects. Atom-for-atom substitution could occur in these so-called copulas, even substitution by electrically opposite elements, without much affecting the properties of the molecule as a whole.

Some chemists criticized Berzelius's copula theory as a mere ad hoc retreat and drew a more far-reaching inference from the phenomenon of chlorine substitution. Perhaps the *identity*—electrochemical or otherwise—of the atoms within a molecule was simply not very important. What mattered more, perhaps, was their *physical location* within the molecule. Laurent took just this inferential step and proceeded to develop an elaborate theory regarding the imputed arrangements of the atoms within organic molecules—his "nucleus" theory. Although he had been one of the earliest explorers of chlorine substitution, Laurent's former teacher Dumas at first vigorously disagreed with Laurent's position. Then he changed his mind.

In papers published in 1839 and 1840, Dumas proclaimed that "in organic chemistry there exist certain 'types' which are conserved even when one has introduced, in the place of the hydrogen which they contain, equal volumes of chlorine, bromine, or iodine." He thought of this concept of types as "entirely mechanical" and appeared to intend the idea in a physical—that is, a mechanical or structuralist—sense, for one of his analogies was to the framework of a building that could undergo different architectural variations without changing its essential character.[17] Though Dumas was deliberately vague in his language, this clearly signaled a realist view of molecular constitutions, and implicitly opened the door to the possibility of determining atomic arrangements—about which prospect, however, he continued to express caution. As his student Adolphe Wurtz commented years later, Dumas here "compared [molecules] to buildings, in which atoms, in a sense, constitute the bricks and mortar"; molecules were conceived as "molecular structures [édifices] that were susceptible in some cases to modification, by the substitution of one part by another."[18]

Dumas's "type theory" was not the only development of the day that was suggesting a route by which chemists could begin to enter inferentially into the interior of molecules. A new hydrogen theory of acidity had recently been proposed, which sought to replace the earlier oxygen-based theory of acids that traced its ancestry back to Lavoisier himself. Hydracid theory had developed in stages and achieved a kind of maturity in 1838, when Liebig applied it to organic acids: as the essence of

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[17] Dumas, "Mémoire sur la constitution" (1839); Dumas, "Note" (1839); Dumas, "Premier mémoire" (1840); and Dumas, "Mémoire sur la loi" (1840), on 174–75, 177–78.

[18] Wurtz, *La théorie des atomes* (1875), 25.

salt formation Liebig pointed to the substitution of a portion of the hydrogen of the acid molecule by a metal or a base. The theory of hydracids shared three qualities with type theory: it implicitly distinguished between distinct parts of a molecule; it did so in a non-electrochemical manner; and it invoked substitution rather than dualistic addition (juxtaposition of two components) as the primary mode of reaction.

A largely independent but convergent theoretical development was the new (and likewise non-electrochemical) conception of organic radicals that Liebig and Wöhler had pioneered. In their landmark 1832 coauthored paper on the "benzoyl radical" (modern C_7H_5O), Liebig and Wöhler portrayed the benzoyl family of compounds as formed by substitution of one-sixth of the hydrogen of the oil of bitter almonds (= benzoyl hydride, C_7H_6O) by (e.g.) a chlorine atom. They could thus chemically distinguish the hydrogen of benzoyl itself—in Liebig's words, the hydrogen that was "inside the radical"—from the hydrogen that was substitutable by other atoms or groups—the hydrogen "outside the radical." Liebig later confessed that in using these expressions he was already thinking in 1832 of the analogy between this phenomenon and his incipient hydracid theory of organic acids.[19] One-fourth of the hydrogen of acetic acid (modern $C_2H_4O_2$), for example, could be replaced by an atom of sodium to form sodium acetate; this replaceable hydrogen could be viewed, like that of benzoyl hydride, as being located outside the main body of the acetic acid molecule. As Berzelius pointed out privately (and vexedly) to Liebig, his language of "inside or outside the radical" was actually derived from Laurent's structuralist theory of organic molecules, an association that Liebig really did not want to acknowledge.

A former student of both Liebig and Dumas, Gerhardt decided that a wholesale reform of chemical theory was required, and he attracted the attention of Laurent in this endeavor. Between 1842 and 1846 the two Frenchmen developed the outlines of their reform, which had two major thrusts. The first was yet another revision of atomic weights. Although Gerhardt proclaimed this system as radically new, in fact it was nearly identical to what Berzelius had arrived at by 1826, which most German (but not French!) chemists had long used. The second thrust, which likewise addressed the problem of how to derive molecular formulas from analytical data, was designed to resolve what Gerhardt and Laurent thought was one of the greatest failures of chemical theory of that day.

[19] *CA,* 195.

This failure was the inconsistent use of molecular magnitudes, namely, the indiscriminate employment of what were called "two-volume" and "four-volume" molecular formulas. The latter have doubled atomic coefficients relative to the former so that twice as many atoms of all types were thought to compose the presumed molecule.[20] In the first half of the nineteenth century, most inorganic substances were represented by two-volume, most organic substances by four-volume formulas, but even in the organic realm some compounds, such as ether and oxalic acid, were given two-volume formulas. Atomic theorists had adopted this mixed usage early on, in order to avoid a troubling quandary following Gay-Lussac's announcement of the law of combining volumes (1809). This inconsistency of volumes would have seen a kind of resolution had chemists adopted the independent and similar proposals of Amedeo Avogadro (1811) and André-Marie Ampère (1814), namely, that under similar conditions equal volumes of elementary gases contained equal numbers of their fundamental particles, and that those particles divided in two in certain reactions. But there were many compelling objections to these purely hypothetical suggestions, and chemists understandably balked at accepting them. Consequently, few chemists trusted relative vapor densities as a *general* indication of relative molecular size.

When the two adjustments recommended by Gerhardt and Laurent were applied, it became impossible to formulate many compounds in a manner consistent with electrochemical-dualist precepts. The two reformers regarded this as an advantage of the new system, for, as advocates of substitutionist and type-theoretical chemistry, they opposed electrochemical-dualist theory anyway. One would think that the two leaders of the international chemical community ca. 1840, Liebig and Dumas, would have warmly welcomed this innovation. After all, each had recently battled electrochemical-dualist theory himself—Liebig by invoking substitutable non-electrochemical radicals and by interpreting organic acids as hydracids, and Dumas by developing his theory of types. However, in a remarkable parallel turn, both men defected from their own theories immediately after proposing them, and gave Gerhardt and Laurent no support whatever.

In the previous few years the discipline had been so disturbingly roiled by the rapid replacement of one theory after another, one system

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[20] Readers should note that this kind of inconsistency is distinct from the "atomic weights" versus "equivalents" problem discussed earlier. For example, the two-volume formula for marsh gas (methane) was CH_4 in atomic weights but C_2H_4 in equivalents; the respective four-volume formulas were C_2H_8 and C_4H_8. For details on this problem, see *CA*.

of atomic weights and molecular formulas after another, that to these and many other chemists the prospect of uniting on a single, permanent, truly empirical system was attractive. The best candidate system appeared to be that defended many years earlier by Wollaston—the explicitly pragmatic system of so-called equivalents. During a pleasure trip undertaken in September 1838 by Liebig, Wöhler, Gmelin, Heinrich Rose, and Gustav Magnus, Gmelin convinced his travel companions that Wollaston's 1814 concept was purely empirical, and independent of all theories.[21] These five prominent chemists concluded a pact not only to adopt equivalents in their own work, but to lobby for it in the international community.

Liebig abandoned the hydracid formulations that he had championed just a few months earlier and immediately ceased his work on chlorine substitution and his flirtations with type theory. After a few years of vacillation, he adopted the old dualistic formulations expressed in equivalents and no longer spoke favorably of the concept of atoms. Dumas's pathway was similar. Immediately after having published four papers in rapid succession on type theory in 1839–40, he left the subject completely and, like his German friend and rival, abandoned active participation in virtually all theory. Nearly coincidentally, the French government's official syllabus for the national curriculum of the lycées and university faculties was altered to eliminate any mention of the word "atom," and a similar change was engineered in the École Polytechnique.

This turn toward what appeared to be more empiricist, even positivist, modalities seems to have been a Europe-wide movement ca. 1840. Comte was still publishing his multivolume *Cours de philosophie positive,* with the crucial third volume, covering chemistry, appearing in 1838; most chemists paid little attention to the support for the chemical atomic theory that he expressed there, preferring to read him in a more radically antihypothetical way. Even Gerhardt felt the pull. After 1842 he rejected any attempt to discern the arrangements of atoms within the molecule; in his mind, the reforms he advocated so strongly were based on formalist logic and taxonomic rationalization, not realist molecular theory. He explicitly denied any and all atomistic interpretations of his formulas—they were simply "reaction formulas," convenient summaries of empirical chemical facts, nothing more. So-

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[21] Though rarely doubted in his own day, subsequent analysis has cast serious doubt on Gmelin's claim. The following material is based on sources cited and discussed in greater detail in *CA,* 177–82, and *NS,* 96–98 and 382–86.

called rational formulas should be considered as nothing more than "contracted chemical equations."[22]

Berzelius and others had long used the term "rational formula," in contrast to "empirical formula," to indicate ideas about the distribution of the atoms within the molecule—"rational" here signifying "pertaining to the exercise of reason," i.e., theoretical. Hence, the *empirical* formula for oil of bitter almonds was C_7H_6O, regarded as a simple expression of chemical analysis. One possible *rational* formula for this substance was $H{\cdot}C_7H_5O$, which, by distinguishing one hydrogen atom from the others, goes beyond the empirical data to make a theoretical statement about the internal details within the molecule. By contrast to this established usage, Gerhardt's "rational" formulas simply summarized reactions; such formulas can vary, according to the reactions that one happens to use for a particular formulation of a particular compound. For example, Gerhardt noted, one could equally well represent the oil of bitter almonds as containing *either* the radical C_7H_5O *or* the radical C_7H_5, depending on the reaction one intends to represent: "[My] principle that *one and the same body can be represented by two or more rational formulas* will doubtless be contested by chemists who presume to represent the absolute constitution of molecules by chemical formulas . . . [But] when one in a sense freezes a compound into a single formula, one often conceals from oneself chemical relationships that another formula would immediately make evident."[23]

Laurent disagreed with Gerhardt's rejection of inquiries into the constitutions of molecules. He was convinced that it was necessary to apply molecular theory to do any good chemistry at all, even if theory were only regarded as an instrumental stepping-stone, as a heuristic aid rather than a true depiction of the microworld. Laurent agreed with Gerhardt that the reformed system created a more beautiful, rational, and consistent chemical taxonomy, but he also pointed to its conformity with recent ideas in the science, such as the newer theories of types, radicals, and hydracids, each of which asserted something about the actual constitutions of molecules.

Gerhardt did not follow Laurent's advice. He even used equivalents, temporarily abandoning his own reform of atomic weights in his massive textbook *Traité de chimie organique* (1853–56) until the last half of the last volume, when he turned back to his newer atomic weights. The final fascicle of this fourth volume appeared just three months before

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[22] Gerhardt, *Traité* (1856), 4:566.

[23] Ibid., 4:580.

Gerhardt's death of a sudden fever. His comrade Laurent had succumbed to tuberculosis three years earlier. Neither man had reached the age of forty-five.

Williamson and Graham

When Williamson arrived in Paris in August 1846, the ideas of Gerhardt and Laurent had reached maturity, but they were not much respected, either in France or internationally, and neither man had proper employment. It is clear from subsequent surviving correspondence that Williamson formed a close personal and professional bond with Laurent (who was in Paris when Williamson arrived there) and with Gerhardt (who arrived from Montpellier in March 1848). He was wholeheartedly converted to the reformed chemistry they had outlined. Williamson's unconstrained individualism, imaginative approach to theoretical innovation, and youthful confidence seem well matched to Laurent's fecund molecular theorizing, as well as to Gerhardt's skepticism and severity toward hypotheses.

While in Paris, Williamson's intellectual formation was to experience one more influence, that of Thomas Graham (1805–69).[24] Between about 1833 and midcentury Graham was the leading British chemist. A native Glaswegian, Graham was educated at the University of Glasgow, partly under the direction of Thomas Thomson. In 1837 he succeeded to the chair of chemistry at University College London. At the time of his call to London Graham was still a young man, but he had already made a name for himself with groundbreaking work on the diffusion of gases and on the constitutions of the phosphoric acids.

In 1833 Graham announced his discovery of the law of gaseous diffusion: any two gases in contact with each other diffuse "by an interchange in position of indefinitely minute volumes of the gases, which volumes . . . being . . . inversely proportional to the square root of the density of that gas." This statement is taken from the first sentence of Graham's paper. His last sentence was: "The law at which we have arrived (which is merely a description of the appearances, and involves, I believe, nothing hypothetic) is certainly not provided for in the corpuscular philosophy of the day, and is altogether so extraordinary that

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[24] Relatively little historical work has been done on this major figure, and his importance to the development of nineteenth-century chemistry has not been sufficiently appreciated. See *DSB;* Partington, *History* (1964), 265–75, 729–39; Swords, "Graham" (1973); Stanley, "Graham" (1979); and Stanley, "Making of a Chemist" (1987).

I may be excused for not speculating further upon its cause, till its various bearings, and certain collateral subjects, be fully investigated."[25] This mixture of empirical caution combined with deep concern with the philosophical investigation of causes is thoroughly characteristic of Graham's work. All who have worked on Graham have agreed with Edward Thorpe's opinion that "the main principle which constitutes the basis of the most original, and perhaps the most important section of his labours, was the conception of molecular motion." The editor of Graham's collected papers commented, "Graham is as strict an atomist as perhaps can be found."[26]

These judgments have been further elaborated and confirmed by subsequent work, which has clarified many of the details of Graham's ideas on molecular theory and atomic-molecular motion. In fact, he appears to have been attracted neither to the static view of gases typical of caloric theorists, nor to the kind of random rectilinear motions suggested by early kinetic theorists, whose work he obviously read. Rather, in 1864 Graham wrote that all matter may be composed of a single type of particle "existing in different conditions of movement. . . . The more rapid the movement the greater the space occupied by the atom, somewhat as the orbit of a planet widens with the degree of projectile velocity." The characteristic combining weights of chemical elements are not, he wrote, due to the masses of the constituent particles, but rather to the volume occupied by each particle, moving with an "inalienable primordial impulse." The lighter elements, composed of more rapidly moving particles, are merely less dense than heavier elements. These tiny particles, Graham suggested, make up the ponderable atoms and molecules that "Herapath, Krönig, Clausius, and Maxwell" had recently proposed in the kinetic theory of gases. "We have indeed carried one step backward and applied to the lower order of atoms ideas suggested by the gaseous molecule, as views derived from the solar system are extended to the subordinate system of a planet and its satellites. The advance of science may further require an indefinite repetition of such steps of molecular division."[27]

Graham's other early landmark publication was on the three different phosphoric acids known at that time. Berzelius had suggested that this was simply a case of triple isomerism whose ultimate cause was

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[25] Graham, "Diffusion of Gases" (1833); Graham, *Researches* (1876), 44, 69.

[26] Thorpe, *Essays* (1911), 264; Smith, in Graham, *Researches,* v, xv; and Swords, "Graham," passim. The best and most thorough discussion of Graham's views on atomic motion is in the fine but unfortunately poorly accessible dissertation by Stanley, "Graham," 347ff.

[27] Graham, "Speculative Ideas" (1864); Graham, *Researches,* 299–302.

unknown, but Graham provided evidence that the three compounds could be distinguished by their unique and fully determinable molecular constitutions. In particular, he showed that the so-called metaphosphoric acid could form a salt with but a single molecule of base, while pyrophosphoric acid could react with two, and the ordinary (ortho-) phosphoric acid could unite with three molecules of base.[28] This discovery meant that salt formation could no longer be represented as Berzelius proposed, that is, as the simple dualistic *addition* of an anhydrous acid to a molecule of base. Rather, what had to be happening was the *substitution* of molecules of water, hitherto chemically bound to the acid as part of its essential constitution, by molecules of base.

Graham's article on phosphoric acid was published a year after Liebig and Wöhler's work on the benzoyl radical, and Liebig immediately understood its concordant implications: Graham was asserting that members of the phosphate series, just like those of the benzoyl series, are related by molecular substitutions, not dualistic additions. Liebig incorporated Graham's work into his evolving theory of hydracids: it wasn't *molecules* of combined *water* in phosphoric acid that were being substituted (as it appeared according to Graham's electrochemical formulations) but rather single *hydrogen atoms,* entirely analogous to the substitutable hydrogen of benzoyl hydride. In Liebig's view, orthophosphoric acid was "tri-basic," in that one, two, or three atoms of hydrogen of the acid could be replaced by one, two, or three atoms of a metal or molecules of base. Liebig applied this point of view to organic compounds. He argued that dibasic tartaric acid, for example, has two hydrogen atoms that can be substituted by metals. The fact that the compound has *any* substitutable hydrogens makes it an acid; the fact that it has *two* makes it a dibasic acid. Considering their related chemical interests, it is not surprising that Liebig formed a close collegial and personal connection to Graham following their first meeting in 1836.

The Graham-Liebig work on polybasic acids added a fifth strand to the four interconnected developments discussed in the last section—chlorine substitution, type theory, a modified radical theory, and the hydrogen theory of acidity—all of which worked against electrochemical-dualist theory. A molecule of a polybasic acid, in Liebig's hands, was depicted as a molecular entity that could hold together additional molecular components; it formed the hub, as it were, of a more complex molecule. It appears that Williamson likewise saw Graham's work on phosphoric acids in this way, for in an obituary of

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[28] Graham, "Phosphoric Acid" (1833); Graham, *Researches,* 321–48.

Graham, Williamson wrote of this early work, “One would fancy that Graham had been acquainted with the modern doctrines of types and of polybasic acids . . .”[29] This concept of polybasic *molecules* was generalized in the next few years to *radicals,* then further developed to apply to *elements*—which marked the origin of what became known as the theory of valence. Valence theory then begat the structural theory of organic molecules, as developed independently by August Kekulé and Archibald Scott Couper in the late 1850s.

All of this will be detailed in subsequent chapters, but what is important for present purposes is to note that Laurent, Gerhardt, Liebig, Dumas, Graham, and others had already assembled by ca. 1840 nearly every element of chemical theory that would provide the necessary preconditions for the revolution to come. Ironically, as we have seen, Liebig and Dumas retreated fully from the theoretical dialectic, simultaneously and independently, just about that time. Laurent and Gerhardt attempted to complete the revolution whose signs were so clearly in the air, but they failed. It would be Williamson and others influenced by him who would succeed.

Early in 1849 Graham traveled to Paris and met Williamson, presumably for the first time. He urged Williamson to apply for the professorship of “Analytical and Practical Chemistry” at University College London, which had just become vacant due to the early death from tuberculosis of George Fownes in January of that year. It is likely that the purpose of Graham’s visit to Paris was specifically to recruit Williamson to the post; certainly, Fownes’s long illness would have allowed appropriate advance planning for the hire. Fownes, like Williamson, had been a student of Liebig, and had recently (1845) taken possession of the new Birkbeck Laboratory at UCL, the first purpose-built academic laboratory building in Britain. Williamson applied for the post on 26 April, and three weeks later he sent a printed booklet containing testimonials in his favor from sixteen luminaries of the field. He was subsequently elected by unanimous vote of the UCL Council; he accepted the offer on 25 June, arrived the first of September, and began his thirty-eight-year career there in October.[30] Considering the close relationship between Graham and Liebig, it is likely that Graham had asked Liebig’s counsel on the hire of both Fownes and Williamson; Liebig’s support would surely have been crucial for both elections.

Graham and Williamson had much in common, including their

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[29] Williamson, “Graham” (1869), 21.

[30] Documentation is held in DMSWL.

Scottish roots and their association with UCL (Williamson's father had been one of the university's founders). Michael Swords has explored how greatly Graham's work was influenced by Thomas Reid and the Scottish school of Common-Sense philosophy, for whom the idea of motion was so central, and I have above suggested the probable influence of Reid, Dugald Stewart, and John Herschel on Williamson.[31] Graham, who was nineteen years older and quite eminent by this time, must have provided at least stimulation and possibly mentorship to the young Williamson. Certainly there was plenty of common ground in the powerful orientation of both chemists to theories of atomic and molecular motion, as well as to a robust regard for the "philosophy" of chemistry.

Four months after Williamson entered into his duties at UCL, in February 1850, Graham published a paper on the interesting and much-controverted subject of etherification. Six months later, in August of that year, Williamson presented his "springtime for chemistry" paper on the same subject. Unfortunately, other than this overlap of subject matter, we know few details about the relationship between these colleagues, and it is difficult to say how much Graham may have influenced Williamson's thinking. As Michael Stanley has thoroughly demonstrated, Graham was one of the most brilliant and productive visual thinkers among nineteenth-century chemists. But the younger man was to succeed where Graham had failed. Namely, Williamson would provide a substantive route from visual hypothesis, to experimental evidence, to convincing argumentation regarding those ephemeral entities, atoms and molecules.

Grasping the Ether

The various formula sizes used in chemical theory during the years ca. 1820–50 maintained an uneasy coexistence at best. But problems became acute when disparate kinds of formulas were involved in one and the same chemical reaction, as in the formation of ether.

The chemical substance simply called "ether" (now referred to as diethyl ether) had been known since the sixteenth century, but since it could not easily be related to a salt-forming organic acid, its formula weight could not easily be determined.[32] But ether *could* be generated

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[31] Swords, "Graham," 11–15, 33–50. He comments, "Common Sense philosophy made 'motion' and 'phenomena' practically a tautology. Motion was the ground of all phenomena" (14n).

[32] The following summary is much simplified, as the evolution of theories of etherification is complex. For a review, see Partington, *History* (1964), 262–63, 341–52, and 448–50.

by simply distilling grain alcohol from solution in sulfuric acid. Since sulfuric acid was known to be a strong dehydrating agent, Dumas and Liebig separately concluded that ether was nothing more than dehydrated alcohol. The idea worked schematically only if one employed a four-volume formula for alcohol and a two-volume formula for ether, but this circumstance did not trouble them. Expressed in formulas typical of the 1830s, this theory of ether formation was:

$$\begin{array}{ccc} C_4H_{10}O\cdot H_2O & \longrightarrow & C_4H_{10}O + H_2O \\ \text{alcohol} & \text{yields} & \text{ether} + \text{water} \end{array}$$

Gerhardt and Laurent *were* troubled by this. To them, Dumas and Liebig were guilty of invoking inconsistent molecular magnitudes for no other reason than to maintain a theory. If a single yardstick were used, expressing all formulas in the two-volume convention, one could see from one's written formulas that the ether molecule was nearly twice the size of the alcohol molecule. (That is: everyone agreed that the atomic-weight formula for ether should be $C_4H_{10}O$; however, for Gerhardt and Laurent alcohol was not $C_4H_{12}O_2$, but half that, C_2H_6O.) These chemists thus argued that *two* molecules of alcohol had to come together, losing a molecule of water in the process, to form each molecule of ether. Following the so-called contact (catalytic) theory of Berzelius—more about this in a minute—Gerhardt and Laurent portrayed alcohol as the "ethyl" radical C_2H_5, united with an oxygen and a hydrogen atom. Following their own lights, they portrayed the ether molecule as consisting of two ethyl radicals and an oxygen atom. Symbolizing C_2H_5 as "Et," they pictured the reaction of ether formation as:

$$\begin{array}{ccc} \mathrm{EtOH} + \mathrm{EtOH} & \longrightarrow & \mathrm{EtOEt} \quad + \; H_2O \\ \text{two molecules of alcohol} & \text{yield} & \text{one molecule of ether} + \text{water} \end{array}$$

Gerhardt and Laurent argued their case on the basis of logical consistency, taxonomic heuristics, and esthetics of formulation (including Ockham's razor), rather than from any evidence from new experiments that were specifically designed to test these ideas. A critic of the 1840s could legitimately say—many *did* say—that Gerhardt and Laurent had not provided any compelling reasons to relinquish the prevailing opinion and adopt a new one; they had not offered experimental proof of the truth of their theory, or of the insufficiency of that of Dumas and Liebig. Considered more broadly, various chemists over the years had provided ingenious alternative formula systems that were consistent with various lines of evidence, but none had yet succeeded in demonstrating the truth of one of those viewpoints to the exclusion of the others. Thus far no one had, in this strong sense, entered into the world of atoms and molecules in an epistemically robust way. No wonder there was a sense in many minds that the best stance was that of empiricist caution—until experimental proofs were to arrive.

Newly installed in his London post, Williamson set himself the task of providing such proof. He started from a position of belief and trust in the Gerhardt-Laurent system, and he thought very hard about this crucial reaction, the formation of ether. It must have occurred to him that the only reason that the theory of Dumas and Liebig could survive their use of inconsistent molecular magnitudes was the fortuitous symmetry of the ether molecule, a result of the circumstance (according to the theory of Gerhardt and Laurent) that two *identical* molecular pieces—the two alcohol molecules—were joining together in the reaction. If one could bring two *different* alcohol molecules together, to produce an *asymmetrical* ether molecule, then the inconsistent magnitudes would be revealed to the world, and the Gerhardt-Laurent theory would be proved.

Williamson discovered that he could form ether from the recently discovered “ethylate of potash” (potassium ethoxide) by reacting the latter with ethyl iodide. In this new reaction, instead of water splitting off as in normal etherification, potassium iodide was released, along with the product ether. Thus far, the new reaction was entirely analogous to the familiar (symmetrical) etherification. However, he now had in his hands the means to make the asymmetric reaction happen, by combining ethylate of potash with *methyl* iodide. By the theory of Liebig and Dumas, the product of this novel reaction ought to have been equal amounts of *two different symmetrical* ethers, whereas the Gerhardt-Laurent theory correctly predicted the formation of *a single asymmetric* product, ethyl-methyl ether (Et = ethyl = C_2H_5; Me = methyl = CH_3):

$$C_4H_{10}O\cdot KO + C_2H_6\cdot I_2 \longrightarrow C_4H_{10}O + C_2H_6O + KI_2$$

Liebig and Dumas

$$EtOK + MeI \longrightarrow EtOMe + KI$$

Williamson

"In this experiment," Williamson wrote, "the two theories cross one another, and must lead to different results,"[33] with the actual result demonstrating the ideas of Gerhardt and Laurent. He underlined the point even more strongly by preparing additional novel asymmetric ethers, namely ethyl-amyl ether and methyl-amyl ether. The argument was proven, he asserted—a beautiful example of an unanswerable experimentum crucis.

As brilliant as this gambit was, there was much more in the paper, namely some important new ideas on the dynamics of reactions. The etherification reaction was complex, partly due to a proliferation of minor products depending on conditions, and partly to the mysterious action of the sulfuric acid. Years earlier, Berzelius had argued that the acid was a simple catalyst operating by physical contact, the details of whose operation were not known and possibly could never be known. Liebig, on the other hand, had asserted the necessary chemical intermediation of a product often found in the reaction mixture called sulfovinic acid (ethyl hydrogen sulfate). In February 1850 Thomas Graham demonstrated that the reaction could be made to work in sealed tubes, apparently without any participation of sulfovinic acid, and so he threw his weight behind the contact theory. As a concomitant of that theory, he emphasized, as Berzelius had done, that it must take two molecules of alcohol to make one of ether, thus (implicitly) also suggesting support for the new chemistry of Gerhardt and Laurent.[34]

In his August 1850 paper, Williamson proposed a reaction mechanism for etherification that invoked a central chemical role for sulfuric acid. He suggested that in this reaction, ethyl radicals continuously shuttle from the alcohol, to the sulfuric acid, then to another molecule of alcohol, thereby making a molecule of ether. The alcohol molecule that is abandoned by its ethyl becomes water, one of the products; the sulfuric acid molecule that acquires ethyl becomes sulfovinic acid; the sulfovinic acid molecule that loses ethyl to a molecule of alcohol becomes sulfuric acid once more. The overall process ineluctably carries alcohol to ether and water, essentially doubling the size of the alcohol molecule, while the sulfuric acid remains unaltered over the course of the entire reaction.

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[33] Williamson, "Theory of Aetherification" (1850), 352. Williamson was using Gerhardt's and Laurent's atomic weight for potassium. Following Berzelius's lead, Liebig and Dumas used a doubled weight for potassium, so they used half the number of atoms. This disagreement was not relevant to the point Williamson was making here.

[34] Graham, "Observations" (1850). See Stanley, "Graham," 253–54.

In Williamson's vivid conception, this process happens continuously and randomly, promoted by the constant kinetic motion of the molecular participants and pushed to completion by the stability of the resulting products, ether and water, and their removal from the site of reaction. He illustrated his mental vision of this molecular dance by means of formula tableaux that made clear the various displacements of the ethyl radicals. His paper thus contains what is probably the first competent and empirically plausible proposal for an important reaction mechanism, a viewpoint that was founded upon the "broader basis of atomic motion."

The Experimental Dissection of Molecules

Williamson was not finished with the subject of etherification. After ten months of public silence, within a span of twenty-six days in the early summer of the following year he presented three connected papers in rapid succession: a "Friday Evening Discourse" at the Royal Institution, a formal paper at the Chemical Society, and a presentation at the annual meeting of the British Association for the Advancement of Science, held that year in Ipswich. Though overlapping and closely related, each of these three papers had distinct styles and messages. The net effect of the three papers was to chart the early stages of an investigative route towards the systematic conceptual dissection of organic compounds, offering the promise of a secure pathway into the bewildering jungle of organic chemistry. In the course of examining these three papers, we will see further evidence of Williamson's imaginative molecular visions.

The discourse at the Royal Institution on 6 June 1851, "Suggestions for the Dynamics of Chemistry derived from the Theory of Etherification," was intended for a broad audience, as was generally the case in this famous lecture series begun twenty-five years earlier by Michael Faraday.[35] Williamson averred that the "dynamics of chemistry will commence by the rejection" of an "unsafe and unjustifiable hypothesis, namely that the atoms are in a state of rest"; "the various phenomena of change, which are now attributed to occult forces, [will] reduce to [the] one fact" of atomic motion. "A little reflection is sufficient to show that such a motion actually exists," he suggested, citing the "fact

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[35] Williamson, "Suggestions" (1851).

of diffusion" as a prominent example. And there are other "mechanical evidences of the communication of momentum from masses to atoms, and inversely." So also for substances in solution. Static appearances in chemistry are as deceiving as the apparent constant whiteness of a spinning color wheel, Williamson asserted; in fact, atoms of molecules in solution, such as hydrogen chloride molecules in water, are undetectably engaging in continuous rapid mutual displacements. Underlying the ostensible stability of "double displacement" reactions are actually opposing atomic currents constantly moving in each direction of the reaction; and "chemical force must be proportional to the velocity of these interchanges."

Williamson had of course recently published on a reaction that illustrates just such a phenomenon. For the benefit of this mixed audience, he visually diagrammed his proposed reaction mechanism for etherification with formulas on a lecture placard on which an oblong card rotating on a pivot was overlaid, in order to represent an example of the rapid shuffling of atoms and radicals undergoing a reaction (such as **Na** and **Et** trading places between EtO and I, transforming EtO**Na** and **Et**I to EtO**Et** and **Na**I).[36] The two steps of his proposed reaction mechanism were more than just a hypothesis, he argued. He revealed that "their reality [was] proved" by his recent success in experimentally separating the two steps, by reacting alcohol directly with sulfamylic acid (amyl hydrogen sulfate). The isolation from the reaction mixture of ethers and sulfovinic acid, but no sulfamylic acid, was positive proof, he wrote, that the sorts of molecular exchanges that he had posited the previous year really do take place.[37]

Williamson ascribed the basis of this model to Claude-Louis Berthollet. Berthollet had denied the existence of "elective" (absolute) affinity, emphasizing instead the role of "chemical mass"; he had also elucidated the importance of precipitation, "efflorescence," and "elasticity" (gas formation) in removing products from the "sphere of chemical

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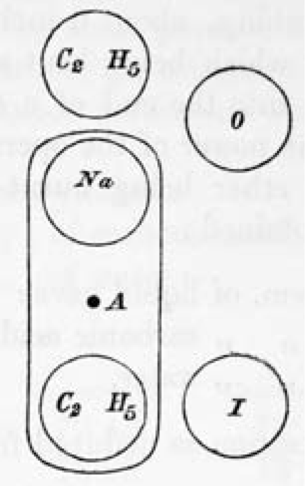
[36] Williamson, "On Etherification" (1851), 231. This is the "Williamson ether synthesis" using sodium (Na) compounds. I have bolded the molecular pieces thought to be shuffling, but Williamson's pivoting card makes the concept much clearer. The pivoting card is mentioned in the Royal Institution talk and was apparently demonstrated to the audience, but was not illustrated in the published version.

[37] These details, like the image of the lecture placard, are also taken from Williamson's presentation to the Chemical Society on 16 June 1851. The third-person description of the Royal Institution talk that appeared in the journal of the Royal Institution (the only source) includes only an allusion to the separation of the two steps of the mechanism, by using successively two different alcohols, as proving the truth of his supposition. It is not known whether Williamson included all these chemical details in the Royal Institution talk.



1 Williamson's lecture placard, with pivoting card. Source: Williamson, *Journal of the Chemical Society* 4 (1851): 231.

activity," thus forcing an unfavorable equilibrium to completion.[38] In the opening of his *Essai de statique chimique* (1803) Berthollet had famously analogized molecular interactions to the motions of the planets ruled by gravitation, adding: "It is a very natural thought that the principles of chemical theory will show more and more agreement with the principles of mechanics, to the degree that they become more general."[39]

We will see below how Williamson would adduce the same gravitational analogy—following the lead of Graham (cited above) as well as Berthollet. But Williamson had gone beyond Berthollet in two ways. First, as he noted, he had applied the atomic theory to Berthollet's mass-action ideas. And second, he had articulated, for the first time, a concept of *dynamic* equilibrium, that is, the idea that equilibrium consists not in cessation of molecular motion, but rather in the equalization of reaction rates running continuously and simultaneously in opposite directions. The Norwegian chemists C. M. Guldberg and P. Waage later generalized the phenomena discussed by Berthollet, Williamson, and others, into the mathematical law of mass action (1864–67).

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[38] Berthollet, *Essai* (1803). Williamson used the phrase "circle of decomposition" in the same way Berthollet referred to the "sphere of chemical activity."

[39] Ibid., 1:1–4. For more on these matters, see the first section of chapter 8, this volume.

Ten days later Williamson spoke on etherification before the Chemical Society of London.[40] As he had in his first ether paper, he played the role of peacemaker. "Now I submit that the theory here laid before you, with its experimental conclusions, combines the requisitions of the several parties in this great discussion, and may be considered as closing it amicably, by shewing that each point of view contained part, and an important part, of the facts."[41] Having synthesized three "intermediate" (asymmetric) ethers the preceding year—ethyl-methyl, ethyl-amyl, and methyl-amyl ethers—he now revealed the synthesis of two additional novel symmetrical ethers using the same molecular pieces (dimethyl and diamyl ethers). By establishing the identity of the products of the two reactions: methylate of potash + ethyl iodide, and ethylate of potash + methyl iodide, he reasoned that for this "three-carbon ether . . . [ethyl and methyl] are contained in *like* manner in it."

Here before his professional peers at the Chemical Society, Williamson made his private mental world public, just as he had done to a broader audience at the Royal Institution. He again illustrated the mechanism of etherification using a placard with a pivot, around which he rotated the symbols of the molecular pieces that he hypothesized were exchanging places. But this was more than a hypothesis: he once more adduced, as he had a few days earlier at the Royal Institution, what he regarded as conclusive proof of the reality of the mechanism, by showing how he had experimentally separated its two steps.

Then Williamson applied the same experimental design that he had used for ethers on a new molecular system. He had already suggested the preceding year that acetic acid had to have the smaller (two-volume) formula advocated by Gerhardt and Laurent, namely, a formula containing only two carbon atoms ($C_2H_4O_2$), for this acid could be easily generated by oxidizing ordinary alcohol, which was now securely known from the etherification work to have only two carbon atoms. Williamson now announced that he had devised an even more direct way to determine that the smaller formula for acetic acid was correct. He synthesized a novel asymmetric analogue to acetone (dimethyl ketone, CH_3COCH_3) using the same reasoning as he had applied to his novel asymmetric ethers. This substance is now known as methyl butyl ketone, $CH_3COC_4H_9$. With the new light that this reaction threw on the subject, he could now establish that acetic acid and its relatives (propionic, butyric, valeric, etc.) had to have the smaller

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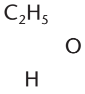
[40] Williamson, "On Etherification."

[41] Ibid., 230.

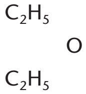
(Gerhardtian) formulas, in an exactly parallel fashion as he had proven the smaller formulas for the alcohols.

This was a stunning series of achievements. Taking the schematic key from Gerhardt and Laurent, Williamson had ingeniously devised investigative pathways that for the first time compelled belief *by reasoning from new experimental evidence*. Williamson asserted that one could now not just suggest, but *prove,* that alcohol consisted of molecules that actually contained exactly two carbon atoms, exactly six hydrogen atoms, and one oxygen atom; and that acetic acid was the same as this, but with two of the hydrogen atoms removed and one additional oxygen atom added. Furthermore, the fact that one could extract one of the six hydrogen atoms of a molecule of alcohol to make ethoxide, and extract one oxygen and one hydrogen from another molecule of alcohol to make ethyl iodide, and then, in effect, stick the two molecules together, meant that alcohol must be composed of an ethyl group, C_2H_5, united with an oxygen and a hydrogen atom, and that the sixth ("basic") hydrogen must be uniquely associated with the oxygen atom, and not directly with the ethyl group. Water, alcohol, and ether were, therefore (in Williamson's preferred rational formulas):[42]

$$\begin{array}{ll}\mathrm{H} & \\ & \mathrm{O}\\ \mathrm{H} & \end{array}$$

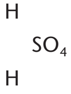


$$\begin{array}{ll}\mathrm{C_2H_5} & \\ & \mathrm{O}\\ \mathrm{H} & \end{array}$$

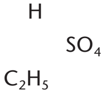


$$\begin{array}{ll}\mathrm{C_2H_5} & \\ & \mathrm{O}\\ \mathrm{C_2H_5} & \end{array}$$

Sulfuric acid and sulfovinic acid were:

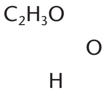


$$\begin{array}{ll}\mathrm{H} & \\ & \mathrm{SO_4}\\ \mathrm{H} & \end{array}$$



$$\begin{array}{ll}\mathrm{H} & \\ & \mathrm{SO_4}\\ \mathrm{C_2H_5} & \end{array}$$

And there was more. The two hydrogen atoms that are removed and replaced by a single oxygen atom when alcohol is oxidized to acetic acid could only have come from the ethyl radical, where all the hydrogen of acetic acid that is not involved in acid formation was located. From this evidence, the rational formula for acetic acid had to be written:



$$\begin{array}{ll}\mathrm{C_2H_3O} & \\ & \mathrm{O}\\ \mathrm{H} & \end{array}$$

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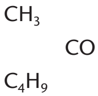
[42] The first five of the following formulas appeared in Williamson's first ether theory paper of August 1850.

The new radical C_2H_3O, which Williamson had thus shown must exist in acetic acid, he named "othyl," from oxygen-ethyl. Acetone, he stated, was obviously othyl associated with a methyl radical. And his novel asymmetric ketone had to be formulated:



$$\begin{matrix}\mathrm{CH_3} & \\ & \mathrm{CO} \\ \mathrm{C_4H_9} & \end{matrix}$$

Though Williamson did not say so explicitly, he was clearly affirming that one could now confidently specify (and represent in a rational formula) the sequential order in which certain atoms and radicals were arrayed within certain molecules. Some aspects of the intramolecular arrangements of atoms, at least in certain cases, were no longer the subject of mere speculation, but of systematic and confident experimental determination.

And his formulas suggested even more. Whenever a central oxygen atom appeared on the right side of one of these triangular formulas, exactly two constituents—never more, and never fewer—always appeared to the left. If one of the left-hand constituents was removed, like a hydrogen atom from the alcohol formula, then another constituent had to come in its place, like an ethyl radical to form ether. Williamson was clearly (though still only implicitly) creating two distinct categories of submolecular constituents. One category comprised those entities that could appear at the right of his formulas, namely O, SO_4, or CO; the other category comprised those entities that could appear on the left, namely an atom of hydrogen, or of chlorine, or certain of the metals, or a hydrocarbon radical, or the othyl radical. He had created these categories not by arbitrary fiat, but by induction. However, he did not make this induction explicit—probably because the empirical base for it was still rather narrow.

Here we may see the influence of Graham's and Liebig's theories of polybasic acids, for Williamson was portraying carbonic oxide CO (for example) as "bibasic" in a fashion analogous to how Graham described pyrophosphoric acid, or to how Liebig described tartaric acid, both as dibasic acids. In each case, a central molecular moiety had the power to hold together precisely two other pieces into a single larger molecular system. When, soon after Williamson's work, certain *atoms* were explicitly proclaimed as intrinsically monobasic, dibasic, tribasic, etc., the theory of atomic valence was born.

Two weeks after his Chemical Society paper, Williamson traveled to Ipswich to present a theoretical paper to the Chemical Section of the British Association.[43] After proclaiming his continuing desire to strongly support and develop the chemical ideas of Laurent and Gerhardt, Williamson categorically rejected Gerhardt's principle that formulas should never presume to indicate the actual arrangements of the atoms that form the molecules of the substance. Instead, following the example of Berthollet, Williamson affirmed that formulas can represent "an actual image of what we rationally suppose to be the arrangement of constituent atoms in a compound, as an orrery [a mechanical planetarium] is an image of what we conclude to be the arrangement of our planetary system."[44] Just as Lavoisier had taught chemists that a substance's "written name should be made to represent what we conceive a compound *to be,*" so also its formula should be taken seriously in this explicitly realist sense, Williamson averred; moreover, we should strive to follow chemical reactions by tracing the actual molecular changes that are effected, and by reflecting those changes in corresponding chemical formulas. This realist sense of formulas was the great contribution of the theory of types, he added, and Dumas deserved the gratitude of his colleagues for this service.[45]

Many "triangle" formulas appear in this paper and build further on the ideas expressed in his earlier publications. Williamson now began to use the term "bibasic" to describe the radicals on the right side of his formulas, which could unite and "hold together" two monobasic atoms or radicals on the left. Such bibasic entities included CO, SO_4, SO_2, and (by implication) oxygen atoms. The two entities that could appear on the left, being held in the same molecule by the single entity on the right, included hydrocarbon radicals, ethoxide or methoxide, othyl, H, Cl, NO_2, K, Na, CN, OH, NH_2, and a few others. Williamson asserted in his formula-language that CO could unite two ethoxide moieties into "oxalic ether" (diethyl oxalate), or two NH_2 groups into urea; he implied that an oxygen atom could unite two hydrogen atoms into water, or two ethyl radicals into ether, or an othyl and a hydrogen into acetic acid; finally, he implied that two oxygen atoms could bridge between a single bibasic SO_2 radical and two hydrogen atoms to make the bibasic sulfuric acid molecule. He even suggested the possible existence of two othyl radicals held together by an oxygen atom, which, if the synthesis

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[43] Williamson, "Salts" (1851).

[44] Ibid., 351.

[45] Ibid., 354.

could be accomplished, would be the true form of anhydrous acetic acid (i.e., acetic acid anhydride).

All this can be simply summarized. First, Williamson was issuing an explicit and unambiguous call for a realistic interpretation of formulas and for the potential determinability of at least some aspects of intramolecular atomic arrangements. Second, he provided a compelling model for how such an investigative program could be conducted. He placed that model in the tradition of the mechanical "type theory" as defined by Dumas in 1839–40, and according to the reformist notational and taxonomic proposals of Gerhardt and Laurent. And third, this paper contains implicitly an idea that atoms and radicals have fixed capacities to combine with one, two, or some other definite number of other atoms or radicals. Others would soon develop this theme into what today is known as "valence." However, he stated no such theory explicitly. These conclusions were accurately captured by Adolphe Wurtz in his early history of structural ideas when he wrote that the essence of Williamson's accomplishment was to have shown that ether quite truly ("bien réellement") contains two ethyl molecules.[46]

Williamson ended this third paper with a return to his concern for dynamical theories of atomic motion by proclaiming that his ultimate goal was the "exact determinations of the relative momentums of atoms in various compounds, the proportion of which to their masses determines their physical and chemical properties." What Williamson meant by this enigmatic statement is hard to say,[47] but in any event it carries considerable irony. Williamson was continuing, sincerely but abstractly, to profess a Heraclitean metaphysics (molecular reality is nothing but motion and change), while at the same time in quite concrete terms carrying out a Parmenidean investigative program (one really can determine the actual enduring form of unseen submicroscopic molecules—or, to use Williamson's exact words, including his emphasis, "what we conceive a compound *to be*"). There may not have been as irreconcilable a conflict between these positions as it may seem—after all, Plato and Aristotle were able to bridge the apparent gulf between their two great pre-Socratic predecessors—but there was at minimum a certain tension between these tendencies. This tension was fully parallel to that between Williamson's French mentors, the Heraclitean Ger-

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[46] Wurtz, *Cours* (1864), 31–32.

[47] The ratio of momentum to mass is velocity. Is this a reflection of, or influenced by, Graham's ideas on the intrinsic motion of atoms? In any case, the statement is consistent with similar statements in Williamson's other papers of 1850–51.

hardt and the Parmenidean Laurent. But beyond question what we see at work here, in *both* of these philosophical modes, is one of the great visual imaginations in mid-nineteenth-century science, allied with brilliant investigative skills.

Excursus: Isolated Radicals?

While Williamson was still in Paris, another important story line was playing out. The Englishman Edward Frankland (1825–99) and the German Hermann Kolbe (1818–84), then fellow assistants of Lyon Playfair at the Museum of Economic Geology in London, presented a joint paper to the Chemical Society in April 1847. Kolbe and Frankland reported that they had succeeded in transforming methyl, ethyl, and amyl cyanide into the corresponding organic acids. In equivalent-weight (C = 6, O = 8) Berzelian-dualist (copula) formulas, they portrayed these reactions as:

$$\begin{array}{ccc}
C_2H_3{\cdot}C_2N & \longrightarrow & C_2H_3{\cdot}C_2O_3{\cdot}HO \\
\text{methyl cyanide} & & \text{acetic acid} \\
\\
C_4H_5{\cdot}C_2N & \longrightarrow & C_4H_5{\cdot}C_2O_3{\cdot}HO \\
\text{ethyl cyanide} & & \text{propionic acid} \\
\\
C_{10}H_{11}{\cdot}C_2N & \longrightarrow & C_{10}H_{11}{\cdot}C_2O_3{\cdot}HO \\
\text{amyl cyanide} & & \text{caproic acid}
\end{array}$$

Kolbe had been a student of Wöhler and Bunsen, both Berzelians, but unlike them was passionately interested in chemical theory, especially the quest to determine molecular "constitutions" (identification of the particular radicals that combine to form a given molecule). He had imbued Frankland with the same passion, contrary to the positivistic tenor of the day. Kolbe and Frankland thought that this work strongly supported the Berzelian copula formulas in which they expressed their reactions.

Aside from the question of copulas, Frankland later asserted that this paper established "for the first time the internal molecular structure of these acids."[48] Whether one agrees with this judgment or not, it

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[48] Frankland, *Sketches* (1901), 70. The standard source for the life and work of Frankland is Russell, *Frankland* (1996).

is probably true that these were the earliest planned reactions in which the core carbon content of an organic molecule was deliberately altered. "The isolating of the alcohol [i.e., alkyl] radicals," Frankland later reminisced, "was, at this time the dream of many chemists, whilst others doubted or even denied their existence. I was also smitten with the fever and determined to try my hand at the solution of the problem."[49] He and Kolbe, who then traveled to Marburg together for the summer semester 1847 to work directly with Bunsen, were notably successful in this quest. In 1848 and 1849 (spending much of this time acquiring a Ph.D. with Bunsen and then working for a semester with Liebig in Giessen), Frankland used zinc metal to liberate the gaseous methyl and ethyl and the liquid amyl radicals from their corresponding iodides. Meanwhile, Kolbe had ever greater success with his electrolyses, isolating the "valyl" radical from valeric acid and the methyl radical from acetic acid. The isolation of all of these radicals, Frankland wrote, "excludes every doubt of their actual existence, and furnishes a complete and satisfactory proof of the correctness of the theory" that ethyl is actually contained in alcohol and ether, and methyl is actually contained in acetic acid.[50]

Gerhardt and Laurent contested the interpretation of these results. They asserted that Kolbe's and Frankland's inconsistent use of molecular magnitudes had only made it appear that they were isolating actual radicals. If all molecules were formulated consistently at the same number of volumes, they wrote, then the formulas for the free gases and liquids that were produced in Kolbe's and in Frankland's reactions would need to be doubled. Their "radicals," Gerhardt and Laurent argued, were stable only because they were in fact doubled molecules (today we call them dimers). Laurent had long used a simple empirical rule, called the "even-number rule," to test for consistent magnitudes. This rule dictated that organic-chemical formulas should always have an even number of hydrogen atoms; if there seemed to be an odd number, the formula was to be doubled. Kolbe's and Frankland's free gaseous "methyl," C_2H_3, they wrote, is not methyl at all, but its dimer, $C_2H_3 \cdot C_2H_3$, or, as expressed in Laurent's and Gerhardt's atomic weights ($C = 12$, $O = 16$), CH_3CH_3 or C_2H_6.

In 1850 Kolbe wrote a long review article interpreting his and Frankland's work in the context of the development of chemistry over the last

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[49] Frankland, *Sketches,* 175.

[50] Frankland, "Isolation" (1849); Frankland, "Researches" (1850), 46–47; Kolbe, "Elektrolyse" (1849).

generation.[51] In his view, Dumas, Laurent, Gerhardt, and other French chemists had been too hasty in rejecting Berzelian electrochemical-dualist theory and the ideas of the radical theory for the uncertain world of "types." All one needed to do in order to maintain the validity of the radical theory was to admit (with Berzelius) that copula radicals could undergo substitution. His and Frankland's success, he wrote, proved the point. One could now say with certainty that acetic acid (for instance) really was constituted as the molecule $C_2H_3 \cdot C_2, O_3 \cdot HO$. The C_2 group between the dot and the comma, Kolbe wrote, "presents the exclusive point of attack for the powers of affinity of oxygen, chlorine, &c." This dissection and schematic analysis of a molecule with the help of Berzelian theory is proof that the latter is "a trustworthy guide in the difficult field of organic chemistry, and has preserved us most securely from the errors of a code of laws like that which has been laid down by Laurent and Gerhardt . . . [C]hemistry is indeed something better than a mere arithmetic problem, into which Laurent and Gerhardt endeavor to convert it."[52]

The sense of triumph of Kolbe and Frankland was to be short-lived, for, coincidentally, Williamson's first ether paper appeared at the same time as Kolbe's major review paper. Curiously, though, on a deeper level the work of Frankland and Kolbe had much in common with Williamson's, for all three chemists were atypically interested in questions that did not much exercise their colleagues: striving toward the determination of absolute constitutions of molecules and expressing those constitutions using rational formulas that could be interpreted mechanically and realistically.

The Spread of Williamsonian Theory

Gerhardt was thrilled by Williamson's first ether paper (Laurent was already mortally ill and could not participate fully in these developments). Over the next six years he combined Williamson's new reactions with those of Adolphe Wurtz, the chemistry professor at the Faculté de Médecine in Paris, and those of August Wilhelm Hofmann, the director of the Royal College of Chemistry in London, to outline a new version of type theory. In Gerhardt's telling, Williamson's work had given birth to a "water type," Wurtz's and Hofmann's efforts had cre-

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[51] For a more detailed explanation of these developments, see *QR*.

[52] Kolbe, "Radicale" (1850), 69; Kolbe, "Radicals" (1850), 76.

ated an “ammonia type,” and Gerhardt himself added what he called a “hydrogen type” (later also a “hydrogen chloride type”) by which to theoretically encompass and organize organic compounds.

But Gerhardt did not agree with Williamson’s realist conception of formulas, continuing to view them simply as empirical summaries of chemical reactions—as “contracted chemical equations.” The formulation of the sulfuric acid molecule can serve as an example. Whereas Williamson had depicted a central SO_2 radical as replacing *one hydrogen atom each from two different* water molecules, holding the two resulting HO radicals into the same H_2SO_4 molecule, Gerhardt’s formula had the SO_2 radical replacing *two hydrogen atoms from the same* water molecule, the symbol for the second water molecule simply sitting beside the new “SO_2O” moiety, to make up H_2SO_4.[53] Gerhardt explicitly denied the atomic linking function so clearly portrayed in Williamson’s approach, since his (Gerhardt’s) formulas were founded upon a different philosophy and had a different function. To put it plainly, Gerhardt did not view the constitution of sulfuric acid in a different way from Williamson; rather, his formula intentionally avoided advocating *any* constitutional idea.

However, Gerhardt obviously appreciated the persuasive force of Williamson’s arguments from the synthesis of asymmetric varieties of ether and acetone, comprising, as they did, affirmations of the truth of what he had been preaching for years. In this regard, at least, Gerhardt followed Williamson’s lead. In the spring of 1852 he succeeded in synthesizing the acetic acid anhydride that Williamson had predicted in his 1851 Ipswich paper—a symmetrical doubled version of acetic acid with loss of water, the perfect analogue to the doubling of alcohol with loss of water to form ether. Gehahrdt then took the next (Williamsonian) step. He succeeded in synthesizing novel *asymmetric* versions—mixed anhydrides between acetic, benzoic, salicylic, and other organic acids. The argument for the smaller (Gehardtian) formulas for all of these organic acids followed along precisely the same lines as Williamson’s arguments from his asymmetric ethers and ketones. This fine contribution marked Gerhardt’s personal career breakthrough, for the result convinced several of his powerful former enemies that he might be on the right track after all.[54]

The theoretical ground in European chemistry began perceptibly to

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[53] Gerhardt and Chiozza, “Addition” (1853), 1054.

[54] Gerhardt, “Recherches” (1852); Grimaux and Gerhardt, *Gerhardt* (1900), 228–36, 239–41, 401–13.

shift in the early 1850s. One of the important voices at midcentury was that of Hofmann, a youthful student of Liebig's lured away from the University of Bonn as the first director of the Royal College of Chemistry. Hofmann and Kolbe were exact contemporaries, arrived in London the same month (October 1845), and became fast friends. Hofmann's work on aniline appeared initially to fully support Berzelius's copula theory, for he formulated all of his compounds using the copula $C_{12}H_4$, joined to ammonia NH_3. But in the fall of 1849 Hofmann found that some reactions simply could not be represented this way. He concluded that aniline could not be $C_{12}H_4,NH_3$, but rather must be $C_{12}H_5,NH_2$; that is, aniline was not a copulated ammonia, but a *substituted* ammonia. Hofmann had thus entered the type-theoretical world of the French chemists. He discovered that he had tapped a rich vein. Even before the end of that year Hofmann revealed his creation of an astonishing array of new organic-substituted ammonias, his so-called secondary and tertiary amines—i.e., NH_3, in which respectively two or three hydrogen atoms are substituted by organic radicals such as methyl, ethyl, or phenyl. The *primary* (once-substituted) amines had been discovered earlier in the year 1849 by Hofmann's good French friend (and former comrade in Giessen as a fellow Liebig student), Adolphe Wurtz.

In March 1850 Hofmann argued before the Chemical Society that Laurent and Gerhardt must be correct in their interpretation of Kolbe's and Frankland's "radicals." There were strong analogical reasons, he noted, to have expected that free radicals such as methyl and ethyl, if isolable at all, would be highly unstable and reactive. But Kolbe's and Frankland's isolated "methyl" and "ethyl" gases were unreactive in the extreme. They bore strong family resemblances to known hydrocarbon gases such as methane, to ordinary hydrocarbon liquids such as those found in petroleum, and to solids in paraffin wax. Also, their boiling points strongly suggested that they were larger molecules than their discoverers thought; if Kolbe's and Frankland's two-volume formulas for the "radicals" were doubled, the boiling points would fit in a beautifully precise series with those of other hydrocarbons known not to be radicals.[55] Hofmann was now publicly favoring the chemistry of Laurent and Gerhardt.

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[55] Hofmann, "Note" (1850). For instance, the known hydrocarbon amyl hydride (today called pentane), $C_{10}H_{12}$, was known to boil at 30°C, while the newly discovered purported "amyl radical," $C_{10}H_{11}$, boiled at 155°C. Why would removing a single hydrogen atom produce such a dramatic change in physical properties? If "amyl" were really di-amyl, $C_{20}H_{22}$ (today called decane), on the other hand, this and other physical properties of "amyl" would make perfect sense. The data on boiling points was supplied by Hermann Kopp.

In December 1850, following the publication of Williamson's first ether theory paper, the London chemist Benjamin Brodie, Jr., adduced additional arguments in favor of the dimer formulas for the purported "radicals." Then Brodie suggested an experimental test that would settle the issue definitively. He (and Hofmann, and Gerhardt and Laurent) were suggesting that in Kolbe's and Frankland's experiments *two identical* radicals were actually coming together—that is, dimerizing—to form symmetrical doubled hydrocarbon molecules. If one could make an *asymmetric* hydrocarbon by stitching together *two different* radicals, then one could prove the dimer formulas correct, exactly as Williamson had just done with the ethers. For this attempt he used Frankland's experimental technique, reacting a mixture of ethyl iodide and methyl iodide with zinc metal. But he could not get the reaction to work well. He commented in a footnote at the end of the paper that Hofmann—also obviously following Williamson's example—had told him that he had tried essentially the same reaction by reacting ethyl zinc with methyl iodide or with amyl iodide. But Hofmann had not been successful either.[56]

Soon thereafter, Kolbe's comrade-in-arms, Frankland, submitted for publication a landmark paper that, similar to Brodie's and Hofmann's work, pointed toward serious anomalies in the copula theory. As a master (indeed, the founder) of organometallic chemistry, Frankland adduced examples of reactions that indicated that tin, zinc, mercury, antimony, arsenic, phosphorus, and nitrogen exhibit fixed maximum combining capacities with other atoms or radicals. Arsenic and antimony, for instance, seem to combine only with three or with five equivalents of other atoms or radicals. If the maximum capacity is reached, then only substitution, not addition, of other components can occur. Frankland had turned: he now allied himself with the ammonia type theory of Hofmann and Wurtz, for the semimetals antimony and arsenic seemed to follow exactly the pattern established by the new organic nitrogen compounds of the latter chemists. The theory of copulas, he declared, could no longer be maintained.[57]

There appears to be much in common between these statements and Williamson's avowal a year earlier that certain radicals and atoms are "bibasic" and can suffer substitution but not addition reactions. Both claims have legitimately been interpreted as early approaches to what came to be known as the theory of atomic valence. (Frankland's had

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[56] Brodie, "Observations" (1850), 411n.

[57] Frankland, "New Series" (1852); Russell, *Frankland,* 108–13, 118–21.

greater potential generality, but suffered from the disadvantage, from the perspective of later atomists, of being expressed in the concepts of chemical equivalents and organometallic radicals.)[58] Frankland, using almost the same words as Williamson had before him, added that his suggestions promised "to assist in effecting a fusion of the two theories which have so long divided the opinions of chemists, and which have too hastily been considered irreconcilable."[59] The parallels in their work were not, however, matched by any close personal connections between these two men.

These new developments worried Kolbe. Williamson's arguments for the new formulas for alcohols, ethers, and organic acids, Gerhardt's for the new acid anhydrides, and Brodie's and Hofmann's for the hydrocarbon radicals, all supported the ideas of Gerhardt and Laurent and provided an effective rebuttal to his and Frankland's putative isolation of the radicals and consequent purported proof of Berzelian copulas. After much effort, in the fall of 1853 Kolbe devised an experimental argument that, he thought, decisively refuted the Williamson-Gerhardt theory, using their own argument turned back upon them.[60] But Kolbe's purported refutation was itself flawed, as Williamson immediately pointed out; among other problems, Kolbe had failed to translate correctly between his atomic weights and formula conventions and those of the reformers. Kolbe's mistakes were symptomatic of a larger issue: he had never fully worked his way through the French (and now French-English) theories. We must not be too hard on Kolbe, who was truly a master chemist and a prolific and important theorist. These formula translations were by no means simple, and many of the finest nineteenth-century chemists became confused in trying to think through all these issues.

There is a parallel here to the problems that Galileo had faced more than two centuries earlier. To understand the Copernican system, one needed a healthy dose of visual imagination, for it was necessary to think of oneself as standing on a spinning and hurtling globe called the Earth, and to imagine vicariously the other motions of the planets, and all the resulting apparent phenomena as seen from the earth. Galileo paired that visual imagination with a realist understanding that one was not just "saving phenomena" abstractly and mathematically, but

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[58] For a vigorous and thoughtful championing of Frankland's undiluted claim to valence theory, see Russell, *Frankland*.

[59] Frankland, "New Series," 441.

[60] For details, see *QR*, 142–55.

riding a real planetary body around a real sun and directly viewing the results; his challenging task was to convince others to follow the same mental gymnastics. In a similar sense, superadded to his investigative brilliance, Williamson's secret weapons were his extraordinary visual imagination and the realist philosophy to which he connected it.

TWO

The Architect of Molecules

It may sound quite strange, but for me, as for other scientists on whom these kinds of imaginative images have a greater effect than other poems do, no science is at its very heart more closely related to poetry, perhaps, than is chemistry. JUSTUS LIEBIG[1]

Now you meet with none of these afflictions in [a London] omnibus; sameness there can never be. . . . We believe that there is no instance upon record, of a man's having gone to sleep in one of these vehicles.
CHARLES DICKENS[2]

After a lackluster period, around midcentury London suddenly became an exciting city in the world of chemistry. Hofmann arrived there in 1845, Kolbe spent from 1845 to 1847 there, Frankland spent most of the period from 1845 to 1851 in or near London, Williamson joined Graham at UCL in 1849, and others, such as John Stenhouse, Benjamin Brodie, Jr., and William Odling, were also valued members of the community. Most of these men had been associated with Liebig at some point. It was the right time for the arrival there of a bright, ambitious, and self-confident young chemist—and another member of the Liebig club—August Kekulé.

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[1] "Es mag recht sonderbar klingen, allein es geht mir wie anderen Naturforschern auf welche diese Art von phantasiereichen Gebilden mehr Eindruck als andere Gedichte machen und keine Wissenschaft ist der Poesie vielleicht ihrer inneren Natur nach mehr verwandt als wie die Chemie." Written in Liebig's hand on the back of a letter from Kekulé to Liebig, dated 20 November 1854, in Anschütz, 1:54n.

[2] Dickens, *Sketches by Boz* (Penguin edition, 1995), 167. This sketch first appeared in 1834.

The present chapter will follow Kekulé's early years, through his London period. In the process we will review the mutually interacting ideas of several of Kekulé's predecessors and contemporaries that were developed into the concept that is now known as valence. We will also provide a preliminary assessment of his famous autobiographical tale of a striking vision he later claimed to have had while dozing aboard a horse-drawn London omnibus, which (he said) led him from valence theory to the much more consequential theory of chemical structure.

The Education of August Kekulé

Born 7 September 1829, (Friedrich) August Kekulé[3] was the son of Emil Kekulé, chief military adviser to Ludwig I, the Grand Duke of Hesse, and Emil's second wife, Margarethe. He enjoyed a comfortable bourgeois childhood in Darmstadt, the capital of the Grand Duchy, where Liebig had also grown up. During his six years in the Grand-Ducal Gymnasium he won particular praise in science, mathematics, and languages. In drawing and painting he had considerable enthusiasm and talent; every Sunday he took lessons in the studio of an engraver, and some of his early artistic efforts survive. From an early age he also developed his powers of memory to an extraordinary degree, a faculty and habit that stayed with him to old age.[4] Henry Armstrong, who, as a student and partisan of Kekulé's rivals Frankland and Kolbe, knew Kekulé personally during the last thirty years of the latter's life, confirmed that "he had an astounding memory."[5]

Although by profession a military man, Emil Kekulé's passionate hobby was architecture. When August showed artistic and mathematical gifts, Emil determined that his son should study architecture for a profession. He obtained small architectural commissions for his son; thus it happened that even as a teenager August drew up the plans for several houses in town. Unfortunately, Emil died shortly before August graduated from the Gymnasium. In the fall of 1847 Kekulé traveled to

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[3] Kekulé's birth name was Friedrich August Kekulé, but he never used "Friedrich." The surname, of Bohemian origin, had gained the French acute accent during the Napoleonic occupation of Hesse; Emil had wanted to preclude native French speakers from saying the name incorrectly in two syllables (which would then sound like a crude French epithet). When August Kekulé was ennobled in 1895, he adopted the new name "Friedrich August Kekule von Stradonitz," without the French accent, and it is this name that is seen today in most encyclopedias and library catalogs.

[4] Anschütz, 1:7–9, 657–58; Hafner, *Kekulé* (1980), 22, 43–44.

[5] Armstrong, "Doctrine" (1930), 808.

Giessen, the Grand Duchy's university town, to begin his higher studies. Without a breadwinner, the family was no longer prosperous, and August needed to choose a profession with pecuniary promise. As his father had wanted, he enrolled as a student of architecture and pursued the subject conscientiously for two semesters. He enjoyed the study and was more than satisfied with the celebrated professor of architecture Hugo von Ritgen. But in summer semester 1848 he attended Liebig's public lecture course on "Experimental Chemistry," and this experience put an end to Kekulé's architectural career.[6]

Kekulé's extensive notes on this course were preserved and were eventually published, both in facsimile and in a modern professionally edited version.[7] What excited Kekulé above all else was the "philosophy of chemistry," especially the many mysteries concerning the manner in which the elementary atoms combine to form complex molecules. But his family was not so delighted with August's new passion. Upon inquiry, it was learned that there were only three civil-service chemistry jobs in the entire state of Hesse-Darmstadt—the professors of chemistry at the University of Giessen and at the Darmstadt School of Trades,[8] and the master of the mint. Even considering just the civil service, architecture was far more promising, especially for someone with August's obvious talent. Holding the purse strings as they did, family members persuaded him to remain in Darmstadt at least for the winter semester 1848–49 to ponder his future, allowing him to enroll in the city's School of Trades. He heard lectures by the well-known professor of chemistry Friedrich Moldenhauer, and took a Praktikum in chemical analysis. In his leisure time he continued to exercise his artistic and craft skills, learning modeling in clay, as well as woodcarving and woodturning. He also became a superior glassblower, able to fabricate the complicated Liebig potash-bulb apparatus in a few minutes.[9]

Kekulé's resolve was firm, and he was allowed to return to Giessen for the start of summer semester 1849, attending Liebig's lectures on experimental, theoretical, and agricultural chemistry. He spent four more semesters in Giessen, learning the science from masters of the field. For

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[6] Anschütz, 1:8–11, 665.

[7] Liebig, *Experimentalchemie* [1927]; Krätz and Priesner, *Liebigs Experimentalvorlesung* (1983). The former is a facsimile publication of Kekulé's handwritten notes from 1848, for whose history see Krätz and Priesner, 363–64; the holograph original is in AKS.

[8] I.e., the Höhere Gewerbeschule, the predecessor of the Darmstadt Technische Universität—in whose Institut für Organische Chemie Kekulé's papers are housed today.

[9] Anschütz, 1:11–13, 51.

three semesters he attended the laboratory practicum of Heinrich Will, in Liebig's branch laboratory that had had to be constructed a few years earlier to handle the crush of students. In Kekulé's last semester in Giessen, winter 1850–51, he gained entry, now as an advanced student, into Liebig's own famous lab. Kekulé also took courses from ausserordentlicher Professor Hermann Kopp in stoichiometry and mineralogy, and from Heinrich Buff and Friedrich Zamminer in physics. Kekulé greatly impressed Kopp with his facility for rapidly orienting complicated crystals. "You do this much better than I was able to, at your age," Kopp had said, then thought a moment, and added " . . . but of course you also had a much better teacher than I did"—referring slyly to himself.[10] In his last semester he took a course in advanced organic chemistry from a capable Privatdozent, Adolf Strecker.

Kekulé later reminisced that Liebig used to tell his students that whoever does not ruin his health from overwork has no hope of making it as a chemist. Kekulé said that he faithfully followed this advice. "For many years 4 or even 3 hours of sleep were enough. One entire night spent over my books was nothing; only if I did this two or three nights in a row did I think I had earned some merit." He added that his friends used to say that his memory was more reliable than the pages of Berzelius's *Jahresberichte* (annual reports on the progress of chemistry).[11]

Kekulé's closest friend was his classmate, roommate, and cousin by marriage, Reinhold Hoffmann, who later provided Kekulé's biographer Richard Anschütz with extensive reminiscences. Hoffmann recollected that even as a young student Kekulé sought to "trace the sources of our knowledge," and in private he became a mentor to Hoffmann. Kekulé began increasingly to "concentrate on theoretical matters," and in particular he (and Hoffmann as well, under Kekulé's tutelage) began to view the orthodox (Berzelian) radical theory ever more skeptically. Hoffmann added, "I think I can say that the origin of this [critical] feeling derived from Will's lectures on organic chemistry." In lectures, Liebig habitually exuded epistemological confidence even when treating matters that were still quite obscure; by contrast, Will often cast doubt "even on uncontested questions regarding the constitutions of organic compounds."[12]

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[10] Ibid., 1:23–24. The anecdote (told by Kekulé to Anschütz) illustrates not only Kopp's quick wit, but also suggests Kekulé's manipulative and visualizing talents.

[11] Ibid., 2:944.

[12] Reinhold Hoffmann, holograph MS entitled "Erinnerungen an A. Kekulé," dated 26 November 1900, in AKS, excerpted passim in Anschütz; see esp. 1:16–17.

In such public moments, Liebig and Will could well have been alluding to contemporaneous developments. Frankland was a postdoctoral researcher in Liebig's laboratory in the fall of 1849, when Kekulé and his cousin were students in the branch lab overseen by Will. It was then that Frankland isolated the purported radicals methyl, ethyl, and amyl, to which event Liebig responded privately to A. W. Hofmann, "So what was desired as the foundation of the [radical] theory is now from this side finally here."[13] In other words, Liebig appears to have interpreted Frankland's work, as Frankland himself did, as positive proof of the existence of isolated monomer radicals. But Kopp's boiling-point regularities suggested that this interpretation was incorrect; this anomaly was followed up by Hofmann and others in London, as we saw in chapter 1. Kopp and Will were close friends as well as colleagues, and it is likely that Kopp's presumed private doubts regarding the Frankland-Liebig interpretation may have been reflected in Will's lectures. In any case, this testimony suggests that even as early as the late 1840s the younger faculty in Giessen were more open to the reform movement than Liebig was.

In 1851 Kekulé was passed by for an assistantship in Giessen. Still a predoctoral student, Kekulé scouted for his next move. Fortunately, Kekulé had a much older half-brother, Karl (Charles) Kekulé, who had emigrated to London and had made a fortune in the grain commodities market. Karl offered to finance a foreign Wanderjahr, and August considered Berlin, London, or Paris, inclining toward the first. But Liebig counseled, "Go to Paris. You will widen your horizons, you'll learn a new language, you will get to know life in a large city; but you won't learn any chemistry."[14] En route to Paris, Kekulé happened to see a copy of Gerhardt's new book, *Introduction à l'étude de la chimie,* in a Frankfurt bookshop, and read it on the journey. Living in Paris from May 1851 to March 1852, Kekulé attended lectures by Jean-Baptiste Dumas, Adolphe Wurtz, Victor Regnault, and others. He formed particularly close personal relations with Wurtz and with Charles Gerhardt, with whom he regularly consorted (but not with Auguste Laurent, who was very ill). Gerhardt even proposed to Kekulé that he lead the teaching in his private laboratory school, but the financial conditions were not acceptable—Gerhardt had just one customer at that time. But Kekulé had many long conversations with Gerhardt—his very first one, he said, lasted twelve hours—and Gerhardt allowed him to read the manuscript

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[13] Liebig to Hofmann, 8 December 1849, in Brock, *Liebig und Hofmann* (1984), 88.

[14] From Kekulé's 1892 reminiscences, in Anschütz, 2:949.

of his yet-unpublished *Traité de chimie organique.*[15] Given the serious Europe-wide recession in the job market for chemical professorships, Kekulé began seriously to consider the possibility of taking an industrial position, but only out of dire necessity; his real love was theory.[16]

Kekulé returned to Darmstadt in March 1852 when his mother became very ill; he took his Giessen doctoral degree that summer, awarded magna cum laude. This was just when Liebig was transferring to Munich, and Kekulé again hoped that Liebig would hire him as his assistant in the Bavarian metropolis. But Liebig only proposed him for two possible postdoctoral assignments. To the surprise of family and friends he accepted the less likely of the two, an assistantship with an independently wealthy private chemist, Adolf von Planta, in Chur, Switzerland. This gave him the opportunity, as he later described it, to spend fourteen months honing his organic-analytical skills, while also pondering, in the beautiful Alps, all that he had learned in Paris. He became personally close to Planta.[17]

In the fall of 1853 the specter of unemployment appeared once more, and Kekulé turned again to his mentor. Liebig proposed him for an assistantship with his former student John Stenhouse, at St. Bartholomew's Hospital, London. Kekulé did not think much of Stenhouse as a chemist, and was inclined to demur. But fortuitously, Robert Bunsen, who happened to be visiting relatives in Chur, met Kekulé for the first time and persuaded him to accept, saying, just as Liebig had about Paris, that even though he would learn no chemistry, in London he would at least learn a new language, and that is more than enough reason.[18] Bunsen would be proved just as wrong about London as Liebig had been about Paris.

Kekulé in London

On his way from Chur to London, Kekulé stopped in Munich to visit Liebig, and there he met a former student of Friedrich Wöhler's named

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[15] Anschütz, 1:24–29, 666; 2:943, 949–50.

[16] Kekulé to Planta, 13 December 1851, AKS. Five years later he wrote to the same recipient, "Ich hatte mich dazu entschlossen, mein Lieblingsfach Theorie an den Nagel zu hängen und auf dem Weg der Praxis selbst praktisch zu werden. Mein Schicksal wollte das nicht!" (9 February 1856, ibid.).

[17] Anschütz, 1:29–38; 2:943, 950. Kekulé related his extended decision-making process in letters to Planta of 13 December 1851, 12 January, 26 June, 5 July, 8 July, 5 August, and 31 August 1852, in AKS.

[18] Anschütz, 2:950.

Hugo Müller. Müller had traveled from Göttingen to Munich in order to ask Liebig to help him find a postdoctoral position, and Liebig, as usual, had one up his sleeve—with an independently wealthy London chemist, Warren De la Rue. In the meantime, Williamson had met Kekulé's Giessen chum Reinhold Hoffmann and had offered him an assistantship at University College. Kekulé arrived in London in the last week of 1853, Hoffmann just a few days later. As they had done in Giessen, Kekulé and Hoffmann decided to lodge together; they found a flat at 56 College Place, east of Regent's Park.[19] Kekulé told Hoffman to expect that Müller would arrive in London soon, as well. Hoffmann remembered Kekulé remarking, "Den können wir brauchen, der kommt von Göttingen und weiß etwas" (roughly: "We can use that guy; he's from Göttingen and knows a ton"). And he did know a ton, Hoffmann later confirmed. "Our triple friendship [Dreibund] was secured. Whereas previously we had considered questions from two sides, now we examined them even more thoroughly from a third side."[20]

Reinhold Hoffmann provided Anschütz with extensive reminiscences of their London experiences during most of the year 1854 (Hoffmann fell ill and returned to Germany that fall). He related that Kekulé was not thrilled with Stenhouse or his job at St. Bartholomew's, but Kekulé was accustomed to picking up Hoffmann at the Birkbeck laboratory, University College, on his way home in the late afternoon, and so he quickly became well acquainted with Williamson.

> If [William] Odling happened to be [at the Birkbeck] as well, friendly battle was soon joined over the relationships of the atoms and radicals among each other, and to their field commanders Gerhardt, Laurent, Kolbe, etc., and the blows fell thick as hail. . . . Hugo Müller's input [on these matters of discussion] generally could not be obtained until the following Sunday's excursion, for he lived too far away [in Islington, north London] to be able to consort with [Kekulé] every evening. But [Kekulé and I] often spent time together, also with [Müller], and always at such times the conversation was directed, in an unconscious and unplanned way, to the subject of contemporary theoretical controversies.

Under Kekulé's leadership, the three young Germans were "united in the effort to push to the limits of knowledge," Hoffmann reported.

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[19] Kekulé's and Hoffmann's London address is revealed in Kekulé's first letter to Erlenmeyer, dated 6 June 1854, AKS.

[20] Anschütz, 1:39.

If Kekulé's development reached maturity in London, as Hoffmann averred, it was partly, he wrote, under the influence of such discussions. The essence of the theory of chemical structure "developed from such seeds," and it required Kekulé to take only "a small step" to develop his ideas to the full theory as announced in 1857–58.[21] After Hoffmann left London, Kekulé wrote Planta in October 1854, commenting how much he missed his cousin's discussions filled with "theoretisch-chemische Speculationen."[22]

Kekulé and Williamson impressed each other greatly. At the time of Kekulé's arrival in London, Williamson's lab was "in peak activity, certainly far better than in any previous session," to use Williamson's own language in a letter to Henry Roscoe, with no fewer than eight research projects going on—probably more than at any other time in his career.[23] Two months after arriving in London, Kekulé wrote Planta about his position in Stenhouse's lab: "Boring, that's all I can say about it, and moreover the fellow (who is otherwise quite generous) is so indecent as to make a face when someone wants to do something for himself. . . . Regarding Williamson [I'll write] another time, for once you start in on him you're not soon finished, he has too many sides to be able to be characterized in a few words."[24] In a Latin curriculum vitae for the University of Heidelberg (January 1856), Kekulé wrote, "I must not fail to make mention of Williamson, that wisest of men and most learned of philosophers, who was not my teacher but my friend, and to whom I owe so much."[25] As for Williamson, he wrote of Kekulé in November 1854,

> These brilliant researches have gained Dr. Kekulé an european reputation among scientific chemists, and I am convinced that he will bring to high renown any chair of Chemistry to which he may be appointed. He possesses the faculty and habit of explaining scientific truths with singular clearness, and his personal character and

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[21] Anschütz, 1:40–41.

[22] Kekulé to Planta, 28 October 1854, AKS.

[23] Williamson to Roscoe, 5 December 1853, HERC. Williamson told Roscoe here of his decision to use barred C and O letters to designate atomic weights (C = 12, O = 16) rather than equivalents (C = 6, O = 8). Kekulé was shortly to adopt this convention and introduce it into Continental chemical journals.

[24] "Langweilerei, das ist alles was ich darüber sagen kann und dabei ist der Mensch (sonst sehr nobel) so unanständig das Gesicht zu verziehen, wenn man etwas für sich selbst thun will . . . Von Williamson ein andermal, denn wenn man von ihm anfängt, wird man so bald nicht fertig, er hat zu viele Seiten um mit wenig Worten charakterisirt werden zu können." Kekulé to Planta, 3 March 1854, AKS.

[25] "Non possum, quin Williamson commemorem, virum sagicissimum philosophum eruditissimum, qui non praeceptor sed amicus mihi erat, et qui de me magnopere meritus est." Anschütz, 1:664.

demeanour will not fail as hitherto to win him the esteem and affection of every body with whom he is brought in contact.[26]

Kekulé's remark to Planta about doing something for oneself and Williamson's mention of "brilliant researches" in the letter just cited refer to a small but important research project that occupied Kekulé early in his London period. Here is how he reasoned. Since the "hydrogen sulfide type" (H_2S) is analogous to Williamson's water type (H_2O), and since then-known organic sulfur compounds bear analogies to alcohols and ethers, then it is reasonable to believe that a more extended parallelism could be established by creating sulfur analogs of organic acids, acid anhydrides, and esters. One might accomplish this, he thought, using a sulfur analog of the known chlorinating reagent phosphorus pentachloride. So, Kekulé's notion was to make phosphorus pentasulfide, and then use that substance to attempt to sulfurate organic acids and esters (i.e., to replace an oxygen atom in them by a sulfur atom). In this way one might expand Williamson's "water type" theory from oxygen to sulfur.

Kekulé told Williamson of his idea—it must have been soon after his arrival, in January or February 1854—and Williamson was enthusiastic. But Kekulé had little free time and no laboratory in which to do the work, and so he stalled. Finally Williamson declared, "This must be tried. If you don't do it, I will." So, without Stenhouse's permission, Kekulé used his boss's lab in the hours before his official duties began at 9 a.m. There was, of course, no way to hide the powerful aromas of sulfur compounds, but Stenhouse let the work continue. Kekulé's labmate Edward Divers commented, "Stenhouse murmured sometimes at Kekulé's giving too much time to it, that was all." On 3 March Kekulé reported to Planta that fortunately Stenhouse was currently indisposed, which gave Kekulé free rein in the lab.[27] Kekulé must have worked efficiently in March, for Kekulé's finished paper, "On a New Series of Sulphuretted Acids," was formally presented in the 6 April 1854 meeting of the Royal Society of London. The paper was also published in Liebig's *Annalen,* and excited interest in the chemical world, as we shall shortly see.

On 20 February of that year, about the time Kekulé was beginning his research project, a meeting of the Chemical Society garnered con-

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[26] From a letter of reference dated 22 November 1854, in Anschütz, 1:56.

[27] The story of the conversation between Kekulé and Williamson derives from Kekulé's oral reminiscences to Anschütz, and Divers's testimony is in a letter to Anschütz, date not cited. Anschütz, 1:45–46, 50; Kekulé to Planta, 3 March 1854, AKS.

siderable attention in the London chemical world.[28] A paper by Kolbe was formally read, containing an attempted refutation of Williamson's theory of the constitutions of ethers and acids. Williamson attended, and answered the paper orally. His rebuttal was detailed, substantive, and rhetorically brilliant—even humorous, often employing a light but incisive hand with an undercurrent of ridicule. For instance, he suggested that Kolbe had evidently failed to first understand the views he was opposing. "I would particularly recommend the papers of [Laurent and Gerhardt] to Dr Kolbe's perusal, as they would probably save him from many surprises to which he would otherwise be exposed."[29] Not all of his comments were equally fair. For instance, Kolbe had contested Williamson's idea that atomic interchanges were ubiquitous in mixed fluids, and Williamson's response to Kolbe was far from convincing. The heart of Williamson's response mocked Kolbe's penchant for arbitrarily introducing various kinds of punctuation symbols into his chemical formulas.[30] The critique obviously made an impression on his young German friend, for many years later Kekulé recalled: "Williamson insisted on clear formulas, without commas, or Kolbe's buckles, or Gerhardt's brackets. That was an excellent education, which made the mind independent."[31]

In October 1854 Kekulé learned from the London newspapers of a rare opening for a chemistry professorship, namely in the newly established institute of technology in Zurich. Unsure whether he should even try for the position, he wrote to Planta of his pessimism. Such jobs, he said, are won only by "Connectionen"; he might decide to apply anyway, he wrote, but only out of desperation. He was nearly resigned, he said, to the very unpalatable idea of going into the industrial job market, as he had considered doing off and on since 1851. He did decide to apply for the Zurich professorship, and toward that purpose garnered glowing letters from Williamson (excerpted above), Bunsen, Gerhardt, and A. W. Hofmann. But the one letter he most needed he did not get: he wrote three increasingly anxious letters to Liebig, without receiving any reply. Though Kekulé had no way of knowing it, Liebig had already recommended Georg Staedeler, Wöhler's capable assistant, and it was Staedeler who got the job. Meanwhile, Kekulé's wealthy merchant half-brother Karl (Charles) had been pressuring him to get

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[28] See, e.g., Henry Watts to Roscoe, ca. early February 1854, and Williamson to Roscoe, 9 February 1854, HERC.

[29] Williamson, "Additive Formulae" (1854), 129.

[30] Ibid., 134.

[31] Anschütz, 2:950.

a “real” job. When the bad news arrived, Kekulé was resigned. “So my decision is now final, to become a chemical boot-polisher,” he wrote unhappily to Planta.[32]

Excursus: The Road to Valence[33]

Reinhold Hoffmann returned to Germany in fall 1854, so that is when his reminiscences of Kekulé in London conclude. Partly for this reason we know few details about Kekulé’s second year there (he left England ca. September 1855). But we do know that this was a fast-moving time for chemical theory. The years 1854, 1855, and 1856 saw the publication of a host of articles by leading theorists, all beginning to explore what chemists then called the saturation capacity, or basicity, or equivalent value, or substitution value, or magnitude of affinity, of atoms and molecules. By the late 1850s this phenomenon had become known as “atomicity,” then by about 1870 as “valence.” The formulation of the earliest theories of atomic valence led directly to the formulation of ideas relating to molecular structures.

But these developments were complex. Not only did a host of protagonists participate in the story, many of whom did not always clearly understand, or in many cases were not even immediately aware of, others’ contributions in real time; there were also many different scientific and methodological issues that were so tightly interfiliated that none can be dealt with cleanly in isolation. In this section we review some of these developments in order to understand more clearly why various leading chemists chose the formulas they did, what they actually meant by some of their words and formulas, and why all of this happened at such a furious cadence. This background is also helpful in order fully to comprehend the particular path taken by Kekulé, our main focus here.

Let us first examine some aspects of the interconnected problem of atomic weights, formulas, and molecular magnitudes. In chapter 1 we noted much disunity and confusion in the chemical community on these questions, such as the crucial issue of the formula for water. What Williamson had done in 1850–51 was to present the first direct experimentally based argument that in the water molecule there *really is* one indivisible oxygen atom weighing 16. That water *really is* H_2O

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[32] Anschütz, 1:52–57; Kekulé to Planta, 28 October and 28 December 1854, AKS: “Mein Entschluss steht also fest, einen chemischen Stiefelputzer zu werden.”

[33] The standard and still quite indispensable source on this subject is Russell, *History of Valency* (1971).

rather than HO (or H_2O_2, as many advocates of "equivalents" had begun to write), and that the two hydrogen atoms are subject to substitution, was the essence of his "water type" theory. In this theory, ether, like water, cannot split apart into two identical molecules, because to do so would require dividing a chemical atom. So, for example, just as one can make a water molecule asymmetric by replacing one of the two hydrogen atoms by, say, an ethyl radical (to make alcohol), so also one could make an asymmetrical ether, like ethyl methyl ether. Kolbe had tried to counter Williamson's argument by suggesting that the ethyl ether and the methyl ether were in fact separately formed as required by the older theory, but that the two ethers hung together as a single molecule anyway. This is entirely analogous to suggesting that OH and OH hang together into the equivalentists' H_2O_2 water molecule. In response to this gambit, Williamson turned the tables on Kolbe with the retort: "The reasonings by which he tries to convince us that . . . ethyl [ether] *may* combine with . . . methyl [ether] are excellent, but perhaps almost superfluous after I have proved that they *do* combine."[34]

Although clever, this response was not substantive, for Kolbe had indeed shown a way to accommodate Williamson's new evidence to the older theory. The legitimate charge against Kolbe's gambit was not the fallacy of *petitio principii* (assuming what is to be proved), as Williamson implied, but rather one of stretching credulity and chemical common sense, which is a question more of judgment than of logic. Williamson's research of 1850–51 did not, in fact, constitute a true *experimentum crucis,* and Kolbe's position was not the uninterrupted series of gaffes and blunders that Williamson tried to suggest (although Williamson was surely right that Kolbe's paper exhibited misunderstandings and inadequate consideration of his opponents' views).

There were also unresolved discussions over the weights of atoms that were known to have *variable* equivalents. Frankland had pointed out already in 1852 that nitrogen, antimony, and arsenic combine with either three or five equivalents of other atoms. Most metals, he noted, exhibit the same variability. A particularly puzzling case was that of iron, which forms oxides in two different patterns, ferrous oxide and ferric oxide—modern FeO and Fe_2O_3. Did the Fe atom really weigh 56, as Berzelius thought, and as was implied by these two formulas? Or did it weigh half as much, suggesting the respective formulas Fe_2O and Fe_4O_3? Or twice as much—FeO_2 and FeO_3? All of these formula pairs seemed a bit ugly, though many chemists in the 1850s, including re-

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[34] Williamson, "Additive Formulae" (1854), 126.

formers such as Gerhardt and Williamson, inclined to the assumption that Fe = 28.

Many chemists attempted answers to these and related puzzles in a rapid-fire tempo. The contributions summarized in the following subsections all appeared in the three years 1854–56.

Laurent

How, indeed, can the existence of two distinct series of iron compounds be understood? Laurent proposed that the answer might be found in hidden subatomic entities that combined in different ways. Let us imagine that there exist two different kinds of iron atoms, "ferrosum" atoms, symbol "Fe," which form ferrous (modern FeO-type) compounds, and smaller "ferricum" atoms, symbol "fe," which form ferric (modern Fe_2O_3-type) compounds. Let us suppose that the fe atom weighs exactly 2/3 whatever the Fe atom weighs. If we posit that Fe weighs 28 relative to H = 1, then ferrous oxide can be formulated as Fe_2O, analogous to water, and ferric oxide will then have the same pleasingly simple parallel formula fe_2O. But then how might one explain the fact that these distinct kinds of iron atoms are each reducible in bulk to one identical material substance, the metal we recognize as iron? Well, let us imagine that the *true* ultimate iron particle is neither the ferrosum nor the ferricum atom, but is actually a much tinier subatomic entity, "f," weighing 2.33 relative to H = 1, such that 12 of these come together to form each ferrosum atom $Fe = f_{12} = 12 \times 2.33 = 28$. The ferricum atom would then simply consist of 8 rather than 12 of these subatoms, exactly 2/3 the size of ferrosum, as is required ($fe = f_8$). We have here used the example of iron, but the same ideas are applicable to other elements, as well.

Laurent explored this hypothesis in the pages of his book *Méthode de chimie,* published posthumously in 1854. He wrote,

> Even if we agree that there is a limit to the divisibility of matter, nothing compels us to identify this limit of divisibility with the atoms of chemists; and we could very well understand the cause of the law of definite [i.e., multiple] proportions by the supposition that chemical atoms are nothing but molecular compounds composed of a certain number of smaller atoms [petits atomes]. . . . Is this hypothesis not in perfect harmony with the atomic theory; is it not confirmed by experience [expérience]?[35]

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[35] Laurent, *Méthode* (1854), 123–33, esp. 125–27. I have slightly modified Laurent's nomenclature here, for greater clarity.

Laurent thought: if several identical groups of atoms could connect themselves together in the well-known phenomenon called polymerism, then by a similar mechanism at an even subtler level one might suppose that several identical groups of subatoms could connect themselves together to form atoms of various sizes, but all of the same element. We will see versions of this idea reemerging several times in the 1850s and 1860s.

Gerhardt and Williamson

In his *Traité de chimie organique* (1853–56), Gerhardt developed his theory of types, arraying most organic compounds according to the four pattern-formulas of hydrogen (H_2), water (H_2O), ammonia (NH_3), and hydrogen chloride (HCl). It was an excellent treatise—massive, thorough, and meticulous. But it was all done as if it were an exercise in accounting, true to the empiricist avowals in his preface. The question remained whether Gerhardt's formulas represented simple empirical fact, or whether—as Williamson held—they indicated something about actual molecular structures. Although with the clarity of hindsight one can see more than a hint of valence regularities in Gerhardt's four infinitely substitutable types, there was no molecular realism here, no arrangement hypotheses, no evidence of the exercise of visual imagination. In accordance with his rigid methodological principle, Gerhardt insisted that a mental blind be drawn over the molecular world.

But this was not the only available choice. In a brief summary of recent chemical theory published in 1863, Williamson described how, in the late 1840s, Gerhardt had attempted to construct chemical ideas solely from empirical "synoptic" formulas, but had initially gained few adherents. Such formulas "represent in the simplest terms the *result* of a chemical reaction, but they give no *physical image* of the progress by which the reaction is brought about. The introduction, in this country, of the water type in connexion with polyatomic as well as monatomic radicals, was found to satisfy the requirements of the synoptic formulae. Gerhardt was the first to adopt them [in his *Traité*] from us."[36] Williamson was trying to phrase all this modestly, but his opinion cannot be mistaken. Gerhardtian positivism, he thought, was an unpromising cul de sac, which was fortunately rescued and transformed, from 1850 on, by Williamson's molecular realism, assisted by his (mental) "physical images" of chemical processes.

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[36] Williamson, address to the Chemical Section (1863), emphasis added.

Such realism was further revealed in a paper that Williamson read to the Royal Society in February 1854. It was already known that sulfuric acid, SO_4H_2 in the Gerhardtian formulation, could be chlorinated by phosphorus pentachloride to form SO_2Cl_2, a reaction in which Cl replaces OH twice. Williamson revealed that it was possible to arrange for the chlorination to occur in two separate stages, and he was able to isolate the once-chlorinated intermediate (or asymmetric) compound, chlorosulfonic acid, HSO_3Cl. In this compound, the "bibasic" SO_2 radical was obviously uniting two different entities, OH and Cl, for otherwise "we should have obtained a *mixture,* not a *compound* of the chloride with the hydrate."[37] This is a reprise of the same kind of argument that he had used in 1850–51, and that several others had used in the meantime (e.g., Hofmann, Brodie, and Gerhardt). As we have seen, even opponents of the reform movement found this "asymmetric synthesis" argument compelling. It was another indication not only of the truth of Gerhardt's weights and formulas, but also of the fruitfulness of Williamson's realist scientific style, assisted as it was by the "physical image" of the molecules that he manipulated in his mind's eye.

Odling

William Odling (1829–1921) had a recent London University M.D. and was lecturer in chemistry at Guy's Hospital at the time of Kekulé's arrival in London. During Kekulé's London period, Odling was a close associate of Williamson and a respected younger member of the progressive circle of London chemical theorists. His substantial contributions to the emergent valence theory consisted of a paper on what he called the "substitution value" of atoms and radicals, and a second more general essay on the nature of organic radicals.

About the time Kekulé arrived in London, Odling presented to the Chemical Society what he said was largely an elaboration of Williamson's work on the "water type." He suggested that acids and bases of almost any degree of complexity could all be schematically represented by the water molecule, multiplied as many times as required, and appropriately substituted according to the "replaceable, or representative, or substitution value" of various atoms or radicals.[38] As an accounting mechanism he suggested the use of single, double, or triple prime marks after the element or radical symbol to indicate the respective

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[37] Williamson, "Note" (1856), 14.

[38] Odling, "Acids and Salts" (1854).

substitution-value of the atom or radical of one, two, or three. At one point he seemed to express Williamsonian molecular realism, for he commented that in the water molecule, “the separable equivalents of hydrogen are held together by the indivisible oxygen.”

But careful study of his myriad formulas leaves no doubt that he was most strongly influenced by Gerhardtian molecular positivism. His formulas were constructed to create an equal number of prime marks on both sides of the bracket, not to express presumed sequential physical arrangements of atoms within the molecule—much less any presumed linking function of atoms or radicals. For example, for hyposulfuric acid, sodium hyposulfite, anhydrous carbonic and sulfuric acids, and metaphosphoric acid, he wrote:

$$\left.\begin{matrix} \mathrm{SO_2'SO_2'} \\ \mathrm{2H'} \end{matrix}\right\} \mathrm{2O''} \qquad \left.\begin{matrix} \mathrm{SO_2''} \\ \mathrm{2Na'} \end{matrix}\right\} \mathrm{O''+S''} \qquad \left.\begin{matrix} \mathrm{CO''} \\ \mathrm{CO''} \end{matrix}\right\} \mathrm{2O''} \qquad \left.\begin{matrix} \mathrm{SO_2''} \\ \mathrm{SO_2''} \end{matrix}\right\} \mathrm{2O''} \qquad \left.\begin{matrix} \mathrm{PO'''} \\ \mathrm{H'} \end{matrix}\right\} \mathrm{2O''}$$

all of which are difficult to imagine in a Williamsonian “linking” sense.[39] Nonetheless, this paper represents a significant expansion of the incipient doctrine of the “substitution-values” of atoms and radicals.

A little more than a year later, on 16 March 1855, Odling presented a Friday Evening Discourse at the Royal Institution entitled “On the Constitution of the Hydro-carbons.” His goal was to demolish the whole notion of radicals as preexisting parts of molecules. Radicals, he averred, are nothing more than a convenient means of accounting for and notating the components of compounds, and have no further signification. For instance, he reproduced the following four formulas, listing his understanding of their originators under the first three:

$\mathrm{H{\cdot}CH^3}$	$\mathrm{H^2{\cdot}CH^2}$	$\mathrm{H^3{\cdot}CH}$	$\mathrm{H^4{\cdot}C}$
Liebig	Dumas	Odling	

The last formula—a stable compound, not a radical—is that of marsh gas, today known as methane. Some, following Anschütz, have understandably seen in this paper the proposal of a fifth chemical “type” to add to Gerhardt’s four, namely the “marsh gas type,” and a modern chemical eye sees an implicit suggestion of carbon tetravalence here.

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[39] In the late 1860s Odling opposed Williamson’s strong public defense of atoms. In 1898 he conceded that this opposition had been unwise; he said that he had always been content to follow in Williamson’s footsteps, but that unfortunately he had more than once lagged behind (Odling, comment, *Chemical News*).

But we must be careful. The same modern eye sees the implication of monovalence, divalence, and trivalence in Gerhardt's other types, and here it becomes even more striking, since Odling uses atomic weights and molecular formulas that match ours today. But it was not Odling's intent to claim that the carbon atom is tetravalent. Even the more plausible position that he was suggesting that carbon has a "substitution-value" of four is uncertain. In fact, his purpose here seems not to have been to explore substitution-values at all, as he had done a year earlier, but to attack the very idea of radicals from a position of Gerhardtian molecular agnosticism. Nonetheless, the paper surely influenced contemporaries, Kekulé foremost among them. Kekulé may well have attended Odling's lecture.[40]

Will and Kopp

When Liebig transferred to Munich in 1852, his erstwhile junior colleagues Hermann Kopp and Heinrich Will became his joint successors in Giessen. In the presence of the master, both had been publicly cautious and noncommittal in the theoretical realm. But in the fall of 1854 each declared himself in favor of Williamson's new approach. Although neither man contributed in a direct or substantial way to the emergent ideas about atomic valence, this simultaneous move gave the movement of the valence theorists a further impulse.

In Liebig's *Annalen* for October 1854, Will published a paper "On the Theory of the Constitution of Organic Compounds." We now know, he affirmed, that carbon and oxygen have the higher atomic weights (12 and 16, respectively), and that there are no oxides in salts and no water in acids. Williamson's study of organic acids in particular, he wrote, "allows us to look into the inner construction and arrangement of the smallest particles, which gives us ever more information . . . The reform of chemistry in this direction was prepared by Gerhardt, and there can be no doubt that it will prevail."[41] Will's concern with the "inner construction and arrangement" of the atoms within organic molecules and his reference to "bonding patterns" demonstrate how receptive he was to the various novel ideas then being floated.

A paper by Kopp appeared in the very next monthly issue of the

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[40] 40. Odling, "Hydro-carbons" (1855); Anschütz, 1:109–12 (who incorrectly stated that Kekulé was no longer in London at this time).

[41] 41. Will, "Theorie" (1854), 292.

same journal. The Gerhardt-Williamson theory of the constitution of organic compounds provides not only “empirically-supported clarity” in a *chemical* sense, Kopp wrote, but in a *physical* sense as well, regarding regularities he revealed here in the specific volumes of liquid substances. Whether the theory is true or not, he cautioned, is still an open question. But Kopp indicated, subtly but clearly, and for the first time, his definite preference for this theory.[42] These declarations of Will and of Kopp, both of whom were respected midcareer chemists, gave additional momentum to molecular ideas in development.

Frankland and Kolbe

We have seen that in 1852 Frankland unequivocally rejected copulas, embraced substitution, and proclaimed a form of what became known as atomic valence. Between 1851 and 1856 Frankland explored a wide variety of organometallic compounds, and we can see in this work his steadily increasing accommodation to type-theoretical ideas. He was interested in his novel organometallics not only for their own sake, but also to employ them as tools that might allow him to “ascend the homologous series of organic bodies”—that is, systematically and in a controlled way to increase the carbon content of hydrocarbons—in order to obtain “clearer views of [their] rational construction.” But during this period Frankland was not yet ready to accept all of the Gerhardtian apostasies. He embraced neither the reformed notation nor the new atomic weights, and he even retained some elements of electrochemical-dualist theory.[43]

At first strongly opposed to Frankland’s substitutionism and rejection of copulas, Kolbe was gradually persuaded by the flood of evidence that came out in these years, especially the various applications of Williamson’s “asymmetric synthesis” argument. By the beginning of 1856 Kolbe had quietly conceded the accuracy of Frankland’s 1852 generalization. During the course of that year the two friends exchanged further correspondence, and in December Kolbe submitted to Liebig’s *Annalen* a paper that offered a new type-theoretical way of looking at the construction of carbon compounds, all based on the type of carbonic acid. The paper appeared in Kolbe’s name alone, though Frankland later stated, both publicly and privately, that the paper was actually

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[42] Kopp, “Volume” (1854), 24–28.

[43] Russell, *History of Valency,* 118–28; *QR,* 181–83.

joint-authored, Kolbe having omitted his name by mere inadvertence. Although Kolbe partially conceded Frankland's point, the whole truth of the matter is complicated.[44]

Kolbe's formula for carbonic acid was $2HO.C_2O_4$, where C = 6, O = 8, and pre-formed water (expressed in equivalents as HO, technically a half-molecule) exists in the compound. In Berzelian theoretical terms, the formula indicates the bibasic character of the acid by depicting two substitutable water molecules outside the radical to the left—sodium carbonate, for instance, being formulable as $2NaO.C_2O_4$. The Kolbe-Frankland theory amounted to the idea that successive substitutions of hydrogen atoms or hydrocarbon radicals for the four oxygens in carbonic acid could generate the schematic starting points for all organic acids, ketones, aldehydes, and alcohols:

$2HO.C_2O_4$	$HO.(C_2H_3),C_2O_3$	$(C_2H_3)_2C_2O_2$	$(C_2H_3)HC_2O_2$	$HO.(C_2H_3)H_2,C_2O$
carbonic acid	acetic acid	acetone	aldehyde	alcohol

So, for instance, acetic acid is carbonic acid with one oxygen substituted by methyl, acetone has two oxygens replaced by methyl radicals, aldehyde is the same except one of the two methyls is replaced by hydrogen, and alcohol is aldehyde with a third oxygen atom of carbonic acid replaced by hydrogen. (In Kolbean terms, one ignores the water molecules HO to the left of the period.)

This paper formed the basis for the later claim of both men to have been the first to state what became known as the tetravalence of the carbon atom, and we can certainly see their point. Instead of starting out with a fully reduced *hydrogen* compound and depicting successive substitutions of hydrogen atoms, as the type theorists had done (e.g., starting with H_2O or NH_3), Kolbe and Frankland started with the fully *oxygenated* compound and depicted successive substitutions of oxygens. This worked well from an equivalentists' standpoint, for the oxygen symbols, as equivalents, operated as monovalent entities, just like hydrogen. To concur with Kolbe's and Frankland's claims to have been the discoverer of the tetravalence of the carbon atom, one must also, of course, take their tetravalent entity to be the "double atom" (= two equivalents) of carbon, C_2. So while we can sympathize with Kolbe and Frankland, we can also understand why reformers, now thinking thoroughly in terms of reformed atoms and atomic weights, would not want to accept this point of view.

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[44] Kolbe, "Zusammensetzung" (1857); Russell, *History of Valency,* 123–27; *QR,* 184–87.

Wurtz

Despite the traditional chemical formulations in Adolphe Wurtz's early work to 1853, there were more than occasional hints of reformist thinking, including a predilection for mechanical-structural language and metaphor.[45] At such times Wurtz probably thought that here he was being entirely consistent with the type theory of his mentor Dumas, who, as we recall from chapter 1, also used mechanical-structural language in his papers of 1839–40.

From 1853 on, Wurtz accepted most of the leading propositions of the reform movement, but differed strongly from Gerhardt in chemical ontology and epistemology. For Gerhardt, all deep theory, especially molecular theory, was to be avoided. Chemical "types" were quite arbitrary assignments, being merely synoptic summaries of empirical evidence (chemical reactions), and the same substance could sometimes be equally well represented by formulas from two different "types." For Wurtz, on the other hand, type formulas had a "true molecular signification," and must indicate the chemist's understanding of the actual arrangements of the atoms within the molecule.[46] Wurtz and Williamson were of the same mind in this regard, and so it is not surprising to see them joining forces. Late in 1853 Wurtz asked Williamson to supply him, as one of the editors of the *Annales de chimie,* with a summary in French of his ether theory papers of 1850–51—for none of the four papers had yet appeared in French translation in a major French chemical journal. This summary was published early in 1854, prefaced with an editorial note by Wurtz. Wurtz subsequently told Williamson that it had "created a sensation."[47]

Stimulated by further work by Williamson and by Marcellin Berthelot, in April 1855 Wurtz further extended his thinking. He wrote that the radical of the monobasic alcohol propyl alcohol (C^6H^7) can be converted into the radical of glycerin (C^6H^5), a tri-alcohol, simply by schematically abstracting two hydrogen atoms. This alteration, Wurtz suggested, changed a monobasic into a tribasic organic radical. Moreover, one can understand glycerin as composed of three distinct hydrocarbon groups that substitute, one hydrogen atom each, into three water molecules—that again explains the molecule's tribasicity. It is the glyc-

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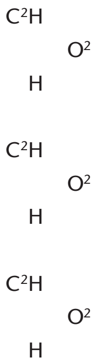
[45] Wurtz, "Acide sulfophosphorique" (1847), 480–81; Wurtz, "Alcaloïdes" (1850), 444–46, 495–507. The following discussion summarizes material in *NS,* 20–22, 155–75, 189–211.

[46] Gerhardt and L. Chiozza, "Recherches" (1853); Wurtz, "Dédoublements" (1853); Wurtz, "Amides" (1853); Gerhardt, "Amides" (1853); Wurtz, "Nouvelles observations" (1853).

[47] Williamson, "Théorie" (1854); *NS,* 192–98.

eryl radical that provides the material connection ("lien") between the three linked ("conjuguées") water molecules, just as oxygen holds two hydrogen atoms into a single molecule of water. In the course of this paper Wurtz provided perhaps the first-ever proposal of an empirically supported and fully resolved constitutional formula for a complex organic compound. He expressed the constitution of glycerin as:[48]



$$\begin{array}{rl} \mathrm{C^2H} & \\ & \mathrm{O^2} \\ \mathrm{H} & \\ & \\ \mathrm{C^2H} & \\ & \mathrm{O^2} \\ \mathrm{H} & \\ & \\ \mathrm{C^2H} & \\ & \mathrm{O^2} \\ \mathrm{H} & \end{array}$$

One should note that Wurtz was still using conventional equivalents, so that it is necessary to halve the number of oxygen and carbon atoms in order to translate this formula into a Williamsonian atomic weight formula. But similar to Williamson, one sees no brackets, braces, buckles, parentheses, or punctuation. As with Williamson's formulas, Wurtz expressed his ideas about the constitution of a molecule solely by the spatial relationships of the letters that symbolize the atoms it contains.

Two months later (June 1855) Wurtz announced the successful synthesis of five novel mixed or asymmetric hydrocarbons (ethyl-butyl, ethyl-amyl, butyl-amyl, butyl-caproyl, and methyl-caproyl), all produced by the reaction of iodides of the radicals with sodium metal—e.g., ethyl iodide and butyl iodide react with sodium to yield, inter alia, the new substance ethyl-butyl. This is precisely what Hofmann and Brodie had tried but failed to accomplish, pursuing Williamson's "mixed ether" strategy, in December 1850. It is a testament to Wurtz's experimental artistry that he succeeded.[49]

But even more important were his theoretical conclusions. Citing Williamson's etherification argument as his model, Wurtz argued that these asymmetric or mixed radicals proved that the larger Gerhardtian

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[48] Wurtz, "Combinaisons glycériques" (1855).

[49] Wurtz, "Radicaux organiques" (1855).

(dimer) formulas were correct. (If the Kolbe-Frankland formulas were true, then the product of Wurtz's reaction should have been mixtures of monomer radicals, rather than single asymmetric products.) Moreover, he said, his work leads to the conclusion that the putatively monomeric gas molecules H, O, and N must likewise now be regarded as dimeric H_2, O_2, and N_2; that O = 16 rather than 8, and hence C = 12 rather than 6; and that two-volume formulas must be regarded as universally reflecting molecular reality. In sum, he averred, the truth of the Gerhardt-Laurent theories was now placed beyond question by experimental evidence.[50]

And something more. Perhaps (he wrote), a nitrogen or a phosphorus atom is analogous to a tribasic radical like glyceryl. Here he adopted Laurent's subatomic speculation, but with an interesting new twist. The nitrogen atom, he suggested, might be "formed from three juxtaposed and inseparable [sub]atoms." Let us symbolize the nitrogen subatom by "n," with each n weighing 1/3 what the nitrogen atom weighs (i.e., n = 14/3 = 4.67). So the nitrogen atom, $N = n_3$, is tribasic, because each of the three nitrogen subatoms is separately capable of uniting with a hydrogen or a chlorine atom (that is to say, each subatom is monobasic), but because the three subatoms are indissolubly combined into one nitrogen atom, the NH_3 molecule is a stable entity—just like the glyceryl radical holding three other components into a single molecular unity. In this sense N is really n_3, P is really p_3, and so on. In other words, just as the *molecular* structure of the glycerin *molecule* explains its tribasicity, so also might the *atomic* structure of the nitrogen *atom* explain its tribasicity (later called "trivalence"). "But as this notation rests on considerations that are not susceptible of rigorous demonstration," he wrote, "I renounce them for the moment."[51]

A few months later, in his paper on glycol and its compounds, Wurtz introduced a new synonym for what he had hitherto called a "tribasic" atom or radical, namely, that it is "triatomic," signifying what we now would call trivalent. It is likely that this change of terminology is connected to his new idea. If his subatomic speculation were true, a "triatomic" atom can form connections to exactly three other atoms or radicals because it consists of precisely three permanently connected subatoms; a single atom is thus in a very literal sense tri(sub)atomic. Thus, the new terminology, which was adopted almost immediately by

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[50] Ibid., 312–13.

[51] Ibid., 306–7n. Again, I have slightly altered Wurtz's symbolism for the sake of clarity. Adopting Odling's prime marks for substitution values, he actually wrote $Az''' = az^3$ and $Ph = p^3$.

Berthelot, then by Kekulé, then more generally by others in the European chemical community, may have encoded a veiled reference (by *some* but not all who availed themselves of the terms) to Wurtz's subatomic speculation.[52]

Wurtz's speculation probably had been sparked by his reading of Laurent's book, published just months earlier, but we see that Wurtz had applied the idea of subatoms in quite a different way and for quite a different purpose than Laurent had. Wurtz's subatomic speculation had an interesting life after its birth in the summer of 1855. In any case, the work described here opened a floodgate of new reactions and syntheses that poured forth from Wurtz's laboratory in the following few years. In the words of his friend A. W. Hofmann, Wurtz "conjure[d] a galaxy of new compounds before the mental eye of chemists."[53] And especially before the mental eye of one chemist in particular, as we will see in the next section.

Molecular Dreams

In the second section of this chapter we summarized Kekulé's research on the sulfuration of organic acids. In this paper Kekulé made the same argument about the sulfur atom that Williamson had about oxygen. Sulfuration yields a single product, "which," he wrote in the English-language version, "according to the bibasic nature of sulphur, must have been expected."[54] In the longer German-language version, Kekulé explained this point more fully. In sulfuration reactions, by contrast to chlorinations, the reaction fragments remain united, because "the quantity of sulfur that is [chemically] equivalent to two atoms of chlorine is not divisible." Therefore: "It is not merely a difference in notation, but [it is] rather an actual fact, that one [molecule] of water contains two atoms of hydrogen and only one atom of oxygen; and that the quantity of chlorine equivalent to *one* indivisible atom of oxygen is divisible by two, while sulfur, like oxygen itself, is *dibasic,* so that one atom is equivalent to two atoms of chlorine."[55]

Kekulé was surely influenced by Odling's recent paper on "substitution values" of atoms and radicals and by Williamson's paper on chlo-

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[52] See Wurtz, *Histoire* (1869), 277; Wurtz, "Glycol" (1856), 203.

[53] Cited in Bauer, "Erinnerungen" (1919), 117.

[54] Kekulé, "Suphuretted Acids" (1854), 37.

[55] Kekulé, "Schwefelhaltige Säuren" (1854).

rosulfonic acid. But here Kekulé was extending an idea to oxygen and sulfur *atoms* that Williamson had only explicitly applied to radicals, and Odling's molecular positivism would have inhibited the kind of realist argument exhibited here. Frankland's major 1852 paper may also have had an effect on Kekulé's thinking, but Frankland was still loyal to electrochemical dualism and had proceeded very cautiously; his influence on Kekulé remains uncertain.

Kekulé later asserted that this paper contains the first explicit statement of the "bibasic" character of oxygen and sulfur atoms, namely, that each atom of either of these two elements can form a material link between two monobasic entities. That constitutes a kind of claim to the concept of valence. Others made competing claims, especially Frankland (on the basis of his 1852 paper), Kolbe, and Wurtz; and of course one must also take into account the powerful influence of Williamson. The point here is not to try to adjudicate these disputes; the preceding section of this chapter suggests how useless any such endeavor would be. The object is rather to understand how and why so many different chemists, indeed, most of those who were theoretically active in the science, were simultaneously approaching the same set of ideas.

Once chemists conceived of atomic valence—that certain kinds of atoms can connect to just one other atom, others to exactly two, others to exactly three, still others to four other atoms—they could explore the possibility of constructing molecules, in thought, following those valence rules. This led, in some minds then and now, to a kind of stripped-down, simplified conception of structure theory that has much in common with the popular American Tinkertoy set for children (patented in 1914). I presented this analogy in the preface and noted there that this gamelike characteristic constituted one of the greatest advantages, and also one of the greatest disadvantages, of the theory. The advantage was its simplicity and appeal; the disadvantage was that to many observers it seemed far too childish to be a probable depiction of nature.

Much later, Kekulé stated on three separate occasions[56] that he had privately developed his structure theory during his years in London, though he only published the theory in two articles of 1857–58, after moving to Heidelberg. In both of those published papers he disclaimed originality, at least "for the most part," for the leading ideas within

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[56] Anschütz, 1:558; 2:940, 951 (1883, 1890, 1892). For more details, see chapter 3, this volume.

them. In his 1857 paper, which offered a partial and preliminary announcement of certain structure-theoretical ideas, he wrote:

> In order to avoid detailed historical comments, I want to say at the outset that I make no claim for originality in what follows, for the most part at least; it is, rather, nothing more than a further development of leading ideas that Williamson has from time to time communicated—what one might call the "theory of polyatomic radicals"; ideas that Odling first further developed in his paper on the constitution of acids and salts; which, since Gerhardt partially adopted them in the fourth volume of his *Traité* (without, however, as can easily be shown, conceiving them strictly in Williamson's sense), have often been repeated in German journals, and whose utility now . . . can probably no longer be contested.

In the second article of 1858, containing the first full statement of structure-theoretical principles, especially the extended application to carbon, he wrote:

> In this connection, I must once more emphasize that I consider a large portion of these views as in no way stemming from me; rather, I am of the opinion that in addition to the earlier-named chemists (Williamson, Odling, Gerhardt), from whom more detailed discussions of these subjects can be had, others as well share at least the fundamental ideas at the heart of this theory; above all, Wurtz, who, never thinking it necessary to develop his ideas more fully, nevertheless permitted others of us to infer them by reading between the lines of each of his classic researches, through which the development of my views first became possible.

These are careful statements. Kekulé appreciated the complex interplay between these five leading personalities, counting himself; it is unfortunate, though not surprising considering their personal relations, that he omitted Frankland's and Kolbe's names. His acknowledgment of the contributions of Williamson, Odling, Gerhardt, and Wurtz is unusually frank and generous. We see at the end of the first quotation that Kekulé also allied himself publicly to Williamson's philosophy of molecular realism, dissociating himself from the molecular positivism of Gerhardt. Finally, the particularly strong acknowledgment of Wurtz in the second article is suggestive. What "reading between the lines"[57] of Wurtz's papers did Kekulé need to do?

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[57] Advice that Kekulé repeated in his Benzolfest speech of 1890: "He who aspires to be a scientist must study the [works of the greatest researchers] so thoroughly that he is able not only to read between the lines, but even to develop the ability to divine unexpressed thoughts" (Anschütz, 2:945).

At a public celebration in his honor in 1890, in "highly indiscrete revelations of my intellectual life," Kekulé spoke of the origin of his ideas on carbon tetravalence and self-linking.

> During my time in London I lived for quite a while in Clapham Road, near the Common. However, I frequently spent my evenings at the home of my friend Hugo Müller in Islington, at the opposite end of the metropolis. We spoke of many things, but mostly of our beloved chemistry. One lovely summer day I rode once more, by the last omnibus, through the now deserted streets of the otherwise so lively city, "outside," on the upper deck of the omnibus, as usual. I sank into reveries [Träumereien]. The atoms began to gambol before my eyes. I had always before seen them in motion, these tiny creatures, but I had never succeeded in discerning the nature of their motion. This time I saw how two of the smaller ones frequently paired off; how larger ones seized two small ones, how still larger ones held three and even four of the tiny atoms together, and how they all moved in a whirling dance. I saw how the larger ones formed a line, and dragged the smaller ones along only at the end of the chain. I saw what the venerable Kopp, my honored teacher and friend, so charmingly depicted for us in his "Molekularwelt," but I saw it long before him. The cry of the conductor, "Clapham Road!", awakened me from my reveries, but I spent part of the night committing at least sketches of these dream figures to paper. This was the birth of the structure theory.

Let us put ourselves in Kekulé's shoes, in London in the summer of 1855. The science was rapidly changing, even month by month. In March 1855 Odling had orally presented his paper on hydrocarbon radicals, and it is likely that Kekulé was an interested observer. In April Wurtz's article on the constitution of the glyceryl radical was printed. Then in June and July Wurtz published his work on the "mixed" radicals (containing his subatomic speculation) in the *Comptes rendus* of the Académie des Sciences and the *Annales de chimie et de physique,* respectively; we know that these articles appeared in print immediately and so would have been available to Kekulé before his departure from London in September 1855.

I suggest that in this exciting climate the most productive stance turns out to have been the realist-mechanist metaphysics, along with its natural ally for chemists, an unapologetic use of the visual imagination. We have pursued evidence of such a practice in some of the personalities treated in this and the previous chapter, but in this regard Kekulé was arguably the most favorably positioned scientist. His visual artistic and architectural talent and training, his further informal education at the hands especially of the equally visual Williamson, his mastery of the science, his eclecticism, his use of the realist-mechanist approach, his strong predilection for theory, and his powerful scientific imagination[58] all served him well.

So Kekulé meditated on Williamson's water type, with those movable diagrams and shuffling atoms; on Wurtz's resolved formula for glycerin; on Odling's substitution-values and marsh-gas radicals; and on Laurent's and especially Wurtz's subatoms. I suggest that Wurtz's subatomic speculation was literally and intentionally portrayed in Kekulé's notorious "sausage" formulas, which he used in his lectures from at least 1857 and which appeared in print in the first installment of his textbook, published in 1859; I suggest that these formulas also embody the dream figures he portrayed in his "omnibus" anecdote. (In these "sausage" formulas, to be discussed in chapters 3 and 4, Kekulé's representation of an atom of carbon indeed appears sausagelike: four interconnected spherical bulges arrayed in a contiguous line—each bulge representing a single carbon valence, or Wurtzian "subatom"—all covered by a hoodlike casing to make a single atomic entity.) I conjecture that he had just read Wurtz's article that summer day, had talked about it (as he related in the anecdote) with friend Müller, and then, riding home from Islington to Clapham in a tired, relaxed, hypnagogic state—not actually sleeping—his visual imagination had fired up. He saw how his little sausage-atoms of various lengths might connect up together, and how larger atoms might also combine, all according to the prescribed linkages. That, I suggest, constituted his "dream."

Let us examine further details of the anecdote, to help assess its verisimilitude. Kekulé said there that while in London he lived in Clapham Road for "quite a while," but we have no independent confirmation of this. In fact, we noted above that in 1854 he was sharing a flat with Reinhold Hoffmann miles away, in College Place. But Hoffmann departed in September 1854, and Kekulé, having lost his roommate, may then have had to scout for less expensive lodgings. A recent search in the London Public Records Office did not reveal Kekulé's residences but did unearth the fact that in 1854 Kekulé's wealthy half-brother, Charles, was living at 3 Clapham Road, on the Common. So after Hoffmann's departure Kekulé may well have moved into, or near, his brother's residence. We also know that Hugo Müller (the third member of the "triple

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[58] Even his bitterest enemies recognized this gift; when Kolbe opined to a friend that Kekulé "always rides a fiery steed [er reitet immer ein feuriges Ross]," he was not referring to equestrian talents. Kolbe to Erlenmeyer, 25 February 1866, HDN.

friendship" of which Hoffmann had such vivid recollections) resided in Islington and that an omnibus route did in fact run between Islington and Clapham Common.[59] If the anecdote reflects actual events, it is therefore more likely to be placed in summer 1855, not 1854, as has usually been assumed. This timing then also fits with the development of the science. The similarity between Kekulé's sausage formulas, the description of his dream figures, and Wurtz's speculation, allied with Kekulé's powerful (but vague-on-details) public testimony to Wurtz's influence would all then make sense.

As an old man, Kekulé was given two occasions to ponder his own career, and his words on those two days are quite similar. On the first of these, a public and festive occasion, he commented, "[My eclectic education] and the direction that my early architectural studies provided to my mind, gave me an irresistible need for visualizability [Anschaulichkeit]; these are apparently the reasons that 25 years ago it was in my mind in particular where those chemical seeds of thought that were floating in the air found appropriate nourishment." Two years later, in a more intimate and extemporaneous gathering, he said, "Such thoughts [of structure theory] were then in the air, sooner or later they would have been expressed, perhaps one or two years later, perhaps in a different way than I did it. [But] it would have become merely a 'paper chemistry,' only the architect was able to provide the arrangements of atoms a living, spatial conception."[60]

Others have agreed with these judgments. Kekulé was a "hero" of chemistry, J. H. van't Hoff wrote in an obituary of his mentor, partly because of his imaginative visual propensity extending down to the molecular world, and this habit of mind could possibly be traced to his early training as an architect.[61] One early twentieth-century commentator has written, "[Kekulé's youthful] robust power of imagination increased almost to that of a visionary. His thoughts developed into [mental] images, and sometimes he was able, as it were, to visually examine his thoughts."[62] In an obituary, Francis Japp noted that "Kekulé,

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[59] The service ran every eight to nine minutes until approximately 10:30 p.m., and the route took about an hour. These details, including the residence of Charles Kekulé, are revealed in Dayan, "Circumstances" (2006).

[60] Anschütz, 2:944, 951.

[61] Van't Hoff, obituary of Kekulé published in *Die Nation,* 13 July 1896, quoted in Cohen, *van't Hoff* (1912), 59–62.

[62] Wizinger-Aust, "Kekulé" (1966), 8. A less flattering but not incompatible viewpoint was provided by Kekulé's Portuguese Indian student in Heidelberg, Agostino Lourenço, who thought that he was exceedingly clever and always full of ideas, but decidedly lacking in follow-through. Lourenço's judgment was transmitted in 1906 by Friedrich Beilstein, who agreed with it, to Anschütz, who did not; Anschütz, 1:154–55.

in later life, by no means regarded the time [spent as a student of architecture] as wasted; he always laid stress . . . on the necessity which he ever afterwards felt of having before him, if possible, an actual picture of any problem he was dealing with. He was doubtless right. After all, he remained an architect to the last: only it was the architecture of molecules, instead of that of buildings, with which it was his lot to concern himself."[63]

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[63] Japp, "Kekulé" (1897), 97–98.

THREE

Building an Unseen Structure

We must first accommodate our mind's eye to the mental picture that corresponds to the second theory we described [i.e., structure theory]—for convenience, since it is less demanding for us, and also because the idea appeals somewhat better to a sensibility that is still (or perhaps that is once again) childlike. HERMANN KOPP[1]

During his two and a half years as a lecturer in Heidelberg (1856–58), Kekulé published ideas that (as he later averred) had been developing in his head since London. In the broadest sense, his theory proposed how to infer from chemical evidence the way individual atoms are linked together to form certain kinds of molecules. But the epistemology of such a move was both complex and risky. Along with many of his contemporaries, Kekulé would make a distinction between the *apparent* intramolecular arrangement of atoms and radicals as deduced from the properties and reactions of a substance—this is what he and others meant by the term "chemical constitution," expressed in what was called a "rational formula"—and the *true* three-dimensional *spatial* arrangement of the physical atoms within a molecule. Kekulé's theory asserted that one could provisionally determine the first, with greater or lesser probability depending on the richness of empirical evidence at one's disposal, but the second was thought to

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[1] *AMW,* 29.

be beyond reach, or more precisely, *presently* beyond reach by *chemical* means. At a time when one did not even know what an atom was, there were limits to the degree that one could assert the determinability of intramolecular constructions, at least at that most thoroughgoing level. As sterile as Kekulé found Gerhardt's total molecular skepticism, he was also repelled by what he viewed as the naïve assurance of those, such as Hermann Kolbe, who made claims to be able to determine with near certainty the permanent chemical constitutions (but not spatial arrangements!) of molecules.

This careful distinction between *apparent chemical arrangement* and *actual, physical, stereospatial arrangement* of atoms inside the molecule spanned methodology (chemical versus physical investigative approaches), epistemology (how exactly one may aspire to knowledge of a realm one cannot directly perceive, and how much certainty one is warranted to attach to that knowledge), and ontology (what is meant by, and how exactly one conceives, molecular reality). Kekulé was trying to steer his intellectual craft between the Scylla of radical skepticism and the Charybdis of naïve realism, and always there was the knotty practical problem of how to connect the massive (and steadily accumulating) experimental evidence to the conceptions that one wished to defend regarding that unseen molecular level. Considering all this, discretion was the better part of valor. As we follow Kekulé's career in Heidelberg in this chapter, including the formulation and publication of his path-breaking theory, we will find hesitations and equivocations that were sometimes in tension with one another.

But however hedged, the emergent theory proved to be powerful and productive. In short, Kekulé's theory, like that of his independent rival A. S. Couper, would provide the basis for *atomic mappings* or *orderings* within the molecule, really a problem of two-dimensional topology, rather than physical arrangements in three-dimensional Euclidean space. The idea that one could accomplish the former task, from the evidence of chemical reactions and using the algorithms provided by "atomicities" (what we now call valence), was the central core of Kekulé's "theory of atomicity of the elements" of 1858—later called structure theory.

The birth of the theory of structure was substantively connected to the contemporaneous emergence of a reformed system of atomic weights and molecular formulas, a system that the first structuralists had come to regard, on the basis of experiments such as those of Williamson, not as convention but as ontology—that is, as permanent and true.[2] (Note that this ontological transition did not require the adoption of naïve Daltonian atomic realism; the careful epistemological distinction described in the first two paragraphs of this chapter was unaffected by the move.) Ursula Klein has well argued that the symbolic systems for chemical formulas of the nineteenth century could be interpreted as having both logical and iconographic features.[3] With the emergence of theories of valence and structure, the iconographic features, hitherto often intentionally suppressed, increased in prominence; psychologically this made sense, for the structuralists now believed in the permanence of their system of chemical atoms. In the hands of the new structure theorists, chemical formulas retained their immense formalist value as paper tools, analogous to mathematical formulas; but they also widened the opportunities for imagery—physical models and mental visualizations—as substantive heuristic aids. The present chapter begins to trace these transitions.

The Start of a Teaching Career

From the 1830s on, teaching in German universities had come to be viewed as deeply interconnected with research, and advanced students became indispensable collaborators with professors. Kekulé held these convictions throughout his career, treating his best students as colleagues, and often as friends. His first and subsequently most famous student, Adolf Baeyer (later Adolf *von* Baeyer, who became Liebig's successor at Munich and who won one of the earliest Nobel Prizes in chemistry), wrote about their earliest relationship: "In [Kekulé's Heidelberg] lectures, and in conversations with him, a new world dawned for me. Younger chemists have no conception from the literature of the influence that the young Kekulé exerted on his contemporaries. . . . Carried away by the logical consistency of the new theory that later was named structural chemistry, he constructed before his enthusiastic audience the edifice of theoretical chemistry in which we still today [in 1905] dwell."[4]

But Kekulé's road from his London postdoctoral position to the start

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[2] I refer to the Laurent-Gerhardt reform of 1846, as well as to that advocated from 1858 by Stanislao Cannizzaro, who made additional small but significant adjustments to the new system. See *CA* for details.

[3] Klein, *Experiments, Models, Paper Tools* (2003), 5, 12, and passim.

[4] Baeyer, *Erinnerungen* (1905), 8–9.

of his teaching career in Heidelberg was not an easy one. The post with Stenhouse, he wrote his friend Planta, offered no prospects for advancement. Having abandoned hope of a university career due to the near absence of appropriate openings throughout Europe, Kekulé tried to find employment in industry, but there was nothing at all to be found, not even poorly paid jobs. His much older half-brother in London, the wealthy commodities trader Karl Kekulé, offered to set him up in business there as an analytical chemist, but the prospect drew only a grimace from the younger man. At this, as Kekulé reported to Planta, Karl withdrew his offer, saying, "better you should let it be, and do what you want to do!" There followed a series of negotiations between the two, which finally culminated in Karl offering to lend his half-brother sufficient funds to support an attempt at a scholarly career back home.[5] The first step for such an ambition was "habilitation" (teaching certification) at a university, which qualified one to be "Privatdozent" (lecturer) there.

Kekulé left London for Darmstadt in early fall 1855, secured his brother's money in November, and then decided on the University of Heidelberg (in the Grand Duchy of Baden) as the most favorable site for him to habilitate. A new laboratory, the largest and best-equipped in Germany, had been built there to attract the great Robert Bunsen from Breslau, and Bunsen was just then completing his first semester of teaching in the new building. Moreover, since Bunsen was strongly averse to theory and was uninterested in organic chemistry, there appeared to be a niche for an instructor like Kekulé, who was deeply engaged in organic-chemical practice and theory. Although they were regulated by the state's education ministry and by the local professoriate, university Privatdozenten received no salary; their income was derived solely from modest fees paid directly to them by students. Hence, student demand was important.

Kekulé moved from Darmstadt to Heidelberg shortly after the New Year, submitting the official application for habilitation on 12 January.[6] The process required delivering a colloquium, a separate sample lecture, a scholarly disputation, and payment of a fee. The colloquium

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[5] "[M]ein Bruder erklärt, was man nicht mit Liebhaberei betreibe, betreibe man auch nicht mit Energie und ohne Energie komme nichts dabei heraus; 'da riskire ich mein Geld nicht, und Du lässt es besser sein und treibst was Du willst.'" These events in Kekulé's life, from summer 1855 until the date of the letter, are all related in Kekulé's long letter to Planta of 9 February 1856, AKS. Kekulé's reminiscences as an old man track this contemporaneous account precisely. "Man wollte mich in England zurückhalten," he stated in 1892; "ich sollte Techniker werden, aber mich zog es nach der Heimat" (Anschütz, 2:950).

[6] Universitätsarchiv Heidelberg, H-IV 102/52, 57–73, and PA 1817, 1–15 (on 3).

took place on 8 February; Bunsen and Gustav Kirchhoff stated that they were "completely satisfied" by the answers of the candidate, but the final evaluation was marked with the rector's laconic judgment of "sufficiently capable" (hinreichend befähigt). The sample lecture took place on 11 March, on a topic selected by Bunsen: "Description of the most important theories of the constitution of organic compounds, with critical attention to the leading principles that form the foundation of these theories." The final disputation took place four days later. Kekulé defended seven Gerhardtian-Williamsonian theses against the assigned opponents Leopold von Pebal and Hans Landolt (Kekulé was fortunate here, for these two colleagues were fellow advocates of the reform camp).[7] By 15 April Kekulé was prepared to begin the first semester of his long teaching career.[8]

As the site of his operations Kekulé rented the upper two floors of a three-story house at Hauptstrasse 4, owned by a flour merchant named Goos, across from the Darmstädter Hof Hotel. Kekulé and most of his chemical friends took their midday dinner together at the hotel.[9] The ground floor was Goos's shop; on the second floor Kekulé set up a residence; on the third a lecture room with a capacity of ten students (for which the university loaned him a few tables and chairs), along with a small private laboratory in a neighboring room, adjoining a small kitchen. His first Praktikant was his old friend Reinhold Hoffmann, who had still not completed his doctorate due to the illness that had taken him from London, and from whom we have more recollections from this time; his second was a young man named Adolf Baeyer. He soon offered to share these tight premises with an acquaintance whom he had briefly met in London, Emil Erlenmeyer.

Hoffmann reminisced to Anschütz about the narrowness of the spaces and the absence of proper facilities in what the young chemists called their "Academy of Sciences at Goos's Flour Shop."

> There soon gathered . . . around Kekulé as leader a circle consisting of numerous other ambitious young scientists, who had come from the world over to Heidelberg to complete their studies in Bunsen's large new laboratory, which was the best-

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[7] Ibid., H-IV 102/52, 60–72.

[8] *Anzeige der Vorlesungen der Universität Heidelberg* (Heidelberg: Groos, semiannual series); *Adressbuch der Ruprecht-Karls-Universität in Heidelberg* (Heidelberg: Groos, semiannual series); both held in Universitätsarchiv Heidelberg.

[9] Beilstein to Anschütz, 31 July 1906, AKS, from which Anschütz drew a number of anecdotes of Kekulé's early time in Heidelberg. Beilstein overlapped with Kekulé in Heidelberg for one year, from April 1856 to April 1857.

> equipped of its day. But what was lacking there was provided by Kekulé, in a brilliant but modestly-expressed way, in his lectures on organic chemistry, which were highly welcomed by all. Since the students were mostly the same age as he, or even older, the interactions quickly became very friendly and extremely informal. . . . The serious discussions in this circle of friends mostly turned around the textbook that Kekulé was planning, especially the arrangement and delimitation of the material, and its provision with new drawings of apparatus that he himself sketched.[10]

Since Hoffmann was in Heidelberg for only one semester before graduating and taking a position in private industry, we can place this testimony in the summer of 1856. Besides Kekulé and Hoffmann, the circle referred to included Erlenmeyer, Baeyer, Lothar Meyer, Ludwig Carius, the Swiss Hans Landolt, the Austrians Adolf Lieben and Leopold von Pebal, the German-Russian Friedrich Beilstein, the Russian Leon Shishkov, the American Frank Storer, and the Italians Angelo Pavesi and Agostino Frapolli (Frapolli, Pebal, and Erlenmeyer were all three to five years older than Kekulé; Lieben, Beilstein, and Baeyer, several years younger).

The same considerations that had led Kekulé to Heidelberg had induced all of these men to make the same decision, and it must have been a lively place in those years. Some of them were inclined to the modernist French chemistry, including (besides Kekulé) Landolt, Pebal, Lieben, Frapolli, and Shishkov; others—nearly all the native Germans—were more traditional radical-dualists, or theoretically agnostic. In his memoirs, Baeyer recalled that while walking with him shortly after his arrival in Heidelberg, Kekulé told him about the new laboratory he was fitting up. Half in jest Baeyer said, "Then I'll be your first Praktikant!" And that, Baeyer wrote, came to pass (apparently Baeyer was not counting Reinhold Hoffmann).

So early in 1857 Baeyer chose to turn his back on the finest laboratory in Germany to go work in Kekulé's jury-rigged hole of a place. In his autobiography Baeyer wrote:

> In Bunsen's laboratory I had certainly learned analysis and become comfortable with gasometric methods, but had profited little from pure [i.e., theoretical] chemistry. Bunsen had lost all interest in organic chemistry . . . This explains why modern organic chemistry, which had its origins in France and England and was imported into Germany by Kekulé (just as years earlier the chemistry of Gay-Lussac had been imported by Liebig), remained without protection or support in this country. . . .

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[10] Hoffmann to Anschütz, 26 November 1900, AKS; Anschütz, 1:64–65.

> Kekulé's laboratory was extremely primitive. It consisted of a one-window room with two work-benches, without any sort of ventilation.[11]

Nonetheless, the workplace was sufficient for a series of substantial papers by Hoffmann, Baeyer, Theodor Kündig, and Kekulé himself, during the five semesters he was there.

In Heidelberg Kekulé had entered a surprisingly crowded field. As mentioned, Bunsen had just moved into his large new laboratory, while the old university chemistry lab of his predecessor (Leopold Gmelin), housed since 1818 in a medieval Dominican monastery, was given to the professor of pharmaceutical chemistry in the Faculty of Medicine, Wilhelm Delffs. Bunsen's assistant Ludwig Carius offered courses on the side, as Privatdozent, and there were several other chemical Privatdozenten teaching at the same time as Kekulé. Including Bunsen, Delffs, Carius, and Kekulé, the university's course roster lists no fewer than nine Ph.D. instructors offering courses in chemistry in winter 1857–58, and this with a total of only about a hundred Heidelberg students studying medicine, pharmacy, or chemistry. Since neither Bunsen nor the university was willing or able to assist them, each of these men had had to set up their own private facilities—for all of these courses required laboratory demonstrations or exercises.[12]

But more important than his facilities for instruction were the ideas that Kekulé was retailing. In his old age Baeyer pondered the differences between his mentor and him. He wrote that unlike himself, Kekulé was never interested in chemical substances for their own sake, but only as means to test his ideas. Such a passion for theory, he thought, could not be taught, which is why Kekulé never really founded a "school" and why he published only a modest number of papers for a scientist of his enormous influence.[13] We find similar descriptions of Kekulé from other witnesses. In his obituary of Leopold von Pebal, speaking of their friendship in Heidelberg, Lothar Meyer wrote:

> It was a very contentious and often also a very stimulating time for chemists. Gerhardt's great textbook was coming out, but the fourth volume, containing the key to the entire system, had not yet appeared. Nonetheless, the type theory was daily gaining adherents—to be sure, most of whom induced only by the indistinct feel-

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[11] Baeyer, *Erinnerungen,* 4–6.

[12] *Anzeige der Vorlesungen* and *Adressbuch;* Curtius, *Heidelberg* (1908), 23–24. The other chemistry Privatdozenten at this time were Emil Erlenmeyer, Gustav Herth, Friedrich Walz, August Bornträger, and Heinrich Meidinger.

[13] Baeyer, quoted in "Vorfeier" (1905), 1621.

> ing that a deeper meaning dwelt in the pattern-formulas of this theory, the key to which no one yet knew where to seek. This is when Kekulé came to Heidelberg to habilitate, and he eagerly agitated among us as an apostle of the theory. I still vividly remember the debates that lasted hours, even days, in which he won ground step by step.

Meyer noted that Pebal was closer to the type theory than many of his comrades, who had been prejudiced against these ideas (as he himself had been) by the hostility of their honored master, Bunsen. But he said that despite this extended resistance, Kekulé managed to persuade most of them "to gradually come over to the new camp."[14] This all must have happened in Kekulé's first summer in Heidelberg, for Meyer moved to Königsberg in fall 1856.

Adolf Kussmaul, a young ausserordentlicher professor of medicine at the time who later became a prominent full professor at Strasbourg, wrote in an autobiographical memoir that the young chemists of his acquaintance eagerly looked forward to the beginning of Kekulé's Heidelberg lectures, for many of them already knew of him. "Out of curiosity I myself attended for a full semester [summer 1858] a weekly Publikum[15] in theoretical organic chemistry that he had announced," Kussmaul recalled. "The lectures comprised the essence of the theoretical portion of his famous textbook of organic chemistry, whose first volume appeared later [1859]. . . . His most fruitful stimulation had come from Gerhardt and Williamson; he cited their names in his lectures often and gladly." Kussmaul and Kekulé became personal friends. "In conversation, a slightly ironic cheerfulness suffused over Kekulé's prominent features, which, when lecturing, increased to a very definite smile whenever he discussed his valence theory. He seemed to take delight in the ingenious game with the atoms, like a master playing dominos."[16] Baeyer summarized: "Kekulé had such a dazzling personality that he irresistibly won over all his students. . . . He dominated his entire entourage by his lively personality and his sparkling intellect."[17]

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[14] Meyer, "Pebal" (1887), 1000. Meyer's long letter of 30 January 1881 to Kolbe (ADM 3535) provides an invaluable personal perspective on this contentious period, and one that is consistent with these comments.

[15] A Publikum was a course offered to students gratis; it was unusual for a Privatdozent to offer such a course, and this was the only time Kekulé did this in Heidelberg.

[16] Kussmaul, "Dreigestirn" (1902), 180–83. Kussmaul went on to say that "Kekulé visited me once in the 1880s and described to me the disturbances in his health, including his own curious notions about the nature of his illness, which I was not exactly able to follow; he accompanied these astonishing hypotheses with the same smile with which he had once explained his valence theory to the audience in his Heidelberg class" (ibid., 184).

[17] Baeyer, quoted in "Vorfeier," 1621.

If upon his arrival in Heidelberg Kekulé was already in possession of some of the ideas that he revealed only later to a wider public, as he later repeatedly asserted, why did he publish so hesitantly? As is the case with Wurtz, one must sometimes read between the lines of Kekulé's public statements to perceive his true convictions. For allied with Kekulé's theoretical brashness was a distinct element of professional caution. It was one thing to engage with students and to pursue entertaining forensics with his friends, but it was quite another matter for a not-yet-established scholar to enter in print too boldly with new theoretical notions. One would want first to prepare the ground carefully.

Early Work in Heidelberg

Before the end of 1856 Kekulé completed his first experimental paper from his new lab. Kekulé attempted to make the case for a proposed molecular constitution for the troublesome family of compounds known as the fulminates. Silver fulminate had been the subject of Liebig's very first investigation in 1822, and a generation later no one had yet solved the puzzle of how the elements of hydrogen, oxygen, carbon, and nitrogen were combined in this explosive compound. Most chemists had assumed that the molecule must contain a nitro group, because most other explosive substances were known to be nitro compounds, but Kekulé, choosing mercury fulminate as his subject, fixed on the circumstance that nitrile (also known as cyano) compounds were often also found as decomposition products of fulminates. His solution was to consider that nitro and nitrile groups may both be present in the molecule, making mercury fulminate a species of a new genus he called the "marsh gas type," marsh gas itself being C_2 H H H H (here he was using equivalents, i.e., C = 6, O = 8, hence a doubled carbon atom). He then wrote nine molecular formulas fitting this pattern, mercury fulminate being formulated as $C_2\ NO_4\ Hg\ Hg\ C_2N$.[18]

In proposing this "marsh gas type," Kekulé was doubtless carrying further the suggestions of William Odling's March 1855 paper on hydrocarbon radicals. But the predecessor whom Kekulé explicitly named was not the atomic skeptic Odling, nor Gerhardt, but rather Dumas, who in 1840 had published a table similar to Kekulé's, headed by a formula for marsh gas.[19] Choosing his words carefully, Kekulé stated that he was

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[18] Kekulé, "Constitution des Knallquecksilbers" (1857), 204.

[19] Dumas, "Mémoire sur la loi" (1840), 163.

proposing this new schema not in the sense of *Gerhardt's* type theory (whose positivist philosophy Odling had also followed), but "rather in the sense in which [the word 'type'] was first used by Dumas," namely, in the sense of a *physical or mechanical structure*. In a second paper on this subject he emphasized once more that all the substances in his table belong to "a single series, a single *mechanical* type."[20]

Although these two papers contain no theoretical statements other than those just cited, their content is consistent with the idea that Kekulé was deliberately building the factual groundwork for a future more general statement about how one might use the substitution-values of atoms schematically to build up proposed molecular constitutions. It is even possible that Kekulé may have chosen precisely the fulminate series for his efforts because it so clearly illustrated the "tetratomic" (i.e., tetravalent) nature of carbon.[21]

If Kekulé was as ardent a follower of Williamson's lead as I suggest here, it may seem curious that he used equivalent-weight formulas in these two papers, rather than Williamson's atomic weights, and indeed any incipient structure-theoretical interpretation of the formulas in these papers is masked by the consequent doubling of numbers of presumed carbon and oxygen atoms in "equivalentist" formulas. The circumstance is even more puzzling when one considers (as we saw in chapter 2) that in 1854 Kekulé had declared that "it is not merely a difference in notation, but rather an *actual fact*" that the oxygen atom weighs 16, sulfur 32, and (by clear implication) carbon 12, relative to hydrogen 1. But in Heidelberg in 1857 Kekulé was writing in a local context in which this retreat made sense as a temporary tactical move. After all, no one else at that time and place was using atomic-weight formulas, and these two papers were not explicitly theoretical. He had made something of a splash in England; he needn't *yet* do that in Germany.[22]

Counting Kekulé's second fulminate paper, seven papers appeared from Kekulé's tiny lab in the course of 1857, three of which were by his

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[20] Kekulé, "Constitution des Knallquecksilbers" (1857), 204–5, and "Constitution des Knallquecksilbers" (1858), 283 (my emphasis). His later historical judgment was that "Gerhardt's Typen waren Reactionstypen . . . Die Typen von Dumas aber waren Constitutionstypen. Ich meine, es bedarf keiner weiterer Auseinandersetzung." Kekulé to Ladenburg, 14 July 1886, AKS.

[21] This suggestion was made by Erwin Hiebert, in "Experimental Basis" (1959), 326. Kekulé's constitution for the fulminates is quite different from the modern view, in which mercury fulminate is HgO–N=C. But the chemistry of these and related compounds is complicated.

[22] For more on this issue, see Kolbe's critique in *Journal für praktische Chemie* 132 (1881): 398; and Kekulé's unpublished response to Kolbe in "Zur Geschichte der Valenztheorie," in Anschütz, 1:498, 558; also Anschütz's own commentary, 1:85.

students. One was from his old friend Reinhold Hoffmann, who had finally finished his doctoral project, the preparation of monochloroacetic acid. It had been relatively easy to prepare the fully chlorinated acid—Dumas had done that as early as 1838—but to insert just one chlorine atom had proved to be a challenge. Unfortunately, in the six months between the printing of Hoffmann's dissertation and its publication in Liebig's *Annalen,* Wurtz had announced the same preparation, achieved in a different fashion.[23]

Then Kekulé himself showed that the substance that Hoffmann had produced could be hydrolyzed to form glycolic acid (this was glycol with one of the two alcohol functions converted into a carboxylic acid, or, alternatively, oxalic acid with one of its two acid functions converted into an alcohol). Wurtz had already recently produced the novel glycolic acid by simple oxidation of glycol, but Kekulé now had done it in a new way. In the process he had demonstrated for the first time (he wrote) how a "monoatomic" (einatomig) substance (acetic acid, the starting material for monochloroacetic acid) could be transformed into a "diatomic" (zweiatomig) substance (glycolic acid).[24] By this he meant that acetic acid could combine with only one molecule of base, while glycolic acid, which was both an alcohol and an acid, could combine with two (that is, if the base were strong enough, such as with sodium or potassium metal).

Kekulé's increasing concern with the "atomicity" of organic compounds led him inexorably toward exploring atomicity (in modern terms, valence) in radicals, then in elements. By the summer of 1857 he was ready to take the final steps.

The Theory of Polyatomic Radicals

Kekulé published his theoretical ideas in two papers, the first of which (dated 15 August 1857, published in the November issue of the *Annalen*) outlined a "theory of polyatomic radicals," and the second (dated 16 March 1858, published in the May issue of the *Annalen*) announced a "theory of atomicity of the elements." A careful reading reveals them to be closely related, essentially two parts of the same set of ideas. Why the cautious, piecemeal method of publication? At the "Benzolfest" in 1890, Kekulé said,

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[23] Hoffmann, "Monochloressigsäure" (1857); Wurtz, "Aldehyde" (1857), 61.

[24] Kekulé, "Glycolsäure" (1857); Wurtz, "Vrai formule" (1857).

> My ideas about the chemical valence of atoms and the way they combine together—what we today call the theory of structure—were already formulated during my stay in London. As a young Privatdozent in Heidelberg I brought these ideas to paper and shared the work with two of my closer friends [Erlenmeyer and Baeyer?]. Both shook their heads in doubt. I thought, one of two things is not yet ripe, either my theory or the time, and put the manuscript away in a drawer: *nonumque prematur in annum*.[25] Over a year later a paper by Limpricht provided the external inducement for publication, naturally in altered form. The work was not really improved by this change. It would have been better had the polemical part not been printed; in my opinion the original form was better.[26]

If this testimony is accurate, it provides an approximate date for the first draft of the theory. Since the paper by Limpricht to which Kekulé seems to be referring appeared in print in June 1857, this suggests that the two unnamed friends shook their heads doubtfully in the spring of 1856.[27] As we have seen, the various testimonies of his friends at the time are at least consistent with this scenario, though no one ever wrote that he had seen an early written draft of the theory.[28]

Heinrich Limpricht (1827–1909), an ausserordentlicher professor in Göttingen, had been the first in Germany to write a textbook based on type theory, *Grundriss der organischen Chemie* (1855). But Limpricht's development of the theory was by no means to Kekulé's taste, retaining as he did the old conventional equivalents without qualm—treating, for instance, water as HO or H_2O_2. A paper by Limpricht and his student Ludwig von Uslar on the constitution of sulfobenzoic acid provided Kekulé a platform to offer his critiques. Another of Limpricht's students, Otto Mendius, in a related and nearly simultaneous paper, assigned sulfonated salicylic acid to the class of "copulated" compounds.[29]

The stated purpose of Kekulé's polyatomic radical paper was to demolish the copula theory for good.[30] Tarring Limpricht and Uslar with the same brush he was using on Mendius, he declared the copula theory to be complicated and unnecessary. Rejecting copulas was beneficial, for then *all* compounds could simply and clearly be represented as

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[25] The advice of Horace, *Ars poetica* 388–89. When you have written a poem, "let it rest even unto the ninth year," and only then, if you still think it has worth, should you publish it.

[26] Anschütz, 1:940–41.

[27] Limpricht and Uslar, "Sulfobenzoësäure" (1857).

[28] In his biography of Baeyer, Karl Schmorl asserted that Kekulé had described his theory to Baeyer early on, that Baeyer had urged Kekulé to publish immediately, but that Kekulé had hesitated. Schmorl's warrant for these statements is not clear. Schmorl, *Baeyer* (1952), 39.

[29] Limpricht and Uslar, "Sulfobenzoësäure"; Mendius, "Sulfosalicylsäure" (1857).

[30] Kekulé, "Theorie der mehratomigen Radicale" (1857).

combinations of polyatomic radicals.[31] But Kekulé made clear that he was after bigger game than this. In his opening sentence he noted that by way of response to Limpricht it was his intention to communicate here "some fragments of a way of thinking about chemical compounds which I have used for quite some time, and which I believe provides a clearer conception of many relationships of chemical compounds than the hitherto customary one does." This new general conception, he wrote, might be called "the theory of polyatomic radicals." He did not believe that these views were entirely original to him; many others shared at least the basic idea, especially Williamson and Odling, and then it was also adopted by Gerhardt (without, Kekulé noted, his conceiving it strictly in Williamson's sense); indeed, the theory now could "probably no longer be doubted." He also noted that he would henceforth use the atomic weights recommended by Gerhardt and by Williamson, namely C = 12 and O = 16, drawing a bar through the respective symbol to distinguish them from the C and O symbols for equivalents.[32]

Kekulé wrote, "The molecules of chemical compounds consist of juxtaposed atoms. The number of atoms of other elements (or radicals) united with one atom . . . is dependent on the basicity, or magnitude of affinity, of the components." The various elements can be divided into three main categories, classed according to their "magnitude of affinity": monobasic or monoatomic, such as H, Cl, Br, or K; dibasic or diatomic, such as O or S; and tribasic or triatomic, such as N, P, or S. But there was even a fourth category. "As can easily be shown, and as I will discuss later in more detail, carbon is tetrabasic or tetratomic [vierbasisch oder vieratomig]; that is, one atom of carbon C = 12 is equivalent to four H," as can be exemplified in formulas such as CH_4 and CCl_4. Later in the paper, Kekulé affirmed that CH_3Cl, for instance, acts as a compound of the monoatomic radical methyl, CH_3—or at least it does so "if the [chlorine atom] is located in an attackable position [in the molecule]." This statement accords with his definition of a radical, which he defined in this paper simply as "that portion [of a molecule] that remains unattacked in any given reaction."[33]

This way of looking at chemical compounds not only provides

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[31] Ibid., 141.

[32] Ibid., 130. On the origin of this convention, see chapter 2, this volume, note 23.

[33] Ibid., 132–33, 143, 145. I translate Kekulé's term "Verwandtschaftsgrösse" as "magnitude of affinity," and his term "Verwandtschaftseinheiten" as "affinity units"; both refer to what later chemists called valence units or valence bonds. I translate his phrase "eine Aneinanderlagerung von Atomen" as "juxtaposed atoms."

schematic clarity, Kekulé wrote, but there are experimental arguments for its truth, at least in certain cases, such as for oxygen or sulfur atoms. In support of this statement he cited both his own 1854 paper on thiacetic acid and Frankland's 1855 paper on diethyl zinc.[34] Whether mono-, di-, tri-, or tetratomic, a polyatomic atom or radical is the "cause of the cohesion" of the various parts of the molecule. A monoatomic atom cannot hold anything together, he wrote; it cannot serve as the basis for the cohesion of any molecule. Here, as an example, Kekulé cited one of the many formulas of Gerhardt that are "inadmissible according to the theory of polyatomic radicals"; that is, inadmissible if one has a realist-mechanist idea of atomic linkages. It was Wurtz, not Gerhardt (Kekulé averred) who had proclaimed the correct notion of atomic linkage.[35] He also gave many specific examples of how various molecules can be schematically analyzed and represented by these "atomicity" rules. Almost none of these cases, however, were analyzed all the way down to each constituent atom.

At the end of this bold paper appeared an unusually timid Kekulé, with concluding phrases that are perhaps understandable coming from an ambitious man who until now had been pummeled by the job market. He was far from wanting to assert, he wrote, that his way of viewing chemical compounds was the only permissible one; indeed, it hardly mattered whether one were to use this or the "customary" set of ideas. But what *is* important is that chemists should not think we see only contradictions in our formulas where in fact there are revealing correlations and analogies to be uncovered. He was implying that the concept of "copulated" compounds misleadingly led to the former, whereas his new "theory of polyatomic radicals" helpfully offered the latter.

We know something about what Kekulé was teaching his students at this time, due to the fortunate survival of a 494-page set of lecture notes taken over two semesters by a student named Moritz Holzmann.[36]

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[34] Ibid., 133–34. He cited Frankland's 1855 paper rather than Frankland's 1852 paper on the saturation capacities of atoms, perhaps because doing so was a way of justifying his own priority in the question.

[35] Ibid. Kekulé illustrated the point by reproducing Gerhardt's formula for glycerin, which displayed two oxygen atoms on the right side of the bracket, and three on the left (Gerhardt, *Traité,* 4:629). This formula violates the atomicity rules that Kekulé and others had informally established to determine which atoms could be linked together, and how.

[36] The course in winter semester 1857–58 was "Organische Chemie, durch Versuche erläutert," conducted Monday through Friday at 8–9 a.m. The course in summer semester 1858 was "Einleitung in das Studium der unorganischen und der organischen Chemie, nach der neueren theoretischen Ansichten," a twice-weekly Publikum. Holzmann was a twenty-two-year-old medical student from Leipzig, later a physician in Zurich. (These details are from the *Adressbuch,* the

Parallel to his usual practice in publications at this time, Kekulé appears to have continued to follow the pattern established by Gerhardt's *Traité* of using equivalent weights in experimental contexts, and the newer atomic weights specifically to discuss theoretical ideas. Consequently, Holzmann's notes for Kekulé's course in organic chemistry in winter 1857–58 exhibit formulas using equivalents nearly exclusively, combined with the customary type-theoretical brackets, prime marks, and so on.

However, close to the end of the winter course Kekulé introduced his students to the use of novel molecular formulas using the newer atomic weights (C = 12, O = 16); his symbols for the atoms were given sausagelike shapes. He also illustrated these new graphic formulas using painted wooden atomic models that constituted three-dimensional versions of the written "sausage" formulas.[37] In his specifically historical-philosophical course in summer 1858—the same one that Kussmaul had attended, along with Erlenmeyer, Beilstein, and Aleksandr Butlerov—he employed Gerhardtian-Williamsonian atomic weights exclusively, and made liberal use of the graphic sausage formulas and wooden atomic models.[38]

I argued in chapter 2 that Wurtz's choice of the terms "triatomic," "polyatomic," and "atomicity" (Atomigkeit) (for what chemists later called trivalent, polyvalent, and valence) may have directly reflected his subatomic speculation, which pictured (e.g.) the "triatomic" nitrogen atom as an indissoluble accretion of three subatoms, each exerting one unit of valence that constitutes the ability to link with an affinity unit of another atom. I suggested further that this visual model may have formed the basis for Kekulé's omnibus vision and for his theory of "atomicity of the elements." His choice of the term "affinity units" for what we now call valences is another indication that this was how he was thinking.

Whether or not these speculations are true, it seems clear that

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Matrikel, and the *Anzeige der Vorlesungen* of the University of Heidelberg.) Holzmann's bound holograph Kollegheft treats the first course on pp. 1–400 (with atomic weight formulas on pp. 345–84), and the second course, with separate numbering, on new pp. 1–94. The volume is held in the Kekulé-Sammlung and is briefly discussed in Anschütz, 1:71–72, 160–63, and 655.

[37] Gillis, "Molecuulmodellen" (1967). These models will be discussed in more detail in the next chapter.

[38] In figure 2, the wooden model of a methyl chloride molecule is a modern replica following the pattern of surviving examples of Kekulé's models (courtesy of Museum voor de Geschiedenis van de Wetenschappen, University of Ghent). The four black spheres are connected together and represent a single tetravalent carbon atom. The printed "sausage" formula is from *LB,* 1:162n (1859). Holzmann's handwritten sausage formulas following what Kekulé wrote on the blackboard in 1857–58 are substantially similar to what later appeared in print.

2 Kekulé's methyl chloride as a "sausage" formula, and as a molecular model. Source: Kekulé, *Lehrbuch der organischen Chemie* (1859), 1:162n; Museum for the History of Sciences, University of Ghent.

Wurtz's concept of subatoms is embodied in Kekulé's "sausage" formulas. Kekulé was probably already thinking in terms of a four-unit sausagelike carbon atom at the time of his "polyatomic radicals" paper, even though he had not yet revealed his graphic formulas to the chemical public. We can say this because his stipulation there that the Cl atom in CH_3Cl needs to be "in an attackable position" to reveal a methyl radical makes sense on this basis, for a chlorine atom in an end position (one attaching to valence unit number one or unit number four) on the linear four-unit carbon atom would obviously be more accessible to attack than would a Cl attached to one of the more protected middle positions (unit numbers two or three).

The two courses represented in Holzmann's notebook covered most of the new ideas that Kekulé introduced in his two theoretical publications of 1857–58 and the first installment of his textbook published in 1859, including carbon tetravalence and self-linking. Consistent with Kussmaul's testimony, the names of Gerhardt and Williamson appear often, and Holzmann's notes show that Kekulé gave clear preference to Williamson's realist theory of atomic linkages rather than to Gerhardt's conventionalist viewpoint.[39] What he was teaching his students orally towards the end of that winter semester—ca. February 1858—turns out, not surprisingly, to have been nearly identical to what he was simultaneously proposing to his colleagues in published form.

The Theory of Atomicity of the Elements

Limpricht was confused by Kekulé's paper, and published a response. Kekulé really ought to have attacked Mendius alone, he wrote, rather than him, for he agreed with Kekulé on the need to eliminate the copula concept; that, in fact, had been part of the purpose of his and Uslar's paper. He also appears to have disliked Kekulé's tone.[40] In response, Kekulé published a long theoretical article that finally laid out his ideas systematically and completely. This article is the one usually cited by historians as enunciating the theory of chemical structure (which Kekulé himself long called the "theory of atomicity of the elements"). The fact that the paper was dated just seventeen days after the issue date of the *Annalen* number that contained Limpricht's response strongly suggests that Kekulé had this text already in hand, and only needed to add an appropriate introduction to it, responding to Limpricht's comments. This is what he later affirmed had happened, expressing regret for the polemical tone of the introduction.[41]

After a few pages of inconsequential offensive cavils and defensive parries, Kekulé came to the heart of his dissatisfaction with Limpricht's views. Limpricht had claimed to be an advocate of the theory of types (Kekulé wrote), but he had only adopted its "external form" while abandoning, deliberately or inadvertently, "the idea at its heart." He had affirmed that the formula for the water *molecule* was HO, but the basis for his water *type* was H_2O_2. This made no sense to Kekulé, who, by contrast, assigned only those compounds to the same type that had the same "cause for cohesion," for example two monoatomic atoms or radicals "held together into an indivisible unit, a molecule" by a single diatomic atom or radical. "For me, the water type only makes sense if Limpricht's two atoms of oxygen [in H_2O_2] are an indivisible unit, an atom; I do not understand how the similarities of organic compounds

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[39] Holzmann Kollegheft, WS 1857–58, 361–62, 365, 367–68; SS 1858, 16, 18, 48; in AKS.

[40] Limpricht, "Bemerkungen" (1858).

[41] Kekulé, "Chemische Natur des Kohlenstoffs" (1858). An excellent annotated translation is in Benfey, *Classics in the Theory of Chemical Combination* (1963). See Anschütz, 1:113–25; 2:941.

with water can induce us to place them in the type H_2O_2, if water itself is to be understood as HO; in a word, I do not understand the water type, if water does not belong to its own type."[42]

For Kekulé this was the nub of the matter. Although he did not say so explicitly, it is clear that Kekulé had come to the conclusion that Gerhardt himself had never understood the implications of type theory, "the idea at its heart," and that misunderstanding was now threatening the advance of the science. What was desperately needed was a good dose of Williamsonian mechanistic theory. The fact that this "profound difference of viewpoint appears to be rather generally overlooked" suggests, Kekulé wrote, that it was high time for a more detailed discussion of first principles, which he now was prepared to offer. Here is where he once more emphasized that the discussion that followed was nothing more than a further development of ideas already sketched out by others. And now, as we have seen, he added Wurtz to the list of his predecessors given in his last paper, and in fact he now gave Wurtz the pride of place in his honor roll.

"I consider it necessary," he wrote, "and, in the present state of chemical knowledge, in many cases possible, to go back to the elements themselves which compose compounds, in order to account for the properties of chemical substances." It was time to give up type theory as the quest for mere abstract pattern-formulas, he wrote; we can and should strive to resolve formulas as far as possible, indeed right down to the very atoms themselves, whenever experimental arguments exist that support the endeavor. For instance, we know much more about sulfuric acid than is revealed simply by the empirical formula H_2SO_4. We know that there is a portion of the molecule that we can denote as SO_4, that this portion is diatomic, and that it unites two OH groups (the hydrogen atoms of these groups accounting for the dibasic character of the acid). We also know that the SO_4 group can be further resolved to a diatomic SO_2 group that engages one "affinity unit" of each of two oxygen atoms; the resulting SO_4 group is diatomic because the second affinity unit of each of these oxygen atoms is thus free to form attachments. But the SO_2 group can itself be resolved right down to one S and two O's, following exactly the same pattern as just described.

We can therefore arrive at a fully resolved formula for sulfuryl chloride, or for sulfuric acid—that is, a formula in which every single atomic connection is specified—and each level of resolution is warranted by

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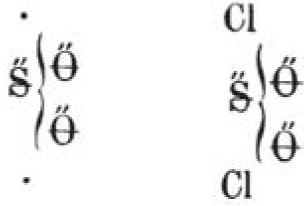
[42] Anschütz, 1:134–35.



3 Kekulé's sulfuryl radical, and sulfuryl chloride. Source: Kekulé, *Annalen* 106 (1858): 152.

existing experimental evidence.[43] In principle, this is nothing more than what he had already laid down in his first theoretical paper, only now he was clearly indicating that one could go all the way to each atom, specifying the sequential patterns in which each atom was connected to each other atom in the molecule, always following the rules of "atomicity" (valence).

One could even apply this procedure to carbon compounds, something he had only briefly touched upon in his "polyatomic radicals" paper. There he had already proclaimed carbon as tetratomic. To the simplest compounds containing a single carbon atom, such as CH_4, CCl_4, CH_3Cl, and $CHCl_3$ (several of which he had already noted in his first paper), one could add other one-carbon patterns, such as $COCl_2$, CO_2, CS_2, or HCN. One could also suggest that carbon atoms could form links to each other, each atom using one of its affinity units for this purpose, forming what he coined a "skeleton" of carbon atoms (Kohlenstoffskelett). The simplest such case is two carbon atoms connected by one affinity unit each. Left over are three affinity units for each atom, and if all of these are satisfied by monoatomic hydrogen atoms, we have ethane, C_2H_6. Five hydrogens and one monoatomic OH group on the ethane skeleton, on the other hand, gives us alcohol; five hydrogens and one NH_2 group yields ethylamine; three hydrogens, a diatomic oxygen, and an OH group gives us acetic acid; and so on. More carbon atoms can add to this two-carbon molecule, he explained. Each link in the carbon chain uses one affinity unit at each end to attach to its neighboring carbons, and so has two affinity units remaining to bond to (e.g.) two hydrogen atoms. Hence emerges the empirically long-accepted unit of homology, CH_2.

We are thus building schematic, Tinkertoy-like models of organic compounds, but always following the rules of atomicity—monoatomic

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[43] Ibid., 1:152.

hydrogen, diatomic oxygen, triatomic nitrogen, and tetratomic carbon—and always proceeding in ways that are supported by the empirical evidence provided by chemical reactions. Sometimes two carbon groups are held together by a single oxygen atom, as in Williamson's ethers, or by a nitrogen atom, as in Hofmann's secondary amines. Sometimes new compounds can be formed upon the same carbon skeleton, such as alcohol converted to aldehylde, acetic acid, glycolic acid, or oxalic acid. Sometimes chemists' manipulations can increase the size of the carbon skeleton (build it up synthetically), or decrease it (break it apart analytically). And sometimes one finds a "denser arrangement" of carbon atoms than in the paraffinic series headed by marsh gas, such as for derivatives of olefins (ethylene-like compounds), or benzene. The structural details of the latter he did not attempt to specify.[44]

How should empirical evidence from chemical reactions be interpreted to help us proceed along this schematic program? Kekulé offered some guidelines. In reactions that proceed without loss of carbon, one may legitimately assume that the carbon skeleton does not change in the course of the reaction. Barring information to the contrary, homologous series are to be constructed by the simplest arrangement of skeletal carbon atoms, that illustrated by ethyl or ethane. And when the carbon skeleton *is* attacked and broken up, aspects of the constitution of the original molecule may be deduced from the constitutions of the fragments.[45]

At the end of the paper Kekulé sketched "Principles of a Classification Scheme for Organic Compounds," which he said he had been privately using for a long time (the taxonomy can indeed be seen in Holzmann's lecture notes). The scheme was based on ideas that Kekulé only publicly revealed later, in subsequent papers and in the pages of his textbook. There he referred to atoms that are only *indirectly or incompletely* bonded to the carbon skeleton, that is, those atoms in which not all of their affinity units are bonded to one and the same carbon skeleton, as "typical" atoms, or "atoms of the type." Examples include the hydrogen and oxygen atoms in alcohols or acids, nitrogen atoms of amines, oxygen atoms of ethers, and so on. For the purposes of this classification scheme, a "radical," on the other hand, is a group consisting of the carbon skeleton plus all of the atoms that are *directly and completely* bonded to it—that is, excluding any "typical" atoms. The hydrogen of the ethyl radical and the oxygen atom in Williamson's othyl

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[44] Ibid., 1:153–57.
[45] Ibid., 1:155–56.

radical are examples of “atoms of (or in) the radical,” as well, of course, as all the carbon atoms themselves.[46]

An unusual but instructive case was the formation of acetone (Me_2CO) from acetic acid ($MeCO_2H$). Kekulé suggested, as Williamson had earlier, that in this reaction one molecule of acetic acid acquires a second methyl group from another acetic acid molecule, losing OH to its neighbor in the process. One acetic acid molecule is thus transformed into acetone, a second into carbonic acid. In this single reaction, now referred to as an example of “disproportionation,” two identical molecules combine after splitting in different ways. This case thus proves a more general point, Kekulé argued, namely, that “radicals” and “types” are conventional concepts only, that they depend on the particular reaction being studied, and that one can often assign the same substance to different types or ascribe to it different constituent radicals. A “radical,” he repeated from his last paper, is just the part of a molecule that happens to be unattacked in any given reaction, and a “type” is simply the conventional model from which one chooses schematically, and ultimately rather arbitrarily, to construct a formula.[47]

This relativist definition of “radical” is at odds with that implicit in his classification scheme, which provided an absolute taxonomy based on the structure of the molecule. Kekulé recognized that his absolute taxonomic definition of a radical was, in fact, a purely conventional choice: pedagogically expedient, hopefully heuristically valuable, but not reflecting an ultimate reality in the real world of atoms and molecules. It was the basis of his chemical taxonomy, but he understood that basis as being artificial in the Linnaean sense; artificial not because that was a desirable quality per se, but because a fully *natural* taxonomy was just as far out of reach for chemists as it had always remained for Linnaeus.[48]

Molecular Epistemology

The point just discussed was important to Kekulé: although useful for conventional purposes, neither “radicals” nor “types” correspond

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[46] These ideas were made explicit first in *LB,* vol. 1 (1859), 131, 156–57, 164, 174, 224; vol. 2 (1864), 244–45; Kekulé, “Acide succinique” (1860); and Kekulé, “Acides itaconique et pyrotartrique” (1861) (Anschütz, 2:153, 204).

[47] Kekulé, “Chemische Natur des Kohlenstoffs,” 147.

[48] For a perceptive review and a different interpretation of Kekulé’s taxonomic work, see Fisher, “Organic Classification before Kekulé” (1973); and Fisher, “Kekulé and Organic Classification” (1974).

to any intrinsic molecular ontology. Such skepticism is justified, he thought, because of chemical epistemology: what chemists know about the constitutions of substances is derived mainly from the study of chemical reactions, and, to a much smaller extent, from the study of physical properties of stable molecules that are not undergoing reactions. Chemists express their theories of molecular constitution by using "rational formulas," as opposed to the "empirical formulas" given directly by experiment. But "rational formulas are reaction formulas, and can be nothing more in the present state of the science," Kekulé affirmed. "Every formula that expresses certain reactions of a substance is therefore *rational*. Of the various possible rational formulas, the *most rational* is the one that expresses the largest number of reactions at the same time."[49]

In a footnote, Kekulé expanded on this point. Some chemists had recently expressed more optimism than he thought was justified concerning the possibility of determining the actual spatial positions of atoms within a molecule. In strong agreement with Gerhardt, whom he cited, he had grave doubts about this program.

> It is clear that the manner in which atoms leave a substance that is changing and undergoing destruction cannot possibly provide proof of how they were previously arranged in the stable and unchanging substance. Although it assuredly must be considered to be a task of science to determine the constitution of matter, and hence, if you will, the arrangement of the atoms, one must concede that the means to this end cannot be provided by the study of chemical reactions, but rather by a comparative study of the physical properties of stable compounds. Kopp's excellent investigations will perhaps provide a point of attack for this. . . . But even when [the determination of absolute constitutions] is successful, different rational formulas (reaction formulas) are still permissible, because a molecule, created as it is by atoms arranged in a certain fashion, can split in different ways and in different positions, depending on conditions.[50]

This expression of doubt about the determinability of "constitutions" would seem to be in tension with, or even contradictory of, much of his treatment that preceded and followed it. These words of Kekulé could have been taken straight from passages in Gerhardt's *Traité de chimie organique*. They seem to contradict Kekulé's many avowals of the mechanical connections between atoms, of the Williamsonian

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[49] Kekulé, "Chemische Natur des Kohlenstoffs," 149.

[50] Ibid., 147n.

vera causa of molecular cohesion traced to a single atom or radical that holds pieces of the molecule together. And what about his guidelines, proclaimed just a few pages later in the very same paper, for how one legitimately *can and should* deduce molecular constitutions from chemical reactions? For that matter, what about his deliberate, repeated, and emphatic efforts over the preceding four years, documented in this and the preceding chapter, to distinguish his Williamsonian brand of molecular realism from the barren schematism of Odling, of Limpricht, and of Gerhardt himself?

One possible explanation is that Kekulé was simply airing fashionably positivistic rhetoric. One often encounters among many in this collegial circle, and not just in Kekulé, avoidance of hypotheses and a tendency to stress, even to *over*stress, one's empiricist bona fides. Such dissimulation would be particularly important for those, like Kekulé, who were still professionally insecure. As we shall see, Kekulé carried over into his *Lehrbuch der organischen Chemie,* whose first part was published a year later, the language I have just cited here. But in his memoirs in old age Baeyer stated that in his textbook Kekulé "was often unfaithful to his own viewpoints" as expressed in personal conversations and in his lectures.[51] It may have been to these sorts of expressions that Baeyer was referring. And it was in the same rhetorical mode, perhaps, that Kekulé concluded his 1858 paper:

> Finally, I think I need to emphasize that I myself place only a subordinate value on such [theoretical] considerations. But since, in the total absence of exact-scientific principles in chemistry, one must at present be content with conceptions based on probability and convenience, it seemed appropriate to communicate these views, since, it appears to me, they give a simple and rather general expression especially for the most recent discoveries, and therefore their application may perhaps facilitate the discovery of new facts.[52]

As we know from Holzmann's lecture notes, Kekulé allowed himself greater freedom talking to his students. The theory he outlined in his course in winter 1857–58 was substantially identical to that of this paper. This theory, as Holzmann's notes reproduce Kekulé's words, "can truly be expanded to all other more complexly constituted compounds. . . . But this developed viewpoint always allows for a greater generality than all [theories] hitherto proposed, and therefore appears for now to

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[51] Baeyer, *Erinnerungen,* 9.

[52] Kekulé, "Chemische Natur des Kohlenstoffs," 159.

be the most suitable and closest to the truth."[53] These stronger words surely better reflect Kekulé's true feelings.

But a more substantive response to the ostensible anomaly is to suggest that there is less of an anomaly than it appears. It seems that Kekulé often walked the kind of epistemological tightrope discussed in the introduction to this chapter. Contemporaries faced the same issues. A few months after Kekulé's paper appeared, on 3 January 1859, Wurtz presented to the Académie des Sciences a substantial review paper on glycol and its reactions. After writing his preferred type formula for glycol, which portrayed two hydrogen and two oxygen atoms separately from the C_2H_4 core of the molecule, he commented, "This formula is not intended to show the exact position of the atoms in the compound. It is merely an expression for a certain number of metamorphoses which glycol undergoes. It shows that two atoms of hydrogen in the compound possess different properties from the other four hydrogen atoms." Again, these words would seem to suggest an orthodox Gerhardtian conviction, and we do in fact find Wurtz strongly defending here the purely "synoptic" significance of rational formulas, very much as Kekulé had done.[54]

But the situation with Wurtz, as with Kekulé, was more complex and more interesting than that. This was the first paper in which Wurtz finally abandoned equivalent-weight formulas and adopted the barred C and O symbols that indicate atomic weights. He now clearly signaled his acceptance of the theory of polyatomic radicals, which he referred to by that name. Kekulé's "extremely important theoretical article" of a few months earlier, and before that, the etherification project of Williamson, "whose work has had such a large part in the development of this theory," had led (he wrote) to an important new interpretation of types, in which the linking ("lien") function of polyatomic radicals was placed in the foreground.[55]

The objection (by Kolbe, though Wurtz did not name him) that the multiple-type formulas of Williamson, Kekulé, and Wurtz are "imaginary" because the pieces are not isolable or otherwise empirically warranted, "is not serious," Wurtz declared, for the theory clearly stipulates

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[53] This theory—the theory of structure—can "wirklich auch auf allen übrigen complicirter zusammengesetzten Verbindungen ausdehnen lassen. . . . Die durchgeführte Anschauungsweise lässt jedoch immer eine grössere Allgemeinheit zu, als alle bisher aufgestellten, und sie erscheint daher für jetzt als die zweckmässigste u. die der Wahrheit am nächsten liegende." Holzmann MS, 384 (ca. February 1858), in AKS.

[54] Wurtz, "Glycols" (1859), 474–75, 477.

[55] Ibid., 471, 474.

that a polyatomic binding radical must be present to tie the pieces together. Organic radicals "offer more points of attack" to reagents than do inorganic radicals, leading to "fragility" in the "molecular edifice"; that is the only essential difference between them. "The ideas, the hypotheses if you will, which express the molecular structure [structure moléculaire] of the first, are exactly applicable to the second."[56] All of this has a tone reminiscent of Kekulé's: brave talk about mechanistic linkages between atoms and radicals and the "structures" of molecular edifices, intermixed with cautious (and justified) empiricist admonitions, and behind it all a broad attempt to create robust connections between the chemical evidence and the theoretical conceptual schemes that can be built on that foundation.

As we noted at the beginning of the chapter, a standard demur among structuralists was developing, namely, that their formulas purported not to represent "physical" positions of the atoms in a molecule, but rather "chemical" positions. This demur was rooted in the ideas of Kekulé and Wurtz that we have just reviewed, but it was given particularly cogent and influential form by Kekulé's notable Russian rival Aleksandr Butlerov in 1861. Those who used this terminology appear to have attached one negative and one positive meaning to this distinction. The negative meaning, as we have seen, is that the formulas were not intended to designate the actual stereospatial locations of real atoms; that, they thought, was presently beyond anyone's power to determine. Positively, however, one could indeed investigate how the atoms appear to be arranged with respect to each other, in the sense of being grouped or tied together in a particular way that one might be able to ascertain. More particularly, the cumulative evidence from chemical reactions could give chemists confidence, for certain well-understood compounds, that they could specify the *sequential order* of all the atoms in the molecule. For instance, for ethyl alcohol, three hydrogen atoms are associated directly with one carbon atom (and not to each other directly); that carbon atom is not only associated with the three hydrogens but also with another carbon atom; to the second carbon atom are connected two more hydrogens, plus one oxygen atom; and one last hydrogen atom is also connected to this oxygen atom, but to nothing else. This is an example of the two-dimensional atomic mappings described in the introduction to this chapter.

In 1860 Kekulé unburdened himself on this subject in a long letter to his friend Lothar Meyer. He had just finished reading Marcellin

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[56] Ibid., 463, 474–78.

Berthelot's massive and tendentious treatise *Chimie organique fondée sur la synthèse,* and hated it, especially Berthelot's doctrinaire use of empirical formulas and his refusal to countenance rational formulas, since Berthelot regarded them as hypothetical.

> Regarding this formula mischief, if [Berthelot's] book creates a backlash I will be very pleased. I myself have had my fill of this mischief. . . . The principle which you and I use to construct formulas (you and I, and by the grace of God others as well) is *correct* and will remain so . . . [W]e and science will calmly continue on our way between the mischief of those who play with constitutional formulas and the indolence of those who deny formulas, toward the shining star of a fundamental syntheses beckoning from afar.[57]

In this program both Wurtz and Kekulé were preceded, and surely influenced, by Alexander Williamson. In chapter 1 we traced Williamson's intellectual formation, which included both positivist Comtean elements and realist-mechanist ideas; we also suggested that there was not as much intrinsic conflict between these two tendencies as might be thought. Hence we find Williamson scorning unmeaning formula notations and rejecting any incautious (empirically unsupported) invocation of unseen causes, while at the same time passionately seeking microcosmic *verae causae* that can explain chemical phenomena—especially those "true causes" that are amenable to mental visualizations. Williamson was both clever and wise, and, as we have seen, he provided a productive chemical model for both method and epistemology to which others could and did aspire.

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[57] Kekulé to Meyer, 23 October 1860, in Anschütz, 1:205.

FOUR

A Barometer of the Science

The book under review here [*Lehrbuch der organischen Chemie,* vol. 1] distinguishes itself in its thematic intent from all other textbooks of organic chemistry. It is intended neither as an elementary primer nor as a detailed handbook. Rather, it is designed to give special consideration to the *speculative* part of the science . . . We can consider it as a kind of barometer of the science, from which we can read off its current height. FRIEDRICH BEILSTEIN[1]

Textbooks are normally intended to communicate accepted knowledge to students learning the discipline. However, writing a chemistry textbook in the middle years of the nineteenth century was challenging, for major parts of the science were both hotly contested and rapidly evolving. Consequently, the best chemistry textbooks of this time contained almost as many new ideas as were to be found in the journal literature of that day. Moreover, not only was the science a moving target; so, often, was the book itself. Nineteenth-century presses often published larger works gradually and piecemeal, in installments or fascicles, for binding was usually done by booksellers or customers anyway, rather than by publishers. Kekulé's *Lehrbuch der organischen Chemie* was published serially in six 240-page fascicles that were collected into two volumes, during the years from 1859 to 1866 while Kekulé was professor in Ghent, Belgium.[2] An examination of this

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[1] Beilstein, review of Kekulé (1863), 493–94.

[2] Kekulé, *Lehrbuch der organischen Chemie,* 2 vols. Volume 1 appeared in three fascicles, in June 1859, fall 1860, and September 1861; the volume 1 imprint was 1861, which has led many to misdate the publication of the earlier fascicles as 1861. Volume 2 also appeared in three fascicles, in 1863, 1864, and

textbook in the present chapter will carry us through many lively issues of that day, including how best to imagine the transformations of those invisible entities, atoms and molecules. It will allow us, as Beilstein expressed it, to read off the height of the science in those years.

But first we need to see Kekulé from Heidelberg to Ghent. In September 1858 the Belgian chemist Jean Servais Stas undertook a government-commissioned journey through Germany in order to fill the chemistry professorship at the Flemish (though thoroughly francophone) University of Ghent. He was initially inclined toward Limpricht, at Wöhler's urging, but Liebig and Bunsen persuaded him to look at Kekulé. Their first meeting went very well, and an offer ensued the following month, for not only had Limpricht made an uncomfortably high salary demand, but Stas also judged Kekulé's spoken French better than Limpricht's.[3]

Still, there were bumps in the road. The Belgian students, along with the press, exploded with indignation that the government had hired a foreigner—worse yet, a German. Kekulé arrived in Ghent on 8 November, after classes had already begun, never before having set foot in Belgium. He was afforded protection by undercover police for his first lecture, eight days later, against a deafening uproar by unhappy students. But Kekulé had prepared well in advance, and presented a well-structured lecture in perfectly acceptable French, accompanied by striking experiments. The students were won over, and Kekulé remained one of the most popular professors at the university until his departure for Bonn in 1867.[4]

"Young, energetic, poor, and ambitious," Anschütz wrote, " . . . fluent in French and English, famous as a reformer among the German chemists, no other of his contemporaries was so well suited to mediate scientific relations between his German colleagues and the French and English chemists."[5] Not to mention the Belgians. Kekulé was overjoyed at finally acquiring a permanent post, but his happiness was dampened by the primitive nature of the laboratory facilities and, despite Stas's confident judgment, by the challenge of lecturing in French. But within two or three months of his arrival he had set up laboratory facilities for

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1866; the volume 2 imprint was 1866. The work was continued, with coauthors, under an altered title: *Chemie der Benzolderivate oder der aromatischen Substanzen,* 3 vols. (1867, 1882, 1887); it was never fully completed.

[3] Gillis, "Kekulé te Gent" (1959), 11–43.

[4] Ibid. The story of Kekulé's first lecture derives from Anschütz (1:144), who had it orally from Kekulé.

[5] Anschütz, 1:133, 141.

himself and his research group (including Baeyer and Kündig, who had come with him, joined as well in fall 1859 by Williamson's assistant George Carey Foster), had begun attracting large audiences of now enthusiastic students, and had initiated a research program. By fall 1860 his laboratory also accommodated a capable Belgian assistant, Theodor Swarts, a second assistant, Eduard Linnemann, and the talented Hans Hübner, who later succeeded Wöhler at Göttingen.

Writing a Textbook

Shortly after arriving in Ghent Kekulé completed writing the first fascicle of his soon-famous textbook. The book had had a long gestation. When in November 1856 Williamson had written to Kekulé to tell him of his hopes to write a textbook for English chemistry students,[6] Kekulé expressed pleasure. "Our textbooks, particularly the smaller ones, are without exception bad, and most are very bad," he wrote; "[b]ut it is even more essential that chemistry, especially inorganic, be treated in an elementary textbook on a new plan, and free from the whole swindle of electrochemical-dualist addition."[7] What he did not tell Williamson was that he was already working on a new textbook of his own; he was developing the system of classification, expanding his theoretical ideas, and sketching the illustrations. A contract between Kekulé and his publisher, Ferdinand Enke of Erlangen, had been signed in July 1856, prescribing a schedule that would turn out to be wildly optimistic.[8] We know that Kekulé was already working on the book in the summer of 1856, and he appears to have been writing assiduously in the fall of 1857.[9] The first two proof sheets (32 printed pages) were printed before he left Heidelberg, and early in 1859 he finished writing the first fascicle (240 pages).[10]

A letter from Kekulé to Erlenmeyer of 29 January 1859 tells of his activities during that first semester in Ghent, including the writing of his book.

> You can see from this that I am working on my textbook again. . . . Once again I work regularly until 1 or 2 [a.m.]; just as I did in Heidelberg, I often work on

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[6] Williamson to Kekulé, 11 November 1856, AKS.

[7] Kekulé to Williamson, 23 November 1856, Anschütz, 1:69–70.

[8] Enke file, AKS. Enke wanted the entire book finished in two years.

[9] Roscoe to Kekulé, 21 November 1857, AKS: "I hope your book is getting on well. How soon will part 1 be out?"

[10] Anschütz, 1:64–65, 69–70, 150, 157.

> my textbook until 11:30 or 12 and only then start getting my lectures into proper shape. . . . I go to the laboratory at 9, and give lectures three times a week from 10 to 11:30. . . . At 12 a frugal bite to eat in the lab, at 4:30 dinner—the high point of the day and my only pleasure, other than cigars (real Havanas, I can afford them now!). Then a solid cup of coffee and at 6 or 6:30 back to my digs, occupied first with digestion and later with work. My lifestyle is simple. Diversions there are none, except for Sundays, when I eat at 1:00 and then take an obligatory constitutional walk. No more theater; concerts and balls are neglected; no beer; no social visits. If I don't succeed in becoming a "scholar" with this sort of lifestyle, it is not my fault; there's little enough left of a "man."[11]

In April and May, after the semester ended, Kekulé visited his friends in both Heidelberg and Paris, partly in company with Baeyer. He was with Wurtz for five days and afterwards raved about the experience to Erlenmeyer: "a great chap. It's not possible for two people to agree more in a general way about a science than we do."[12] It was on this occasion that Kekulé first told Wurtz his idea about organizing an international chemical conference in order that the community might talk over, and hopefully agree on, some burning issues in the science; Wurtz was enthusiastic. Kekulé, Wurtz, and Karl Weltzien proceeded to organize this epochal conference (with important assistance from Baeyer, Roscoe, and Williamson), and it took place over three days in September 1860 in the southwest German city of Karlsruhe.[13]

The first installment of Kekulé's textbook was published in June 1859. It contained a "General Section," consisting of introductory material and a brief history of organic-chemical theory over the last thirty years, and a "Theoretical Section," which was a significantly expanded and revised version of his two theoretical papers of 1857–58. In the foreword, dated 21 May 1859, Kekulé explained, in reference to what he called an "absolute revolution" in the theory of chemistry, that:

> a perspective [Anschauungsweise] has very recently arisen, principally under the hands of Williamson, Odling, Hofmann, and Wurtz, which embraces within itself the advantages of earlier theories which in their strict form had often appeared in conflict, and thus [this perspective] is the most general expression of our contemporary experience, while also providing an account of the causes of chemical phenomena that is better than any of the earlier theories. The present work intends

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[11] Kekulé to Erlenmeyer, 29 January 1859, in Anschütz, 1:150–51.

[12] Kekulé to Erlenmeyer, 16 June 1859, in Anschütz, 1:152.

[13] Bensaude-Vincent, "Karlsruhe" (1990); *NS,* 226–33.

> to take these views, currently scattered in the massive material of individual articles, and summarize them into a single clear system.[14]

One of the first colleagues to whom Kekulé sent a complimentary copy of the fascicle was Wurtz, accompanied by a cover letter declaring how important Wurtz's views had been to him. Beilstein, who had gone from Heidelberg to Paris to study and was present when the gift arrived, recalled many years later Wurtz's actual immediate reaction: "Wurtz cut the pages open, sniffed around a bit in it, then turned to me and said, 'Je crois que c'est un excellent ouvrage!'"[15]

The book had enormous influence, right from the start. Beilstein wrote an extremely positive review of the first volume, completed with the publication of the third fascicle in 1861. He particularly praised the thoroughness, accuracy, and rigor of the "general" section, as well as the clear and lively presentation and the "flowing" style; but he wondered whether it would be appropriate for beginners.[16] In his diary, the young organic chemist Rudolf Fittig (1835–1910) wrote of reading the first fascicle in September 1859. He was captivated, devouring the book page after page, hardly able to put it down. This is an unusually strong reaction to a science textbook. And the testimony is particularly powerful, for Fittig had not yet met Kekulé; he was a student of Wöhler and Limpricht at the University of Göttingen, had undoubtedly been taught from Limpricht's *Grundriss der organischen Chemie,* and if anything might well have had an initial presumption *against* Kekulé's book. Many chemists, old as well but especially the young, had an experience similar to Fittig's. "In a sense, we were all students of Kekulé," Fittig later averred.[17]

Formulas, Models, Reality

Writing a book is a different experience from writing articles for publication in scientific or scholarly journals. In comparing Kekulé's two theoretical papers of 1857–58 to the corresponding passages in the 1859 published fascicle of his *Lehrbuch* (114–230), one sees that much

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[14] *LB,* 1st fascicle (1859), v. Note the omission of Gerhardt's name here.

[15] Beilstein to Anschütz, 16 June 1906, in Anschütz, 1:154.

[16] Beilstein, review of Kekulé, 500.

[17] Fichter, "Fittig" (1911), 1361. The testimony of reading the book comes from Fittig's diary for 17 September 1859; the second quotation is from a speech he gave at the 1904 St. Louis World's Fair.

language from the papers was simply reused verbatim for the textbook, but there are interesting differences, as well.

At the end of his short history of organic-chemical theory, Kekulé described the rise of the "theory of polyatomic radicals" at the hands of Williamson, Odling, and Wurtz, then provided a stronger demur against Gerhardt than he had at the beginning of his 1857 paper. He wrote, "These views were since adopted by Gerhardt and used in the fourth volume of his *Traité;* to be sure at times not quite with Williamson's viewpoint, and not carried out fully consistently." He explained why it made much more scientific sense to adopt the larger values C = 12 and O = 16, employing Williamson's barred letters to indicate that these were atomic weights, rather than the so-called equivalents of C = 6 and O = 8. In fact, he argued that the choice between atomic weights and equivalents was not mere convention; properly speaking, equivalents are (or should be) purely *relative* quantities that depend on the particular reactions being studied. For chemical formulas, one must adopt unchanging atomic weights that are empirically justified, as he had done—following Williamson and Laurent.[18]

In a section entitled "Necessity and Significance of Rational Formulas," Kekulé stated that the use of different rational formulas is always possible for one and the same substance, simply because one may wish to use a particular formula to highlight one particular reaction of the compound, or to illustrate one particular manner (of several) in which the molecule may be decomposed. Does this circumstance mean that rational formulas are useless? By no means. For instance, there are three substances with strikingly different properties, all possessing the same *empirical* formula $C_3H_6O_2$: propionic acid, methyl acetate, and ethyl formate. If one refused to represent them with three different *rational* formulas, these facts would remain utterly mysterious. Kekulé asserted that of the various common ways of writing rational formulas, the "type" style, with its customary triangular array and curly bracket, is most useful; and of the various possible rational "type" formulas for a given compound, that which resolves the formula right down to the very atoms is the most revealing and the most complete.

However, there is often a disadvantage in showing *too much* detail, especially if that level of detail is unnecessary for the purpose at hand, for the excess and unnecessary detail will only obscure that particular purpose. Consequently, apart from special highly theoretical con-

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[18] *LB,* 1:94, 98–100, 111 (1859).

texts, it is almost always best (Kekulé wrote) to choose a less-resolved formula.[19] Two years later, in the third published fascicle of his book, he returned to the same theme.

> A comprehensive rational formula for a compound for which very numerous reactions are known must not only separately indicate each individual atom, it must also group the atoms such that the atoms which remain united in individual reactions are placed adjacent in the formula, and also such that the relative positions of the atoms in the formula give a precise accounting of the principal properties of the compound. . . . [However,] it is clear that . . . a completely comprehensive rational formula is not appropriate for ordinary use, even if one can be specified by the present state of the science. Rather, one of the rational formulas derived from a specific group of reactions must be chosen, since it will be more appropriate for the purpose at hand.[20]

This pragmatic point is partly what Kekulé meant when he repeated the language of his 1858 paper in the first fascicle of his textbook: “rational formulas are reaction formulas, and can be nothing more in the current state of the science.” There were, of course, methodological and epistemological dimensions to this statement, as well. As he had done the preceding year, in 1859 he rejected the possibility of determining the physical arrangement of the constituent atoms in a molecule from the study of chemical reactions, since chemical reactions necessarily alter the arrangements of the atoms of the molecule. But he added an additional explanation, not provided in the 1858 paper: “No special proof is required to show that this is impossible; it is intrinsically clear that we cannot represent the positions of the atoms in space by placing letters next to each other in the plane of the paper, even if those arrangements were discernible; we would rather require for this purpose a perspective drawing or a model.”[21] Two years later, in the third published fascicle of his textbook, Kekulé elaborated further:

> For complicated compounds, a completely comprehensive rational formula is probably not possible; first, because the atoms positioned spatially in the molecule cannot be grouped next to one another in the plane of the paper, such that the atoms which remain united in various reactions are placed adjacent to one another in a single formula; and second, because atoms which were not adjacent in the stable

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[19] Ibid., 1:152–57 (1859).

[20] Ibid., 1:521–24 (1861). And he repeated all this once more in a fascicle published in 1864: ibid., 2:243–51.

[21] Ibid., 1:157–58 (1859).

> molecule may come together and unite with each other during the course of the decomposition.[22]

Kekulé was not denying the determinability of constitutions, but he was asserting certain epistemological limitations. In his opinion, one was indeed justified in writing rational formulas specifying apparent groupings of atoms, as determined from chemical evidence; that in fact was his principal theoretical goal. What one could not hope to do was to determine actual stereospatial atomic arrangements—absolute formulas in a physical and ontological sense, given once for all time. Not only was this not justified from the purely *chemical* evidence at our disposal, given the possibility of rearrangements during the course of the reaction, but it also posed a representational or notational problem due to the quasi-architectural challenge of representing what must obviously be three-dimensional objects on two-dimensional paper. One might write molecular diagrams analogous to architectural elevations, plans, or perspective drawings, but any one of them could capture only part of the truth. And in no case was direct observation of the stable molecule ever possible. All was by inference alone, and often very *distant* inference.

The situation was in many ways analogous to the well-known South Asian fable of the blind men exploring the elephant. The "truth" of elephant-ness depends on what part of the elephant one happened to have observed: a snake (the trunk), a tree (the leg), a fan (the ear), a spear (the tusk), a wall (the side), or a rope (the tail). Kekulé and most of his colleagues were, I suggest, acutely aware of these epistemological problems, and we see considerable evidence of their efforts to grapple with them, often in careful and sophisticated ways. But the efforts to steer between the shoals sometimes produced muddy, inconsistent, occasionally even apparently contradictory dicta.

In the 1859 fascicle of his textbook, Kekulé then plunged into questions of the "Constitutions of Radicals" and the "Chemical Nature of Carbon and the Constitutions of Carbon-Containing Compounds." It is essential to understand Kekulé's language here. Molecules, he wrote, are composed of atoms that are juxtaposed in a contiguous fashion (aneinander gelagert). Polyatomic (mehrwerthig or mehratomig) atoms, such as diatomic (zweiatomig) oxygen or sulfur, triatomic (dreiatomig) nitrogen, or tetratomic (vieratomig) carbon, can create molecules by binding, connecting, uniting, or holding together (binden, sich verbin-

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[22] Ibid., 1:522–23 (1861).

den, vereinigen, zusammenhalten) other parts of the molecule. They do this using the property called atomicity (Atomigkeit) or chemical value (Werth), which is directly dependent on their power or magnitude of affinity (Verwandtschaftsgrösse). The measure of this is the number of chemical units or affinity units (chemische Einheiten or Verwandtschaftseinheiten) to which an atom is equal—that is, how many hydrogen atoms it can hold together. From about 1870 this phenomenon was called "valence."

In his imagination, it appears that Kekulé represented a monoatomic (monovalent) atom, such as hydrogen, by a tiny sphere. Putting two hydrogen-spheres together and covering them with a single hoodlike casing provides a graphic depiction of a diatomic (divalent) atom, such as oxygen. The spherical subatoms are inextricably bound together—hence the casing—but each still retains its original atom-binding power, represented by what Kekulé called an affinity unit or a chemical unit (what we call a valence unit); hence we have diatomic (divalent) oxygen. Three of the spheres covered by a casing provide a graphic representation of a nitrogen atom, and four represent carbon. I have suggested that all of this is derived from Wurtz's subatomic suggestions from 1855.[23]

In 1867 Kekulé became more explicit, stating that the appearance of his graphic formulas was intended to express the idea that "with respect to their chemical values, polyvalent [mehrwerthige] atoms can be viewed in a sense as a conglomeration of several monovalent atoms." He had arrived at this formula style, he said, after much trial and error, and thought that it was preferable to alternatives due to the range of combining relations that it was able to portray.[24] Apparently for simplicity and clarity, Kekulé depicted these forms in an exclusively horizontal *linear* fashion; this convention also has the advantage of not misleading readers into thinking that this was his notion regarding the actual physical appearance of these atoms. The formula convention thus depicts interatomic connections, what were later called valence bonds, exclusively in a *vertical* direction.

Here is how Kekulé publicly introduced (in a footnote) what soon began to be called his "sausage" (Wurst-)[25] atoms and formulas, which

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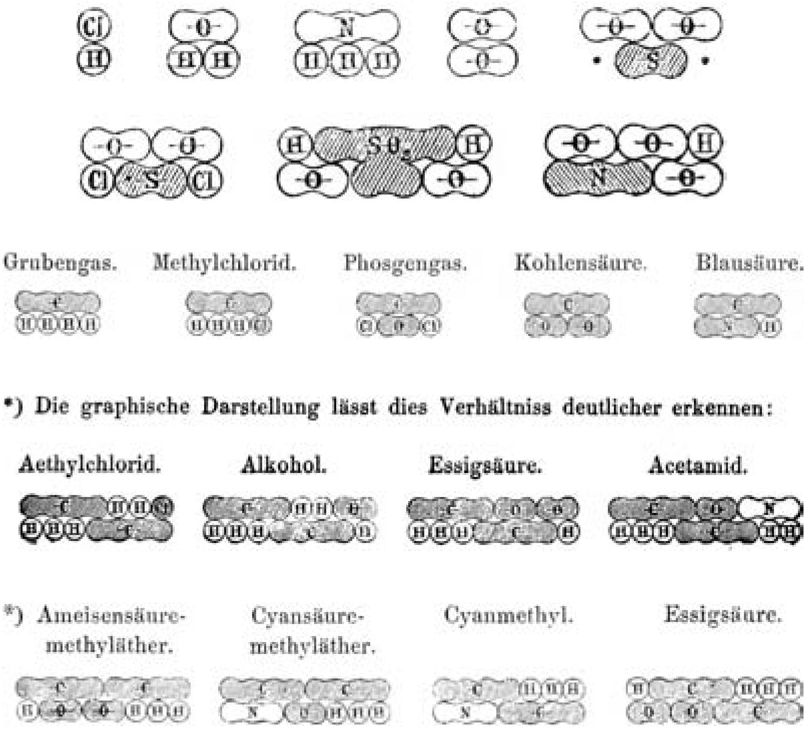
[23] See the last section of chapter 2, this volume; also Rocke, "Subatomic Speculations" (1983).

[24] Kekulé, "Constitution des Mesitylens," (1867), 217; Anschütz, 2:529–30.

[25] No one knows who coined this jocular term. It has long been thought that the first use of the term was in the "Durstige Chemische Gesellschaft" lampoon of 1886, but twenty years earlier Alexander Williamson referred to the "string of beads (or 'sausages' as they have been



4 First appearance of Kekulé's sausage formulas in print. Source: Kekulé, *Lehrbuch* (1859), 1:160n, 162n, 164n, 165n.

he had been using in his lectures at least since 1857, in both written or printed mode as well as in the form of wooden models: "One can illustrate these atomic arrangements by a graphic representation in which the basicities of the atoms are indicated by drawing them in different sizes [i.e., lengths]. This distinction in size is not intended to express a difference in the true size of the atoms, but merely signifies the number of chemical units which an atom possesses, hence the number of hydrogen atoms to which it is equivalent. The following examples are intelligible without further comment."[26] Depicted were simple compounds of oxygen, sulfur, and nitrogen. In the following five pages of his textbook three more footnotes further develop the theme: depict-

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humorously termed) of Kekulé"; see Williamson, presidential address (1866), 17. It may well have been Williamson's coinage.

[26] *LB,* 1:159–60n (1859).

ing one-carbon-atom compounds illustrating the tetratomic character of carbon; the *direct* bonding of carbon atoms to each other, by using one of the affinity units of each carbon atom; and the *indirect* bond of (e.g.) a hydrogen atom bound to an oxygen atom, which is itself bound to the carbon skeleton. In another footnote, Kekulé cautioned a second time "that the indicated sizes of the atoms are not intended to express the actual size relationships, but only the atoms' basicities [i.e., valences]; and that the position of the individual atoms should in no way be taken to be representative of their positions in space." Type formulas express ideas about chemical constitutions "to a certain degree," Kekulé suggested, but the graphic formulas express the same ideas "more clearly."[27]

In his book review, Beilstein praised the sausage formulas as having "excellent effectiveness," especially for understanding the constitutions of more complicated organic molecules, and he noted that the author had used these formulas "earlier, to show the arrangements of the atoms."[28] Beilstein was surely referring to Kekulé's courses, which he had attended. In Moritz Holzmann's lecture notes of Kekulé's two Heidelberg courses conducted between October 1857 and August 1858 there appear no fewer than 128 graphic formulas; we see from these notes that Kekulé drew many sausage formulas on the blackboard, such as methyl formate, propane, dimethyl amine, glycolic acid, and oxalic acid, which he chose not to reproduce in the 1859 publication.[29]

These are the only printed appearances of Kekulé's graphic formulas in this fascicle of his *Lehrbuch,* though he *mentioned* them once more, in a note on page 174. He used them just once in the second fascicle (444n, 1860), and just once in the third and final fascicle of the first volume of his *Lehrbuch* (523, 1861). In volume two (published in three fascicles in 1863, 1864, and 1866), he used them regularly, but only sparingly, and only twice, in journal articles published in 1865 and 1866, did he use them outside the pages of his textbook.[30]

He tried to be clear about all this. A well-investigated substance can

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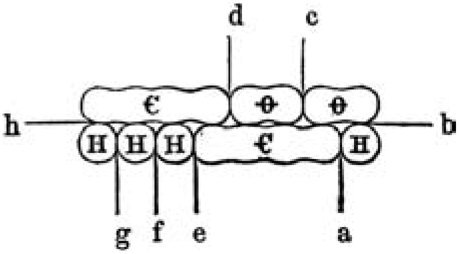
[27] Ibid., 1:162n (quoted), 164n, 165n. On chemical formulas and molecular models more generally, see Dagognet, *Écriture* (1973); Ramsay, "Molecules" (1974); Laszlo, *Parole des choses* (1993); Francoeur, "Forgotten Tool" (1997); Francoeur, "Molecular Models" (2001), 95–115; Klein, *Experiments, Models, Paper Tools* (2003); and Chadarevian and Hopwood, *Models* (2004).

[28] Beilstein, review of Kekulé, 498.

[29] Holzmann MS, part 1, 363, 378–84; part 2, 18, 44–49, 70–75, 80; in AKS.

[30] He *mentioned* them in *LB,* 2:2n, 7 (1863), 246, and 250 (1864); he *illustrated* them on 2:410–11 (1864), 498, 501–2, 510, 515, 672, and 744 (1866). He also used them in the initial publication of his benzene theory: Kekulé, "Substances aromatiques" (1865), and "Aromatische Verbindungen" (1866).



5 Sausage formula for acetic acid. Source: Kekulé, *Lehrbuch* (1861), 1:523.

obviously have but one constitution, unambiguously represented by a unique, fully resolved formula, such as his graphic formulas provide. However, it is equally obvious that a single graphic representation can be translated into type notation in different ways, using different formula styles. Moreover, as he had repeatedly emphasized, for most purposes one need not, and indeed should not, depict a molecule's constitution in its fullest resolution; one usually wants to emphasize this or that reaction of the compound by writing the formula in this or that fashion. This is why many different rational formulas for the same substance can be equally well justified, and why rational formulas are only reaction formulas. And this is the reason why, Kekulé concluded, he made only rare use of his own fully resolved graphic formulas, despite the fact that "*only* completely-resolved formulas—such as [my] frequently-mentioned graphic formulas—are able *fully* to express the views which we have offered concerning the mode of combination of the constituent atoms in the molecule."[31]

In his lectures in Ghent, Kekulé used the same molecular models[32] to illustrate his ideas as he had in Heidelberg. Made of painted wood—carbon was black, hydrogen white, oxygen red-orange, nitrogen blue, and chlorine green—these models had (and have) the appearance of the printed "sausage" formulas, the sausage atoms being connected to each other, one atomic bulge to the respective bulge on another atom, with small bent brass rods.[33] Some examples of these models are preserved in the Museum of the History of Science at the University of Ghent, along with much additional Kekulé memorabilia. Baeyer was

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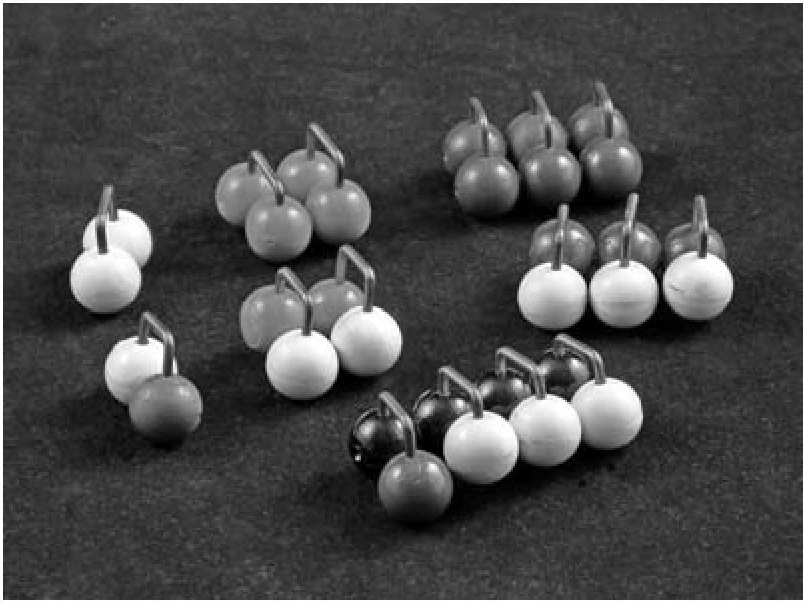
[31] *LB,* 2:243–51 (1864), quote from 250, with my emphasis added.

[32] Figure 6, clockwise from the top right: N_2, NH_3, CH_3Cl, H_2O, HCl, H_2, O_2. These are replicated models on the pattern of surviving Kekulé models, courtesy of Museum voor de Geschiedenis van de Wetenschappen, University of Ghent.

[33] Gillis, "Kekulé et son oeuvre" (1966), 21–23, 29; Gillis, "Molecuulmodellen" (1967), 175–80; Meinel, "Molecules" (2004), 259.



6 Inorganic sausage models. Source: Museum for the History of Sciences, University of Ghent.

using sausage formulas in his letters to Kekulé at least from 1861; he also adopted the corresponding wooden models and was using them in his lectures at the Berlin Gewerbeschule in 1865.[34] As we shall see, the fundamental idea behind Kekulé's graphic formulas—depicting atomicities by the length of the symbol for the respective atom—was subsequently adopted by many chemists in the 1860s.

Excursus: A Case in Point

Two of the most interesting substances under intensive scrutiny during the 1850s were lactic and glycolic acids, and as they exemplify many of the issues chemists were then facing, a brief examination will be helpful. To understand the nature of the lactic acid molecule from our current perspective, picture a tetravalent carbon atom to which is attached

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[34] Sausage formulas appear in Baeyer's letters to Kekulé dated 28 November 1861, 19 March 1865, and 26 April 1865 (AKS). Carl Graebe remembered the models from his student days with Baeyer, and praised their pedagogical utility: Graebe, *Geschichte* (1920), 236.

four different monovalent entities: a hydrogen atom, a methyl group, a hydroxyl (OH) group, and a carboxyl (CO_2H) group. Glycolic acid is the same, except with a second hydrogen atom in place of the methyl group. These molecules are what organic chemists call difunctional, which means that chemically they behave sometimes like an alcohol (due to the hydroxyl group) and sometimes like an organic acid (due to the carboxyl group). They also have interesting and complicated isomeric relationships. As a consequence of all this, the two compounds were difficult puzzles to crack, despite their relative simplicity.

It should be noted that most mid-nineteenth-century organic chemists defined "typical" atoms—or atoms "of the type"—as the separate atoms joined together by the bracket symbol when molecular constitutions were written in usual type-theoretical style. The most common cases were the replaceable hydrogen atoms, or hydroxyl groups, of water, of sulfuric acid, or of organic alcohols and acids. For instance, in acetic acid, the hydrogen atom that is replaced by sodium to form sodium acetate was regarded as belonging to the type, or as being a "typical" hydrogen atom, whereas the hydrogen atoms of the methyl group in acetic acid were thought to belong to the radical.

Adolf Strecker, then Privatdozent at Giessen, published the first synthesis of lactic acid from naturally occurring alanine in 1850 (at the very time he had a student in his organic chemistry lecture course named Kekulé), but its molecular constitution was still uncertain. In 1857 Wurtz suggested that the compound was dibasic, since two of its hydrogen atoms and two of its oxygen atoms could be substituted by chlorine.[35] Hermann Kolbe contested this viewpoint; he preferred to view lactic acid as monobasic, namely, as a substituted propionic acid. What emerged out of the ensuing public dialogue between Wurtz and Kolbe was the understanding that lactic acid did indeed have two replaceable hydrogen atoms, as Wurtz had originally claimed, but that they were not equally easily replaced. One hydrogen atom behaved more or less like the replaceable hydrogen of alcohol. The other behaved very much like the replaceable hydrogen of acetic or propionic acid. Wurtz summarized these facts by maintaining that lactic acid was "monobasic" but "diatomic."[36]

Glycolic acid posed many of these same issues. Kolbe once more emphasized the close relationship of monobasic acetic acid to the likewise

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[35] Strecker, "Bildung der Milchsäure" (1850); Wurtz, "Recherches sur l'acide lactique" (1857); and Wurtz, "Sur un nouvel acide lactique" (1857).

[36] Wurtz, "Recherches sur la constitution de l'acide lactique" (1859). See *QR,* 214–24.

monobasic glycolic acid. In response, Wurtz applied the same reasoning to glycolic as he had to lactic acid. In both cases there were two different kinds of "typical" hydrogen atoms, and two different kinds of "typical" hydroxyl groups—one of alcoholic and one of acidic character. It was unfortunate that the type formulas could not make any such notational distinction, for both kinds of hydrogens, and both kinds of hydroxyls, were customarily written in the same triangular bracketed form.

In his textbook, Kekulé discussed these questions in a section entitled "Influence of the Relative Positions of the Atoms." Type formulas did an excellent job, he wrote, of distinguishing between hydrogen atoms "of the radical" and hydrogen atoms "of the type," only the latter of which were normally replaceable by metals, bases, or other organic groups. But sometimes one encounters different kinds of "typical" hydrogen atoms, and type formulas are powerless to indicate these differences. For instance, each of the two "typical" hydrogen atoms of lactic or of glycolic acid exhibited distinct chemical properties: one behaved like the replaceable hydrogen of an alcohol, the other like the replaceable hydrogen of an acid. This difference was "clearly caused" by the fact that the first was located next to *one* oxygen atom, while the second lay next to *two* oxygens. This difference could be illustrated "particularly clearly" by his graphic (sausage) formulas, he thought—certainly more clearly than by type formulas, which made no symbolic distinction between the two chemically distinct environments.[37]

These issues continued to spark debate between Wurtz and Kolbe. Wurtz affirmed that lactic acid could equally well be represented by totally different type formulas, e.g., by one that illustrated its relationship to other alcohols, or by one that showed its family resemblance to organic acids.[38] Kolbe quickly responded, "I confess that I do not have so broad a chemical conscience. . . . [T]o assign a compound two different rational formulas . . . is to maintain an impossible proposition."[39] Wurtz replied: As to their consciences,

> Mine is less delicate concerning formulas. I envision them as expressing the mode of derivation, parental ties, and reactions of compounds, and in no way share the opinion of M. Kolbe, who endeavors to express the exact grouping of the atoms with the aid of his rational formulas. . . . [W]e do not have any means of assuring ourselves in an absolute manner of the arrangement, or even the real exis-

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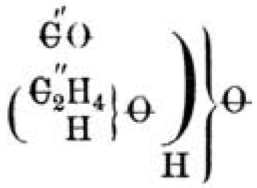
[37] *LB,* 1:174.

[38] Wurtz, "Nouvelles recherches" (1859).

[39] Kolbe, "Milchsäure" (1860), 225–26.



$$\left.\begin{matrix}\overset{\prime\prime}{\text{C}}\text{O} \\ \left(\left.\begin{matrix}\overset{\prime\prime}{\text{C}}_2\text{H}_4 \\ \text{H}\end{matrix}\right\}\text{O}\right) \\ \text{H}\end{matrix}\right\}\text{O}$$

7 Wislicenus's "type" formula for lactic acid. Source: Wislicenus, *Annalen* 128 (1863): 44.

> tence of the groups which appear in our rational formulas. . . . I merely express parental ties.[40]

With Wurtz, unlike with Kolbe, we see the same epistemic tension as we see in Kekulé. On the one side, there was a burning desire to imagine the molecular world, reaching out to it with chemical tools and methods, and striving for some degree of confidence in the pictures we make for ourselves that attempt to portray that world. Indeed, no one believed in the utility and reality of atoms and molecules more ardently than Wurtz. But on the other side there was reasonable caution and an epistemically sophisticated standpoint that acknowledged a degree of arbitrariness in notational preferences, as well as the potential pitfalls in proceeding from evidence drawn from the dynamic world of chemical reactions to static images of stable molecules. There may also have been a psychological element of professional caution, for it was never professionally healthy to be seen as too strongly oriented toward hypotheses. Laurent had shown the dangers of that route.

Many chemists adopted the views and approaches of Kekulé and Wurtz. The Zurich chemist Johannes Wislicenus provided an appropriate postscript to the exchange between Kolbe and Wurtz by summarizing the various proposed formulas for lactic acid, including his own, and then commenting:

> The radicals in them are identical, and the *mode* of mutual saturation between them is the same; they are only altered in their *sequential* order. . . . As long as chemical formulas are only pictures of one and the same body drawn from different sides, that is, drawn with these proximate components shown bound purely in a different *sequential order,* not in a different *mode* of combination, then even the strongest chemical conscience can make no objection against the writing of multiple formulas.[41]

[40] Wurtz, "Recherches sur l'acide lactique" (1860), 161–91 (on 182–83).

[41] Wislicenus, "Studien" (1863), 1, 44, 46.

Erlenmeyer and Molecular Theory

When early in 1856 Kekulé set up his improvised laboratory and lecture room in the "Academy of Sciences at Goos's Flour Shop," he invited Emil Erlenmeyer (1825–1909) to share the lecture room. Erlenmeyer also temporarily established a laboratory there, but two years later he set up a new lab in a ramshackle structure not far away, in the Karpfengasse. Erlenmeyer attended some of Kekulé's lecture courses, but he and the slightly younger Kekulé were more collegial friends than teacher and student; in fact, Erlenmeyer was probably Kekulé's closest friend during his Heidelberg years. In his first months in Ghent, Kekulé regularly mailed newly written portions of his textbook manuscript to Erlenmeyer for copyediting and trusted the latter's work so thoroughly that he asked that the edited manuscript then be sent directly to the publisher.[42] But Erlenmeyer's role as Kekulé's sounding board and editor would gradually shift over the decade in which Kekulé's textbook was written and published (1856–66). By the early 1860s Erlenmeyer became a not-always-friendly rival in the competitive trade in new ideas on the nature of chemical compounds. Both for his role as a silent collaborator on Kekulé's *Lehrbuch* and for his importance as an increasingly independent theoretician, in this and the next section we will examine Erlenmeyer's ideas and influence.

The son of a pastor, Erlenmeyer was a Ph.D. student of Liebig and Will in Giessen before qualifying as a pharmacist.[43] On a trip to London in 1854 he became acquainted with Kekulé. In 1855 Erlenmeyer abandoned pharmacy and moved to Heidelberg with the intent to habilitate, while earning a living as an industrial consultant for pharmaceuticals and artificial fertilizers. He finally habilitated at the beginning of May 1857. The subjects of his early courses at Heidelberg included chemical technology, stoichiometry, and analytical and inorganic chemistry, and he also conducted a practicum. After Kekulé left Heidelberg in the fall of 1858, Erlenmeyer's courses tended more toward the organic field, to which he exclusively devoted his efforts from 1861 on. Many of his students were Russian, for Tsar Alexander II had recently liberalized the empire's travel laws, and Erlenmeyer's teaching (and Heidelberg geographically) proved attractive to Russians.[44] In 1863 Erlenmeyer was promoted to ausserordentlicher professor. Then in 1868 he was called

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[42] Anschütz, 1:150–51.

[43] Conrad, "Erlenmeyer" (1910); Krätz, "Erlenmeyer" (1972).

[44] Krätz, "Turgenyew" (1987).

to a full professorship at the Technische Hochschule in Munich, where he remained until his retirement in 1883.

When Kekulé went to Ghent, Erlenmeyer took over the editorship of a journal that Kekulé had recently started in collaboration with two Heidelberg colleagues. The *Kritische Zeitschrift für Chemie, Physik, und Mathematik* was initially designed as a review organ intended "in some measure to stem the tide of the steadily increasing flood of claptrap [Schmier-literatur]," as Kekulé put it in a letter to Liebig.[45] After Kekulé's departure, the journal was retitled *Kritische Zeitschrift für Chemie und die verwandten Wissenschaften und Disciplinen*. Erlenmeyer edited the third volume alone, the title now having changed once again, to *Zeitschrift für Chemie und Pharmacie*. In the preface to volume 3, dated December 1859, Erlenmeyer stated that the journal would henceforth appear on a prompt biweekly schedule, that he would now accept original papers, that such a fast-publication outlet was all the more necessary considering the "ferment in our views" in recent days, and that he would henceforth only use atomic-weight formulas in preference to equivalent weights. Privately, he promised colleagues that he would publish their work more quickly than was usual for the *Annalen,* his chief competitor, which had become irritatingly dilatory at a time when prompt publication was becoming ever more urgent.[46]

In Erlenmeyer's hands, volumes 4 through 7 (1861–64) became the major forum for theoretical chemical discussions in Germany. Erlenmeyer used the *Zeitschrift für Chemie,* as many other journal editors did in the nineteenth century, as a convenient organ for his own speculative, critical, and sometimes caustic essays, and his incautious language cost him many friends—including Kekulé for several years. After Erlenmeyer stepped down as editor, Beilstein complained to Butlerov, "His occasional good thoughts were simply drowned by the large amount of sauce that he poured over everything. I finally just stopped reading his long essays."[47] In fact, Erlenmeyer's sharp pen nearly drove the journal out of business; when he gave up the editorship at the end of 1864, there were only 150 subscribers (more than half of whom were Russian), and complete runs of the *Zeitschrift* are difficult to find today.

At first Erlenmeyer's ideas had a strong Kekuléan cast, but they developed in unique ways. His first theoretical article, an essay on "a somewhat altered way of considering alcohols and their derivatives," appeared

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[45] Kekulé to Liebig, n.d. [1858], in Anschütz, 1:130.

[46] Kolbe to Erlenmeyer, 19 February 1860, HDN.

[47] Beilstein to Butlerov, 24 November 1866, in Bykov and Bekassova, "Beiträge" (1966), 280.

in his journal early in 1861. He asserted that chemists had now come to understand that one cannot determine the absolute constitutions of molecules, only multiple expressions of the various ways they split apart [Spaltbarkeiten]; the more different ways we have to express this, and the more flexible they are, the better. This, he wrote, is a real advantage of type formulas, which are capable of the greatest flexibility.[48] Much more was soon to come. Early the next year he wrote, "one must require of every science the possession of a theory which should be under unremitting development. It is not possible to study a *science* without clear insight into its theory."[49] He would aggressively follow his own advice. It would not be easy thereafter accurately to track, or even simply to characterize, Erlenmeyer's mercurial trajectory.

Constant or Variable Atomicity?

One of the most contentious points that Erlenmeyer and Kekulé disputed was whether a given element's atomicity (valence) was necessarily constant, or whether it could vary. The issue was unintentionally brought to a head by George Carey Foster (1835–1919), an assistant to Williamson, and then an early and enthusiastic disciple of Kekulé. Foster was foreign correspondent for both Erlenmeyer's *Zeitschrift* and Wurtz's *Répertoire de chimie pure*.[50] In September 1859, he presented a "Preliminary Report on the Recent Progress and Present State of Organic Chemistry" to the British Association meeting in Aberdeen. The report is a skillful recapitulation of the new ideas of the past nine years, developments fathered by Williamson, Odling, Wurtz, and especially Kekulé.[51] A month after this meeting, on Williamson's recommendation he traveled to Ghent to join Kekulé's research group. He stayed with Kekulé for two years, then worked briefly with Wurtz before returning to London in 1861.

Soon after his return to London, Foster reported favorably for the *Répertoire* on Peter Griess's research on diazo compounds at the Royal College of Chemistry, but he took issue with Griess's assumption that the atomicity of nitrogen could vary. "The idea of atomicity, or capacity of combination," he wrote, "is a property of elementary atoms just

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[48] Erlenmeyer, "Vorläufige Notiz" (1861).

[49] Erlenmeyer, "Theorie" (1862), 31.

[50] See the obituary in *Journal of the Chemical Society* 115 (1919): 413–27. Foster became professor of physics at University College.

[51] Foster, "Report" (1859).

as fixed and unalterable as their weight, and appears to us to be the one idea which, in the present state of the science, can serve as the basis for a general theory of chemical combinations." Writing later that year in the same journal, Wurtz disagreed with Foster, asserting that although atomicity "tends to a maximum," it can vary.[52] Early in 1862 Erlenmeyer commented on this subject. Two assumptions in addition to those of Dalton, he wrote, are necessary to explain the laws of chemical combination: "that each atom contains at the same time an unchanging number of affinities (G. C. Foster); and that not only the affinities of dissimilar atoms, but also those of atoms of the same element may enter into combination with each other (Kekulé)."[53]

Kekulé had never publicly asserted the constancy of an atom's atomicity in the explicit manner that Foster had done, but in fact the constancy of atomicity had always been fundamental for him. Throughout his textbook Kekulé avoided any suggestion that (e.g.) carbon could be diatomic, or nitrogen pentatomic. He was thus quite at a loss to explain the constitution of carbon monoxide, and his depiction of ammonium chloride required the auxiliary hypothesis of "molecular compounds" (two molecules held together by an unspecified attraction weaker than that of true chemical combination).[54] So Foster must have been a little embarrassed to see the doctrine of constant atomicity ascribed to him when he had obviously imbibed it from his German mentor. He wrote Kekulé, "What do you think of Erlenmeyer's [paper]? I think it is the best statement I have seen of the essential questions at issue between the old and new schools. It was very insane of him, all the same, to mention my name in it."[55]

But Erlenmeyer was not a supporter of constant atomicity. He cited the example of carbon monoxide, in which only two affinities of the carbon atom are engaged, and pointed out that the other affinities of that carbon atom are only capable of combining with those of certain kinds of atoms—chlorine or oxygen, for example, but not hydrogen. Hence, "From all that we know about the matter, the individual affinities of polyatomic [mehraffiner] bodies appear to play highly specific roles with respect to the quality of the elements, and it appears to be by no means indifferent to one and the same element whether it combines with this or that affinity of a polyatomic atom."[56]

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[52] *Répertoire de chimie pure* 3 (1861): 273n (Foster) and 419–20 (Wurtz).

[53] Erlenmeyer, "Theorie," 27.

[54] *LB,* 1:162n, 444n.

[55] Foster to Kekulé, 12 February 1862, in Anschütz, 1:218.

[56] Erlenmeyer, "Theorie," 31.

Erlenmeyer clarified this obscure statement the following year in a long theoretical paper. He defined a "limiting equivalent" (Grenzäquivalent) as the atomic weight of an element divided by its atomicity (e.g., H = 1, C = 3, N = 4.7, O = 8, and so on). In the case of carbon, for example, four of these limiting equivalents are indivisibly bound into a single complex (Äquivalentencomplex) that constitutes the chemically active tetratomic atom. When n equivalents are bound into an n-atomic atom (such as four carbon equivalents weighing 3 each, into a tetratomic atom of carbon of weight 12), each equivalent still retains its power of chemically bonding to an equivalent of another atom. All this explains the phenomenon of polyatomicity (Atomigkeit, valence).[57] This is clearly a verbal version of the subatomic speculation begun by Wurtz and pursued in various ways by Kekulé. Erlenmeyer's "limiting equivalents" are Wurtz's subatoms, or Kekulé's sausage-bulges.

Erlenmeyer returned to the same subject early in 1864. "We can imagine," he wrote, that the four equivalents of a single carbon atom (e.g., in methane, which he now depicted as four vertically arrayed CH groups gathered by a large bracket) have affinity units of intrinsically varying attractive power. Perhaps the reason "methyl" gas and "ethyl hydride" gas, both possessing the identical empirical formula C_2H_6, are distinct (as chemists then believed that they were) may be because their two carbon atoms are connected by different sorts of affinity units in the two cases.[58] (This idea had been broached by Butlerov as early as 1861.)

In yet another paper that he inserted into his journal a few months later, Erlenmeyer suggested that this hypothesis offered a way to understand other aspects of chemical behavior connected with valence and structure. He wrote: "I believe that every elementary atom possesses a constant number of points of attack for chemical affinity (i.e., affinity units), all of the same weight, of which each is capable of *directly* attracting exactly the same weight—no more and no less—of other substances." But the intensity of attraction of these equal-weight affinity units for other elements might vary. Thus a single sulfur atom consisting of a complex of six affinity units might attract six affinities (i.e., three atoms) of oxygen to form SO_3, but only four affinities of chlorine to form SCl_4, or two of hydrogen to form H_2S. By the same token, if one assumed that carbon affinities had different intrinsic degrees of attrac-

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[57] Erlenmeyer, "Betrachtungen" (1863), 66–73, 103.

[58] Erlenmeyer, "Hypothesen" (1864), 6–10.

tive power, one might be able to explain certain cases of isomerism that had not yet been understood.[59]

In France, the same idea was taken up in February 1864 by Alfred Naquet, a former student of Wurtz and a future republican senator, who offered a "rough hypothesis" (hypothèse grossière) to help readers conceive what was meant:

> If one imagines for example certain hook-shaped appendages fixed to the atoms, which can serve for hooking onto the corresponding appendages of other atoms, thus resulting in the formation of a compound, it is clear that the number of hooks possessed by a single atom would represent its absolute atomicity. Now if these hooks are not able to bond equally well with the appendages of other bodies, it is conceivable that the effective or relative atomicity of a radical could sometimes remain below its absolute or true atomicity.[60]

This is a particularly striking example of a mental visual image at the heart of a chemical theory.

Kekulé then entered the discussion, responding to Naquet in the *Comptes rendus* of the Académie des Sciences, and wishing to strongly affirm the *constancy* of atomicity. He proclaimed, "The equivalent can vary, but not the atomicity." To maintain his stance he defended the concept of molecular compounds for substances such as ammonium chloride, and he cited the phenomena of dissociation and water of crystallization as evidence that this suggestion was not foolishly ad hoc. He was also intent to show that if one were to accept the variability of valence, one would enter a slippery slope toward theoretical chaos—for then how could one *limit* the possible variability? Erlenmeyer reprinted Kekulé's paper, equipping it with his own parenthetic editorial exclamation points, question marks, and sarcastic footnotes. It severely strained the relationship of the two former friends.[61]

In rebuttal, Naquet questioned the worth of the idea of molecular compounds, preferring to subsume dissociation under the broader rubric of thermal instability. Wurtz also entered the debate. He did not deny that molecular compounds may exist, for water of hydration is an example of this, but he doubted that ammonium chloride, phosphorus pentachloride, or iodine trichloride had constitutions such as Kekulé had proposed. The only reasonable possibility for the varying atom-

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[59] Erlenmeyer, "Sättigungscapacität" (1864).

[60] Naquet, "Atomicité de l'oxigène" (1864).

[61] Kekulé, "Atomicité" (1864); reprinted with editorial notes in *Zeitschrift für Chemie* 7 (1864): 689–94.

icities of organic radicals was that of the varying atomicity of carbon. For instance, in the bromination of allyl alcohol a monoatomic radical becomes triatomic; Wurtz believed that this was because a diatomic carbon atom becomes tetratomic.[62]

I conjecture that one reason Kekulé was so attached to the idea of constant atomicity is because it seemed to be implied by the use of his graphic formulas. Namely, since in his formulas the length of an atom is a direct measure of its atomicity, sausage atoms of constant length suggest constant atomicity (and if this speculation is correct, it is another illustration of the heuristic importance of visual mental images). Carbon monoxide was an obvious problem for this view, but it was an isolated case. One could also see ethylene (C_2H_4) and other unsaturated carbon compounds as another problem for the constant valence of carbon, and some theorists did construct ethylene formulas from two *tri*atomic carbon atoms, or one tetratomic and one diatomic carbon.

For some years Kekulé avoided committing himself on the question of the structure of ethylene (and of the structure of all olefins, of which ethylene is the simplest instance). In 1858 he drew attention to the issue, but only vaguely referred to the need, in the case of such "carbon-rich hydrocarbons," to assume "a denser arrangement of carbons," or the "next-simplest" bonding pattern. In 1859 he graphically depicted double bonds between carbon and oxygen or carbon and nitrogen atoms, but avoided the subject of unsaturated carbon compounds. (He was not so reserved in his lectures; in early 1858 he wrote a sausage formula on the blackboard depicting two olefinic carbon atoms that were positioned so that two bulges of each atom were aligned—a sausage double bond.)[63] In 1862, as we will see in the next chapter, he suggested that certain unsaturated acids had carbon skeletons that were "in a sense shoved together," a clear implication, considering the character of his sausage formulas, of carbon-carbon double bonds. But we will see that at the same time he suggested that these unsaturated structures might also possibly have "gaps" in them, namely, carbons with two unsatisfied affinities. Kekulé apparently made a distinction between a tetratomic carbon atom with two unsatisfied affinity units, which was allowable in his view, and a *di*atomic carbon atom, which was not. Again, this was perhaps a consequence of the circumstance that he was thinking in terms of imagined sausage atoms, which have constant lengths.

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62. Naquet, "Atomicité des éléments" (1864), 675–78; Wurtz, "Atomicité" (1864).

63. Holzmann MS lecture notes, part 1, 381, AKS.

By contrast, Wurtz had no compunction about depicting diatomic carbon atoms using his own graphic formulas that he introduced in 1863. He explicitly stated that these formulas were modeled directly on Kekulé's sausage formulas, but they utilized square boxes instead of round bulges, hence were presumably easier on typesetters. Wurtz discussed several times during the 1860s the subatomic speculation on which both graphic systems were founded. These little particles, corresponding to Erlenmeyer's "limiting equivalents," he referred to as "petits atomes," "sous-atomes" or "atomes primordials."[64] In addition to Wurtz, Kekulé, and Erlenmeyer, Charles Delavaud, Alfred Naquet, and Christian Blomstrand also used Wurtz's subatomic speculation during the 1860s.[65] But everyone abandoned it around 1870, undoubtedly partly because of its speculative character, but perhaps also because it was difficult on that basis plausibly to account for variable valence, which had begun to look ever more probable.

Some advocates of the new theory of atomicity of the elements, such as Erlenmeyer and Butlerov, were troubled by certain passages in the fascicles of Kekulé's *Lehrbuch* published in 1863 and 1864, especially those places where Kekulé suggested the existence of molecular compounds, or where he occasionally seemed to suggest two distinctly different structures for the same compound. The first of these gambits, as we have seen, was an auxiliary hypothesis that Kekulé had adopted to salvage the constancy of atomicity. The second issue appears to be a more serious violation of the tenets of structure theory, but it is not necessary to conclude that Kekulé had suddenly reverted to Gerhardtian structural skepticism, after vigorously remonstrating against it for years. Rather, these instances would seem to be the result of the operation of Kekulé's habitual caution (implying that there was too little evidence yet to justify confidence in either structural assignment), and his equally habitual caginess. For when Erlenmeyer complained of obscure passages in the textbook, Kekulé responded that the obscurity was quite deliberate, for "I wanted to preserve for myself the priority for a future idea to be developed later in more detail."[66] If one omitted all reference to an idea, one might be scooped; but one also wanted not to commit oneself or be too explicit before one could provide convincing evidence. Keeping such references vague or ambiguous, or on occa-

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[64] Wurtz, *Répertoire de chimie pure* 3 (1861): 419; Wurtz, *Leçons* (1864), 114–15; Wurtz, *Cours* (1864), 56, 74–76; Wurtz, "Histoire" (1868), 1:lxx; Wurtz, *Théorie atomique* (1879), 148–49.

[65] Rocke, "Subatomic Speculations."

[66] "Ich wollte mir für eine später ausführlicher zu entwickelnde Zukunftsidee die Priorität wahren" (Kekulé to Erlenmeyer, 13 June 1860, AKS).

sion providing two hypotheses for the same molecular structure, might preserve as much priority as possible, while also buying time.

We have seen similar wariness before: in Kekulé's piecemeal and hedged publication of structure theory; in his obscure references to "a denser arrangement of carbons," or the "next-simplest" bonding pattern in olefins and aromatic compounds; in his failure immediately to make explicit his definition of "atoms of the radical" and "atoms of the type"; in his reticence to actually use his graphic formulas in print or even to clearly explain what the bulges were intended to mean; and in his apparent simultaneous advocacy of two incompatible ideas that could explain unsaturation. We will see these habits come into play in the future, as well, for example in the publication of his benzene theory.

Kekulé behaved this way out of perceived self-interest, but we will see in the next chapter that his actions created enough obscurity to allow others to claim significant parts of what Kekulé retrospectively thought he himself had already accomplished. What we are really seeing in these years, and what is illuminated by these disputes, is an entire community slowly moving in the same direction, with several leading theorists developing similar ideas roughly simultaneously, but not always very self-aware and not always proceeding with full understanding of others. What we have followed here, and will continue to follow in the next chapter, is a generation of chemists learning scientifically to "see" the molecular world.

FIVE

The Heuristics of Molecular Representation

The atomic conception . . . made its way more slowly, for the fear of metaphysics still governed many acute minds. . . . Too much learning is sometimes in the way, and clogs the flight of that imagination by which the greatest discoveries are made. F. W. CLARKE[1]

As we have seen, Kekulé's ideas in the years from 1854 to 1859 emerged out of a rich context of data and hypotheses concerning the intimate constitutions of molecules, a context that had been in gradual development by many hands and minds since the earliest days of Dalton's atomic theory. We have seen Kekulé making certain claims for originality while also acknowledging deep debts to many of these workers. Still others entered the field simultaneously with Kekulé or soon thereafter, and it is revealing to study the sorts of molecular representations developed by these younger rivals.

This complex case study of relatively simultaneous discovery has a substantive connection to the theme of images and imagination, for one purpose of this book is to investigate how so many people could concurrently have been following similar paths, exploring imaginative routes to the microworld in ways that could be justified by experiment. Indeed, matters of priority became contentious partly because the imagined molecular world necessarily had both *speculative* and *private* character. Moreover,

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[1] Clarke, "Atomic Theory" (1903), 8–9.

by 1858 the context had been drawn so carefully, and the evidentiary and psychological prerequisites supplied so completely, that even relative tyros, if they were sufficiently perceptive, bold, and creative, found themselves in a position to be able to take the final conceptual steps into the interior of molecules. As F. W. Clarke suggested in the epigraph quotation above (referring to John Dalton), perhaps less "learning," less professionalized indoctrination or inhibition, may have even aided the free play of imagination in certain minds.

But to appreciate these matters fully it is necessary to pursue an explicitly personal—that is, biographical—approach. The four scientists considered in this chapter—two Scotsmen, an Austrian, and a Russian—were all novices, outsiders, or both. The first was a star-crossed chemist who never held a professional position.

Couper

The only surviving son of a wealthy textile mill owner, Archibald Scott Couper was born near Glasgow in 1831.[2] Between 1851 and 1854 Couper studied philosophy as well as classical and modern languages at the universities of Glasgow and Edinburgh, as well as intermittently in Germany. In Edinburgh he attended the lectures of William Hamilton on logic and metaphysics. Hamilton, who had traveled and studied in Germany, was concerned to introduce contemporary Continental philosophy into Great Britain, and he was at pains to reconcile Immanuel Kant's ideas with Scottish Common-Sense philosophy, of which he regarded himself as the culmination. Couper may have been inspired to travel and study in Germany by Hamilton's example or advice.

In chapter 1 we noted the probable influence of the Common-Sense school on Couper's fellow Scots/English chemists Williamson and Graham. In reference to the 1826–27 atomistic formulas of the Glaswegian chemist Thomas Clark, W. V. Farrar has seen "a climate of thought in Scotland favourable to naïve structuralism," and argued for a culmination of this trend in the formulas of Couper and Alexander Crum Brown.[3] More broadly, Richard Olson has explored the influence of Scottish Common-Sense philosophy on British physics. This philosophical school arose in Thomas Reid's opposition to the skeptical writings

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[2] Anschütz, "Couper" (1909); Dobbin, "Couper Quest" (1934); Jacques, "Boutlerov, Couper" (1953); and O. T. Benfey's biographies in the *DSB* and *Dictionary of Nineteenth-Century British Scientists*.

[3] Farrar, "Dalton" (1968), 295.

of David Hume; adherents emphasized a more pragmatic, empirical, and nonhypothetical epistemological approach that above all sought *simplicity* and *derivation from first principles* in explanations of phenomena. As the school developed at the hands of Dugald Stewart and William Hamilton, an increasing role for the productive use of hypotheses was allowed, and there developed an affinity toward analogies, models, and visual explanatory elements. Olson argued effectively for the influence of these ideas on Scottish science in general and increasingly, over the course of the nineteenth century, on British science. Among those most strongly influenced Olson counted John James Waterston, John Herschel, and James Clerk Maxwell. It was no coincidence, Olson remarked, that it was the Scottish-trained Thomas Thomson and William Henry who were two of the earliest and most ardent supporters of the atomic hypotheses of John Dalton.[4]

In the fall of 1854 Couper returned to Berlin to begin studying chemistry—why chemistry, we do not know. In August 1856 he moved to Paris and obtained a place in Wurtz's private laboratory at the Faculté de Médecine, where he remained for two years. Couper thus was with Wurtz during perhaps the most important stage of the latter's career, joining an international polyglot community and experiencing the intellectual excitement of this period. Wurtz had just published his studies on the "mixed radicals," on glycerin, and on glycol, and was beginning to turn out papers on polyfunctional organic compounds in rapid succession. This was also the time when the theory of atomicity of elements was being developed, and ideas from many sides were being floated regarding the constitutions of types and radicals.

Still a neophyte, Couper was to achieve the astonishing accomplishment in Paris of proposing the two pillars of structure theory, the tetravalence and the self-linking ability of carbon atoms. Couper's formulation of structure theory was certainly independent of Kekulé's, but it takes nothing from Couper's brilliance to consider the context out of which this discovery emerged. To the extent that Wurtz's work helped to prompt Kekulé's bright ideas about molecular structures, as I have suggested, then Couper may well have had similar stimulation. Moreover, in Paris there were many connections to Heidelberg, not just through Wurtz but also through several of his students. Fellow students or postdocs with Couper in Paris included the Austrian Adolf Lieben, the Italian Agostino Frapolli, and the Russians Aleksandr But-

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[4] Olson, *Scottish Philosophy and British Physics* (1975).

lerov and Leon Shishkov, all four of whom had recently been consorting with Kekulé in Heidelberg. Couper also overlapped with Beilstein, who arrived in Paris (likewise from Heidelberg) in April 1857. Moreover, by early 1858, when Couper first wrote down his theory, he had had the benefit of pondering Kekulé's two published fulminate papers of 1856–57 and his first theoretical paper of late 1857, in which Kekulé had stated the idea that carbon was "tetratomic."

Not counting translations and alternate versions, Couper published three papers over the course of about a year (August 1857 to August 1858), and nothing else ever thereafter. The first of these was on the bromination of benzene, a project presumably suggested to him by Wurtz. The next was on the chlorination of salicylic acid. And his last paper was "On a New Chemical Theory," published in a condensed form in the *Comptes rendus* of the Académie des Sciences on 14 June 1858, and then in a considerably more detailed form in both French and English, in the respective August 1858 issues of the *Annales de chimie* and the *Philosophical Magazine*.[5] His new chemical theory announced both the tetravalence and self-linking of carbon atoms, the second statement appearing, as he thought, for the first time. Unfortunately, Kekulé's "theory of atomicity of the elements" paper defending the same proposal had already appeared in print, in May 1858.

The most unhappy aspect of the matter is that earlier that spring (probably in March or April) Couper had asked Wurtz to present this paper to the Académie, but Wurtz was not yet a member of the Académie and so had to request the favor of a colleague. Eventually it was Dumas who presented Couper's paper, but too late to procure priority for the thesis of carbon self-linking. Couper was distraught at the disappointment, and he angrily confronted Wurtz. Wurtz then asked him to leave the laboratory.[6] Couper returned to Scotland, having been offered the position of second assistant to Lyon Playfair at the University of Edinburgh, to start 2 January 1859. Unfortunately, on 15 May 1859 he suffered a breakdown and entered a mental institution as a private patient. Released on 14 July, he almost immediately suffered a relapse (due to sunstroke, it was said), and sought further treatment until No-

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[5] Couper, "Benzine," (1857); "Acide salicylique" (1858); "Nouvelle théorie," *Comptes rendus* 46 (1858); "Nouvelle théorie," *Annales* [3] 53 (1858); "New Chemical Theory," *Philosophical Magazine* [4] 16 (1858).

[6] The story was told years later, in letters to Anschütz, by Adolf Lieben, who was there at the time, and by Albert Ladenburg, who had the story directly from Wurtz (Anschütz, "Couper," 200–201). Lieben also mentioned that Couper had privately shown him the manuscript of the paper for comment, even before he had given it to Wurtz for publication. Lieben could therefore verify Couper's independence from Kekulé at first hand.

vember 1862.[7] He was not able to engage in any serious work thereafter, becoming an invalid and finally dying in 1892.

There are many curious aspects to Couper's "New Chemical Theory," not least of which are its abstract philosophical approach and its acerbic tone.[8] The first part of the paper is a fierce polemic against Gerhardt. Couper proclaimed that Gerhardt's type theory was "based on an old but vicious principle, which has already retarded science for centuries," namely that of referring any number of particular instances to a single broad generalization. In the system of Gerhardt, he explained, all chemical compounds are derived, by means of appropriate substitutions ad infinitum, from the one multiple type of nOH_2 (a nonexistent substance, he noted parenthetically). This principle is "fundamentally false," "essentially pernicious," and "simply absurd," as can be seen by applying a linguistic simile. It is like "saying that [Gerhardt] had discovered a *certain word which would serve as a type, and from which by substitution and double decomposition all the others are to be derived,"* including all books in the world. This is an absurdity. "But a principle which common sense brands with absurdity, is philosophically false and a scientific blunder."[9]

The goal of science, Couper wrote, is not to arrive at generalizations (laws), but to propose *theories* that are both empirically adequate and "philosophically true," especially in explaining "the greatest number of facts in the simplest possible manner." Here we can discern the probable influence on Couper of Common-Sense principles, as well as the philosophy expressed in John Herschel's influential 1830 volume, *Preliminary Discourse on the Study of Natural Philosophy.* "The sure and invincible method of arriving at every truth which the mind is capable of discovering," Couper wrote, "is always one and the same. It is that, namely, of throwing away all generalization, of going back to first principles, and of letting the mind be guided by these alone."[10] Gerhardt had denied the very possibility of determining the constitutions of the

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[7] These details come from Dobbin, "Couper Quest." Since Alexander Crum Brown was at Edinburgh University at this time and yet never met Couper, it is likely that Couper never actually reported for work in January 1859; all we know for certain is that he was offered the position, not that he accepted it or fulfilled any duties.

[8] All subsequent quotations are from Couper, "New Chemical Theory" (1858), being both the extended version of the paper, and written in Couper's native language. The French version has one additional formula and a few minor variations of notational style. Whereas the English version uses dotted lines to connect many of the letters signifying the atoms in the formulas, the French version uses many dashes, as well as brackets in the type-theoretical style.

[9] Couper, "New Chemical Theory," 105–6.

[10] Ibid., 104–7.

molecules of substances—a dictum that, for Couper, was equivalent to renouncing chemical research altogether. Couper mentioned Williamson only once in this paper, attributing to him the very same errors that Gerhardt had committed. And if the type theory is false and pernicious, Couper opined, the radical theory is no better. It is "unprofitable" and "injurious to science," since it puts the seal of elementarity on entities that are clearly not that. "Is this explication arbitrary? Is it instructive? Is it science?"[11] No other contemporary is mentioned anywhere in the paper.

Couper's Common-Sense suggestion for a "more rational theory of chemical combination" was to start with first principles. It therefore becomes necessary to go all the way back to the atoms that compose molecules. Affirming that one would be "perhaps not unwarranted to adopt" the view that "the elements are themselves composite bodies," he then proposed to focus on carbon, which, he declared, possesses two important properties: "1. It combines with equal numbers of hydrogen, chlorine, oxygen, sulphur, etc. 2. It enters into chemical union with itself. These two properties, in my opinion, explain all that is characteristic of organic chemistry." The first claimed property is puzzling. Couper could only have meant that carbon combines with equal numbers *of equivalents* of hydrogen, etc. Since Couper had expressed a preference for the view that atoms are perhaps "composites," that is, compounded of even smaller particles, one wonders whether this verbal slip suggests that he was here making oblique reference to Wurtz's subatomic speculation of 1855. Other aspects of the paper reinforce this suspicion.[12]

Having outlined a justification for the proposals of carbon tetravalence and self-linking, Couper demonstrated the power of his new theory with more elaborate and explicit exemplification than Kekulé had done. He provided fully resolved formulas for ethane, for four different alcohols and four organic acids, and for more complex substances such as glycol, glycerin, tartaric acid, and glucose. In many of these formulas there appear, for the first time, dotted lines to symbolize connections between atoms.

There are other intriguing aspects to Couper's paper. In contrast to Kekulé, he averred that the affinity of carbon could be exerted in two degrees, for instance to form the compounds CO and CO_2. In propos-

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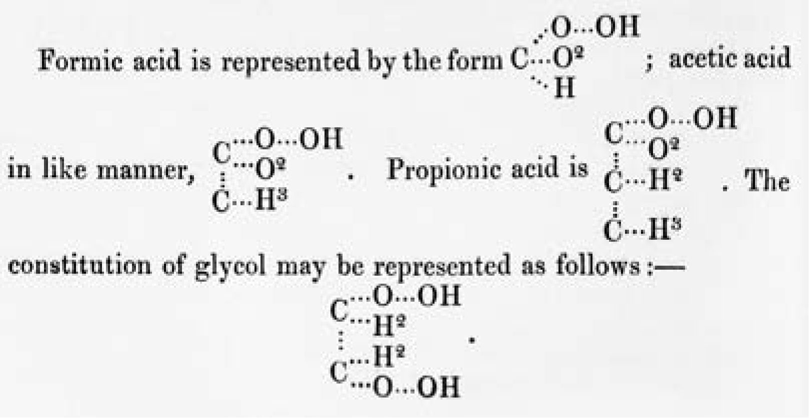
[11] Ibid., 107–8.

[12] See Rocke, "Subatomic Speculations" (1983), 9–10.



Formic acid is represented by the form $\mathrm{C}\begin{array}{l}\cdots\mathrm{O}\cdots\mathrm{OH}\\ \cdots\mathrm{O}^2\\ \cdots\mathrm{H}\end{array}$; acetic acid in like manner, $\begin{array}{l}\mathrm{C}\begin{array}{l}\cdots\mathrm{O}\cdots\mathrm{OH}\\ \cdots\mathrm{O}^2\end{array}\\ \vdots\\ \mathrm{C}\cdots\mathrm{H}^3\end{array}$. Propionic acid is $\begin{array}{l}\mathrm{C}\begin{array}{l}\cdots\mathrm{O}\cdots\mathrm{OH}\\ \cdots\mathrm{O}^2\end{array}\\ \vdots\\ \mathrm{C}\cdots\mathrm{H}^2\\ \vdots\\ \mathrm{C}\cdots\mathrm{H}^3\end{array}$. The constitution of glycol may be represented as follows:—

$$\begin{array}{l}\mathrm{C}\begin{array}{l}\cdots\mathrm{O}\cdots\mathrm{OH}\\ \cdots\mathrm{H}^2\end{array}\\ \vdots\\ \mathrm{C}\begin{array}{l}\cdots\mathrm{H}^2\\ \cdots\mathrm{O}\cdots\mathrm{OH}\end{array}\end{array}.$$

8 Some of Couper's molecular formulas. Source: Couper, *Philosophical Magazine* 16 (1858): 114.

ing a fully resolved formula for salicylic acid, Couper suggested that the formula for benzene was what chemists today call diallene or hexatetraene, $H_2C{=}C{=}CHHC{=}C{=}CH_2$ in modern symbols. This linear formula was the earliest proposal for what the extraordinarily important compound benzene might look like on a fully resolved molecular level. In the French version of the paper, he proposed a cyclical formula for cyanuric acid, implying the presence of a six-membered ring of alternating nitrogen and (divalent) carbon atoms.[13]

There is no question but that Couper was a gifted chemist, in both the experimental and the theoretical realms. In his salicylic acid paper, he reported the synthesis of salicyl trichlorophosphate, for whose formula he suggested another ring structure within the molecule—not, however, in the aromatic nucleus, but in the carboxyl/phosphate portion of the molecule. Several chemists, including Kekulé, tried to reproduce this experimental result, without success. And yet Couper's experiment was indeed correct, as Kekulé's student Richard Anschütz demonstrated in 1885; one simply had to follow to the letter Couper's prescriptions as to reaction conditions. By this time Couper had fallen into utter obscurity; no reference work carried his name, and no one knew even so much as his nationality.

Inspired by his unexpected success in proving the accuracy of Couper's experimental result, Anschütz resolved to learn more about

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13. Couper, "Nouvelle théorie," *Annales,* 489.

the man. He turned back to Couper's original papers. "Mein Gott, I said to myself, why did not Couper continue his work: he was, at the time, decidedly freer than Kekulé was from preconceived ideas." Together with British allies whom he recruited to the task (especially Alexander Crum Brown), Anschütz managed to piece together the biography that appeared, after the deaths of both Couper and Kekulé, in full form in English and in condensed form as sections in his biography of Kekulé. Anschütz concluded, with justice, that Couper was "a meteoric phenomenon" in the history of chemistry, "as distinguished as he was unfortunate," and that "in the history of organic chemistry the sorely tried Archibald Scott Couper deserves a place of honour beside his more fortunate fellow-worker, Friedrich August Kekulé."[14] In particular, Anschütz admired Couper for the many correct formulas he proposed, for the modern form in which he proposed them (he was the first to use something approaching a line signifying a valence bond), and for his suggestion of cyclical formulas.

To later chemists, Couper's formulas do appear more modern and more sensible than Kekulé's. However, Couper's theoretical paper must have been read with different eyes in 1858, before anyone had ever seen a "modern" structural formula or knew what "correct formulas" must look like. The essence of science is the construction of theory, as Couper rightly proclaimed. But that construction cannot be done by fiat; scientists have the obligation to argue for their theoretical ideas *from evidence.* Couper made no attempt to do that for any of his formulas. He laid down formula after formula by saying that this or that compound ". . . has the formula . . . ," ". . . is . . . ," ". . . is to be viewed as . . . ," ". . . is represented by the formula . . . ," ". . . may be represented as . . . ," and so on, with no more explanation or justification than that. There were available in 1858 detailed empirical justifications for most of Couper's simpler formulas, and he surely could have supplied them; that is what Kekulé had done. His failure to do that for *any* of his formulas made it impossible for contemporary readers to separate well-supported ideas from outright conjecture.

There were other problems as well. Couper urged the atomic weight of carbon C = 12, using (without naming him) Gerhardt's argument that when one employs C = 6, no compound is known with an odd number of carbons. But he adopted the equivalent weight for oxygen O = 8,

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[14] Dobbin, "Couper Quest," 335; Anschütz, "Couper," 193, 235; Anschütz, 1:125–29, 177–79, 296–97.

hence doubling the number of oxygen atoms in his formulas. He justified this move with an unclear rationale that is distinctly reminiscent of electrochemical dualism. He then asserted (incorrectly, in the context of chemistry in 1858 as well as of chemistry today) that hydrogen atoms abstracted from a hydrated acid or oxide "are universally accompanied by an atom [O = 8, i.e., a half-atom of O = 16] of oxygen."[15] Chemists ca. 1858 were well practiced at translating different atomic weight systems, but readers must have blinked at this particular argument. Couper was also in error (in hindsight, but also in the context of his day) in asserting that Gerhardt had derived *all* compounds from a multiple water type, and in failing to understand that Williamson was a powerful ally in Couper's own passionate pursuit of common-sense *verae causae,* real philosophical causes in the real world of molecules, rather than being the loyal acolyte of Gerhardt that Couper portrayed.

In fact, Couper had many philosophical allies, though you would not know that from his language. Not only Williamson, but also Kekulé, Wurtz, and even Kolbe in some respects, were pursuing similar aims under similar philosophical convictions as he. His complete silence regarding fellow cultivators of the vineyard—other than those on whom he poured sarcasm and scorn—was unusual for the day, and must have been viewed with distaste by many readers. In this sense Couper's paper contrasts with that of Kekulé, who was at great pains to pay homage to his predecessors and to rhetorically diminish claims of novelty in his own work. In none of his published papers did Couper ever even mention that he had worked under the patronage and in the laboratory of Wurtz—an expected courtesy of that time.

To be sure, one can readily see what Anschütz and others meant when they said that Couper was less under the spell of earlier work—especially the type theory so reviled by Couper—than Kekulé: the dotted lines between atoms are one example, the possibility of a cyclical (heterocycle) ring formula another. By contrast, Kekulé continued to use formulas expressed in the triangular type-theoretical style, even though he meant something different by them than what many type theorists had intended. But in other ways, amid all the creative iconoclastic brilliance, one also sees a certain immaturity in Couper and, ironically, a certain inability to transcend earlier ideas. He, too, used the word "type," and in the French papers employed type-theoretical curly brackets. And then there is the matter of O = 8, chosen not for mere conventional purposes but deliberately and indeed insistently,

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[15] Couper, "New Chemical Theory," 112–13.

with the curious electrochemical-dualist rationale—old-fashioned and outdated by the standards of 1858.

After reading Couper's paper in the *Comptes rendus* of the Académie des Sciences, Kekulé sent off some "Remarks" to the Académie, pointing out, inter alia, that his similar theory had already appeared in print. Then Wurtz published separate critical reviews of Kekulé's and of Couper's theories in the first two monthly issues of his new journal, *Répertoire de chimie pure.* His review of Kekulé's theory was highly favorable, approving of Kekulé's call to "go back to the elements" and praising the development of the ideas in the paper. His review of Couper's theory was mixed. Couper had provided "analogous considerations" to what had already appeared from Kekulé; his conceptions were broader than Kekulé's, admitting as he did diatomic as well as tetratomic carbon, and in general Wurtz judged his ideas "ingenious and acceptable, if one separates from them certain accessory hypotheses and unclarities which plague his exposition."[16]

Most importantly, Wurtz asserted that the main lines of Couper's theory were *not,* despite his protestations, irreconcilable with either radical or type theory, considering especially the most recent modifications of those theories. "In general," he wrote, "I find M. Couper's formulas too arbitrary, too distant from experiment." Rational formulas are not intended to show the "intimate constitution of compounds," only reactions; "hence their advantage." In sum: "It is too much of hypotheses, and it is wrong to present these things as if they were handed down by God. In this respect M. Kekulé, who seems better to have understood the sense and import of the ideas which he was the first to express, wisely wrote at the end of his memoir, 'As for me, I attach but a secondary importance to considerations of this sort.'" Wurtz failed to take this opportunity to affirm that he had Couper's paper in hand at the time Kekulé's second theoretical paper was published. In several subsequent historical accounts of the rise of structure theory, Wurtz mentioned Couper's independent formulation only once, and that in a footnote.[17] It does appear that Wurtz and Couper had clashed personally, and this may have ever after influenced Wurtz's treatment of his former student. His reticence fully to acknowledge Couper's substantial accomplishment is out of character for Wurtz's notably wise and generous personality.

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[16] Kekulé, "Remarques" (1858); Wurtz, *Répertoire de chimie pure,* 1:20–24 (review of Kekulé's paper, October 1858), and 1:49–52 (review of Couper's paper, November 1858).

[17] Wurtz, *Histoire* (1869), 215n.

CHAPTER FIVE

Loschmidt

In December 1861, a forty-seven-page brochure appeared, self-published by a forty-year-old school teacher in Vienna named Joseph Loschmidt (1821–95), which contained a discussion of the theory of atomicity of elements and portrayed hundreds of graphic molecular formulas. The brochure attracted little attention at the time, and was almost completely forgotten for half a century.[18] But in 1913, four years after having resurrected Couper and his work, Anschütz performed a similar service for Loschmidt by reprinting the booklet with extensive explanatory and bibliographic notes and an illuminating introduction. The recuperative baton has since passed to others.[19] Loschmidt is justly famous in the history of science for having provided the first plausible data-driven estimate of the actual sizes of gas molecules (1865), but this chemical essay was in fact his earliest published work in science.

The imprint is 1861, but the brochure must have been printed in the last week of that year, since it contains citations to literature that had been published up until late December. Loschmidt therefore had at his disposal all three fascicles of the first volume of Kekulé's *Lehrbuch*. He made use of Kekulé's and Wurtz's barred atomic symbols C and O to indicate atomic weights, as well as their prime marks to indicate atomicities, and he followed Kekulé's *Lehrbuch* in many particulars, notably the salient principles of structure theory.[20]

In two respects Loschmidt did *not* follow Kekulé's lead: in the choice of graphic formula style and in Kekulé's hesitation to use graphic formulas very often. Loschmidt chose a circle as his basic atomic symbol: a small one to symbolize a hydrogen atom, a larger one for carbon, a double-rimmed circle for oxygen, a triple-rimmed circle for nitrogen, and a lenticular figure for chlorine. A chemical bond between two atoms was symbolized simply by depicting the two respective circles just touching. Like Kekulé, Loschmidt strove to create a consistent theory that would preserve the constancy for carbon of what he called in general "Pollenz" (valence), or in particular "vierstellig" (tetravalent)

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[18] Loschmidt, *Chemische Studien* (1861); Bauer, "Loschmidt" (1913).

[19] Loschmidt, *Konstitutions-Formeln* (1913/1989); Fleischhacker and Schönfeld, *Pioneering Ideas* (1997), esp. the historical papers by Alfred Bader, Christian Noe, Günter Schiemenz, and Robert Rosner.

[20] For an example of Kekulé's influence, see Loschmidt's treatment of isomerism on page 8 (14–16), which closely follows that in *LB,* 1:183–92 (1859) (here and in the following footnotes I first cite page numbers from the original 1861 publication, and then in parentheses the pages from the 1913/1989 republications). This includes Kekulé's concept of "Isomerie im engeren Sinne" (isomerism in the narrower sense).

carbon. One strategy to do this was to posit doubled bonds between certain atoms, such as between carbon and oxygen in CO_2, or between two carbon atoms in cases like ethylene. He symbolized such a double bond by creating an overlap between the two respective circles, with two small dashes within the overlap. Triple bonds had three small dashes.

So Loschmidt's graphic formulas have a very different appearance from Kekulé's; in contrast to the latter, there is no trace of Wurtz's subatomic speculation. Loschmidt was also far less reserved than Kekulé in his willingness to use graphic formulas, thereby pronouncing his opinion regarding the atomic-level detail of the constitutions of scores of organic compounds. He did all this with intelligence, imagination, and a dash of brio. Many of his formula assignments were relatively straightforward exercises, such as the simple hydrocarbons, alcohols, ethers, and acids; in these cases it was simply a matter of translating relatively unambiguous then-well-accepted type formulations into his graphic formula style. For some he provided detailed empirical justifications for particular resolved formulas, for others just hints regarding his choices, and for still others he simply provided the formula without comment, as Couper had done. He often made choices that were nothing more than speculations, without labeling them as such. And a few of his formulas were simply nonsensical as judged by his own standards, or impossible to decipher in a sensible fashion; some of these may have been uncorrected misprints.[21]

Loschmidt provided a graphic formula for glycolic acid that Kekulé had (only textually, not graphically) described in his 1859 fascicle: in modern terms, $HOCH_2CO_2H$. This was a relatively straightforward exercise for anyone who accepted Kekulé's 1858 theory, as Loschmidt clearly did, for there were really no other sensible choices for how to arrange these few atoms according to the valence rules. But Loschmidt also provided a graphic formula for lactic acid, something that Kekulé had deliberately avoided doing, even verbally. Kekulé's caution was wise, because there were two obvious alternative ways of arranging that molecule, and it was by no means clear from then-available empirical evidence which of the two was the true formula. (Namely, it could well have been either $HOCH_2CH_2CO_2H$ or $CH_3HOCHCO_2H$.) So Loschmidt was often not empirically careful; he guessed, and in this case, as in

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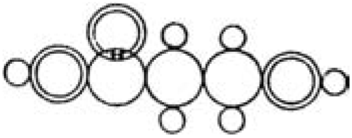
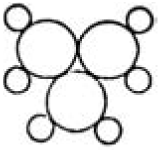
[21] In his 1913 edition, Anschütz provided a detailed and perceptive running commentary in the notes, pointing to Loschmidt's weaknesses as well as strengths. See, for instance, the problems he noted on pp. 7–8 (13–14). But overall, Anschütz certainly admired Loschmidt's performance, and with good reason.



9 Loschmidt's formula for lactic acid. Source: Loschmidt, *Chemische Studien* (1861), 10 (19), Schema 41.



Schema 68.

10 Loschmidt's formula for allyl hydride or propylene. Source: Loschmidt, *Chemische Studien* (1861), 14 (28), Schema 68.

some others, he guessed the "wrong" one.[22] In saying this, my purpose is not to reproach Loschmidt for having made a choice that does not correspond to what we now believe. My point, rather, is to look at these matters as Loschmidt's contemporaries must have done, applying their criteria and not ours. Most scientists at that time, as in ours, reasonably expected to find an *argument* for particular choices, not just an arbitrary choice without comment, which must for that reason appear to have been speculative, even in those cases when it may not have been.

A second example is the compounds of the so-called allyl series, namely, derivatives of the hydrocarbon radical C_3H_5—what we now call propylene, $CH_3CH{=}CH_2$, less one hydrogen atom from the first carbon. Loschmidt first provided a formula that happens to correspond essentially with the modern propylene structure. He wrote that that one should adopt this approach, even though there is not a full chemical parallel between allyl compounds and others in which we presume a carbon-carbon double bond, such as ethylene. But there is another way to solve this problem, he noted, namely, by assuming in the allyl series a *triangular* array of three CH_2 groups, with each of the groups bound to the other two; this preserves carbon tetravalence all around (it corresponds to the formula we now call cyclopropane). "There is nothing improbable about . . . this chaining together of carbon atoms; as we will see below regarding phenyl, it impresses one in many cases as the

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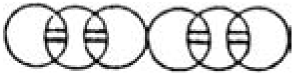
[22] Ibid., 9–10 (16–19).



11 Loschmidt's possible diallene (hexatetraene) structure for benzene. Source: Loschmidt, *Chemische Studien* (1861), 30 (58), Schema 181.

most acceptable supposition."[23] This provides an example of how it was sometimes difficult fully to understand Loschmidt, for here he seemed to be giving preference to both of these ideas—the straight-chain structure with the double bond *and* the cyclical option—with nothing more than hints toward the empirical evidence that could decide the issue definitively.

Loschmidt's treatment of aromatic compounds has excited comment in the last fifteen years. His just-cited hint that what we now call cyclopropane might be relevant for understanding the phenyl series (i.e., C_6H_5, or benzene less one hydrogen atom) has led some to suggest that he understood benzene itself as a cyclical or ring formula, four years before Kekulé's famous proposal of the same idea. The reality is more complicated. When Loschmidt came to discuss the structure of benzene in his brochure, he first raised the possibility that benzene may have Couper's diallene (hexatetraene) structure, where there is a "compression" (Verdichtung) of carbon atoms, by which he meant a series of cumulated double bonds (his Schema 181). This "would be the simplest" resolved formula, he wrote; but he then cited evidence that strongly spoke against this formula. "Under these circumstances one might almost be tempted to explain the unsaturated character [Unvollstelligkeit] of this [benzene] nucleus not through *compression,* but rather through *layering* [Schichtung] of the carbon atoms, and to assign to the C_6 nucleus something like Schema 182."[24]

This figure depicts six contiguous carbon circles, layered three on three. Translated into our contemporary notational system, it corresponds to two cyclopropane rings connected together using three new carbon-carbon single bonds, which produces, in effect, four fused triangular carbon rings composed of a total of six carbon atoms, all connected together with nine single bonds. Six carbon valences remain

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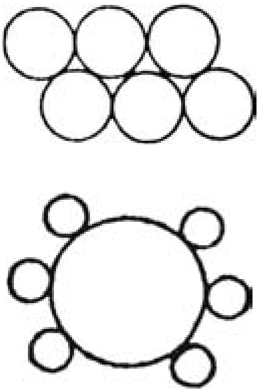
[23] Ibid., 14–15 (27–28). The fortuitous resemblance between some of Loschmidt's graphic formulas and modern molecular-orbital models does not, pace Noe, Wotiz, and William Wiswesser, justify the judgment that Loschmidt had written "the masterpiece of the century in organic chemistry" and "would have been far ahead of his time even in the 1940s." See Wotiz and Noe, "Kekulé and Loschmidt," 223, 225, 236.

[24] Loschmidt, *Chemische Studien,* 30 (58–59), with my emphasis added.



12 Loschmidt's two other possible representations for benzene. Source: Loschmidt, *Chemische Studien* (1861), 30 (59), Schemas 182, 185.

unused, arrayed unsymmetrically around the periphery, just enough to engage the six hydrogen atoms of the benzene molecule. To a modern chemist this appears to be an impossibly strained molecule, even if "legal" by valence rules, but Loschmidt cannot be faulted for knowing nothing about bond strain, and indeed the formula does account for the C_6H_6 formula in a way that sidesteps the problem that benzene does not behave chemically as if it had olefinic double bonds.

"One might almost be tempted," Loschmidt wrote, to advocate this structure for benzene. But having gingerly proposed this possible solution to the problem, and without offering any reasons why one ought to resist that temptation, he backed away:

> However, in the present state of our knowledge it is not possible to come to a definitive result in the matter, and we are all the more justified in suspending judgment, as our [proposed] constitutions are fully independent of the question. We [therefore treat the carbon skeleton of benzene] as if it were a hexavalent [sechsstelliges] element. Benzene, C_6H_6, Schema 185, is in the phenyl series what methane, CH_4, is in the methyl series. Just as the latter must be viewed as methyl hydride, so the former is phenyl hydride.[25]

Schema 185 is thus a single giant circle, signifying the *structurally indeterminate* hexavalent carbon skeleton of benzene, with six small hydrogen circles arrayed around the periphery.

Some recent writers have suggested that this large circle was in-

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[25] Ibid., 30 (59).

tended to signify a single benzene ring formed somehow by the carbon atoms—a conception that would make it very similar to Kekulé's theory first proposed in 1865.[26] However, this assertion is inconsistent with Loschmidt's clear explanation. If he were to speculate, he had told his readers, he would guess that benzene had a structure composed of multiple fused triangular carbon rings, very different from Kekulé's later proposal. But in fact Loschmidt was not willing actually to propose any single theory of the constitution of the benzene nucleus. He used a symbol that was explicitly crafted to signify that we simply cannot yet say what this nucleus may look like. His circular symbol for the benzene skeleton, in short, is a chemical version of the algebraic unknown, *x*.

As we have noted, Loschmidt's booklet contains references to literature that was published throughout the year 1861, but it must have been printed and distributed quickly at the end of the year, for already on 4 January 1862 Kekulé mentioned in a letter to Erlenmeyer that he had read "Loschmidts Confusionsformeln."[27] This derogatory two-word reference is all we have from the private Kekulé, but he also referred once to Loschmidt's formulas publicly (and relatively neutrally), in the 1865 paper in which he first announced his benzene theory; the relevant footnote simply states that he regarded his own graphic formulas as preferable to those that had been proposed by Loschmidt and by Alexander Crum Brown. Interestingly, in Loschmidt's very last publication (1890), in which he returned to a theoretical discussion of the structure of benzene, he did not even mention his 1861 booklet or any proposals therein.[28]

In taking issue with unproductive latter-day priority claims, my purpose is not retrospectively to award accolades or issue reproaches, but simply to attain the clearest possible historical understanding of what Kekulé and Loschmidt thought they were doing when developing their respective concepts of the molecular world. In Loschmidt's case, I believe that he must have formed vivid mental images correspond-

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[26] Wotiz and Noe, "Kekulé and Loschmidt"; also the individual essays by Bader, Noe, and Rosner, in Fleischhacker and Schönfeld, *Pioneering Ideas.* A brief response to an early version of this argument is Rocke, "Waking up" (1993). Schiemenz independently and simultaneously developed an argument similar to mine: "Goodbye Kekulé?" (1993) and "Loschmidt und die Benzol-Formel" (1994). Heilbronner and Hafner have developed this refutation of Noe, Bader, Wotiz, and Rosner more thoroughly than anyone else: "Loschmidts Benzolformel" (1998).

[27] Cited in Anschütz, 1:305; the date on the original letter, preserved in HDN, is clear and is confirmed by internal content. One may presume that Loschmidt sent a number of copies to important chemists throughout Europe. No copy was found in Kekulé's personal library at the time of his death (*Konstitutions-Formeln,* Anschütz ed., 105).

[28] *Konstitutions-Formeln,* Anschütz ed., 109.

ing to at least some aspects of what he thought the molecular world was like. The conjecture that Loschmidt habitually thought about the microworld in a visual-realistic stereospatial fashion is consistent with the path-breaking work he did four years later in the physics of gas molecules, providing a means to estimate their real sizes.

To see this, we need to explore his conceptual world more fully. The opening pages of Loschmidt's chemical essay describe a generalized theory of matter strongly reminiscent of Boscovichean point-force atomism. Curiously, he characterized this view as uniformly accepted by chemists of his day, and as traceable to Liebig—both of which are doubtful assertions. He then introduced his graphic atomic symbols, whose sole purpose, he declared, was the "direct visualization [Anschaulichkeit] of relationships." Loschmidt seems to have intended any two atomic circles in contact to symbolize (or visualize) the potential energy wells that keep the point-atoms at certain characteristic separations, according to Rudjer Bošković's eighteenth-century theory: "The desired graphic clarity [Anschaulichkeit] appeared to me to be achieved when I tried to surround each [point-]atom with a sphere that represents, as it were, its equilibrium sphere, the radius of which indicates the distance at which the atom that enters into chemical combination maintains its separation from the equilibrium sphere of each other atom with which it is immediately bound by its molecular force."[29] Loschmidt also noted that the atoms must "oszillieren" around this equilibrium position. His repeated reference to "equilibrium *spheres*" of force before introducing his graphic "circles" demonstrates that he understood the difference between real atomic interactions in the world of Euclidean space, of which one could make private hypothetical mental images, and conventional planar representations suitable for the customary paper medium of the professional world. His remark that all of this was a matter of representational convenience, rather than any intended indication of actual relative distances, does not weaken the sense that we can gain a real glimpse of his thought patterns here.[30]

On one point, at least, Loschmidt's latter-day defenders are right: Loschmidt's graphic formulas were more powerful heuristically than Kekulé's sausage-shaped graphic formulas. This is probably because they appear, as I have suggested, to have been modeled after an explicitly stereospatial mental conception, in contrast to Kekulé's essentially

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[29] Loschmidt, *Chemische Studien,* 2 (4).

[30] Ibid., 1–2 (3–5). This viewpoint is skillfully developed by Schuster, "From Curiosity to Passion" (1997), 269–76.

linear sausage formulas. But we will postpone a discussion of the heuristics of Kekulé's formulas until later in this chapter.

In the broadest sense, the cases of both Loschmidt and Couper demonstrate how wide the prospects must have appeared when structure-theoretical ideas began to be developed in the late 1850s. It was as if a door had suddenly been opened to a whole new world of understanding of the unseen microworld, and all one had to do was walk through that door. The problem was that there was a great temptation to run rather than walk. By this I mean that structuralist precepts, which could be taught to a complete beginner in Tinkertoy fashion in a few minutes, allowed anyone easily to proceed in minutes from "empirical" formulas (such as $C_3H_6O_3$ for lactic acid, C_3H_5 for allyl, or C_6H_6 for benzene) to a variety of possible resolved structural formulas—especially for those who were untroubled by epistemic doubt. However, chemical understanding, wisdom, and experimental artistry were required to decide how chemical and physical evidence might allow one to effectively argue for this or that alternative.

Neither Couper nor Loschmidt were complete novices, and both provided valuable development of the theory; indeed, Couper's theory was substantially the same as Kekulé's. However, both men were, in different ways, sometimes overly enthusiastic and optimistic in the application of simple structure-theoretical precepts. The most experienced chemists, such as Kekulé, were often the most reticent—sometimes *too* reticent—to commit themselves, for they had the best understanding of the sometimes subtle evidentiary complexities and epistemological pitfalls. For the historian to understand such reticence requires, inter alia, a full appreciation and evaluation of what evidence for each hypothesis was available at the time.

Butlerov

When in 1958 the centennial of Kekulé's and Couper's theory of chemical structure was commemorated, the Soviet Union waited three more years for their corresponding celebrations, for Soviet scholars dated the theory to a landmark paper in 1861 by one of their countrymen. The author of that paper, Aleksandr Mikhailovich Butlerov (1828–86), was a student of Nikolai Zinin and Karl Klaus at the University of Kazan, and was named professor there in 1857. During the mid-1850s he was already inclined toward the reform camp, but Butlerov's full development awaited his first trip to western Europe (from August 1857 to July

1858), which became possible after Tsar Alexander II acceded to the throne and quickly liberalized the empire's travel laws.[31]

Butlerov had several long conversations with Kekulé in Heidelberg in the fall of 1857, and also worked a while in Erlenmeyer's laboratory. But his longest stay was in Paris, from December 1857 through May 1858. For two months he worked in Wurtz's laboratory, where he was a member of a particularly stimulating international community including Couper, Lieben, Beilstein, and Shishkov, and where he performed his very first published experimental work in chemistry. He was one of the earliest members of the Société Chimique de Paris, and those early meetings were characterized by much discussion of chemical theories. On 17 February 1858 he presented a theoretical paper to the Société that outlined a theory of a marsh gas type, which he called a "type of molecular structure" explicitly following Dumas's "mechanical type" theory; it is reminiscent of Odling's and Kekulé's ideas on the methane type.[32] He was still in Paris when Couper submitted his paper "On a New Chemical Theory" to Wurtz, but he was already on his way back to Kazan by the time Couper's paper appeared in print.

On his way east, he stopped again in Heidelberg and attended lectures of both Kekulé and Bunsen. He heard at least portions of Kekulé's theoretical "Publikum" of summer semester 1858, which was organized around Kekulé's full new theory of atomicity of the elements. In his journal for 19 May, Butlerov praised Kekulé's "extremely clear and astute" lectures, and described parts of the new theory; coincidentally, this was the issue date of the monthly issue of the *Annalen* in which Kekulé's second theoretical paper appeared.[33] In a report to his government regarding this trip, Butlerov characterized Kekulé as "outstanding among German chemists representative of the new direction in science." His lectures were "well attended and merited complete attention for their clarity and precision of expression, and for the originality and novelty of some of the views introduced by this young scientist into the field of theoretical organic chemistry."[34]

In December 1858 Butlerov sent some comments on Couper's theory to the *Annalen*.[35] The goal of science, Butlerov averred, is not theory, as

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[31] For a recent biographical review, see Brooks, "Butlerov" (1998). Brooks characterizes Butlerov in 1857 as "a provincial encountering the scientific center for the first time" (23).

[32] The paper was never published, but Butlerov published a résumé of it in his paper "Bemerkungen" (1859), 55, 63–66.

[33] Butlerov, *Sochineniia [Collected Works]* (1953), 3:337–38.

[34] Ibid., 3:72–73.

[35] Butlerov, "Bemerkungen."

Couper had claimed, but the discovery of laws based on facts. Couper had gone too far in rejecting all of Gerhardt's ideas, especially Gerhardt's useful generalization of types. It is true (he wrote) that one cannot investigate the detailed constitution of molecules using Gerhardt's theory, but progress had been rapid since Gerhardt's death, and even Gerhardt would rejoice in such investigations were he still alive. Finally, "many other theoretical views of [Kekulé] are analogous to those of Couper, and, since they were expressed earlier, [Kekulé's] priority must be granted." Butlerov did concede that Couper had discussed the self-linking of carbon atoms in greater detail than Kekulé had. On the other hand, he excoriated Couper for his assumption of (and confusing justification for) O = 8.[36]

In 1861 Butlerov made another six-month trip to the west, visiting many of the places and people he had seen the first time, including Kekulé. At the annual Naturforscherversammlung (meeting of the Society of German Scientists and Physicians) in Speyer on the Rhine in September, he delivered a paper "On the Chemical Structure of Compounds" that Russian scholars have considered the origin point not just for the earliest prominent appearance of the phrase "chemical structure," but for the theory itself.[37] The paper was in effect a hortatory address. We need to get fully beyond both the older and newer versions of the type theory, he declared. This theory had given good service in its time, especially the idea of "mechanical types," which had led to the increasingly fine schematic dissection of molecules. But all type theories have a fatal flaw in that they seek to identify a central focus for the molecule, namely, the atom outside the bracket of the type formula. For Butlerov this was artificial, a distortion of chemical reality, and even the most progressive theorists were still being tainted by it. Rather (he wrote), we need to seize the principle of atomicity and carry it through with absolute consistency. This means that no atom in a molecule is privileged; all are connected together equally according to the atomicity rules, to form a single molecular "structure."

Butlerov emphatically stated that it was not yet possible to determine actual *physical* molecular reality: "chemistry, which only deals with bodies in a state of transformation, is powerless to judge this mechanical structure, as long as physical investigations are not brought to bear on the question." However,

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[36] Ibid., 53–54.

[37] Butlerov, "Chemische Structur" (1861).

> we cannot deny, leaving the concept of *physical atoms* entirely to the side, that the chemical properties of a body are determined in particular by the chemical context of the elements which form it. Proceeding from the assumption that there inheres in each *chemical* atom only a specific limited quantity of chemical force (affinity) with which it participates in the formation of bodies, I would designate this chemical cohesion, or the manner of mutual bonding of the atoms in a compound body, by the name *chemical structure.* The familiar rule that states that the nature of a compound molecule is determined by the nature, quantity, and *arrangement* of its elementary components could thus *temporarily* be altered to the following: *the chemical nature of a compound molecule is determined by the nature and quantity of its elementary components, and by its chemical structure.*[38]

On one level, this is (and in 1861 was) familiar. By speaking of *chemical* atoms, *chemical* force, *chemical* cohesion, *chemical* context, and *chemical* structure, Butlerov was making the same epistemological distinction that Kekulé and others had often already made: physical and stereospatial claims were to be avoided, since the evidence comes from chemical reactions and we know nothing about the physical details of atoms, much less of molecules. But there was a new urgency here: he wanted to use this distinction to go further than others had gone in the *consistency of application* of the new ideas. This will eventually lead, he thought, to "truly rational" formulas, and when that happens, only one resolved formula will be possible for any given substance.

Can type formulas express this purified idea of chemical structure? Yes, he affirmed, and indeed Butlerov continued to use formulas in the type style for the next few years. But these formulas are not ideal for expressing chemical structure, he cautioned, partly because readers might then assume that some sort of type theory, rather than structure theory, was being utilized. He did not advocate for any particular new graphic formula, leaving it to "time and experience" to decide how best to notate the new formulas of chemical structure. He concluded,

> I am far from thinking that I am proposing a new theory here; on the contrary, I believe that I have expressed views to which very many chemists subscribe. I must even remark that a similar thought formed the basis of the viewpoint and formulas of Couper, whose too absolute and exclusive conclusions I contested at the time; but this thought was neither clearly enough perceived nor expressed by that chemist. My remarks today were only intended to suggest that it is time to apply the idea of atomicity and of chemical structure in every case, and entirely free from the type

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[38] Ibid., 551–53.

> viewpoint, as the foundation for considering chemical constitutions, and that this would seem to provide a means of helping chemistry from its present uncomfortable position.[39]

It is curious that he did not mention Kekulé in this article, after having made a particular point of emphasizing Kekulé's priority over Couper in his December 1858 commentary. The first volume of Kekulé's *Lehrbuch* had appeared in the meantime, and it is probable that Butlerov did not like aspects of what he saw there; it is also possible that the two men may have clashed in their conversations. Butlerov certainly seems to have had Kekulé in mind in speaking of those who had not freed themselves fully of remnants of type-theoretical thinking—he would later express this opinion explicitly—and not mentioning him at all would at least be more courteous than mentioning him in a critical fashion.

After publishing this manifesto, Butlerov produced a series of important experimental investigations in quick succession, while also acquiring a reputation as one of the most productive theoreticians of the 1860s. He suggested an intrinsic difference in the four affinity units (valences) of carbon atoms, as a way to understand hitherto mysterious examples of isomerism; he tentatively suggested, purely for its heurism, that the carbon atom might form an "irregular tetrahedron"; he synthesized the tertiary butyl alcohol predicted by Kolbe, as well as other tertiary alcohols; he synthesized an acid containing the first quaternary carbon atom; he produced many novel saturated and unsaturated hydrocarbons; and he emphasized the need to represent double bonds between carbon atoms in unsaturated compounds, as opposed to free affinities or divalent carbon (both of which ideas he had flirted with in 1861). But probably his two most influential papers (published in 1863 and 1864) were devoted to applying the theory of structure to explain difficult cases of isomerism and to predict novel substances. He also used these ideas in an influential textbook.[40]

It is difficult to gain full clarity on the subtleties of how Butlerov himself conceived "chemical structure," and how he distinguished it from Kekulé's, Couper's, and others' ideas, because his statements on this subject are not fully consistent. In a portion of his textbook written in 1863, Butlerov wrote that Kekulé and Couper were the first to

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[39] Ibid., 560.

[40] Butlerov, "Erklärungsweisen" (1863); "Systematische Anwendung" (1864); *Vvedenie* (1864–66); *Lehrbuch* (1868).

"clearly express" the ideas of carbon tetravalence and self-linking, but the use of the type theory had led to a certain artificiality and distortion; it was "but one more step" to arrive at the "more encompassing concept of the complication of molecules resulting from the atomicity of the elements." This idea of "chemical structure" may be defined as "the sequential order of reciprocal action, the manner of mutual chemical bonding of the elementary atoms in a molecule,"[41] which some had called "constitutions," but since this word had been used in different ways, we need a new name for it. This idea of structure "appears to have formed the basis for the ideas and formulas of Couper (1858); they were then formulated more clearly in 1861 [i.e., by Butlerov]." One sees the structural principle in Kekulé's *Lehrbuch,* too (he wrote), but only "fairly clearly" and only "here and there."[42]

In his important 1863 paper, written about the same time as these words, Butlerov made masterly use of structural theory to provide a better understanding of many of the most troubling isomerisms, and he expressed judgments that do not seem to be fully consistent with those just cited. He illustrated his ideas using formulas in the type style (because, he wrote, they will be easier for his colleagues to understand). He also was careful to say that he was not claiming to have proven his conclusions; only "that the principle of chemical structure (constitution, affinity attack-points), if consistently carried out, leads inexorably to these or similar considerations, and that the necessity of applying this principle in all its consequences necessarily arises from the generally accepted concepts regarding the atomicity of elements and the chemical molecule." Immediately following these words he discussed Kekulé's *Lehrbuch.* Kekulé's very terse style, he said, makes it difficult to say for certain what he thinks; "but one soon sees," Butlerov noted approvingly, "that Kekulé, who speaks right from the start about the arrangement of the atoms, really understands by this only their chemical connections (constitution in Kolbe's sense, or chemical structure)," rather than stereospatial arrangements. "Be that as it may, most of

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[41] Bykov and other Soviet historians have argued that Butlerov's German language of "Zusammenhang" and "Bindung" (context, connection, bonding) is more concretely and accurately expressed in his Russian definition of structure (stroeniia): "raspredelenie deistviia khimicheskoi cily" or "raspredelenie deistviia srodstva" (distribution of the action of chemical force, or of affinity). See, e.g., Butlerov, *Izbrannye raboty* (1951), 558.

[42] Butlerov, *Lehrbuch,* 36–37, 73–78. These statements apply, Butlerov wrote, to "theoretical views in 1863," when he was writing this part of his textbook. In the section immediately following, he offered some comments on the "current [1867] state of the theory." The term "structure" and the ideas behind it had gained currency, he thought, and were being applied more generally than four years ago; types have now been fully abandoned, and the differences of opinion are relatively small compared to earlier (ibid., 79–81).

Kekulé's as well as Kolbe's formulas are obviously based on the principle of chemical structure."[43]

Butlerov appears to have been troubled by certain passages in the fascicle of Kekulé's *Lehrbuch* that was published in 1863, especially those places where Kekulé suggested the existence of "molecular compounds" or where on rare occasion he seemed to suggest two distinctly different structures for the same compound. Butlerov thought that these problems were at heart due to Kekulé's continued partial allegiance to type theory and his continued use of type formulas. At the end of the last chapter we ascribed these passages to a mixture of caution and caginess on Kekulé's part, but Butlerov cannot be blamed for being a bit mystified, as others were as well. Nor can he be faulted for believing, as he did, that he had played an important role in eliminating such obscurity from the science with his program of advocacy for chemical structure.

In a long, friendly letter, Wurtz offered some polite criticism of the positions that Butlerov had taken in this article. He agreed wholeheartedly with his friend that the idea of atomicity of the elements is at the heart of Gerhardt's types and "gives them their true sense"; he also agreed that when one attempts to express *all* the reactions of a somewhat complex substance using *fully resolved* type formulas ("formules typiques délayées") they become so complex as to lose their value. But why urge the abolition of the more usual kinds of type formulas before having something better with which to replace them? "Are you not struck by the simplicity of type-theoretical interpretations?" he asked.[44] Butlerov responded, grateful for the supportive tone of the letter. He did not think their real positions were very different. "I believe that those typical formulas that suffice for most relationships of substances do nothing more than express their chemical structure, or at least the most salient part of that structure. I believe that in pursuing the idea of the atomicity of the elements one is obliged to express that structure whenever the substance is sufficiently studied."[45]

Many others in the chemical community may have had similar reservations as Wurtz. Butlerov was unhappy when certain chemists seemed to write and behave as though he had contributed nothing but an appealing new phrase, "chemical structure," or worse, ignore him completely. His part was aggressively taken in 1865 by his student, the

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[43] Butlerov, "Erklärungsweisen," 504–5, 520, 532n.

[44] Wurtz to Butlerov, 19 February 1864, in Bykov and Jacques, "Deux pionniers" (1860), 121–22.

[45] Butlerov to Wurtz, undated but ca. March 1864, in ibid., 123–24.

fine chemist V. V. Markovnikov. Butlerov's "true merit," Markovnikov wrote, "consists in knowing how to apply the principle of chemical structure consistently, and in always striving to draw all possible conclusions which could be derived from this principle."[46] Markovnikov was particularly critical of Kekulé. His article caused hard feelings in Germany, for many thought that the real author of this article must have been Butlerov.[47] Two years later Butlerov took up his own pen: "The judgment regarding the manner of mutual chemical bonding of the elementary atoms in a molecule (the principle of chemical structure) is increasingly becoming the basis of most theoretical speculations in modern chemistry; as early as 1861 I referred to the need for this judgment, and I feel justified in asserting that a significant portion of the priority regarding the complete and consistent application of this principle belongs to me."[48]

Lothar Meyer was one of the German chemists whom Butlerov had named as having neglected his contributions. Meyer published "A Defense," in which he expressed astonishment that Butlerov appeared to be claiming priority—essentially, ownership—of certain chemical formulas written in a certain manner. He averred that it mattered little if one wrote one's symbols left to right, like Europeans do, or right to left, like the Hebrews, or even top to bottom, like the Chinese. What mattered was the thought or idea behind the symbols. Moreover, absent careful thought, anyone could formulate Kekuléan structures with abandon. "The establishment of these formulas was derived from a problem solved long ago, namely the calculus of combinations, permutations, and variations, a problem whose application to concrete cases requires neither ingenuity nor great inventive gifts."[49]

In "An Answer" to Meyer, Butlerov acknowledged "Kekulé's brilliant services in both the theoretical and factual branches of our science," but pointed out the limitations in Kekulé's theoretical contributions: his continued use of type-style formulas, his statements that rational formulas were nothing but reaction formulas, and his assertion that that multiple formulas were permissible for the same compound. Butlerov therefore repeated his claim to "a not insignificant portion of this further step, that is, the consistent realization and expanded application of the new principle." The only reason he had said anything about

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[46] Markovnikov, "Geschichte" (1865), 284.

[47] See Leicester, "Kekulé, Butlerov, Markovnikov" (1966).

[48] Butlerov, "Trimethylcarbinol" (1867), 9–10n. He mentioned Meyer, Ladenburg, Lieben, and H. L. Buff as having ignored his contributions.

[49] Meyer, "Abwehr" (1868).

the matter, he concluded, was that he had perceived "a *constant* silence concerning my ideas." And now, he hoped, the matter could be considered completely closed.[50]

And so it was, at least for the rest of that century. Butlerov did not return to the attack, nor to the defense, and when in 1879 he wrote (but only in Russian) a "Historical Sketch of the Development of Chemistry in the Last 40 Years,"[51] his quite reasonable claim there was consistent with that just described: that he deserved significant recognition for the expansion and consistent development of structure-theoretical ideas. This dispute emerged again, with considerable vigor, in the twentieth century; but that is another story.[52]

Crum Brown

The last of our four outsiders is Alexander Crum Brown (1838–1922). Born in Edinburgh, he was the product of three generations of secessionist Church of Scotland divines and the nephew of the chemist Walter Crum (whence his adopted compound surname). He graduated from Edinburgh University M.A. in 1858 and M.D. in 1861, having been taught by the Liebigians William Gregory (d. 1858) and Lyon Playfair; he then spent two semesters in Bunsen's Heidelberg laboratory, followed by a summer semester with Kolbe in Marburg. Upon his return in 1862 he received the first D.Sc. from the University of London. In 1863 he was appointed "extra-academical lecturer of chemistry" at Edinburgh, and in 1869 he succeeded Playfair in the professorial chair. Besides chemistry, his varied interests included mathematics, physiology, East Asian languages, philosophy of religion, the semiotics of diagrams and models, and systems of knitting and knot-tying.[53]

Even before he traveled to Germany, Crum Brown had become an advocate of reformist organic chemistry, as can be seen in his M.D. thesis; eighteen years after its submission, he had it printed "as a contri-

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[50] Butlerov, "Antwort" (1868).

[51] Butlerov, "Istoricheskii ocherk razvitiia khimii v poslednie 40 let," esp. 272–78.

[52] The historiography of this question shifted radically in 1949, when certain Soviet historians began to make aggressive new claims that Butlerov deserved *sole* priority for the theory of chemical structure—an interpretation that gradually penetrated into Western historiography as well. For a discussion, see Rocke, "Historiography" (1981). By contrast, intelligent and scholarly advocacy for Butlerov was expressed by Bykov, e.g., in *Istoriia* (1976). A reasoned response to Rocke, "Historiography" (1981) is Bykov, "K istoriografii" (1982).

[53] Subsequent biographies are principally indebted to Walker, "Crum Brown" (1923). See also Larder, "Crum Brown" (1967), and Ritter, "Graphical Formulas" (2001).

bution to the history of the subject."[54] Just twenty-seven pages long, the thesis is a perceptive history of nineteenth-century atomic theory, with obvious inclination toward the reform movement of the 1850s, and concluding with some interesting conjectures. The theory of polyatomic radicals, he wrote, was due to Williamson, Odling, Wurtz, and Kekulé; Gerhardt, on the other hand, "had not carried it out generally." To demonstrate Gerhardt's incomplete understanding or acceptance of this theory, Crum Brown declared "impossible" the same nonlinking formula for glycerin published by Gerhardt in 1856 that Kekulé had previously cited (*Lehrbuch,* 1859, 94) to make the same point. This marks Crum Brown as an adherent of the mechanist-realist (Williamson-Kekulé) school of thought.[55] And he is one more example of the Scottish theme in our exploration of epistemologically sophisticated and atomistically inclined philosophers.

Crum Brown was intrigued by the fact that in certain cases a single radical seemed to have two different atomicities. The glyceryl radical C_3H_5, for instance, can combine with three "typical" hydrogens and three "typical" oxygens to form glycerin, a molecule that exhibits an atomicity of three. But the allyl radical, also C_3H_5, appears to be *mono*atomic as in the formation of allyl chloride, C_3H_5Cl, and other analogous reactions. "It is probable, he wrote, "that in these latter cases there is some change of relative position of the atoms composing the radical—indeed it is difficult otherwise to conceive how the change of atomicity could take place."[56] If allyl were conceived as a triangular ring of three CH_2 groups (Crum Brown thus preceding Loschmidt in this hypothesis), then its monoatomic status would make sense, for the removal of any hydrogen atom creates the monoatomic radical. But now suppose that one of the "lines of force" connecting the three CH_2 groups were broken; then two new points of attachment to the carbon nucleus would be available, raising the atomicity from one to three—in other words, forming the glyceryl radical. He then cryptically added that the same kind of mechanism might also find application on the *atomic* level to explain alternate atomicities of elements; this might well mean that atoms are not ultimate particles, but have internal structures, too, just like molecules do.[57]

What he meant here was clarified when he addressed the "simple

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[54] Crum Brown, *Theory* (1861/1879). Ritter ("Graphical Formulas") has published photographic excerpts from the holograph manuscript of 1861.

[55] Crum Brown, *Theory,* 11–12.

[56] Ibid., 11.

[57] Ibid., 11–12, 17–18.

polyatomic radicals," which was his designation for what we now call polyvalent atoms. All such atoms, he wrote, may be reduced to "the multiple type of hydrogen": the oxygen atom reducible to a double hydrogen type, nitrogen to a triple, carbon to a quadruple, and so on. This is still somewhat ambiguous, but his accompanying graphic formulas made matters considerably clearer. His resolved molecular formula for alcohol, for instance, places the C, H, or O symbols for each of the nine atoms of this molecule in small circles, with what he called "lines of force," symbolized by dotted lines, connecting up the atomic circles in the accepted sequence. This constitutes the earliest appearance of a recognizably modern structural formula: just remove the circles and replace dots by lines, and it looks exactly like the formulas that appear every day in elementary organic chemistry classrooms today.

But that was not all. This conception, he wrote, corresponds to a parallel diagram he also provided, in which the same graphic formula is repeated, only this time with four tightly grouped hydrogen circles replacing each of the two carbon atoms, and two tightly grouped hydrogen circles replacing the oxygen atom.[58] Although there is no explicit acknowledgment here, this is a direct visualization of Wurtz's verbal subatomic speculation. Crum Brown likely picked up this idea from reading the source article of 1855 and/or from understanding Kekulé's 1859 sausage formulas visually in the same way, even though Kekulé had not yet made this interpretation explicit. Using his graphic formulas, he then illustrated the breaking of the three-membered ring of CH_2 groups to show how monoatomic allyl could become triatomic glyceryl. The same sort of internal rearrangement might well happen with *atoms* of variable atomicity, he said, suggesting the possibility that "these bodies are in reality compounds, and that one line of force less is employed to unite their component atoms [i.e., their component Wurtzian subatoms] together in N^{V}, &c., than in N''', &c." But he hazarded no explicit visual or diagrammatic hypothesis here.[59]

Crum Brown had developed a useful and convenient symbolism, generically similar to Loschmidt's (and preceding it by some months); there is also evidence of possible stereospatial thinking here, though not as obviously so as with Loschmidt. Crum Brown explicitly compared his graphic formulas to Kekulé's, samples of which he reproduced.[60] "It must, however, be remembered," he added not unfairly,

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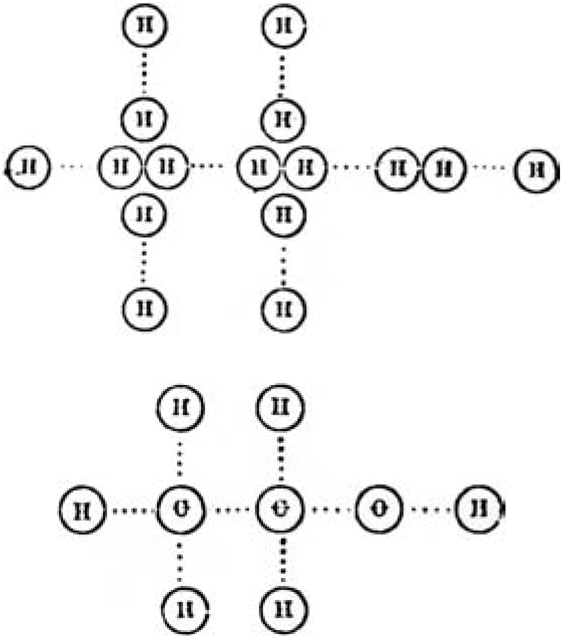
[58] Ibid., 16–17.

[59] Ibid., 17–18. N^{V} indicates pentatomic (pentavalent) nitrogen, i.e., N'''''.

[60] Ibid., 22–23.



13 Crum Brown's alternative depictions of ethyl alcohol. Source: Crum Brown, thesis (1861), 16–17.

"that Kekulé's graphic method is a most artificial one." He provided alternative graphic formulas (in his new style) for glycolic and oxalic acids, suggesting what we now call epoxide structures (three-membered rings consisting of two carbons and one oxygen), rather than carbonyls, hence transforming Kekulé's unsymmetrical structures into symmetrical ones. He did not assert that the new formulas were better, only that Kekulé needed at least to consider these possibilities. In a footnote, he suggested a plausible experimental plan that one might apply to discern which kind of formula, his symmetrical or Kekulé's unsymmetrical ones, should be given preference. Within months after the submission of this unpublished M.D. dissertation, a paper by Wurtz and Friedel accomplished just what Crum Brown had suggested, in an entirely analogous way. The symmetrical option was rendered improbable by their result.[61]

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[61] Wurtz and Friedel, "Mémoire" (1861). They prepared both the ethyl ester and ethyl ether of lactic acid, demonstrating that they are very different substances. That suggests an unsymmetrical placement of the two "typical" hydrogen atoms of the acid.

Of this chapter's quartet of subjects, we see here an outsider of a different sort, namely, a man who professionally was barely coming of age—seven years younger even than Couper—and writing an essay for purely local consumption. In addition to type formulas, before 1861 Crum Brown could only have seen two sorts of graphic molecular formulas, Kekulé's and Couper's. However, Crum Brown's proposals for how best to visualize and iconographically represent the "theory of atomicity of the elements" were astute. They were less indebted to type formulations than Couper's, less "artificial" than Kekulé's (as we shall shortly demonstrate), and superior to Loschmidt's in that they were more readily comprehensible. And Crum Brown knew far better than either Couper or Loschmidt how to argue effectively for his formulations from chemical evidence.

A year after his lecturer appointment, Crum Brown published a major theoretical article.[62] His purpose was to explore whether the "theory of atomicity"—structure theory—was capable of accounting for all cases of isomerism known at that time, and if it was not, what modifications to the theory might be proposed to widen its explanatory scope. Kekulé had defined the relevant concepts: "metamers" were understood to be isomers that could be explained by structural differences; on the other hand, "isomers in the narrower sense"—Crum Brown called them "absolute isomers"—could not; that is, absolute isomers were chemically distinct substances that nevertheless appeared to possess identical fully resolved formulas. Absolute isomers thus represented chemical phenomena that were as yet outside the scope of the theory. Such cases were rare but known to exist.

Investigating seriatim all fourteen cases of purported absolute isomerism known to him, Crum Brown presented arguments that four or possibly five were actually instances of metamerism, and one case might well be an instance of chemical identity. His investigative tool was not wet chemistry, but simply judicious use of the theory of atomicity, *with the essential assistance of his graphic formulas*. This was, in fact, their public debut; the only iconographic difference from his yet-unpublished M.D. thesis of three years earlier is that instead of dotted lines between atoms, each valence was now denoted by a dash emerging from the respective atomic circle; when two dashes from neighboring atoms formed a single "line of force," a small gap remained equidistant between the circles. He explained the formula conventions

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[62] Crum Brown, "Isomeric Compounds" (1864) (reprinted in *Journal of the Chemical Society* 18 [1865]: 230–45).

in a footnote, concluding with the standard "chemical versus physical" demur: "This method seems to me to present advantages over the methods used by Professors Kekulé and Erlenmeyer; and 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."[63]

Excursus: Heurism in Action

The character, and the positive heurism, of Crum Brown's formulas are demonstrated by the way he used them. One straightforward example was the resolution of the isomerism of the two propyl (three-carbon) alcohols as a case of metamerism; namely, excellent chemical arguments were available leading to the conclusion that in the normal alcohol, the OH group must be attached to the *end* of the three-carbon chain, whereas in Charles Friedel's newly discovered isomer, the OH must be attached to the *middle* carbon atom.[64] A more difficult explanatory challenge was the fact that the dehydrogenation of "pyrotartaric" (modern methyl succinic) acid had produced three distinct isomeric products. He provided the graphic formula of the starting material—which corresponds exactly to the modern one—and then simply stated, without further explanation, that "it is obvious that there *may* be three metameric dehydrogenates" (i.e., that the loss of two hydrogen atoms from pyrotartaric acid may occur in three structurally distinct ways).[65]

How had he deduced that pyrotartaric acid—$C_3H_6(CO_2H)_2$, produced by pyrolyzing the straight-chain tartaric acid—must have the formula of methyl succinic acid, a *branched* carbon chain with two terminal carboxyl groups? What were the presumed structures of the three "dehydrogenates" to which he was referring? And how could he assert that it was "obvious" what those structures must be? Regarding the first question, Kekulé had in fact recently suggested a different view of pyrotartaric acid, namely, that it had a *linear* carbon skeleton. But Maxwell Simpson had recently transformed propylene (modern $CH_3CH{=}CH_2$) into pyrotartaric acid by first making propylene [di]bromide, then substituting CN groups for the two bromine atoms, then hydrolyzing both

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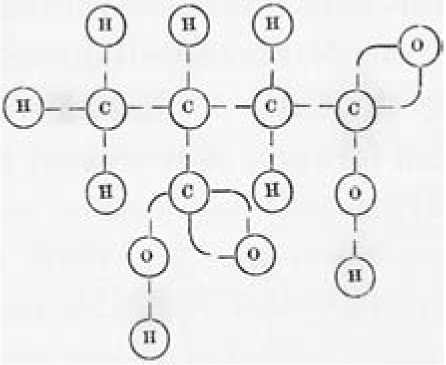
[63] Ibid., 708n.

[64] Ibid., 712–13. See Friedel, "Transformation" (1862); Friedel, "Sur l'alcool" (1863). The isomeric distinction was actually first made explicit by Hermann Kolbe, between the appearance of these two papers, but Crum Brown translated Kolbe's curious formulas into a clear graphic form.

[65] Crum Brown, "Isomeric Compounds," 710.



14 Crum Brown's formula for pyrotartaric acid. Source: Crum Brown, *Transactions of the Royal Society of Edinburgh* 23 (1864): 710.

of the CN groups to CO_2H.[66] When one follows what must be happening in this reaction sequence in Crum-Brownian terms using graphic formulas, one ends up with a branched-chain structure, methyl succinic acid. Now, Crum Brown telegraphically summarized all this in a single phrase ("from the relation of pyrotartaric acid to propylene, and of the latter substance to Friedel's alcohol") and he does not cite Simpson's paper, but there can be little doubt that we have accurately followed here what he had mentally (and semiotically) done.

Regarding our second question, when one dehydrogenates (removes two hydrogen atoms from) an organic compound, in modern terms one removes one hydrogen from each of two adjacent carbon atoms, creating a double bond—an unsaturated two-carbon linkage within the molecule. Although by 1864 this possibility had already been proposed by some chemists, others had suggested that in such cases the two hydrogen atoms might possibly be abstracted from the *same* carbon atom. There were three different ways that various chemists of this era proposed to visualize a single carbon atom that had lost two hydrogens and remained in a stable compound: two *free* affinity units on the carbon atom; or two affinity units that *combine with each other;* or a tetratomic carbon atom that becomes a *diatomic* carbon atom.

But Crum Brown would not countenance any of these three possibilities, strongly preferring the double-bond concept instead. As regards free affinity units, "the theory of atomicity taken strictly does not admit" such a phenomenon. As regards the second choice, he declared flatly that "equivalents of the same atom cannot be combined with one

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[66] Simpson, "Synthesis" (1861).

another." And as for the last alternative, Crum Brown did not want to deny all possibility to it, "but all we know of such 'non-saturated' substances leads to the belief that the atomicity of the carbon radical C_n is reduced, not by one or more of the carbon atoms becoming diatomic," but by the formation of a double bond or a three-membered carbon ring, which Crum Brown did not describe in words but rather in graphic form.[67] Given these constraints laid down by Crum Brown, we can read between his lines and, using his graphic formulas, draw exactly three possible structures for a dehydrogenated methyl succinic acid, no more and no fewer. Two of these have double bonds in the only two possible locations that the molecule permits; in a third possible structure a three-carbon ring provides the unsaturation.

Crum Brown still credited the Wurtzian idea that polyvalent atoms were accretions of subatomic monovalent "equivalent" particles (e.g., a carbon atom C = 12 being a concretion of four monovalent carbon equivalents, each subatom = 3), for he referred to it implicitly several times in this article, for instance in noting that "the two unsaturated [carbon] equivalents of the radical ethylene [must] belong to two different carbon atoms," or in asserting that every polyvalent atom possesses "two or more equivalents, by means of which it may unite with the equivalents of other atoms."[68] As we have suggested earlier, this appears to be the same idea that had inspired Kekulé's graphic formulas, which concretized and visualized each subatomic equivalent as a bulge on the respective atomic symbol. However, Crum Brown intentionally suppressed the visuality of this particular aspect in his graphic formulas by assuming *but not illustrating* each subatom as Kekulé had. He had also recast the linear Kekuléan model to a more flexible spatial style that had greater heuristic power.

Crum Brown was well aware of this greater power, arguing the case in this article, for it was clear to him that Kekulé had been led into error by the cumbersome character of his graphic formulas. One aspect of that awkwardness is that when one uses Kekulé's linear formulas it becomes tricky to express anything other than a linear structure. To be sure, by expressing the formula of pyrotartaric acid as a linear five-carbon skeleton, Kekulé had created a way that he could explain, in a different fashion than Crum Brown had, the fact that there were three distinct "dehydrogenates." Namely, in the linear version of $C_3H_6(CO_2H)_2$ there are exactly three pairs of hydrogen atoms susceptible of abstraction—

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[67] Crum Brown, "Isomeric Compounds," 709–11.

[68] Ibid., 711, 713.

which was *not* the case for Crum Brown's methyl succinic acid. Moreover, succinic acid has exactly two such pairs. Hence Kekulé was suggesting the theoretical possibility of, respectively, three and two dehydrogenated isomers of the two diacids, which accurately matched the actual then-known isomer numbers. "At the place in the molecule where the two hydrogen atoms are missing [from the same carbon atom]," Kekulé wrote, "two carbon affinities are not satisfied; there is at that place a sort of gap." A footnote here reads: "Naturally, one might just as well assume that the carbon atoms are in a sense shoved together, so that two carbon atoms are each bound by two affinity units. This is just another form for the same thought."[69]

Now, not only had Crum Brown provided a superior chemical argument for his alternative structure for pyrotartaric acid—for Kekulé could not, in his linear hypothesis, explain Simpson's reaction route—but he also pointed to internal inconsistencies in Kekulé's treatment. After citing Kekulé's footnote, Crum Brown wrote:

> There is some difficulty in understanding this last statement. For what can be meant by two affinities of the same carbon atom uniting together? unless the definition of either "atoms" or "combination" be completely changed. Or if we take the natural meaning of the sentence last quoted, and suppose two carbon atoms pushed together, so that two affinities of each previously united to hydrogen come to be united together, the two wanting hydrogen atoms do not come from the same, but from two different carbon atoms.

Crum Brown was right: Kekulé's "gap" theory of unsaturation is not at all the same, in either Crum Brown's or Kekulé's own terms, as the theory that there were double bonds between carbon atoms—which Kekulé had hinted at in earlier published writings, specifically proposed in his lectures, and adopted in print for the case of other combinations such as carbon-oxygen or carbon-nitrogen bonding. Erlenmeyer had made the same point against Kekulé the previous year, but had not illustrated his argument with graphic formulas. Whatever the system of representation, the two theories of unsaturation, gaps versus double bonding, specify different molecular structures.[70]

There was a second serious problem with Kekulé's reasoning, Crum Brown noted. He reproduced Kekulé's own proposed graphic (sausage) formulas for succinic acid and pyrotartaric acid (Kekulé himself had not

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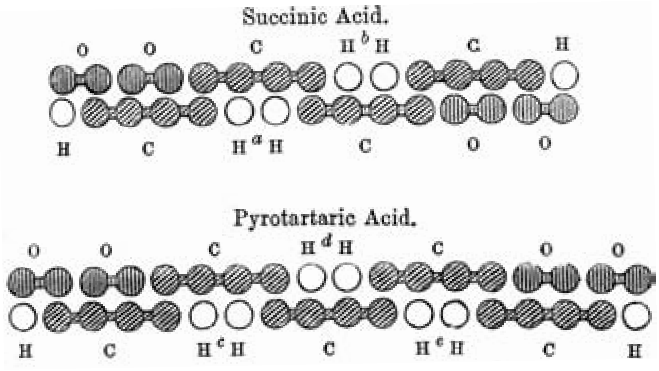
[69] Kekulé, "Organische Säuren" (1862), 115.

[70] Crum Brown, "Isomeric Compounds," 717–18; Erlenmeyer, "Bemerkungen" (1863).



15 Kekulé's succinic and pyrotartaric acid, according to Crum Brown. Source: Crum Brown, *Transactions of the Royal Society of Edinburgh* 23 (1864): 717n.

done this, simply describing the formulas in words, but Crum Brown was an accurate translator from Kekulé's words into images). He then pointed out that "a glance at the diagram is sufficient to show" (!) that removing *either* pair of hydrogen atoms from the sausage formula for succinic acid produces the *same* dehydrogenated product. That means that in Kekulé's own terms, contrary to his claim, he had not provided an explanation for the metamerism of the dehydrogenated acids called maleic and fumaric acids. (Crum Brown couldn't either, and so he concluded that this was, in fact, a genuine instance of absolute isomerism.) Furthermore, when one examined Kekulé's linear sausage formula for pyrotartaric acid (explicitly provided only by Crum Brown), only two, and not three, distinct isomers could be produced by abstracting each of the three pairs of hydrogen atoms in turn, for two of the putatively distinct structures turned out in actuality to be identical—a fact that was only evident when one pondered the graphic formulas. (Here, as we have seen, Crum Brown *did* succeed in explaining the triple isomerism by suggesting three distinct structural formulas, since he was working with a branched-chain rather than a linear formula.)[71]

A little less than a year after Crum Brown's article appeared, Kekulé published a preliminary version of his theory of benzene, and he used his sausage formulas to illustrate his ideas. In a footnote, he commented that these formulas "seem to me to be preferable to the modifications proposed by MM. Loschmidt and Crum Brown." Of the thirty-two sausage formulas in the principal table in the article, a handful were aliphatic (nonaromatic) substances. Two of the latter were two differ-

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[71] Crum Brown, "Isomeric Compounds," 717–18.

ent formulas for the alcohol prepared first by Friedel. In effect, Kekulé seemed to be suggesting that there should exist two distinct isopropyl alcohols, which he called acetonic alcohol and methylic ethyl alcohol. But these two products of different reactions had identical properties and an identical structure; they were the same compound, not isomers at all.[72] He was doubtless led to his erroneous conclusion by the characteristics of his graphic formulas, for isopropyl alcohol, like pyrotartaric acid, is a branched structure that is portrayed in sausage formulas only ambiguously or with difficulty.

Once again, Crum Brown immediately pounced on the mistake. Since he introduced his statement with an interesting historical commentary, I reproduce it at some length:

> The idea of atomicity . . . was employed by Frankland to explain the nature of the organometallic bodies, and its application was further extended by Kolbe to a large number of organic substances. It is, however, to Kekulé that we owe the complete generalization of this idea and its systematic application to all classes of compounds. This first rendered it possible to represent, as it is often advantageous to do, the constitution of compounds by completely dissected formulae. The most convenient way of doing this is to employ some suitable system of graphic notation.
>
> Kekulé himself, in his "Lehrbuch," made use of a system which has the advantage of compactness and clearness, but is limited in its application to those compounds in which the polyatomic atoms form a single chain. In order to obviate this inconvenience, I proposed, in my thesis presented to the Medical Faculty of the University in 1861, a form of graphic notation which, while inferior in compactness to that of Kekulé, appears to me preferable, as being at least equally clear and applicable to every formula in accordance with the theory of atomicity.
>
> In an able and suggestive paper published in the "Bulletin de la Société Chimique de Paris" for February 1865, Kekulé uses a modification of his original notation, which to a great extent removes my first objection to it, but at the same time lays it open to another and more serious one—that of obscurity and ambiguity. That this is not an imaginary or trivial defect is made evident by the circumstance that Kekulé has himself, in the paper referred to, been led into an error by his notation.[73]

Crum Brown then compared Kekulé's, Kolbe's, and his own formulas for the isomeric propyl alcohols, pointed to Kekulé's mistake, and asserted (fairly) that one would not be led into this error using his own graphic formulas. But Kekulé appears not to have been aware of Crum

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[72] Kekulé, "Substances aromatiques" (1865), 100n, 110.

[73] Crum Brown, "Graphic Representations" (1865).

Brown's critique, which appeared in a poorly known Scottish journal, and he repeated the two distinct propyl alcohol formulas in the detailed German publication of the benzene theory that appeared a year later.

It seems likely that Crum Brown was correct in his presumption that it was Kekulé's adherence to his linear sausage formulas that had led him astray (and it would not be the last time that Kekulé was thus misled). This circumstance did not, however, lessen his esteem for the German chemist. As we have just seen, Crum Brown regarded Kekulé as the principal source of the new light that was spreading over organic chemistry. If one is to take as sincere his letter four years later requesting a reference for the professorship that he was about to win, he even thought of Kekulé as a mentor once removed.[74]

The Fate of the New Graphic Formulas

Crum Brown's graphic notation, publicly introduced in a minor Scottish journal in the spring of 1864, experienced rapid acceptance, as such things go, particularly in Britain.[75] On 7 April 1865, shortly before he left London for Berlin, August Wilhelm Hofmann presented a Friday Evening Discourse "On the Combining Power of Atoms" at the Royal Institution, using as visual aids handmade molecular models.[76] Christoph Meinel has pointed out that these were the first physical models fashioned after Crum Brown's diagrams, and he suggests that Hofmann's early architectural study (also the profession of his father) may have been influential for him.[77] The atoms were represented by variously colored table-croquet balls, joined together in an appropriate fashion by short metal tubes. These models soon acquired the generic designation "glyptic" (to distinguish them from two-dimensional pa-

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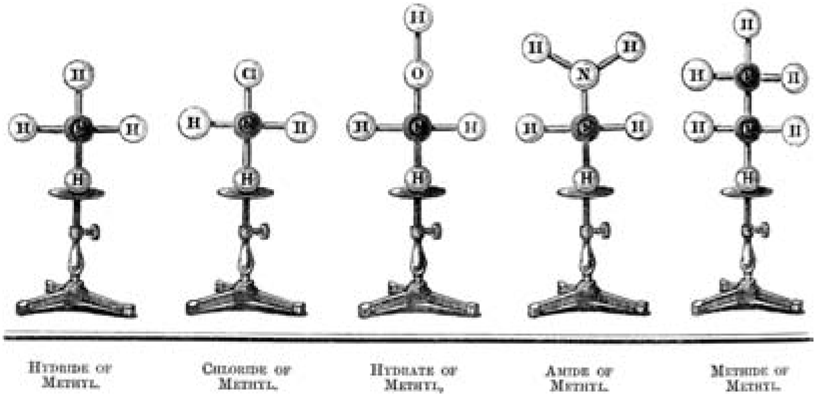
[74] Crum Brown wrote (18 February 1869, AKS), "Although I have never studied in your laboratory I have always considered myself as, in a sense, your disciple, so many of my ideas being derived, directly or indirectly from you."

[75] Colin Russell has plausibly suggested a relationship between the particular success of graphic atomistic representations in England and the popular education movement represented by the mushrooming Mechanics' Institutes, a movement that had no counterpart on the Continent: *History of Valency* (1971), 101–7.

[76] Hofmann, "Combining Power" (1865).

[77] Meinel, "'A World out of Chaos'" (1995), 84–87. Meinel provides the British context and notes that Hofmann had the models in production for use in the Royal College of Chemistry since 9 January 1865: "Molecules and Croquet Balls" (2004), 250. Hofmann's paint colors for his carbon, hydrogen, oxygen, nitrogen, and chlorine atomic balls were the same as those used since 1857 for Kekulé's wooden sausage models.



16 Hofmann's "glyptic" molecular models. Source: Hofmann, *Proceedings of the Royal Society* 4 (1865): 426.

per "graphic") formulas. Nearly all of Hofmann's models were direct translations of Crum Brown's paper formulas into three dimensions, but he differed as regards the constitution of unsaturated compounds, assigning to ethylene and its compounds the "ethylidene" formulation, CH_3CH. He called this structure an "unfinished molecule," that is, a molecule possessing a carbon atom with two unsatisfied or unsaturated affinity units.[78] Wurtz had formulated ethylene in this fashion two years earlier, but rather than suggesting the existence of two free affinities, he asserted that the second carbon atom was diatomic.[79]

By the end of 1865 Frankland began publicly to advocate Crum Brown's notation for use in certain contexts. He probably first encountered it in reading a reprinting of Crum Brown's 1864 paper, which appeared in the *Journal of the Chemical Society* in the summer of 1865. On 28 May 1866 he wrote to Crum Brown, "I am much interested in graphic formulae and consider that yours have several important advantages over Kekulé's." He told Crum Brown that he had used them in his course presented in winter term 1865–66 "with very great advantage." By return post Crum Brown informed Frankland where his publisher could procure the necessary type fonts, and Frankland proceeded to use the formulas systematically in his new textbook.[80] Frankland and his student Baldwin Duppa had synthesized lactic acid and

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[78] Hofmann, "Combining Power," 428.

[79] Wurtz, *Leçons* (1864), 136–37; he cited Couper as having been the first to propose the existence of diatomic carbon.

[80] Cited in Walker, "Crum Brown," 3425.

several of its homologues from the reactions of organozinc compounds with oxalic acid, and they used the graphic formulas in their published papers to clarify the structural relationships of these molecules. Their formula for ethylene, like Crum Brown's, contained a representation of a carbon-carbon double bond. Regarding the utility of the new notation, they commented,

> It is often extremely difficult to trace in symbolic formulae, the exact meaning which the author attaches to the grouping of letters; in graphic formulae no such difficulty can arise; and we therefore think that the use of these formulae, where constitutional expressions are intended, will greatly tend to clearness and precision. It is scarcely necessary to repeat Crum Brown's remark, that such formulae are not meant to indicate the physical, but merely the chemical position of the atoms.[81]

Three months later Frankland wrote to Crum Brown, "There is a good deal of opposition to your formulae here, but I am convinced that they are destined to introduce much more precision into our notions of chemical compounds. The water-type, after doing good service, is quite worn out."[82] A later paper by Frankland and Duppa well illustrated the advantages of Crum Brown's formulas for the increasingly complex structures being synthesized and being determined with confidence.[83]

Frankland discussed the representational significance of constitutional formulas in a paper published later that year. Discussing a formula for alcohol, Frankland commented, "This is a true representation of the internal arrangement of the atoms composing alcohol—not, indeed of their relative positions with regard to each other in space, but of the mode in which they are held together."[84] One cannot exclude the possibility of a limited amount of motion of each atom individually (such as vibration), nor of the possible influence of every atom exerted upon every other atom in the molecule. But the atoms may not *trade places* with each other: "The formula asserts such an exchange to be just as impossible as the wandering of a satellite from planet to planet in

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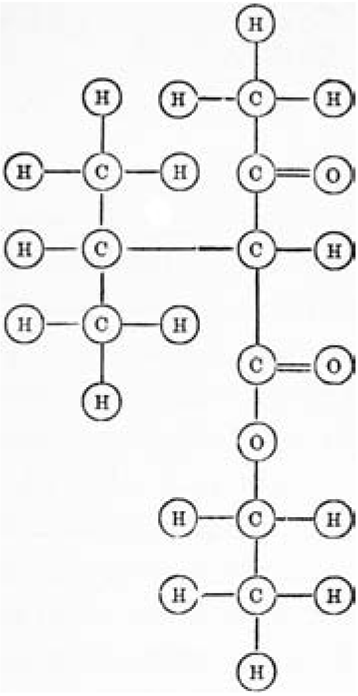
[81] Frankland and Duppa, "Researches" (1866), 345, 349–50n, 352. For the full context, see Russell, *Frankland* (1996), 254–70.

[82] Frankland to Crum Brown, 4 June 1866, cited in Walker, "Crum Brown," 3425–26.

[83] Frankland and Duppa, "Synthetical Researches" (1867). This paper, read 17 January 1867, provided several complex graphic formulas of newly synthesized compounds, e.g., on p. 111, "ethylic isopropaceto-acetate" (today denominated ethyl α-isopropyl-β-ketobutyrate).

[84] Frankland, "Contributions" (1866), 374 (published late summer 1866). He did not use graphic formulas in this paper, but rather introduced his own system of rational formulas in which bolded C's represent carbon atoms to which other carbon atoms are attached.



17 A complex graphic formula by Frankland and Duppa, after Crum Brown. Source: Frankland and Duppa, *Journal of the Chemical Society* 20 (1867): 111.

our own solar system. On no other hypothesis than this of limited mobility, can the facts of isomerism receive an intelligible explanation. . . . This idea of limited atomic mobility, which is one of the fundamental bases of constitutional formulae, forms the essential difference between constitutional and merely typical formulae."[85] Such constitutional formulas, Frankland averred, provide a conception of the order of the bonds connecting the individual atoms. But he did not want his term "bond" to be misunderstood. He did not intend it to imply "any *material* connection," but rather, "the bonds actually holding the atoms of a chemical compound being, as regards, their nature, much more like those which connect the members of our solar system."[86]

Frankland wrote the preface to his textbook, *Lecture Notes for Chemical Students,* shortly after this paper, and there he commented:

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85. Ibid., 374–75.
86. Ibid., 377–78.

> I have extensively adopted the graphic notation of Crum Brown, which appears to me to possess several important advantages over that first proposed by Kekulé. Graphic notation affords most valuable aid to the teacher in rendering intelligible the constitution of chemical compounds, especially when it is supplemented by what may be called the glyptic formulae of Hofmann. . . . 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 positions 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.[87]

Regarding interatomic bonds as resembling the gravitational bonds of the solar system, Frankland reproduced the exact language of his 1866 paper in the first edition of his textbook, but then changed his mind and expurgated both passages in reprints after 1867.[88] He could not see any reason why two atomicities of the same atom could not satisfy one another, thus providing an explanation for the variable atomicities of (e.g.) nitrogen; hence he distinguished between a maximum "absolute" atomicity and an "active" atomicity that could be below the absolute, the remaining units constituting the atom's "latent" atomicity.[89] Crum Brown had suggested something similar in 1861, though we see nothing of this in his 1864 paper.

Thereafter the Crum Brown–Frankland graphic formulas began steadily to penetrate the literature and replace other forms. Jacob Volhard learned them from Crum Brown personally, when they were both working in Kolbe's laboratory in summer 1862; he used them in his lectures at Munich from 1863 on.[90] Even before Crum Brown's 1864 paper appeared, Wurtz, presumably following Couper, reproduced a (vertical) resolved formula for glycol, with lines connecting the atomic symbols but without circles surrounding them. "But is it not obvious," he commented, "that this is nothing more than a type formula that

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[87] Frankland, *Lecture Notes* (1866), preface dated 15 September 1866, v–vi. This work was essentially a transcript of his lecture notes for the winter session 1865–66 at the Royal College of Chemistry, Frankland just having succeeded Hofmann there.

[88] Frankland put out a second edition of his textbook in 1870–72, and an edition of collected papers in 1877 in which his 1866 paper was reprinted. In both spots he replaced the phrase "as regards their nature, much more like those which connect the members of our solar system" with "as regards their nature, entirely unknown." First edition, p. 25; second edition, vol. 1, p. 25; *Experimental Researches* (1877), 9. This change was doubtless prompted by public ridicule that he had suffered for his views in a meeting of the Chemical Society in 1867 (for which, see the end of chapter 7, this volume).

[89] Frankland, *Lecture Notes,* 1st ed., 21.

[90] Volhard to Crum Brown, 19 December 1868, in Crum Brown, *Testimonials* (1869), 40.

has been expanded [délayée] a bit more . . . ?"[91] After Frankland and Duppa, Ernest Chapman and William Thorp began using the formulas in 1866.[92] Also influential was the example of Erlenmeyer, who in 1866 likewise began using this style of graphic formulas.[93] As early as the spring of 1867 commercial molecular model kits were being sold in the English market, clearly patterned after both Crum Brown's graphic and Hofmann's glyptic formulas.[94] After this time, the new notation experienced steadily increasing acceptance. In 1868 Frankland expressed the judgment, with slight exaggeration, that the formulas had been adopted "by a large majority of those chemists who are engaged in original [organic-chemical] research."[95] After Kekulé left Ghent for Bonn (1867), his former students there, Carl Glaser and Theodore Swarts, began using the formulas, and by 1869 Kekulé himself, along with most German chemists, had begun using them.

Nonetheless, this did not happen without some controversy, opposition, and even ridicule, as the following doggerel of 1868 attests:

Though Frankland's notation commands admiration,
    As something exceedingly clever,
And Mr. Kay Shuttleworth praises its subtle worth,
    I give it up sadly for ever;
Its brackets and braces, and dashes and spaces,
    And letters decreased and augmented
Are grimly suggestive of lunes to make restive
    A chemical printer demented.

I've tried hard, but vainly, to realize plainly
    Those bonds of atomic connexion,
Which Crum Brown's clear vision discerns with precision
    Projecting in every direction.

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[91] Wurtz, *Leçons,* 140–41.

[92] Chapman and Thorp, "On the Relation" (1866), 494. This paper, presented 1 November 1866, represents the second paper using graphic formula ever printed in the *Journal of the Chemical Society* (after Crum Brown's reprinted paper the previous year); the paper cited above by Frankland and Duppa represents the first graphic formula ever to appear in the *Philosophical Transactions.*

[93] Erlenmeyer, "Aromatische Säuren" (1866), 345, 351, 353–54; Erlenmeyer, "Process der Einwirkung" (1866), 217–18n, 224n, 231.

[94] Meinel, "Molecules and Croquet Balls," 253–55. Meinel draws a plausible connection between the international Kindergarten movement of Friedrich Fröbel, whose developmental psychology emphasized the importance of model toys, to the conditioned reception of such molecular models.

[95] Frankland to Crum Brown, 8 December 1868, in Crum Brown, *Testimonials,* 28.

In fine, I'm confounded with doctrines expounded
By writers on chemical statics
Whom jokers unruly may designate truly
As modern atomic fanatics.[96]

However, as Colin Russell rightly comments, "Frankland's instinct was perfectly correct, and learners did find the notation of great service, given a little time to get used to it."[97]

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[96] Signed J.C.B. [John Cargill Brough], reproduced in Jensen, "Chemical Satire" (1979). James Kay-Shuttleworth, previously James Kay, was secretary to the Committee of the Privy Council for Education.

[97] Russell, *Frankland,* 302.

SIX

Molecules as Metaphors

Frankly, I consider all these graphical representations . . . as dangerous, because the imagination is thereby given too free rein. HERMANN KOLBE[1]

[I]t is in fact through the imagination that the direction for exact science is often determined. JACOB VOLHARD[2]

Is it true, as Hermann Kolbe asserted, that there is danger in the too-free exercise of the scientific imagination? Kolbe certainly had strong opinions on a leading theme of this book, namely, how chemists should visualize the invisible objects upon which they operate—indeed whether they should engage in such visualization at all. His censure was of course directed at others; whether Kolbe had the psychological insight accurately to assess his own mental processes is a separate question. In any case, the disputes in which Kolbe engaged during the 1860s and 1870s provide historical insight into these important questions: the productive use of imagination and mental visualizations in science, and the way these mental processes can be tied to empirical data.[3]

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[1] Kolbe to Frankland, 23 July 1866, EFA 01.02.1505: “Offen gesagt, halte ich alle diese graphischen Darstellungen . . . für gefährlich . . . weil damit die Phantasie zu freien Spielraum gewinnt.”

[2] Volhard to Kolbe, 9 November 1878, ADM 3516: “es wird ja häufig durch die Phantasie die Richtung für die exakte Forschung bestimmt.”

[3] The following analysis is supplemented and complemented by material in *QR*.

CHAPTER SIX

Natural Types

Kolbe (1818–84) was a student of Wöhler and Bunsen, and was also powerfully influenced by Berzelius and by Liebig. In 1851 he became Bunsen's successor at the University of Marburg, then was called to the University of Leipzig in 1865. In the course of the 1850s, partly in collaboration with Frankland, Kolbe developed a fruitful approach to understanding the constitutions of molecules that had many commonalities with that of Williamson, Wurtz, and Kekulé. There was, however, an essential difference. As we have seen, the Williamson school partially based its development on ideas of Laurent and Gerhardt, who had fervently fought the electrochemical dualism of Berzelius. This "unitary school" no longer thought it necessary to conceive molecular reality in electrical terms. They were open to consider other ways of understanding how atoms might cohere into molecules, or else they simply did not trouble themselves about the question. The manner in which oxygen "holds together" exactly two radicals (to use Williamson's phrase), or its atomic "tie" (Wurtz's "lien") or "connection" (Kekulé's "Bindung") or "contiguity" (Kekulé's "Aneinanderlagerung") or "bond" (Frankland's term) *might* somehow be electrical in nature, but we know too little about it to say for certain. What one *could* say (if one adhered to this school of thought from about the mid-1850s) is that atoms can form limited numbers of links to other atoms—for instance, hydrogen just one, oxygen two, nitrogen generally three, and carbon generally four. What the nature of this link was, no one in the "unitary school" professed to know. But the idea seemed to work well heuristically, even without a more detailed understanding of the nature of the chemical bond. That pragmatic success was what they primarily cared about.

By contrast, Kolbe never relinquished a visceral commitment to electrochemical dualism. The discovery that electronegative chlorine could substitute indifferently for electropositive hydrogen had been a body blow to this belief, but the absence of any fundamental understanding of the nature of chemical affinity that could replace electrochemistry led Kolbe and a few others to stay faithful to some version of dualism. Kolbe remained convinced that the traditional approach of resolving formulas into radicals, taught him since his earliest student days with Wöhler and Bunsen and sanctioned by the authority of the great Berzelius, must not be abandoned. In this approach to chemical theory, radicals combine together *as such* to constitute the molecule. That which holds the constituent parts of the molecule together is not a series of directed links or bonds between individual atoms, but rather *isotropic* *forces operating between radicals as a whole.* This was Kolbe's watchword. For instance, the monoatomic methyl radical (C_2H_3 in Kolbe's formulation) enters into combination as a whole, not through a directed bond from carbon.

We recall from chapter 2 that the formula for carbonic acid proposed by Kolbe and Frankland in 1857 was $2HO.C_2O_4$, where C = 6, O = 8, and preformed water exists in the compound.[4] The two HO groups outside the C_2O_4 radical were the two water molecules (half-molecules in Williamson's terms), which could be replaced by one or two molecules of base to make salts. Successive substitutions of hydrogen atoms or hydrocarbon radicals for the four oxygens of the radical C_2O_4 generate organic acids, acetone, aldehyde, and alcohol:

$2HO.C_2O_4$	$HO.(C_2H_3),C_2O_3$	$(C_2H_3)_2C_2O_2$	$(C_2H_3)HC_2O_2$	$HO.(C_2H_3)H_2,C_2O$
carbonic acid	acetic acid	acetone	aldehyde	alcohol

This was the theory to which Kolbe and Frankland later pointed, in support of their argument that it was they, not Kekulé or Couper, who had first declared carbon a tetravalent element.

In successive fascicles of his textbook, which was published piecemeal starting in 1854, Kolbe gradually adjusted this theory on the margins, and sometimes more than just on the margins. In the fascicle that appeared in December 1857 he began using the term "type" for the first time to describe his theories, and abandoned the copula theory completely.[5] He also now began hesitantly to write in the terminology of "atomicity," though not entirely consistently. Kolbe was proud of his theory; he thought it was distinct from those of the conventional type theorists, and also that it was fruitful in guiding investigations. For instance, just as one can replace the single available hydrogen atom in aldehyde with methyl to produce acetone, one sees that there are two available hydrogen atoms in alcohol that could conceivably be replaced by methyl radicals.

$(C_2H_3)HC_2O_2$	$\longrightarrow$	$(C_2H_3)_2C_2O_2$	$HO.(C_2H_3)H_2,C_2O$	$\longrightarrow$	$HO.(C_2H_3)_2H,C_2O$
aldehyde		acetone	alcohol		unknown dimethyl pseudoalcohol

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[4] Kolbe, "Rationelle Zusammensetzung" (1857). The first "2" applies only to the HO moiety, not to the whole molecule.

[5] Kolbe, *Lehrbuch* (1854–78). This, the fourth installment, comprised pp. 481–672 of volume 1. The section containing this discussion is on pp. 567–75.

In the next fascicle of his textbook, published at the beginning of 1859, Kolbe came even further toward his erstwhile "typist" enemies.[6] He now advocated the doctrine of atomicity quite explicitly, including, for the first time, referring to the "vieratomig" carbon atom—or rather, since he was an advocate of "equivalents," to the tetratomic carbonyl radical, C_2.

All this had been revealed in his textbook, normally a resource for students, not a place where most colleagues would think to look in order to seek out the latest in theoretical innovation. Accordingly, Kolbe thought to publish a summary of his newly developed views in Liebig's *Annalen.* Written in the fall of 1859 and appearing in March 1860, this long essay was entitled "On the Natural [natürlichen] Connection of Organic and Inorganic Compounds, the Scientific Basis of a Natural [naturgemässen] Classification of Organic Chemical Bodies."[7] The title, with its repetition of forms of the word "natural," was carefully chosen. Gerhardt's types, Kolbe wrote, were artificial and unnatural and had led his latter-day followers into a "dead schematism," a meaningless game with mere fictions. Since his own type theory was based directly and materially on substitutions in carbonic acid, an actual compound with important connections to the physiology of both plants and animals, it was real, natural, and organic in the deepest and best sense.

However, in a published review of this paper Hermann Kopp asserted that Kolbe's theory was substantially similar to the Gerhardt-Williamson theory, for both had derived multitudes of organic compounds from inorganic models.[8] In another review of Kolbe's paper, Wurtz concurred with this judgment: both Kolbe's and his opponents' theories had at heart the same fundamental idea, namely, atomicity of the elements, which is "a clear, simple, and general principle, which deserves for this reason to be placed at the foundation of a system of chemistry." But it was not helpful, Wurtz opined, that Kolbe's theory was based on a *disguised* water type, Kolbe's diatomic C_2O_2 radical (in atomic weights, CO) serving the function that diatomic oxygen did for Williamson. So Kolbe in effect "combats Gerhardt's types by counter-

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[6] The fifth installment was pp. 673–848 of volume 1; this material is from pp. 740–49. Volume 1 was finally complete in 1859, but the imprint on the title page is 1854, the date of the first installment.

[7] Kolbe, "Zusammenhang" (1860).

[8] Kopp, in *Jahresbericht über die Fortschritte der Chemie* 13 (1860): 218–22. Cf. his similar judgment of the 1857 Kolbe-Frankland theory that formed the basis of Kolbe's 1860 paper: *Jahresbericht über die Fortschritte der Chemie* 10 (1857): 269–70.

feiting them."[9] As Wurtz had, Kekulé also noted that Kolbe's assumption of O = 8 artificially meant that each single increment of oxidation must involve *two* of his oxygen "atoms." If atomic weights rather than equivalents were used in his system, then a hydrogen compound rather than an oxygen compound would have to be used as the model; but then "this [Kolbe's] viewpoint would coincide with that developed in this [my] textbook."[10]

In contrast to these judgments by Kopp, Wurtz, and Kekulé, Liebig greatly admired Kolbe's paper. Kolbe's and Frankland's 1857 theory had made wonderful sense to him, perhaps partly because it was expressed in the equivalent weights that Liebig had been using for nearly twenty years, partly because it had been developed from the radical theory that he had played such an important role in building, and partly because of Kolbe's careful connection of the theory to physiology. Kolbe's later schematic derivation of malic and tartaric acids from succinic acid (malic is a mono-hydroxy and tartaric a di-hydroxy derivative of succinic acid) was a "triumph," in Liebig's words, and he looked forward to the testing of the various predictions derived from the theory.

What Liebig so deeply appreciated in both Kolbe's and Frankland's work, he told each of them separately, was the clear operation of a scientific idea, rather than what he characterized as thoughtless mechanical manipulations of formulas (which is what he regarded many structure theorists of the 1860s to be doing). To Kolbe he wrote: "all your work demonstrates that you are on the right path." And to Frankland he wrote: "What Wöhler and I saw thirty years ago in dreams, that is, in our imagination, you are now on the road to realizing."[11] To Kekulé he wrote in a similar vein (but avoiding the same kind of direct compliment): "I thank you very much for . . . the extremely interesting

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[9] Wurtz, *Répertoire de chimie pure* 2 (1860): 354–59; Wurtz, *Répertoire de chimie pure* 3 (1861): 418–21; Wurtz, *Leçons* (1864), 113–14.

[10] *LB,* 1:736–37 (1861); 2:247–49 (1864). Lothar Meyer later informed Kolbe that in this period he and many other type theorists were in the habit of routinely translating Kolbe's formulas into type formulas while reading his papers, for otherwise they were not easily comprehensible (letter of 30 January 1881, ADM 3535).

[11] Liebig to Kolbe, 3 April 1860, 2 December 1860, and 15 July 1861, ADM 3603, 3604, and 3606. "[D]ie Hauptsache ist, wie bei Allem, dass man den rechten Weg einschlägt und alle Ihre Arbeiten zeigen, dass Sie auf dem rechten Wege sind. In der organischen Chemie werden jetzt in der That bewundernswürdige Entdeckungen gemacht, im Ganzen genommen ist aber auch viele Formelspielerei dabei, und man vermisst häufig die wissenschaftliche Idee, die [man] denn doch zuletzt zum Ziele haben muss, uns über den Ursprung der Verbindungen aufzuklären" (no. 3606). Liebig to Frankland, 28 January 1866, BSB IIB: "Ihre Arbeiten erregen immer mein warmes Interesse weil sie die Ausflüsse einer grossen wissenschaftlichen Idee sind, deren Wahrheit Sie durch das Experiment beweisen. Was Wöhler und ich vor 30 Jahren im Traume d.h. in der Phantasie uns vorstellten diess alles sind Sie auf dem Wege zu realisiren."

communications about your most recent work. The discoveries now being made in organic chemistry are truly wondrous, and bring to pass what we, Wöhler and I, often spoke with each other as dreams.”[12]

Absolute Formulas

Kolbe’s formulas embodied carefully considered claims about the constitutions of the molecules he was studying. For Kolbe, “constitution” denoted the proximate pieces—radicals—that are assembled together into a molecule and that can substitute for one another under certain conditions; the goal of a formula is clearly and judiciously to depict that constitution. Unlike his “typist” opponents, Kolbe sought to establish *absolute* formulas, only one per compound. To Kolbe, the notion of Wurtz and Kekulé that many different formulas for the same substance were permissible was perverse, a kind of skeptical relativism run wild—or even worse, a contradiction in terms. He did not, however, understand what Wurtz and Kekulé meant by this: simply that with this or that different formula one might wish to emphasize this or that different reaction or mode of decomposition of *the same* molecule. His attitude is a little curious, since despite his protestations Kolbe sometimes did precisely the same thing (for instance, writing the carbonyl group in acetic acid as either C_2O_3 or C_2O_2,O depending on what he wanted to emphasize).

In almost all cases, and contrary to the approach of (e.g.) Wurtz and Kekulé, Kolbe sought to identify and depict a single carbon atom or radical that was central and fundamental to a given molecule. To see this, look again at his formulas (above) for acetic acid, aldehyde, the normal and pseudoalcohols, and acetone. All are built around a central carbon radical C_2. For Wurtz and Kekulé glycol was a symmetrical dialcohol with the constitution:

$$\left.\begin{matrix}C_2H_4\\H_2\end{matrix}\right\}O_2$$

18 Kekulé’s formula for glycol. Source: Kekulé, in Anschütz, 2:161 (1860).

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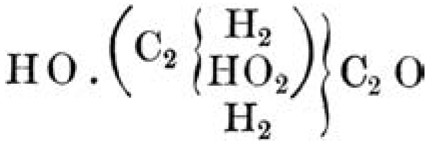
[12] Liebig to Kekulé, 28 December 1863, in Anschütz, 1:238. For further details on all of these issues, see Rocke and Heuser, *Liebig und Kolbe* (1994).

No atom is central in this formula.[13] By contrast, for Kolbe (using C = 6, O = 8), glycol must have the formula:



$$HO\,.\left.\begin{matrix}\left(C_2\left\{\begin{matrix}H_2\\HO_2\end{matrix}\right.\right)\\H_2\end{matrix}\right\}C_2\,O$$

19 Kolbe's formula for glycol. Source: Kolbe, *Ausführliches Lehrbuch der organischen Chemie* (1859), 1:734.

In this formula, we have two tetratomic C_2 radicals, and we see that each has combined with four other radicals—the first (the one on top) with two hydrogen atoms and a hydrogen peroxide group, the second (to the right) with an oxygen atom and two hydrogens, and with each C_2 radical also combining with the other. The C_2 radical contains two atoms, hydrogen peroxide (HO_2) three, but each acts chemically as a unit.

And here is the point: Kolbe chose to portray one of the two "carbonyl" radicals—the one to the right—centrally and asymmetrically, forming the base upon which the molecule is built. And notice also that for Kolbe "atomicity" meant primarily the tetratomicity of "carbonyl," C_2. At least by implication, nearly everything else that appears in his formulas is monoatomic—oxygen atoms, hydrogen atoms, and compound radicals. Kolbe's goal was to identify that single governing radical, which he called the "fundamental radical" (Grundradikal), or "root" or "base" radical (Stammradikal), upon which the molecule as a whole depended.

So whereas the structure theorists sought to create, in effect, a chemical democracy, by writing formulas that assume in principle the equal role of every atom in the molecule, Kolbe's formulas, reflecting his conception of molecular constitutions, was intrinsically hierarchical. In some respects, there was little difference between operating from one or the other of these kinds of formulas, for each kind could rather easily be translated into the other, presuming that one were sufficiently familiar with both sets of conventions. In other ways, however, there were substantive differences. Take, for example, the two different formulas for glycol reproduced above, and imagine replacing one of the two hydroxyl groups, or one of the hydrogens attached directly to carbon, with a chlorine atom. For the case of the structuralists' symmetri-

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[13] *LB,* 1 (1859).

cal glycol, one would predict that such replacement can result in only one isomer. For the case of Kolbean glycol, however, the two hydroxyls or the two sets of hydrogen atoms obviously occupy distinctly different places in the molecule, and so replacement of one or the other will result in one or the other of two different isomers.

As a consequence of such differences, and considering also that Kolbe placed such high heuristic confidence in his formulations, in the late 1850s and 1860s he was not shy about making public predictions concerning the expected discovery of new isomers. In many cases he was disappointed in the outcomes. He often conceded failures of his predictions—he would carry out several such unsuccessful investigations himself—but he also often temporized, suggesting, not unreasonably, that we simply have not yet found the right conditions to produce the expected isomers. According to his own interpretations of his own formulas, for instance, glycolic and lactic acid ought to exist in two distinct modifications each. There should be reduced forms of glycol and glycolic acid that are not identical with those produced by Wurtz. There must exist two oxalic acids, and two distinct ethyl oxalates. One ought to be able easily to dehydrate glycol directly to aldehyde. And so on. All of these were simple predictions inferred from the way he wrote his constitutional formulas. None of these predictions was sanctioned by structure theory, and none was ever realized in the laboratory.[14] And it should be noted that we have here a salient example of the way that the varying heuristics of particular formulas written in particular ways may sometimes obtrude into the more general heuristics of mental imagery. We saw some parallel instances of this in the last chapter.

Kolbe maintained high confidence in his approach, despite these disappointments, partly because several other of his risky public predictions *were* successful. He proved his hypothesis of the relationship of malic and tartaric acids to succinic acid by the simple means of directing a student to reduce the former to the latter, a paper that greatly impressed Liebig, for one.[15] But the most celebrated such case was that of the two "pseudoalcohols," dimethyl and trimethyl alcohol (i.e., isopropyl and tertiary butyl alcohol), whose existence he had foretold in the installment of his textbook published at the end of 1857 and repeated in his 1860 journal article. Charles Friedel, an Alsatian student of Wurtz, produced the first of these in the summer of 1862 by reducing acetone, and Butlerov produced the second the following year by reacting phos-

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[14] *QR,* 190–200, 214–24.

[15] Schmitt, "Umwandlung" (1860), 106–11.

gene with methyl zinc.[16] Kolbe was elated. He was utterly confident that his way of looking at the matter was the right one, and that the "type theorists" (who actually by this time were structure theorists) were building a ramshackle theoretical structure that would soon collapse.

The basis for Kolbe's loathing for the newer structural formulas is difficult fully to comprehend. Surely part of the reason, as explained above, is Kolbe's allegiance to vestiges of electrochemical dualism and radical theory, but that cannot explain the intensity of his feeling. Another part of the reason must be related to psychological, religious, and political factors. To Frankland he wrote disparagingly about "Kekulé, whose imagination long ago bolted with his understanding. It is impossible to gain any picture of the spatial arrangement of the atoms [at this time], and we will probably never get to that point, either. So we should also guard against drawing up an image of this [spatial arrangement] for ourselves, just as the Bible warns us against making a visual representation of God."[17] Kolbe had a personality quite different from Kekulé's, as Kolbe observed. Kekulé loved the visual, and he instinctively (and consciously) relied on imaginative powers. By contrast, Kolbe would never admit to anything like that.

Excursus: Looking through the Stereoscope

We have seen in chapter 4 that during the years 1862–64 Erlenmeyer developed the theory that the multiple valence units of a polyvalent atom may well be distinguishable, and he did so along lines suggestive of Wurtz's subatomic speculation. In this way he could explain why the valence of an atom sometimes appeared to vary: e.g., a carbon atom can form CO because it uses its two strongest valence units to do so; but under some circumstances it can still activate the two remaining weaker units to form CO_2, $COCl_2$, CH_4, etc. This hypothesis could also explain some cases of "absolute isomerism," such as the purported isomerism of "methyl" gas, CH_3CH_3, with "ethyl hydride," C_2H_5H, by assuming that distinguishable (nonequivalent) "affinity units" of the

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[16] Friedel, "Transformation" (1862); Friedel, "Sur l'alcool" (1863); Kolbe, "Chemische Constitution" (1862), 687–90; Butlerov, "Studien" (1863); Butlerov, "Tertiärer Pseudobutylalkohol" (1864).

[17] "[W]ie denn schon z.B. bei Kekulé seine Phantasie mit dem Verstande längst durchgegangen ist. Es ist unmöglich, und wir werden wohl auch nie dahin gelangen, über die räumliche Lagerung der Atome eine Anschauung zu gewinnen. Hüten wir uns deshalb auch, uns davon ein Bild zu entwerfen, wie die Bibel uns warnt, uns von der Gottheit eine sinnliche Vorstellung zu machen." Kolbe to Frankland, 23.7.1866, EFA 01.02.1505.

two carbon atoms are used to form these two compounds. Butlerov had briefly suggested something similar in his September 1861 "chemische Structur" paper.[18]

The following year Butlerov developed this idea further.

> If we take a rough example [ein grobes Beispiel] and imagine the carbon atom as a tetrahedron, each of whose four faces is capable of binding a hydrogen atom, we cannot determine and designate either the position or the action of each of these faces, but nonetheless it is possible for us to assert that the action is different for each face, and this difference can be experimentally demonstrated and characterized, even though we cannot tell which face corresponds to this or that action.[19]

So the four tetrahedral faces of carbon in Butlerov's imagined example were not equivalent: two were "primary" valences, two "secondary." Such a distinction could explain several curious examples of isomerism that otherwise appeared inexplicable. Alexander Crum Brown examined this hypothesis two years later. He argued from known reaction sequences to demonstrate there was no way to formulate the hypothesis in a self-consistent fashion to explain such isomerisms, unless one were also to assume that primary valences can spontaneously become secondary, and vice versa.[20] Crum Brown had effectively closed down this line of argument.

These variable-affinity hypotheses intersected with emergent theories of carbon-carbon multiple bonds. In January 1862 Erlenmeyer became the first to publish the explicit assertion that a carbon-carbon double bond was the explanation for the formula of C_2H_4 for ethylene, and that a triple bond accounted for the C_2H_2 formula for acetylene. These claims reconciled the respective empirical formulas with carbon tetravalence.[21] Kekulé had depicted double bonds between carbon and oxygen and between carbon and nitrogen in his 1859 textbook fascicle, and had hinted at carbon-carbon multiple bonds; he first made this suggestion explicit in the case of unsaturated diacids in the summer of 1862, but also left open the possibility that the unsaturation was produced by two unsatisfied affinities on a single carbon atom. He asserted that these hypotheses amounted to the same thing.[22] Kolbe then pub-

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[18] Butlerov, "Chemische Structur" (1861), 556.

[19] Butlerov, "Verwandtschaft" (1862), 299.

[20] Crum Brown, "Theory" (1864).

[21] Erlenmeyer, "Theorie" (1862), 28. For a general treatment of the history of the double bond, see Baker, *Unsaturation in Organic Chemistry* (1968).

[22] Kekulé, "Betrachtungen," 9–13.

lished an article on the constitutions of the same compounds. He excoriated Kekulé for having attempted to specify the "spatial arrangement of the atoms in a compound, which I consider futile from the start." Kolbe's suggestion for the constitution of these unsaturated substances was that one of the carbon atoms was diatomic (i.e., divalent).[23]

In a commentary on both these papers, Erlenmeyer pointed out an apparent error that Kekulé had committed in suggesting that unsaturated (free) affinities and double bonds are equivalent ideas, and lead to the same formulas. They aren't, and they don't.[24] But he also had some critical comments for his other friend:

> Concerning Kolbe's ideas, they are in fact nothing other than attempts to determine the spatial arrangement of the atoms in a compound, despite Kolbe's comment that he considers such attempts to be futile from the start. It is essentially one and the same thing whether I go back directly to the elements and seek to determine their arrangement, or whether I use as a means to the same end the arrangement of the radicals (which consist of elements and thus involve a conception of the arrangement of these elements).[25]

Erlenmeyer had recently averred that his own chemical formulas were intended to specify the "topographic position" (topographische Lage) of each atom, or to provide a "positional diagram" (Situationsplan) for the molecule. In using such phrases, he wrote, he was certainly not suggesting that one could specify the "actual positions" of the atoms, but rather simply a "topographical analogy of the derivative with the mother substance." It was time, he wrote, to abandon "mere reaction formulas" and embrace "relative constitutional formulas."[26] Using slightly different vocabulary, Erlenmeyer here was ratifying the position that Kekulé, Wurtz, and Butlerov represented. Chemists of this time could not determine exact stereospatial positions of unseen atoms within a molecule. However, pace Gerhardt, their formulas could do more than simply summarize reactions. For many simpler organic substances chemists often could map out the connectivity of the individual atoms—the "chemical structure" of the molecules that compose them.

Erlenmeyer had also already begun to develop in detail his own theory of variable affinities. This theory was described at the end of

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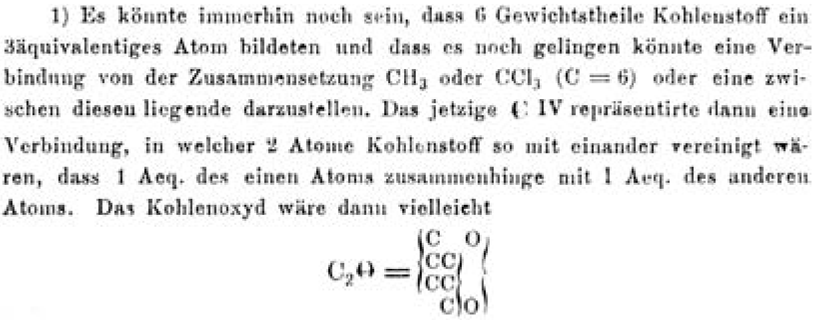
[23] Kolbe, "Isomerie" (1863).

[24] This point was discussed in more detail in chapter 5, as Crum Brown presented the same criticism the next year.

[25] Erlenmeyer, "Bemerkungen zu den beiden vorstehenden Abhandlungen" (1863).

[26] Erlenmeyer, "Bemerkungen zu der vorstehenden Abhandlung" (1862).



1) Es könnte immerhin noch sein, dass 6 Gewichtstheile Kohlenstoff ein 3äquivalentiges Atom bildeten und dass es noch gelingen könnte eine Verbindung von der Zusammensetzung CH_3 oder CCl_3 ($C = 6$) oder eine zwischen diesen liegende darzustellen. Das jetzige C IV repräsentirte dann eine Verbindung, in welcher 2 Atome Kohlenstoff so mit einander vereinigt wären, dass 1 Aeq. des einen Atoms zusammenhinge mit 1 Aeq. des anderen Atoms. Das Kohlenoxyd wäre dann vielleicht

$$C_2O = \left\{\begin{array}{ll} C & O \\ CC & \\ CC & \\ C & O \end{array}\right.$$

20 Erlenmeyer's hypothesis of carbon monoxide formation. Source: Erlenmeyer, *Zeitschrift für Chemie* 6 (1863): 732n.

chapter 4, but I did not mention there an interesting speculation that pertains to the present subject. It could well be, Erlenmeyer wrote, that Kolbe is right that carbon atoms actually weigh 6 rather than 12 relative to H = 1, for such half-sized carbon could be triatomic (i.e., trivalent) rather than tetratomic. One then need only suppose that they normally combine with each other pair-wise, using one of their three affinity units each, such that each C = 6 carbon couple—comprising together one normal carbon atom of C = 12—has four affinities left over and so becomes tetratomic. One can then imagine the possibility of a *double* bond between these two triatomic miniatoms, whence a total of only two affinity units would then remain left over; and that can explain what we normally call diatomic carbon (C = 12).[27] This suggestion that the atomists' C might actually be better expressed as Kolbe's C_2 represents a degree of theoretical rapprochement towards Kolbe, and indeed in the early 1860s these two chemists began to correspond regularly, visit each other occasionally, and develop a real collegial friendship.

At the end of 1863 Erlenmeyer published a paper in his *Zeitschrift* seeking to explain and defend Kolbe's views, which he thought were being neglected and poorly understood in the international chemical community in general, and among the type theorists in particular.[28] Kolbe's theory is a type theory, like Gerhardt's, but there are some obvious differences, Erlenmeyer declared. Kolbe affirms, as not all Gerhardtians do, that a substituting atom or radical comes into the same spot in the molecule that the departing element came from, which is why

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[27] Erlenmeyer, "Betrachtungen" (1863); Erlenmeyer, "Vorläufige Notiz" (1863), 732n.

[28] Erlenmeyer, "Vorläufige Notiz."

he can be more definite that he is writing absolute formulas. But the contradistinction to type theory here (Erlenmeyer wrote) is really misleading, for in practice the "typists" (die Typiker) operate in the same way. When one examines the different multiple formulas for the same substance that typists declare permissible, they usually turn out to be using different symbolic patterns to portray what can be seen to be at heart precisely the same arrangement. To demonstrate this, Erlenmeyer chose as an example—as Kekulé also had in 1859—the various current type formulas for acetic acid.

> Do all these images, which appear to be so different, really express distinct bonding patterns? If one considers them all properly and correctly, they can all, as it were, be stereoscopically united to a single representation, for all these formulas state the same thing expressed in Kolbe's formula, which he proposes as the only possible constitutional formula. The typists are thus unknowingly of the same opinion as Kolbe, that there is only one single rational formula for a given substance.[29]

In the guise of a defense of Kolbe, Erlenmeyer was making the case that there was little substantial difference between Kolbe and the type theorists, and indeed between the various competing versions of type and structure theories. He was urging everyone to take a step back in order to attain a clearer perspective and really try to understand what each was really doing and saying. There were many disputes over details and over the form in which conclusions should be expressed, but Erlenmeyer was right that most active researchers were striving for similar goals and were not disagreeing over fundamentals—or at least not as much as some thought they were. What mattered was that unified inner vision—the look through the stereoscope to see the single image actually intended—rather than being distracted by this or that unessential detail in the particular formula that happened to be chosen to express the structure. In effect, Erlenmeyer was urging that a kind of holistic mental imagery could help to reconcile the (only apparently discordant) heuristics of various written formulas.

No doubt Kekulé and Butlerov each felt that he had been perfectly clear in his respective writings, and had no need to listen to Erlenmeyer's preaching. Kekulé had already broken contact with his former

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[29] Ibid., 730–31. The stereoscope, a common parlor device, visually unites two different photographs of the same scene taken from different angles to create a three-dimensional effect. Erlenmeyer's metaphor was not intended to imply a stereospatial or stereochemical view of formulas. His point was that different formulas are intended simply to view the same molecular object from different (mental) points of view, a point made earlier, e.g., by Kekulé.

friend. Despite his eminence, Kolbe had few allies in the European chemical world; he looked past the various parts of the article that might have been anathema to him had they appeared in a less flattering package, and expressed gratitude.[30] Butlerov also responded positively, and continued to send his highly consequential and influential structuralist studies to Erlenmeyer's *Zeitschrift*.

Molecular Democracy or Autocracy?

In the fascicle of his textbook that appeared in 1864 Kekulé responded to this and certain other claims, such as those of Butlerov. Although he continued to use chemical formulas that had the external appearance of type formulas, he wrote, readers should not be misled into believing that he had failed to move beyond Gerhardt's theory of a decade earlier. He declared that throughout his book he had consistently given preference to one sort of rational formula, namely, that derived from the "theory of atomicity of the elements." To be sure, he had only occasionally considered it necessary or appropriate to use his fully resolved graphic formulas (by which he meant his sausage formulas). Obviously, only one such graphic formula could be assigned to any well-investigated compound. If one uses less-resolved formulas, however, then different formulas are surely permissible for the same compound, to conveniently emphasize different aspects of the substance's composition or reactivity, or to express one's ideas in different formula styles. But even type formulas *can* be used to express a fully resolved formula. *Whenever* one writes such a resolved formula, *however* one writes it, radicals thereby vanish, because we have succeeded in going back to the very atoms themselves; but that is nothing more than the theory of atomicity.

> For that reason it is clear that all formulas that reflect such considerations can express nothing other—or at least nothing more—than the graphic formulas which represent the molecules of carbon-containing compounds as contiguous juxtapositions [Aneinanderlagerungen] of carbon atoms. . . . [O]nly completely-resolved graphic formulas, such as the [sausagelike] graphic formulas to which I have fre-

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[30] "Indem Sie es unternehmen, für meine Ansichten über die Zusammensetzungsweise der organischen Verbindungen, den dagegen allgemein verbreiteten Vorurtheilen gegenüber, ein besseres Verständniss anzubahnen, laden Sie eine etwas gefährliche Arbeit auf sich, denn eine grosse Zahl Chemiker wollen *durchaus* nichts davon wissen, und werden es Ihnen übel nehmen, dass Sie ihnen zumuthen, den chemischen Fragen ein ernstes Nachdenken zu schenken." Kolbe to Erlenmeyer, 12 February 1864, HDN.

> quently made reference, are able fully to express the views which we have offered concerning the mode of combination of the constituent atoms in the molecule.[31]

Kekulé may have hoped that this declaration would finally clear the air, but if so, he was too optimistic. Soon thereafter Erlenmeyer wrote Butlerov: "I think we are the only two chemists in the world who understand each other and everyone else. Besides us, I know of no one else who understands us, and none who understands everyone else, as we do. Most typists understand Kolbe not at all; Kolbe understands the typists not at all; Kekulé doesn't understand himself, Kolbe, or us. Wurtz is in the same position. . . . Who's left?"[32] But Erlenmeyer was surely underestimating the degree to which leading chemists did understand each other.

It was a curious time in the history of the science, especially in Germany. Since around 1840, Liebig, Wöhler, Bunsen, and others had been teaching much larger numbers of students than previously, and during the 1850s and early 1860s there were few academic positions available for the sharply increasing supply of qualified candidates. Simultaneously, there was (as we have seen) a relatively abrupt opening up of the science itself, what I have elsewhere called the "quiet revolution" of the 1850s. But this, too, was a contested and sometimes perplexing extended event. Hugo Müller, Kekulé's friend from London, complained, "it is an accursed business doing chemistry these days; one can never be safe from being overtaken by others."[33]

The result of operation of these separate factors was a fascinating, confusing, dynamic, and above all highly competitive period, in which many younger members of the chemical community were avidly looking for small advantages in theoretical outlook or terminology, as well as in their experimental practice. The same context explains why many chemistry textbooks of this period, coming out as they often did in successive fascicles over many years, make such interesting reading. Younger and midcareer chemists had a strong interest in emphasizing the novelty and distinctiveness of their viewpoints, while some of their older compatriots threw up their hands at the apparent furious pace of change.

In 1871 Erlenmeyer provided a brief interpretive history of structure

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[31] *LB,* 2:245–50 (1864). Kekulé first coined the metaphor of a carbon "chain" (Kette) the following year.

[32] Erlenmeyer to Butlerov, 9 July 1864, in Bykov and Bekassova, "Beiträge" (1966), 192.

[33] "Es ist heutzutage eine verfluchte Geschichte Chemie zu arbeiten, man ist nie sicher nicht von Anderen überrumpelt zu werden." Müller to Kekulé, 28 February 1864, AKS.

theory in the form of a 3500-word (!) footnote that appeared in the published version of a formal oral address to the Royal Bavarian Academy of Sciences. The occasion was Bavarian King Ludwig's twenty-sixth birthday, Erlenmeyer having been appointed full professor at the Munich Technische Hochschule three years earlier. Erlenmeyer wrote that Kekulé had "adhered strictly to types" even after having proclaimed in his landmark paper of 1858 that one must go back to the elements of which molecules are composed, for he had in the same paper declared that "rational formulas are nothing but reaction formulas." Erlenmeyer asserted that both the Williamson-Kekulé type theory and also the Kolbe type theory had been "one-sided," because both theories usually designate a single atom as the foundation for the molecule; the atom or radical on one side of the typist's bracket really is no different chemically than the atoms or radicals on the other side, and ought not be given special status. He went on to assert that in the period between 1858 and 1861 he himself had been a loyal adherent of "Kekulé's type theory," but in 1861 he "began to consider chemical compounds as combinations of radicals, by deriving the valence of the latter from the valence and bonding patterns of their elementary components. I thus broke with the type theory and ceased considering compounds in a one-sided fashion."[34]

Erlenmeyer's autobiographical statement was more accurate than his history. He correctly articulated here a major characteristic of structure-theoretical thinking, namely, the flexibility to imagine the molecule in many different lights, from many different chemical perspectives, thus according each part of the molecule its own chemical importance rather than arbitrarily elevating one feature to fundamental status. But this was not a new idea in 1861, for in 1858 both Kekulé and Couper had been very clear about this central notion. The formulas and models that Kekulé adopted for teaching and textbook from 1857 make his conviction obvious, for *sausages* (like chains) *have equal links*.

Indeed, all of Kekulé's metaphors and images for carbon atoms and their interconnections—sausage models and diagrams, lines, chains, and skeletons—suggest a linked series of equivalent component parts, not a hierarchical structure. And in fact we have seen that much evidence shows that Kekulé broke with Gerhardtian type theory (in a similar sense as Erlenmeyer described as applying to himself) as early as 1854. In 1858–61 Erlenmeyer may, as he stated, have adhered to the type theory in organic chemistry, but he was not engaged with original organic research at all in this period, his activities being more oriented

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[34] Erlenmeyer, *Aufgabe* (1871), 27.

towards pharmacy, inorganic chemistry, and chemical technology. Further, we have seen that during the period 1861 to 1864 Erlenmeyer had acted as a peacemaker between Kekulé and Kolbe, and never criticized either of them as "one-sided."

Kolbe proudly embraced the hierarchical idea of molecular structure, even in the face of Erlenmeyer's criticism of one-sidedness. Ever since his textbook fascicle of 1857 he had been clear that higher hydrocarbon homologues are formed by asymmetric substitutions, not chain formation. Upon gaining the editorship of the *Journal für praktische Chemie* at the beginning of 1870 he acquired an unimpeded platform for chemical sermonizing, and he used it aggressively. In Kolbe's telling, superficial structure theorists simply scribble down carbon chains on paper, taking care only that no valences are left unsatisfied, and pleased that no profound understanding of chemistry is necessary to develop any number of bonding schemes. The real culprit in this sad state of affairs, he wrote in 1870, is the "fashionable delusion that chemical compounds can be compared to chains, open or closed, whose identical links—the identical, equivalent elementary atoms—are all of equal significance, and possess the same rank." The fact that just two years earlier he had finally capitulated and adopted $C = 12$ and $O = 16$ did not reduce his confidence in his own conceptions.

> If a simile is permissible at all, I would compare a chemical compound of any sort rather to an organization, all of whose members are subordinate to a principal, such as in a military command with ranks consisting of superiors and inferiors. In a regiment of soldiers, privates are lower in rank than the commanding officers, but the latter also have various ranks among themselves. Although each of these officers has, or may in principle acquire, the capacity to command the regiment, there can normally be but *one* commander-in-chief, all the others being subordinate in service to him.

So for instance a methyl group can be compared to a commando group consisting of three privates (the three hydrogen atoms) and a corporal (the single carbon atom—now for Kolbe, as for everyone else in Germany, C rather than C_2). This methyl group can substitute as a whole for the hydrogen atom of another hydrocarbon radical, thus becoming a member of a higher-order organization, whose carbon atom will then have a higher rank than corporal (presumably sergeant, though this is where Kolbe left off with military terms). Any number of such further substitutions may take place, and at the head of all is found the "base radical" or the "dominant principal" (Stammradikal, dominierendes Haupt), namely, the single carbon atom upon which the entire molecule depends.[35]

As everyone else did, Kolbe drew his images of molecules from metaphors that spoke to him personally. The following year he came up with a new one: "In my conception, the constitution of a chemical compound is like that of a well-organized constitutional state, with one sovereign and a number of subordinate members standing nearer or farther from him, which is organized such that in place of a given individual, a group consisting of various individuals of equal rank can function." He used the four smallest alcohols—methyl, ethyl, propyl, and butyl alcohols—as a case in point. He provided the four resolved formulas in his usual bracket notation, but this time he added additional graphic features to drive his point of view home. In every case, the base radical was the carbon atom to which the hydroxyl group was attached, and this "C" was printed in a large, bold font to make that clear. Methyl alcohol just had the one (bolded) C, but ethyl alcohol also had a methyl group, now enclosed in a box to make clear that it substituted as a whole, rather than by a carbon-to-carbon bond. As one proceeded through the higher homologues, each substituting hydrocarbon group was printed in an ever smaller font, all were enclosed in nested boxes like Russian dolls, and each formula ended in the last methyl group, which grew ever smaller at each additional step. This methyl "must be considered to be bound as an integral unit to the principal carbon atom of the alcohol, as was the case with the simple hydrogen atom whose place it took."[36]

This article appeared shortly before Erlenmeyer's academic address, and in his 3500-word footnote Erlenmeyer took the opportunity to respond. He agreed with Kolbe that methyl substitutes for hydrogen to form ethyl, but strongly disagreed with Kolbe's conclusion from this. Methyl, he wrote, is a monovalent radical because tetravalent carbon has only three of its units satisfied by three hydrogen atoms. What other conclusion can one reasonably come to than that the fourth valence *belongs to the carbon atom,* rather than to the four-atom group as a whole? Moreover, in the alcohol molecule the hydrogen that the methyl radical replaced was clearly bound directly to the carbon atom that holds the hydroxyl group; so the methyl group must likewise be attached directly to that carbon atom. Thus we can see, looking at both

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[35] Kolbe, "Abkömmlinge" (1870), 292–94.

[36] Kolbe, "Structurformeln" (1871), 128–29.

ends of this bond, that there is a *carbon atom* at each end, not a compound radical considered as a whole.[37]

So Kolbe's logic was faulty, according to Erlenmeyer. Even worse was the "type-theoretical one-sidedness" that Kolbe still refused to abandon, even long after everyone else had done so. He had designated the end carbon as the dominant atom in each of these compounds. But was it not the entire functional group CH_2OH, and not just the carbon atom of that group, that conferred the properties of an alcohol on each of these substances? And how can this carbon atom dominate the others if according to Kolbe it is not the carbon atoms themselves, but rather the radicals, that hang together? And—here Erlenmeyer did Kolbe's military metaphor one better, adding a double entendre on the chemist's word "attack"—would it not be better to consider the CH_2OH group not as the command post, but as the opposite, an advance outpost (Vorposten) in service of the rest of the molecule, for this is where the first attack usually comes?

The most serious problem, Erlenmeyer emphasized, was that Kolbe's hierarchical formulas were empirically deficient. For instance, compare the eighteen-carbon stearic acid with the two-carbon acetic acid. The two substances have very different properties, though by Kolbe's reckoning they are both built upon the same dominant carbon atom. Just as problematical, Kolbe had to assume that in the stearic acid molecule there exist eighteen distinctly different carbon atoms. Then, in a sarcastic aside, Erlenmeyer noted that if stearic acid were to be written in Kolbe's style with radicals of decreasing size enclosed in nested boxes, one would need a microscope to see the methyl group at the end of the molecule. To put it simply, Erlenmeyer concluded: "Kolbe has remained a type theorist while most other chemists have abandoned the type standpoint."[38]

Finally, to Kolbe's argument that structure theory was too seductive for young chemists, for they might imagine that they were doing real chemistry by drawing pretty pictures all day without troubling themselves to think carefully about the substances themselves, Erlenmeyer turned the tables. It was not the structuralists, but Kolbe who was seducing young chemists into an easy but deeply misleading road. Certainly it was a simple matter, in fact far *too* simple, to decide on a "fundamental radical" like CH_2OH or CO_2H, and then imagine that one's job was done, rather than to consider in all their complexities, as structural-

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[37] Erlenmeyer, *Aufgabe,* 28–29.

[38] Ibid., 30–32.

ists needed to do, the chemical roles and functions of *all* of the atoms in the molecule. Taking Kolbe's metaphor of a constitutional state and once again turning the trope on its head for satirical effect, Erlenmeyer wrote:

> Like that of a well-organized state, the constitution of a chemical compound is characterized precisely by the fact that all of its members find themselves in a condition of mutual dependency, the inferior not merely dependent on the superior, and both not simply dependent in the last analysis on the chief of state. In a chemical-constitutional state, every elementary atom has a seat and a vote whenever the chemical fate of the state is to be decided; every radical in the commonwealth brings its justified characteristics into play, by expressing the functions corresponding to its topographical position as well as to the nature, customs, and the habits of its constituents.[39]

In eight years, Erlenmeyer had passed from being the principal (almost the only) defender of Kolbe's unique point of view to being its most acute critic. Kolbe never forgave him; to Kolbe thereafter, Erlenmeyer was a "fantasist," reminiscent of the old Naturphilosophen, "who also speculated without a solid foundation, up into the blue."[40] Erlenmeyer, like Kolbe, had a habit of alienating all of his friends with his critiques; their earlier rapprochement had obviously been doomed from the start.

The Revenge of Jupiter's Children

Kolbe was not the only mature chemist of his day who had little patience or appreciation for structural formulas. In 1868 Otto Erdmann (Kolbe's senior colleague in Leipzig) privately referred to those who used them as "bright-born jovial children of Jupiter," an allusion to a passage in Schiller's astrological drama *Die Piccolomini* (1798), hence analogizing structural formulas to the Hermetic mysteries.[41] The three

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[39] Erlenmeyer, *Aufgabe,* 32–33. I have tried to fashion an English translation that reflects Erlenmeyer's repeated double entendres between chemical and political terminology. The German of the last word of the translation is "Einwohner."

[40] "Er ist als Theoretiker Phantast und gleitet mehr und mehr in die Bahnen der alten Naturphilosophie, die auch ohne festen Boden ins Blaue hinein speculirte." Kolbe to Volhard, 2 July 1874, ADM 3669.

[41] "Die sieht das Aug' nur, das entsiegelte / Der hellgebornen heitern Joviskinder." ("Only that eye can see these things, the unsealed [eye] / Of the bright-born jovial children of Jupiter.") Erdmann was indirectly criticizing Carl Graebe's use of structural formulas (Universitätsarchiv

éminences grises of German chemistry ca. 1870, Liebig, Wöhler, and Bunsen, all ignored modernist chemical theory in general, and structural chemistry in particular, and in private all spoke slightingly or even contemptuously of the proliferation of structural formulas. After Liebig's death (1873) Kolbe urged his two former teachers and longtime good friends, Wöhler and Bunsen, to join him by openly denouncing structural excesses, but both adamantly refused to carry their private negative opinions into the public sphere. There is no evidence that Wöhler or Bunsen had any higher an opinion of Kolbe's formulas than those of his enemies, and in fact Kolbe was the only theoretically active German organic chemist of any prominence after about 1870 who refused all concourse with structural formulas.

Seven years to the day after Erlenmeyer's address to the Bavarian Academy of Sciences, on the same anniversary (King Ludwig's thirty-third birthday) the lecturer was Adolf Baeyer, the recently appointed successor to Justus Liebig at the University of Munich. Since his address was directed to a nonchemical audience, Baeyer treated his subject, chemical synthesis, in a richly imaginative fashion and also in a manner that would be, he hoped, generally understandable. He introduced the idea of atomic valence and carbon chains, then wrote, "If one imagines a large number of atoms linked with each other according to these simple laws, one arrives at shapes that can be compared in their arrangement and branchings to a coral or a tree . . . : matter consists of tree-shaped branched atomic systems called molecules." In a synthetic direction, chemists operate like architects, "only instead of mortar they make use of the force of affinity of atoms." Methane forms a "microcosmic solar system," with carbon as the sun and four hydrogens as planets; if one wishes to unite two such suns, then one of the planets must first be removed. The place where the hydrogen-planet formerly stood is now empty, and the carbon-sun exerts its affinity at that place. If two such entities strike one another, the two carbon atoms "stick to each other," and we have now a planetary system with a double sun. Such a process can repeat ad infinitum, forming a long "chain." If one million carbon atoms could be so joined, it would form a molecule visible through a microscope. To take another example, glucose consists of six carbon atoms, to each of which is connected an oxygen atom that has the ability, in a manner "analogous to a fish-hook," to "catch and hold"

Leipzig, Personalakt 515, f 3r, 3v [August 1868]), but he approved Graebe's habilitation anyway. I thank Elisabeth Vaupel for drawing my attention to this document.

other molecules; this explains the basis of biosynthesis of higher organic substances in plants.[42]

Such extreme liberties with both language and science were too much for Kolbe. In an essay in his *Journal für praktische Chemie* he wrote, "It recently transpired that a German chemist had a dream, wrote it down, and used the text as a formal address . . . This address on chemical synthesis is little different from other dreams; it is rich in baroque ideas, illogical developments, audacious leaps of thought, as well as trivialities and irrelevant matters. . . . Adolf Baeyer holds too elevated a position in the chemical world to be ignored or protected from criticism as a speaker before the Munich Academy, indeed not just a speaker, but the plenary speaker on a high occasion." So Kolbe reprinted the speech verbatim—equipped with his own devastating glosses, of course. Parenthetic and footnoted annotations include question marks and exclamation points, as well as the sorts of severe comments that high school teachers are accustomed to insert in their poorer students' papers. He concluded by expressing his confidence that any attentive reader would agree with him "that the speech was more dreamed than thoughtfully composed, and that it is not worthy of a German scholar."[43]

Seeking reinforcement in his censures, Kolbe wrote to his good friends Friedrich Wöhler and Jacob Volhard. But neither Wöhler nor Volhard provided the support Kolbe was seeking. In fact, Volhard's private response was probably as stern a rebuke as Kolbe ever received. Volhard told his former teacher that his criticisms had been disrespectful, uncivil, inappropriate . . . and scientifically unjustified. If one reads the latest work of Clausius, Maxwell, and other physical theorists, he wrote, one would see pretty much the same sort of "imaginative ideas concerning the form of molecules" as in Baeyer's talk, "for it is in fact through the imagination that the direction for exact science is often determined."[44]

Kolbe never relinquished his conviction that hierarchical hydrocarbon radicals are formed by asymmetric substitutions. Because he assigned each carbon atom in an organic compound a distinctive "rank," and because he also continued to believe that the four affinities of carbon atoms were not equivalent (despite ever-increasing empirical evidence to the contrary), Kolbe's theory suggested the existence of a plethora of isomers that were not predicted by structuralists—and (as

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[42] Baeyer, *Chemische Synthese* (1878).

[43] Kolbe, "Chemische Synthese" (1878).

[44] Kolbe to Wöhler, 15 October 1878, Wöhler Nachlass, Göttingen; Kolbe to Volhard, 27 October 1878, ADM 3683; Volhard to Kolbe, 9 November 1878, ADM 3516 ("denn es wird ja häufig durch die Phantasie die Richtung für die exakte Forschung bestimmt.").

even Kolbe had to concede) that were never found. As a consequence, he failed to convince many others in the collegial community of the advantages of his theoretical ideas.

To Kolbe, structural formulas were a part and parcel of modernist social and cultural developments, many of which Kolbe despised as degenerate and corrupt. Like other disturbing manifestations of the modern world, structural formulas were superficially appealing, but seductive in the worst sense; they also betrayed a coarse, sensual materialism. Science must not rely on "crassly material" aids; it must rather "be conceived by the mind, and not mechanically."[45] This avowal was, however, apparently inconsistent with another line that Kolbe emphasized equally often: his own type theory was founded on natural and real entities, as opposed to those of his opponents, who focused on "idealized entities invented [merely] for convenience," types that were nothing more than formal—in fact, fictional. These theorists built imaginary structures in the air with no more reality or scientific justification than their dreams.[46]

One such theorist was Johannes Wislicenus, the earliest prominent defender of stereochemical theory, and therefore a special object of Kolbe's scorn. In a review of Wislicenus's short textbook of organic chemistry that appeared in his proprietary journal, Kolbe asked him rhetorically: "Are you really able to perceive the bonding sequence of the atoms in a chemical compound, which is nothing more than the order in which they follow one another in the molecule, with the bodily eye, either unaided or fortified?" The obvious answer to this question is that atoms cannot be seen with the human eye, even with technological assistance. But then that means necessarily that "you think you can see with your mind's eye, with your imagination. Such a gift of prophetic vision [Sehergabe] has not been given to me," so he sarcastically begged for instruction from Wislicenus, or from the latter's heros, Kekulé and Baeyer, who were obviously similarly gifted.[47]

In addition to these three chemists, Kolbe could well have also named Volhard, Erlenmeyer, Crum Brown, Butlerov, J. H. van't Hoff, Victor Meyer, and many other structuralists. Kolbe's oldest contemporary comrade in arms was Frankland, and it must have been severely disheartening when his friend went over to the dark side around 1864 and began bandying structural formulas with the best of the "fantasist"

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[45] Kolbe, *Kurzes Lehrbuch* (1883), vi–vii.

[46] Kolbe, "Reale Typen," in *Chemische Laboratorium* (1865), 515–19; also, e.g., *Journal für praktische Chemie* 111 (1871): 122–23n; and *Journal für praktische Chemie* 132 (1881): 405.

[47] Kolbe, "Kritisch-chemische Gänge IV" (1883), 362–63.

crowd. In 1871 Frankland wrote Kolbe: "I cannot coincide in your condemnation of the use of constitutional formulae by young chemists. It seems to me that chemists who make no use of their imagination (Odling & Brodie [Jr.] for instance) do but very little original work. The hard dry facts of the science are not likely to excite the enthusiasm of anyone."[48] At first, Kolbe simply refused to acknowledge the disagreement. He replied:

> I am glad to see that we agree on structural formulas. The main distinction of *my* views on the chemical constitution of chemical compounds from those of the true structural chemists is that the latter deny the real existence of compound radicals in compounds. For these people, methyl, ethyl etc. do not really exist in compounds, but rather are only ideal, conventional quantities. . . . You have misunderstood . . . when you say that I reproach young chemists for using constitutional formulas. . . . What I condemn is the modern doctrine of bonds which does not assume the existence of compound radicals, and by which immature chemists are misled to believe that they are capable of explaining the constitution of compounds without the help of exact chemical research.[49]

The correspondence between Kolbe and Frankland continued spottily for years, without resolving this point. Near the end of his life Kolbe pushed too hard, and Frankland was induced, finally, to declare himself clearly in a letter to his friend. He wrote: "That there should be no more such mistakes in future, I here record my Glaubensbekänntniss [confession of faith]: *Chemistry owes its progress from empiricism to exact science entirely . . . to Strukturchemie. Without Strukturchemie there is no science of chemistry.* And allow me to add,—two of the first Strukturchemiker to whom this progress is due were Berzelius and Kolbe!"[50] Kolbe responded,

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[48] Frankland to Kolbe, 19 April 1871, ADM 3567.

[49] Kolbe to Frankland, 21 April 1871, EFA 01.03.600. "Es freut mich, dass wir über die Structurformeln übereinstimmen. Die Hauptverschiedenheit meiner Ansichten über die chemische Constitution chemischer Verbindungen von denen der eigentlichen Structurchemiker ist die, dass letztere die wirkliche Existenz zusammengesetzter Radikale in den Verbindungen läugnen. Methyl, Aethyl etc. sind für diese keine wirkliche in den Verbindungen existirende Factoren, sondern nur ideelle Bequemlichkeitsgrössen. . . . Sie haben . . . missverstanden, wenn Sie meinen, ich tadele den Gebrauch von Constitutionsformeln von jungen Chemikern. Was ich verurtheile ist die moderne Bindungslehre, welche die Existenz zusammengesetzter Radikale nicht annimmt, und wodurch unreife Chemiker verleitet werden, zu meinen, sie seien im Stande, ohne Zuhülfenahme exacter chemischer Untersuchungen die Constitution der Verbindungen [zu] erklären."

[50] Frankland to Kolbe, 23 September 1883, ADM 3573.

> I will gladly take sins on myself that I have actually committed, but to want to make of me a spiritist is *almost* an insult. If you think you can see into the interior of the molecule . . . and perceive how its atoms are sitting, lying, standing, casting fish-hooks (according to Baeyer) . . . then *you* are a spiritist of the first water. . . . I see now that we do not understand each other.[51]

Their correspondence—as well as their friendship—was over. When Kolbe died a year later, his successor at Leipzig was none other than Johannes Wislicenus. Jupiter's children had won the day.

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[51] Kolbe to Frankland, 28 October 1883, EFA 01.02.1526. "Ich nehme gerne die Sünden auf mich, welche ich wirklich begangen habe, aber mich zum Spiritisten machen zu wollen, ist fast Beleidigung. Wenn Sie vorgeben ins Innere des Moleküls . . . sehen, und wahrnehmen zu können, wie darin die Atome sitzen, liegen, stehen, Angelhaken (nach Baeyer) auswerfen . . . so sind Sie Spiritist von reinstem Wasser. . . . Ich sehe jetzt, wir verstehen uns nicht."

SEVEN

Aromatic Apparitions

> Oh! They're dancing Ring around the Rosie! In each molecule there are six carbon atoms, who form a molecular ring with their dark little faces looking in; each carbon gives two of its four hands to one, and one hand to the other of its neighboring atoms, and each tows a hydrogen atom behind it with the fourth hand. How quick and nimble they are, and at the "all fall down" refrain they quickly crouch; even the tiny hydrogens do it! HERMANN KOPP[1]

The prototype of what chemists call "aromatic" substances is benzene, whose empirical formula was known to be C_6H_6 (expressed in atomic weight values) ever since its first isolation from coal gas by Michael Faraday in 1825.[2] The first important study of a series of substances in this family was Liebig's and Wöhler's classic collaboration of 1832 on the oil of bitter almonds (benzaldehyde), during which they prepared a dozen related compounds and deduced that all of them contained a "benzoyl" radical, formulable in atomic weights as the monoatomic entity C_7H_5O. The attractive, pungent smell of almond oil, and the circumstance that the fragrant resin long known to commerce as benzoin had given its name to benzoic acid and related compounds, probably explains why in 1855 A. W. Hofmann chose the adjective "aromatic" as the chemical name for the family, even though most members of this family were in fact odorless.[3]

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[1] *AMW,* 33–34.

[2] Portions of the following discussion partially summarize and partially expand upon and modify Rocke, "Hypothesis and Experiment" (1985), and *QR,* 290–304.

[3] *QR,* 290.

The very next year Hofmann's student William Perkin discovered mauve, the first coal tar dye. Aromatic compounds thereafter became the object of intense commercial interest, even though the structural details of their molecules were not yet known. Today, the overwhelming majority of the millions of known organic substances contain the benzene nucleus somewhere in their structure and therefore are aromatic in the chemical sense (organic compounds of all kinds comprise about 99 percent of known chemical compounds). Consequently, a satisfying scientific understanding of the constitution of benzene, and thus of all aromatic compounds, was historically of crucial importance to the development of chemistry, both pure and applied.

Of course, this judgment is made only with hindsight, and before 1850 it was not obvious that aromatic substances were as important as that, nor even that the relevant substances should be considered as members of a common family. Others besides Liebig and Wöhler studied aromatic substances in the 1830s, including Berzelius, Mitscherlich, Dumas, and Laurent. Laurent called benzene "phène," from the Greek for illumination, hence the modern name of the "phenyl" radical, C_6H_5 (benzene less one hydrogen atom), and "phenol," C_6H_5OH (phenyl hydroxide, or carbolic acid). It soon became clear that benzoic acid was phenyl carboxylic acid, $C_6H_5CO_2H$, and that its relatives in the benzoyl series all contained the phenyl radical. In the late 1840s Hofmann and his English students at the Royal College of Chemistry took the lead in these studies. Hofmann himself had carried out the first investigation of the components of coal tar, many of which were aromatic, and his student Charles Mansfield continued this work, focusing especially on benzene, toluene (which is methyl benzene), nitrobenzene, and aniline (aminobenzene).[4]

It was in the late 1850s, simultaneous with the rise of the coal tar dye industry, that aromatic chemistry became a recognized subfield of organic chemistry. In the course of this chapter, we will see that the development of the structural theory of aromatic substances is an outstanding example of the heuristic importance, indeed indispensability, of visual symbols and mental images in the pursuit of chemical science.

First Approaches to the Problem

When Kekulé and Couper independently proposed what became known as the theory of structure in 1858, it would have been desirable to use

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[4] Hofmann, "Chemische Untersuchung" (1843); Mansfield, "Researches" (1848).

the new theory to explain the constitutions of all known compounds and elucidate all cases of isomerism, but this was not yet possible. Kekulé and Couper reasonably concentrated on the simplest known organic substances. Kekulé did not hazard a public guess as to the constitution of "carbon-rich" hydrocarbons (in which category he included at this time both olefins—members of the ethylene class—and aromatics), simply hinting that whereas the substances whose constitutions he did specify exhibited the "simplest" arrangement of the skeleton of carbon atoms (presumably he meant that they were connected by single bonds), carbon-rich molecules must be arranged in the "next-simplest" way.[5]

This "next-simplest" bonding of carbon atoms seems to have been a cagey reference to the hypothesis of carbon-carbon multiple bonds, possibly even alternating single and double bonds—a hypothesis that is easily portrayed using the sausage models that he had already employed in his classes and that the following year he began to use in print. The empirical formula for benzene suggested to him that the molecule must possess a "denser" structure, as he put it, and this word distinctly implies multiple bonds when Kekuléan sausage carbons are in mind.[6] However, as we have seen in the last three chapters, there were at least four hypotheses at this time that could supply detailed structures to these empirical formulas. In 1864 Kekulé publicly suggested that the structures of what he was by now calling "hydrogen-poor" (olefinic) hydrocarbons probably had "gaps" (free affinity units), while "carbon-rich" (aromatic) hydrocarbons probably had some sort of arrangement of multiple bonds between carbon atoms. This, at least, was consistent with the experience that olefins eagerly accepted the addition of hydrogen or chlorine atoms, while aromatic substances did not. After all, it would seem logical that free affinity units of olefins would most readily seize hydrogen or chlorine, while the double bonds of aromatics might well be stronger and thus more impervious than single bonds.[7]

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[5] Kekulé, "Chemische Natur des Kohlenstoffs" (1858), 156.

[6] Moving from single to multiple bonds as portrayed in Couper's, Crum Brown's, or Frankland's graphic formulas, no matter what theory of unsaturation is applied, does not increase the *density* of the molecule. But it does if one uses the sausage formulas, for here the carbons actually move more closely together when they form double or triple bonds.

[7] *LB,* 2:398. Again, all this makes most sense when one visualizes "sausage" structures. The terms "hydrogen-poor" and "carbon-rich" appear from a modern perspective to be semantically equivalent, since for hydrocarbons either term implies the other. However, in the Kekuléan context, sausages with "gaps" can indeed be considered "hydrogen-poor," while sausages shoved together to create double bonds are indeed "carbon-rich." This is another datum that suggests

The stock in trade of structure theory was explaining otherwise mysterious cases of isomerism. In the first fascicle of his textbook (1859), Kekulé offered a structural explanation for one case of aromatic isomerism, namely, benzoic acid and salicylous acid.[8] In Kekuléan terms the two substances were "metamers," or what we now call ordinary structural isomers. But subtler sorts of isomerisms were showing up in the aromatic realm. Even before structure theory appeared on the scene, chemists had recognized many cases of isomerism among double-substituted benzene: two distinct dihydroxy benzenes, two distinct nitrophenols, two distinct nitrobenzoic acids, two distinct aminobenzoic acids, two distinct chlorobenzoic acids, and two distinct hydroxybenzoic acids. Kekulé mentioned the last of these in 1859, and declared what he called "oxybenzoic acid" to be an "isomer in the narrower sense" (i.e., a nonstructural isomer) of salicylic acid. He commented that there must be some unknown difference in the composition of the "atomic groups that are assumed as radicals in their formulas."[9]

Aromatic hydrocarbons and aromatic acids proved to be challenging sets of laboratory objects, the former because they were extremely difficult to separate cleanly, and the latter because even the tiniest impurities often significantly altered their properties. Several chemists noticed that the benzoic acid obtained by reducing salicylic acid seemed to be different from (i.e., isomeric with) conventional benzoic acid, and this putative isomer was named "salylic acid." Kolbe and his student Eduard Lautemann were the first to discover the substance, and Kekulé's good friend Hugo Müller (still working with De la Rue in Islington, London) confirmed the work. Kekulé himself studied the two substances and was not certain at first that they were distinct, but was then (apparently) convinced by Kolbe's experiments. Considering how many isomeric twins among the aromatics had already been discovered, Kekulé suggested that there might well exist two extended parallel isomeric series, one following the benzoic/oxybenzoic acid pattern, the other following the salylic/salicylic acid pattern.[10]

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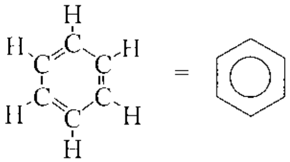
that when Kekulé thought chemically, he thought in terms of his atomic-molecular symbols and models.

[8] *LB,* 1:188. Kekulé's ambiguous type-style formula was probably intended to signify that "salicylous acid" is salicylaldehyde, which is indeed a structural isomer of benzoic acid.

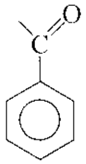
[9] *LB,* 1:188–89.

[10] The first compound in each of these pairs is $C_6H_5+CO_2H$, the second is $C_6H_4+CO_2H+OH$. Kekulé, "Faits" (1860); slightly revised translation "Beiträge" (1861). In the period between these two papers there appeared Kolbe and Lautemann's paper, "Salicylsäure" (1860), and Kekulé commented in the German paper that he now felt more confident that the two substances were distinct.

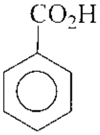
Modern Structural Formulas



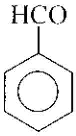
cyclohexatriene (CHT) = benzene



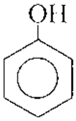
benzoyl



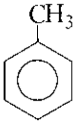
benzoic acid
"salylic acid"



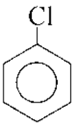
benzaldehyde



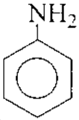
phenol



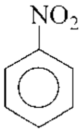
toluene



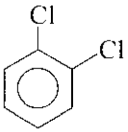
chlorobenzene



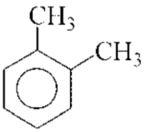
aminobenzene
aniline



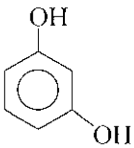
nitrobenzene



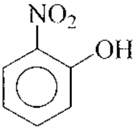
dichlorobenzene



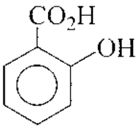
xylene



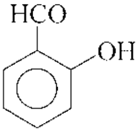
dihydroxybenzene
resorcinol



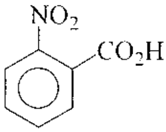
nitrophenol



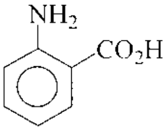
salicylic acid
(hydr)oxybenzoic acid
paraoxybenzoic acid



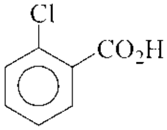
salicylaldehyde
salicylous acid



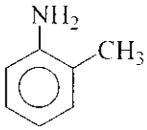
nitrobenzoic acid



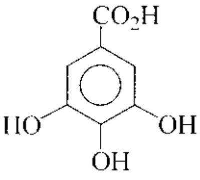
aminobenzoic acid



chlorobenzoic acid



methyl aniline
aminotoluene
toluidine



gallic acid

Kolbe independently made essentially the same proposal, but without the reservations that characterized Kekulé's account. In fact, Kolbe felt so confident as to guess at the different constitutions of the two distinct hydrocarbon radicals (both empirically C_6H_5) that he thought must account for the two different isomeric series.[11] To this, Kekulé responded that the facts of the matter were too few and too insecure to go so far.[12] There were other complications, as well. In the period 1857–59, certain chemists claimed to have isolated an isomer of benzene as well as a lower homologue of benzoic acid. Kekulé tentatively accepted some of these discoveries. But in 1861 experimental doubt was cast on the reality of "salylic acid," and in the following three years such skepticism, also regarding the putative isomer of benzene and the putative lower homologue of benzoic acid, was reinforced by additional work.

By late in the year 1864, well-informed chemists could now say with increasing confidence that certain ideas about benzene derivatives that chemists had generally held in the 1840s and early 1850s were now reconfirmed, namely, that the minimum carbon content of aromatic molecules was six atoms, that the minimum carbon content of benzoic acid derivatives was seven atoms, that there was only one known isomer of benzene, and that there was only one known isomer of each *mono*-substituted benzene molecule (e.g., benzoic acid, phenol, chlorobenzene, aminobenzene, nitrobenzene, or toluene). If all this continued to hold true, the isomeric series to which both Kekulé and Kolbe had drawn attention would be even more puzzling. Consider: although there was always only one isomer of benzene and one isomer of each singly substituted benzene, the moment a *second* substituent came into any aromatic molecule that already held one, chemists always seemed eventually to find *two* isomers corresponding to each formula. The basis for such isomerisms could not inhere in the original starting hydrocarbon, as Kekulé and Kolbe had both once thought, nor even in the singly substituted benzene, for then we would expect to find isomers in these progenitors. How, then, could one explain these di-substituted isomeric pairs?

Then the situation became even more curious. In 1863 chemists began to uncover instances of *three* isomers of certain doubly substituted benzenes. Butlerov's former teacher Nikolai Zinin started the trend with the suggestion, announced in the spring of that year initially only as a preliminary result, that one could in fact distinguish three

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[11] Kolbe and Lautemann, "Salicylsäure," 182–83.

[12] Kekulé, "Beiträge," 161–64.

nitrobenzoic acids; this was definitively verified soon thereafter by Nikolai Sokolov.[13] That summer, two obscure students in Kolbe's Marburg laboratory, Konstantin Zaitsev and Georg Fischer, independently synthesized the same hydroxybenzoic acid, each by a different reaction route, and determined that this new substance was distinct from the two other known compounds possessing the same formula, salicylic acid and oxybenzoic acid. Each man named the substance "paraoxybenzoic acid," the prefix "para" merely indicating, as had become customary, that this was a new isomer of a known compound.[14] Parallel to the nitrobenzoic acids, there were now three distinct compounds that had the empirical formula $C_6H_4(OH)(CO_2H)$.

Four months later, in December 1863, a paper appeared by J. Wilbrand and Beilstein in which they reanalyzed previous work on aminobenzoic acid and suggested that there were in fact three distinct isomers possessing this composition.[15] In a paper published in February 1864, H. Hlasiwetz and L. Barth asserted the existence of a third dihydroxybenzene, which they christened resorcinol.[16] Finally, in a communication dated in August 1864 (though not published until early the next year), Beilstein and F. Schlun announced a third distinct chlorobenzoic acid. They made explicit the obvious regularity that had by now emerged: "What we have stated regarding the chlorobenzoic acids naturally also applies to the other substitution products of benzoic acid. Whereas to date we know but *one* benzoic acid, there are *three* chlorobenzoic acids, and therefore probably three bromo- and iodobenzoic acids; [finally,] Sokolov's experiments have definitely established that there are *three* nitrobenzoic acids."[17] And working with another student at about the same time, Beilstein finally proved without question that "salylic acid" was a phantom; there was but one benzoic acid isomer.[18]

One benzene, C_6H_6, only. *One* isomer only whenever a single substitution for a hydrogen atom takes place in benzene, C_6H_5X, no matter what X is. And now, late in the year 1864, it appeared to those chemists who paid close attention to such matters that *three* isomers would probably always be found whenever a second substitution takes place, $C_6H_4X_2$ or C_6H_4XY, no matter the identity of the substituents X and Y. What was going on?

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[13] Zinin, "Desoxydirtes Benzoin" (1863).

[14] Saytseff, "Paraoxybenzoësäure" (1863); Fischer, "Paranitrobenzoësäure" (1863).

[15] Wilbrand and Beilstein, "Neue Reihe" (1863), 269.

[16] Hlasiwetz and Barth, "Körper" (1864).

[17] Beilstein and Schlun, "Vierte Abhandlung" (1865), 252.

[18] Reichenbach and Beilstein, "Dritte Abhandlung" (1864).

Table 7.1 For each instance, the number of known (or expected) isomers of:

	benzene	monoderivatives (e.g. benzoic acid)	diderivatives (e.g. salicylic acid)
In 1860	2	2	2
In 1862	1?	probably 1	2
In 1864	1	1	3

Enter the Hexagon

The first three years of Kekulé's Ghent professorship were filled with intense work: he published a dozen papers, some of great length and complexity, and completed the first volume of his textbook—in three installments and some 766 pages—all while transforming the teaching of chemistry in Belgium. His letters to friends are filled with business and almost no mention of pleasure, other than the trips he regularly took between semesters. He often complained of the long hours and lack of diversion, appeared to have no particular love for Ghent or Belgium, and expressed homesickness for Heidelberg and the many friends he had made there.[19] But the appearance of the final installment of the first volume of his *Lehrbuch der organischen Chemie* in the fall of 1861 seems to have signaled the need for a slackening of his furious pace. It also appears, having turned thirty-two, that he began to think about marriage.

In equipping his laboratory with gas for Bunsen burners, Kekulé had made the acquaintance of George William Drory, an English engineer who had married a young woman from a well-connected Flemish family and settled in Ghent. Drory was inspector general of the European facilities belonging to the Imperial Continental Gas Association, and directed the gas factory in Ghent; he possessed the additional advantages of both a townhouse and a country estate, and no fewer than five lovely and cultured daughters. The next to youngest (at nineteen), Stephanie, attracted Kekulé's attentions, and he himself proved no less attractive to the young lady.

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[19] In letters to Erlenmeyer of 29 January and 25 November 1859 (HDN) he wrote of his obsessive work habits: "ich bin . . . am allerwenigsten aber zu Vergnügen [gekommen], was hier nun einmal durchaus nicht zu haben ist." Cf., e.g., Kekulé to Baeyer, 24 May 1861 (AKS): "Im Übrigen lebe ich hier zurückgezogener wie je . . . Im Übrigen gehe ich nicht aus, was man so ausgehen nennt . . . alle schönen Mädchen, die wir früher des Ansehens würdigten, sind versprochen."

While courting Stephanie, in the winter of 1861–62 Kekulé began to work on the first installment of the second volume of his textbook. If we are to believe the famous story he told in 1890, it was probably about this time, in the early months of 1862, that another eureka experience occurred.

> During my residence in Ghent, in Belgium, I lived in an elegant bachelor apartment on the main street. However, my study was situated along a narrow alley and had no light during the day. For a chemist who spends the day in the laboratory this was not a disadvantage. There I was sitting, working on my textbook, but it was not going well; my mind was on other matters. I turned my chair toward the fireplace and sank into half-sleep [Halbschlaf]. Again the atoms fluttered before my eyes. This time smaller groups remained modestly in the background. My mind's eye, sharpened by repeated visions of a similar kind, now distinguished larger forms [Gebilde] in a variety of combinations. Long lines [Reihen], often fitted together more densely [dichter zusammengefügt]; everything in motion, twisting and turning like snakes. But look, what was that? One of the snakes had seized its own tail, and the figure whirled mockingly before my eyes. I awoke as by a stroke of lightning, and this time, too, I spent the rest of the night working out the consequences of the hypothesis.[20]

Let us assume for the moment, as we did with the London omnibus dream, that the story is true, or rather, that it was an attempt factually to describe, after a lapse of many years, an experience that Kekulé genuinely remembered having. The only indication of date is the reference to his *bachelor's* apartment (he resided at 72 Rue des Champs or Veldstraat[21]), so it must have occurred before the wedding (24 June 1862). The fireplace suggests, though does not require, cold weather, and if the "dream" occurred in the months before his wedding we would understand why his mind might be on "other matters."

Whether or not the eureka anecdote is biographically accurate, there is reason to believe that Kekulé must have been thinking anew at that time about the problems posed by aromatic substances. By early 1862 alert members of the chemical community would have suspected that isomers of monosubstituted benzene (such as "salylic" acid) were phantoms, and Kekulé probably had early indications that the putative isomer of benzene was, too. We have noted that as early as 1858 Kekulé

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[20] Anschütz, 2:942; Gillis, "Kekulé te Gent" (1959).

[21] Gillis, "Kekulé et son oeuvre" (1966), 17. After the wedding he and his wife moved to no. 12 Drève du Jardin Zoologique.

had hinted at double bonds in aromatic substances. The idea of a cyclical molecular structure for C_6H_6—suggested, according to his reminiscence, by the daydream—combined with carbon tetravalence and at least some double bonds in the molecule could quickly lead one to the hexagon hypothesis that made Kekulé so famous.

Once he had the idea of a cyclical structure for benzene, what "consequences" might he have tried to work out the rest of the night? It is hard to say, since his first papers on the new theory, as we will shortly see, provide two alternative structural suggestions that have different chemical consequences. Moreover, quite a bit happened in the aromatic world in the year or two between the putative dream and the writing of the first benzene theory paper. In particular, at the first date it seemed well established that each double-substituted benzene had *two* isomers; but by the latter date it had become clear that the correct number was probably *three*. For any potential benzene theory the difference is important.

Kekulé stated in 1890 that the benzene theory "lay nearly a year in my papers" until he was induced to publish it by the work of Bernhard Tollens and Rudolf Fittig. (Tollens and Fittig published novel syntheses of aromatic hydrocarbons that brilliantly elucidated the relationships between various side-chain isomers, but they proposed nothing in their paper concerning the aromatic nucleus itself.)[22] If that is the case, then Kekulé must have written the draft paper late in the year 1863 or very early in 1864. Just as with his structure theory papers of 1857–58, Kekulé apparently held his cards tightly, waiting until the last reasonable moment to reveal them. By timing the announcement carefully, he could be certain of making the best possible evidentiary case for the new theory while still getting on record first with the idea.

Many have speculated what might have first led Kekulé to imagine a cyclical structure for benzene. Several historians, starting with Richard Anschütz, have pointed out that Couper published two cyclical structures in his 1858 papers, though neither represented the aromatic nucleus, neither consisted entirely of carbon atoms, and neither was accompanied by an evidentiary argument for its probable truth. In 1861 and 1864 Crum Brown also suggested the possibility of a three-membered ring of carbon atoms in certain molecules, as had Loschmidt in 1861. Other historians seeking influences on Kekulé have pointed to a hexagonal figure for an aromatic substance that appeared in Laurent's *Méthode de chimie* of 1854. However, Laurent made clear that his

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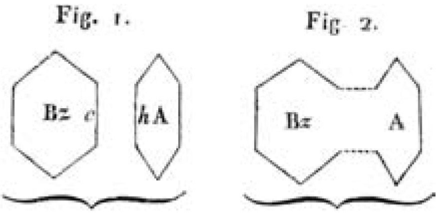
[22] Tollens and Fittig, "Synthese der Kohlenwasserstoffe" (1864).



22 Laurent’s crystal diagrams. Source: Laurent, *Méthode de chimie* (1854), 408.

figure represented a “whole polyhedron” (polyèdre complet) in a crystallographic sense, not a hexagonal molecule; the polyhedral form, depicted in two dimensions as a hexagon, belonged not to benzene but to benzoyl chloride (labeled “Bz”). Laurent also gave a hexagonal figure to ammonia (labeled “A”), which, he wrote, should likewise be regarded as a “whole polyhedron.” Furthermore, ideas on atomic valence and structure theory were still in the future when Laurent was writing this; his context was a fanciful exemplification of his crystallographically based “nucleus theory,” quite different from the sorts of issues with which Kekulé was dealing ten years later.[23]

Kekulé’s own retrospective answer to how he got to the hexagon was simple: “What else was I to have done with the extra affinity units?”[24] He meant that if one imagines alternating single and double bonds in a six-carbon, six-hydrogen molecule, one ends up with two affinity units (valences) left over, one on the first carbon atom and one on the last. Why not bend them around into a ring, thus engaging each affinity unit to form one last bond? In 1890 he said that this was such an obvious thought that someone would surely have arrived at it very soon had he not made the announcement when he did.

It was noted in chapter 5 that Couper in 1858 and Loschmidt in 1861 each suggested the same structure for the benzene nucleus, namely diallene or hexatetraene, $H_2C{=}C{=}CHHC{=}C{=}CH_2$, though Loschmidt then noted that he did not favor it; considering the state of aromatic chemistry at the time, this proposal would appear to be contradicted by what was then known about aromatic isomers.[25] That surely must have

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[23] Laurent, *Méthode* (1854), 407–8; Kekulé cited this text in his 1858 paper, though he did not reproduce the figure. A full discussion of these issues is provided by Brooke, “Doing Down the Frenchies” (1993).

[24] Anschütz, 2:938.

[25] For instance, one would then confidently expect to find two isomers each of aniline and of phenol. This is just one of what would have been many empirical problems with this formula at this time.

been why Kekulé never was attracted by it. But there is possible merit in the suggestion that Loschmidt may have had an indirect influence on Kekulé. Kekulé read Loschmidt's pamphlet in early January 1862, very shortly (as I proposed above) before he may have begun to develop, or may have further developed, his own benzene theory. Loschmidt's tentative proposal for benzene as a highly fused series of cyclopropyl rings would presumably not have made a favorable impression on Kekulé, since it too would fail obvious empirical tests, but it is certainly possible that his preferred symbol for the still-unknown structure of the six-carbon benzene nucleus, a large circle, may somehow have stuck in Kekulé's mind, consciously or unconsciously. Loschmidt proposed literally scores of aromatic formulas, some of them ferociously large and complex, and all those circles are certainly visually impressive—even if highly suspect, due to his failure to actually present arguments in their favor.

Kekulé's apparent hesitancy in publishing his benzene theory was partly connected to events in his personal life. After their wedding, the couple spent four weeks in Switzerland, where Kekulé showed his bride the site of his youthful postdoctoral stay in Chur; then in the fall they attended the International Exposition in London, where Stephanie Kekulé won the hearts of August's English friends. A son was born to the couple prematurely on 1 May 1863. Unfortunately, after the successful delivery, Stephanie developed puerperal fever, declined, and died on 10 May. Kekulé was crushed with grief. He named his little son Stephan, after Stephanie. On the 31st he reported to Stas that "je ne suis pas un moment tranquille" and that he was completely unable to work.[26]

Kekulé was laid low, physically and emotionally, by his wife's death and by the exigencies of a widower caring for a young son (though he surely also had domestic help). For a year and a half he was not able to do much research, though he taught his courses and continued to make progress on his textbook. By the beginning of 1864 he was beginning to write the section on "hydrogen-poor" and "carbon-rich" compounds, among which were aromatic substances. If we can trust his later reminiscences, it was Tollens and Fittig's paper, published in the August 1864 issue of the *Annalen,* that moved him to action. In September, at the annual Naturforscherversammlung in Giessen, he scouted for private assistants. In October he hired two capable young chemists, Carl Glaser (a former student of Strecker) and Wilhelm Körner (a

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[26] Gillis, "Kekulé et son oeuvre," 19.

former assistant of Will), and began to set up for a concentrated period of work.[27]

But it wasn't easy. On New Years Day 1865 he decided to go to Paris to try "to shake myself from my lethargy"; he was there eight days, and the trip did do him good. Soon after having returned to Ghent, he wrote Baeyer:

> Chemically speaking, there's nothing new in Paris . . . Also nothing new here either. I myself . . . have no results at all, and I also see none coming. My students don't have any, either. . . . And now to give a more complete picture of my situation and especially my activity, or rather lack of activity, I must tell you that I have not written a single line on my textbook. In fact, I'm sick, and as a consequence lazy. Stas calls my condition, which has been going on about 8 months, melancholic hypochondria; my friend and personal physician Poelmann says, "vous avez l'esprit frappé." The main point is, I feel so addled that I cannot bring myself to any real work. From time to time it gets a little better—ebb and flow—and then I can work at least a little. Since my return from Paris I am once again better and I will make the most desperate attempts not to sink again.
>
> In these clear intermezzos I have dreamed a lot and sometimes also done some theory; but I suffer from chemical constipation and am too lazy to write. However!!! However, I will nonetheless soon let fly with some theoretical tinder. . . . My plan is . . . to send off a song and dance on the constitution of all aromatic substances to the société chimique. I won't describe these publications to you, so they won't lose the charm of novelty. But don't expect too much; the good parts are not new and the new parts not good.[28]

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[27] Kekulé to Glaser, 9 October 1864; Körner to Kekulé, 8 and 29 October 1864; all in AKS.

[28] "Chemisch Neues gibt es in Paris nicht . . . Auch hier gibt es Nichts Neues. Ich selbst habe . . . durchaus keine Resultate und sehe auch keine kommen. Auch meine Schüler haben Nichts. . . . Um nun das Bild der hiesigen Zustände und namentlich meiner Thätigkeit oder richtiger Unthätigkeit zu vervollständigen, muss ich Ihnen sagen, dass ich am Lehrbuch noch keine Zeile geschrieben habe. Ich bin eben krank und in Folge davon faul. Stas nennt meinen Zustand, der seit etwa 8 Monaten dauert, Melancholic-hypochondriaque, mein Freund und Hausarzt Poelmann sagt: vous avez l'esprit frappé. Hauptsache ist, ich bin so versimpelt, dass ich es zu keinen soliden Arbeiten bringen konnte. Von Zeit zu Zeit geht es etwas besser—Ebbe und Fluth—und dann kann ich wenigstens etwas arbeiten. Seit meiner Zurückkunft von Paris bin ich wieder einmal besser und ich werde selbst die verzweifelsten Anstrengungen machen um nicht wieder zu versinken.

In diesen klaren Intermezzos habe ich viel geträumt und bisweilen auch Thoerie gemacht; aber ich bin zu faul etwas zu schreiben. Indessen!!! Indessen werde ich doch demnächst einigen theoretischen Schwamm loslegen . . . Mein Plan ist . . . der société chimique einen Schwindel über die Constitution sämmtlicher aromatischer Verbindungen einzuschicken. Ich greife den Veröffentlichungen nicht vor, damit der Reiz der Neuheit nicht verlorengeht. Erwarten Sie indessen nicht zu viel, das Gute ist nicht neu und das Neue nicht gut." Kekulé to Baeyer, 11 January 1865, AKS.

This is a curious letter. After aggressively lowering Baeyer's expectations by telling him of his inactivity, total absence of experimental results, ill health, and inability to work, he presents Baeyer a rhetorical drumroll for a major theoretical announcement on a topic of increasing importance in the chemical world. But then he refuses to say anything more about it, other than to lower expectations once more. It is also interesting that he mentioned his *dreaming* in direct connection with his *doing theory.* Considering the events that immediately followed Kekulé's trip to Paris, it seems reasonable to believe that he went there specifically to talk to his good friend Adolphe Wurtz about his new theory.

A few days later, Wurtz presented Kekulé's benzene theory to the Société Chimique in Paris.[29] Kekulé began by pointing out that no one, "as far as I am aware," had attempted to apply the theory of atomicity of the elements to aromatic compounds. He stated that he had had a "fully formed idea" on this question since 1858, having published hints in that direction in his major paper of that year, but he had not regarded it as appropriate to unveil it publicly and in detail until now. The theory that follows is very incomplete, he warned, and may not ultimately be verified, but it may also be very useful in stimulating and guiding experimental work, to confirm or refute it, hence his desire to put it forward now.

This theory of aromatic compounds, which, he declared a second time, "I conceived quite a long time ago," was, in brief, that all such molecules possess the same six-carbon nucleus consisting of a closed chain (chaîne fermée) of carbon atoms, connected together among themselves with alternating single and double bonds. Six carbon affinities are left over, thus explaining the hexavalent character of the aromatic nucleus. To the six-carbon cyclical "main chain" (chaîne principale) may attach one or more "side chains" (chaînes latérales): methyl, ethyl, hydroxyl, carboxyl, nitro, amino, chloro, and so on. Since each carbon of the main chain normally has one hydrogen atom attached, substitutions may occur in either chain; so for instance we have isomeric chloro derivatives of toluene, where a chlorine atom enters into the methyl group to form one isomer, or substitutes into the aromatic nucleus to form another. Similarly, when hydroxyl substitutes into the methyl of toluene we get benzyl alcohol, when it does so into the main chain we get the isomer cresyl alcohol. We can have two side chains of one methyl each, or one side chain of ethyl; the formula will be the same, so there is another example of isomerism. His aromatic

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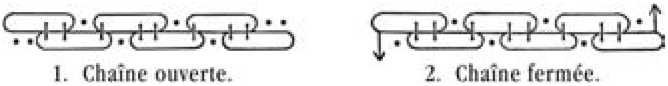
[29] Kekulé, "Substances aromatiques" (1865).



1. Chaîne ouverte. 2. Chaîne fermée.

23 Kekulé's open-chain and closed-chain sausage formulas for benzene. Source: Kekulé, *Bulletin de la Société Chimique* [2] 3 (1865): 108.

theory thus uses the "theory of atomicity of elements" to explain the six-carbon minimum for all aromatic compounds, the seven-carbon minimum for derivatives of benzoic acid or toluene, and a variety of "metameric" (conventional isomeric) relationships among already-known compounds.

Kekulé's tactic here was to demonstrate the value of his theory in explaining certain aromatic metamers by referring these cases to substitutions of hydrogen atoms in different parts of the molecule (i.e., hydrogen of the side chains versus hydrogen atoms attached directly to the aromatic nucleus), and the discussion of such considerations constitutes most of this first paper. This theoretical value could have been "cashed" (and in fact to some degree had already been, e.g., by Tollens and Fittig) without considering details of carbon bonding *inside* the aromatic nucleus—what modern chemists refer to as the hexagonally shaped cyclohexatriene (CHT) structure. Kekulé did indeed propose here that benzene was CHT, but he did not especially emphasize this claim.[30] Nonetheless, the CHT hypothesis soon became the basis of much of Kekulé's fame. In 1865, what *additional* explanatory value did this hypothesis provide?

The first point that Kekulé wanted to make is that his was the earliest such hypothesis for the aromatic nucleus that followed the rules of atomicity, especially carbon tetravalence, *and* that could not immediately be rejected for obvious predictive (or retrodictive) failures. It is true that Couper and Loschmidt had each tentatively suggested structures for benzene, but Kekulé was right that this was the first time that anyone had made a serious, competent, and sustained attempt to develop such a structural aromatic theory and to explore its consequences empirically. It was also the first time that anyone had proposed the CHT structure as the essence of aromaticity.

Secondly, the cyclical shape of the CHT structure had obvious impli-

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[30] A primer on organic-chemical nomenclature: "cyclo" indicates a ring structure; "hexa" indicates six carbon atoms in the formula; and "tri-ene" indicates that there are three carbon-carbon double bonds. Since the unnamed "default" is always the carbon-carbon single bond, there must be three of them, as well. Hydrogen atoms are assumed to fill in otherwise unspecified valences and are not normally named; to maintain carbon tetravalence there must be six in this case.

cations for a new kind of isomerism, namely "positional" isomerism. If the ring is symmetrical, there can be but one isomer of any singly substituted benzene. If a second isomer of any monosubstituted benzene were ever to be found, then either the ring must be asymmetrical or the entire theory must be given up. Kekulé also concluded that for the same reason there should also be but one penta-substituted benzene whenever chemists succeed in creating such a molecule, since, considered in terms of symmetrical geometry, a single absence is equivalent to a single presence. If there are two substituents, however, there should always be *three* isomers corresponding to each formula. One such isomer would have the two substituents attached to neighboring carbon atoms in the six-membered ring; another would position them on carbon atoms number one and three; and a third would have them sit on carbon numbers one and four, directly across from each other in the ring. The theory also predicts that there should still always be three isomers whether these two substituents are the same or are different from each other. By similar reasoning one can easily see that if there are three identical substituents on the ring then again one should expect to discover three isomers corresponding to each formula, and similarly if there are four identical substituents.

That Kekulé had explored these consequences and had come to these conclusions is obvious from his language, though he was decidedly cautious. Mono- and penta-derivatives of benzene, he wrote, should have one isomer only, but di-, tri-, and tetra-derivatives will "probably" be found to have three each. Dimethyl-benzene, which Kekulé and his colleagues already knew as xylene, should have as many isomers as the corresponding dichloro-benzene, and so also for all other alkyl-substituted benzenes. Regarding the case of the triple isomerism of salicylic, oxybenzoic, and paraoxybenzoic acids, this threefold "existence is understood; it is [explained by the three] different positions that the OH group occupies with respect to the CO^2H group," and the nitrobenzoic acids follow the same pattern. There are two phthalic acids so far known, which "can perhaps be explained by the hypothesis that the two side chains [the two CO_2H groups] are located in different relative positions."

Clearly, Kekulé had drawn many of the same conclusions that were soon to become standard regarding the counting of possible isomers consequent to his theory, but he avoided being explicit. Nowhere in this first paper did he explain *why* he thought there should be (e.g.) three isomers of every di-derivative, leaving it to his readers to arrive at the (obvious?) explanation; and he did not even use all of the then-known instances of triple isomerisms to support the new theory empirically. This caution was arguably a reasonable attitude considering the recent history of aromatic chemistry, in which many generalizations had had to be modified or even retracted due to insufficient experience or empirical difficulties with the particular substances being handled.

And yet we also find him here boldly offering a table of sausage formulas depicting the fully resolved structures of no fewer than twenty-eight substances, twenty-four of them aromatic.[31] This, counting also the German version of this paper, was the first and only time he ever used these formulas outside the pages of his own textbook, and was by far the most extensive such tableau he ever printed. In introducing them, he commented:

> The idea that these formulas are intended to express is now fairly well known, so it will not be necessary to go into details. I retain the [sausage] form that I adopted in 1859, when I expressed for the first time my views on the atomic constitution of molecules. The form is moreover nearly identical to that which M. Wurtz has used in his admirable *Leçons de philosophie chimique.* It appears to me to be preferable to the modifications proposed by MM. Loschmidt and Crum Brown.[32]

Having just hired two capable private assistants (Glaser and Körner), in January 1865 he put them to work making some of the innumerable aromatic compounds that his theory predicted must be possible. They, along with his Belgian assistant Theodor Swarts, were soon joined by other advanced Praktikanten and postdocs in Kekulé's Ghent laboratory, such as August Mayer, Albert Ladenburg, and Hermann Wichelhaus. However, even with these major reinforcements, Kekulé's team discovered that they had more on their hands than they ever could have imagined. Kekulé's health, along with his passion for work, had finally returned, and the laboratory was working at white heat. Glaser reminisced about this time:

> The Ghent University laboratory was on the third floor of the main university building. The private lab was next to the lecture hall and had five workbenches, as I recall. My place was next to the boss's, who always thought aloud while working, and discussed the problems that occupied him with whomever was working in the private lab with him. . . .

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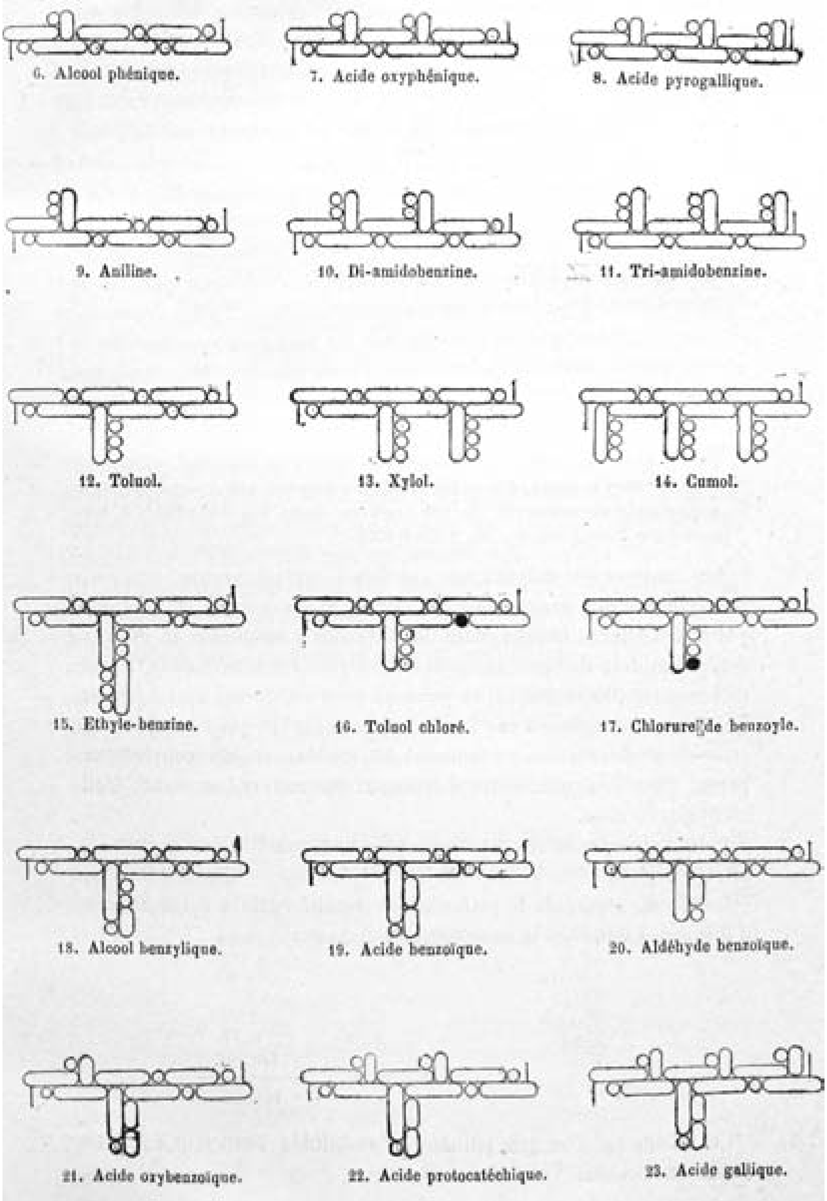
[31] Kekulé, "Substances aromatiques," 108–10.

[32] Ibid., 100n.



24 Kekulé's table of aromatic formulas. Source: Kekulé, *Bulletin de la Société Chimique* [2] 3 (1865): 109.

> Kekulé was a man of great personal warmth and kindliness. Thirty-five at the time, he had a casual, merry, even boisterous personality. He told stories in the most captivating way of his time in Giessen with Liebig, of the Parisian and English chemists. The air-bath for reactions in sealed tubes was located on a platform in the lab. Whereas we all stood on a stool or chair to reach the thermometer column in order to record temperatures, the boss scorned such boring methods, performing an acrobatic leap from his lab bench to the platform, in order to release his excess muscular energy. He always spent 7–8 hours working steadily in the laboratory, then every night he worked from 8 to 12 or 1 on the second volume of his textbook.[33]

Kekulé eagerly wrote his friends Baeyer in Berlin and Müller in London in mid-March: guided by the theory, he and his research group were taking on the aromatics "from A on." By that time results were coming—slowly, but coming. On 10 April he wrote again to Baeyer, now veritably euphoric: the sky was the limit, for "the aromatic theory is an inexhaustible treasure-trove. Now, when 'German youths' need dissertation topics, they will find plenty of them here. . . . Naturally, everything is aromatic, facts to prove or disprove my recent aromatic theory." Müller responded, "I gather you intend to give the benzene series everything you've got, and from the hints you've given, there won't be much left over for others to do."[34]

Müller needn't have worried. It was not just on Kekulé that the publication of the benzene theory worked like the sound of a starting gun; there was more than enough for everyone. His colleagues in the field received the new theory positively, many signing on immediately, others using words of caution, but very few (not even Kolbe, at first) expressing downright opposition. In March 1865 Williamson wrote a review of the first five fascicles of Kekulé's textbook and referred indirectly therein to the benzene work.

> There are not quite two volumes in the hands of the public, but enough has already appeared to secure the admiration and gratitude of chemists. Carbon has been shown by Kekulé to be tetratomic; and although the discovery has already thrown a flood of light upon organic chemistry, it is evident, from recently published papers of our author, that we have by no means got all, that the development of the idea of tetratomic carbon can give us. The book even in its present incomplete state is

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[33] Anschütz, 1:272.

[34] Kekulé to Baeyer, 16 March and 10 April 1865; Müller to Kekulé, 14 March 1865; all in AKS. For more extensive quotations from these letters along with the original German, and for greater detail on the immediate reception of Kekulé's theory, see Rocke, "Hypothesis and Experiment," 369–77.

> one of the most original and masterly productions which chemistry can boast of. But the author is still one of the youngest among chemists of eminence, and is still hard at work discovering, systematizing, and teaching.

Such words from such a valued older friend and former mentor must have meant a great deal to Kekulé—enough so to cite this passage in extenso in a letter to Baeyer, though he disclaimed deriving any great thrill from it.[35]

I stated above that according to Kekulé's theory there should be only one isomer of benzoic acid, toluene, aniline, or phenol, *if the cyclical benzene structure is assumed to be symmetrical*. Everything Kekulé had written in his first article of January 1865 implied that he thought it probably was. However, in his second article on benzene theory, a short French paper published in May in the *Bulletin* of the Belgian Academy of Sciences, he broached the *possibility* that it might not be. The six-carbon cyclical (CHT) structure, he wrote there, must be shaped either so that the hydrogen atoms connected to the carbon ring are arrayed in a symmetrical hexagonal pattern, or arrayed more like a triangle, such that hydrogen atoms are located at the three vertices and in the middle of each of the three sides. He drew an unembellished hexagon to illustrate the first hypothesis—the first aromatic hexagon ever printed—and a simple triangle to illustrate the second, with six marks to designate the positions of the carbon-hydrogen pairs.[36]

It seems strange for Kekulé to suggest even the possibility of a triangular shape in dealing with an entity that so obviously deals in sixes rather than threes, but there is a reasonable conjectural explanation for this move, ably defended more than forty years ago by Jean Gillis. If one manipulates actual Kekuléan sausage models to construct a six-membered CHT ring, there is no way one can produce a symmetrical object. The problem is that each carbon-atom sausage model is four times longer than it is high, and a double bond between any two carbon sausages forces these two atoms into a straight line that is six hydrogen-units long. But it turns out that there are two different ways to join the ends of the hexatriene sausage ring model together. In one of these configurations, both the six hydrogen and the six carbon atoms are arrayed in the approximate form of a triangle, with three hydrogens on the outside and three on the inside of the ring. Applying a longitudinal twist to three carbons creates a second distinct configura-

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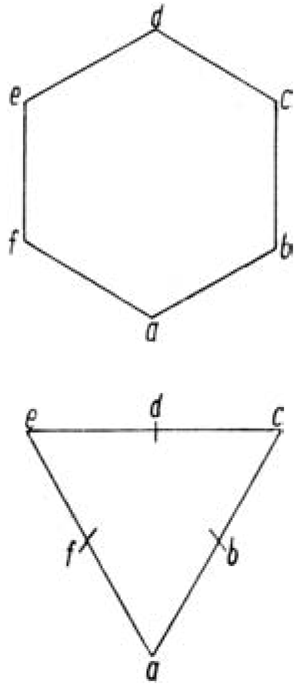
[35] Williamson, in *The Reader,* 1 April 1865; Anschütz, 1:368.

[36] Kekulé, "Produits de substitution de la benzine" (1865).



25 Kekulé's first benzene hexagon, and possible triangle form. Source: Kekulé, in Anschütz, 2:389 (1865).

tion. This structure appears just as triangular when one looks only at the carbon atoms, but now all six hydrogens are symmetrically placed on the outside of the ring, in an approximately hexagonal array. So Gillis concluded that Kekulé himself must have arrived at the two CHT hypotheses of May 1865 through physical manipulation of his wooden sausage models. This would explain why Kekulé would write that the six *hydrogens,* not the carbons, form either a triangle or a hexagon.[37]

Another part of Gillis's evidence for this suggestion is that when Kekulé discussed the possibility of the triangle form for the benzene molecule in his May 1865 paper, he described the hydrogens as not

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[37] Gillis, "Kekulé et son oeuvre" (1966), 21–23, 29–30; Gillis, "Molecuulmodellen" (1967), 176–77. In figure 26, the model on the left is an original, the model on the right a replica (courtesy of the Museum voor de Geschiedenis van de Wetenschappen, University of Ghent). In 1865, Paul Havrez published three-dimensional perspective drawings of aromatic rings formed of Kekuléan sausage models. See *LB,* 2:514–15n; Heilbronner and Jacques, "Havrez" (1998); and Paoloni, "Stereochemical Models" (1992).

26 Kekulé's two alternative benzene rings, formed with original sausage models. Source: Museum for the History of Sciences, University of Ghent.

only forming a triangle, but arrayed such that three hydrogens were, as he expressed it, "on the outside," and three were "inside" of the molecule (he did not mention the sausage models in this passage). One would predict, if this hypothesis were true, Kekulé carefully noted, that any tetra-derivative of benzene would be very difficult to form, because it would require that at least one hydrogen atom in the *interior* of the molecule undergo substitution. But we know that Kekulé already believed that tetra-derivatives were possible, for he had in fact included a sausage formula for such a tetra-derivative (gallic acid) in his January paper, and now, in May, he reported producing a tetra-bromobenzene. Further, his assertion in January that there would be only one possible isomer of benzoic acid (or of toluene, aniline, or phenol) appears to be inconsistent with the triangle hypothesis. So his suggestion of the triangle form in May was no sooner mooted than rejected. But what is most relevant here is the fact that this episode demonstrates that even as late as 1865–66 Kekulé regarded his sausage formulas and models as heuristically important, even if not always reliable in matters of detail, for the development of chemical theory.

Benzene through the Phenakistoscope

When I first studied these issues carefully, I came to the conclusion that in 1858 Kekulé probably had no developed viewpoint about the structure of benzene, only hinting then at the possibility of double bonds, and that it was likely that his first extended development of the theory only occurred after the putative "dream" in early 1862. According to this scenario, Kekulé could not have been candid when he repeatedly claimed in 1865–66 that his private theory dated to 1858. One justification for this conclusion was that Kekulé's papers on salicylic acid of 1860–61 seem inconsistent with the 1865 theory, which suggests that the theory, even in its earliest version, must have been formulated after 1861.[38] But I now think that there is another scenario that, although also conjectural, has greater probability.

Upon reading Kekulé's January 1865 paper, Baeyer wrote his former mentor that just a few months earlier he had innocently lectured on Kekulé's yet-unpublished aromatic theory; he had remembered Kekulé teaching him these same ideas in Heidelberg in 1858, "though to be sure they are now somewhat modified by new ideas."[39] I suggest that in 1858 Kekulé may have discussed with his students one or both of the two CHT hypotheses that he would later outline in May 1865, possibilities that Kekulé had already derived from manipulating his sausage formulas and models. One of these, the symmetrical CHT hexagon, is inconsistent with Kekulé's 1860–61 statements on aromatics, but the other, the CHT triangle, is consistent with them. In 1858 there was insufficient evidence to *prove* either model; however, the CHT triangle would surely have appeared more *probable,* given that there seemed to exist two isomers of benzene and two of benzoic acid. Perhaps it was this idea, the CHT triangle, that he presented in his 1858 lectures, or more informally in conversations, and that Baeyer remembered learning.[40] In 1860–61 he would still have been inclined, from then-accepted evidence, to favor the CHT triangle. However, by 1864 Kekulé would surely have seen the superior empirical merit of the CHT *hexagon,* now that it was known that di-substitution creates *triple* isomerisms. He

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[38] Rocke, "Hypothesis and Experiment."

[39] In reading the published paper, Baeyer said that he "wurde dabei lebhaft daran erinnert wie sehr ich Ihr Schüler bin, da ich vor einigen Monaten die Theorie der aromatischen Gruppe in derselben Form, und beinahe denselben Worten vorgetragen habe. Sie haben diese Ansichten ja schon [18]58 ausgesprochen, wenn auch jetzt durch neueres etwas modifiziert." Baeyer to Kekulé, 26 April 1865, AKS.

[40] To be clear: there would be two benzenes because of the two distinct ways one can form the ring using sausage atoms, and there would be two benzoic acids because one would have the carboxyl group attached to a carbon triangle vertex, the other to a carbon triangle side. Such isomers were believed to exist at this time. However, discussion of these matters cannot be found in Holzmann's notes from Kekulé's lectures in 1857–58 (AKS).

then may have felt enough in the clear on these matters to actually come out publicly with his long-bruited benzene theory.

This conjectural scenario would relieve Kekulé from the suspicion of being disingenuous in his 1865–66 statements about the early origin of his theory. It is also consistent with the hints about aromatics that one finds in his 1858 paper, as well as with his 1859 and 1860 suggestions of two parallel isomeric series. However, accepting it presents us with a new conflict, namely the "dream story" he told in 1890. How could he have had the first idea of the benzene theory in a (day)dream ca. 1862 if he had already formulated the theory in 1858? But I believe that it is entirely possible to continue to credit the sincerity of Kekulé's reminiscence, allowing a formative role for this personal experience even when that experience did not represent the *first* formulation of his aromatic theory.

The Kekulé case, as I will develop it below, would actually fit well with the conclusions that Frederic L. Holmes and others have reached after careful study of similar stories of sudden and mysterious illuminations that are so common in the history of science and that I shall discuss in more detail in chapter 10.[41] Such stories, considered carefully, usually reveal more continuity than is at first apparent, and less a sudden and discontinuous shift. The experiences seem utterly true to the person experiencing them, and genuinely feel from the inside to be sharp breaks with previous thinking, but one can nearly always find significant underlying continuities. In short, the "eureka" is both psychologically real and an important element of the creative process, but can be misleading as an unqualified historical depiction of the trajectory of a research path. In the Kekulé case, whatever conjectural pathway we follow, we see that his trajectory was by no means a smooth one. One of the most imaginative theorists of the century, Kekulé was constantly spinning off ideas and just as constantly modifying them to accord, as best as possible, with the rapidly evolving empirical state of the field. Each one of these twists and turns could feel, from the inside, like a dramatic shift, a "eureka" moment. And as regards aromatic chemistry, we have outlined above how often the empirical ground shifted in the period from 1858 to 1865.

I suggest that Kekulé may have formed the hypothesis of ring closure with alternating double bonds in 1858, but at that time inclined only toward the CHT "triangle" hypothesis—a hypothesis that had been de-

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[41] Holmes, *Investigative Pathways* (2004), 172–88.

rived from actual manipulation of his sausage models. That hypothesis would have fit well with much (but not all!) of the data on aromatics known in the period 1857–61—namely, that there were *two known* isomers of benzene and of every mono-derivative, and *no known* tetra-derivatives. But as we have seen, the empirical ground shifted in 1862 and 1863, so that the triangle hypothesis by then fit few of the facts—it was now known that there was only *one* isomer of benzene and of benzoic acid and other mono-derivatives, and examples of tetra-derivatives were now recognized. The "snake" daydream may have given him the notion that there may be another way to form the ring, one that he had perhaps never hitherto considered (or had forgotten that he had considered), this time in a more symmetrical pattern—what I have called Kekulé's hexagonal CHT hypothesis. Only *that* hypothesis now would have fit the new data, and that would have felt like a true "eureka." (Might this have been what Kekulé meant when he wrote Baeyer that "the good parts are not new and the new parts not good," and what Baeyer was referring to when he noted that the old theory taught to him in 1858 was now "modified by new ideas"?)

Actually, there would still have been at least one empirical problem for the carbon hexagon hypothesis at the time of the putative dream in 1862. Namely, as we have seen, evidence at that time suggested that every di-derivative of benzene exists in two isomeric forms, whereas the symmetrical hexagon hypothesis would suggest that there should probably be three isomers of each di-derivative. Perhaps this was the reason why Kekulé held off on publication. Evidence of triple isomerisms, as we have seen, only began to appear in 1863. Once that phenomenon seemed securely established—by late 1864—he proceeded to write the theory up, and finally he hand-carried it to Wurtz in Paris, for publication in the *Bulletin* of the Société Chimique.

Important parts of this scenario are conjecture. What we can say without hesitation is that in May 1865 he could be definite and explicit about his isomer predictions: always only one for each mono- or penta-derivative, always three for each di-, tri-, or tetra-derivative. He also explained clearly (finally) *why* isomers ought eventually to be found in just these numbers, if the theory is true; he provided a diagram with labeled positions to demonstrate the argument.

> A problem of this type could appear at first to be completely impossible to solve; nonetheless, I believe that it can be resolved by experiment. One need only prepare, by as many different methods as possible, a considerable number of substitution products of benzene. One then examines them particularly with respect to

> isomerism; one counts them, and above all reasons from the particular isomers that one obtains, and ultimately one will arrive at a satisfactory solution.[42]

This is exactly what Kekulé and his students were beginning to do, and what many of his colleagues soon started to do, as well. The theory provided hundreds or even thousands of specific predictions, and each prediction could only be tested by the accumulation of much laboratory evidence. Some of this evidence was of a positive character; for instance, can one make the predicted third isomer of a given di-derivative of benzene—say, for example, bromobenzoic acid—only two isomers of which were currently known? Some of the evidence was negative, which required even more empirical experience; for instance, is the theory correct that it is in fact impossible to make an isomer of benzoic acid or phenol, or a fourth isomer of a di-derivative? Is it impossible to make an aromatic compound with less than six carbons? Are there always exactly three possible isomers of each tri-derivative?

No wonder the theory was such a scientific treasure trove, a virtually inexhaustible source of topics for research papers and doctoral dissertations in chemistry. And the attractions of Kekulé's theory were dramatically increased by three important circumstances. One was that, with relatively few exceptions, the empirical investigations of aromatic compounds carried out in the late 1860s and 1870s repeatedly confirmed the predictions from the theory; some did so in spectacular fashion. The theory started out with positive reviews from most of Kekulé's colleagues and only kept growing in prestige. A second factor was that the benzene theory happened to have been unveiled just when the German academic scientific enterprise was poised for dramatic expansion. Metaphorically considered, the theory provided the cognitive equivalent of a vacuum into which the existing chemical profession could expand.

The third circumstance was that it became increasingly clear that one could make a great deal of money from aromatic chemistry. Nearly all of the dyes that, already in 1865, were beginning to become major industrial commodities, nearly all of the pharmaceuticals, food chemicals, explosives, and plastics that became so lucrative (especially in Germany) were based on aromatic molecules. And it made a great difference for the efficiency of new product development first to understand clearly the nature of the molecules with which these new companies were dealing.

Assisted by his co-workers and advanced students, Kekulé worked

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[42] Kekulé, "Produits de substitution de la benzine" (1865), 554.

diligently preparing and analyzing novel aromatic derivatives all through calendar year 1865. That fall he prepared a major paper on benzene theory for Liebig's *Annalen,* which was the first publication of the theory in German; it appeared in the February 1866 issue.[43] In the spring of 1866 he completed, and that fall was published, the final fascicle of the second volume of his textbook, which contained the most detailed discussion of the aromatic theory to date; the fascicle was the size of a significant monograph.[44] Both of these treatments, the *Annalen* article and the *Lehrbuch* installment, consisted of revised versions of his two French papers of January and May 1865, but with substantial additions. He now explicitly claimed that the carbons and hydrogens in benzene were symmetrically and hexagonally arrayed, in support of which he now cited all four then-known instances of triple isomerism of benzene di-derivatives.

There were two potentially serious problems in Kekulé's theory, both of which were almost immediately noted, but neither of which substantially damaged its reception. The first of these was that benzene did not act like a compound with three double bonds in it, if the model for double-bonded organic molecules was taken to be ethylene, propylene, and other olefins, for the latter compounds easily absorbed hydrogen or chlorine in addition reactions, and the former did not. One way out, as for any dilemma, was to deny the premise. Why should aromatic compounds not be regarded as the true model of double-bonded carbon compounds, rather than olefins? Double bonds might be taken to imply greater strength, hence greater resistance to addition reactions. One would then only need to explain why olefins, rather than aromatic compounds, were the exceptions. By the time this route of argument was closed off, the benzene theory was too well confirmed to be significantly weakened by the apparent anomaly, and chemists just accepted this state of affairs.

The second potentially serious problem was the circumstance that there would appear to be two distinct compounds formed by disubstitution on neighboring carbon atoms in the ring, one where the substituted carbons were connected by a single bond, the other where they were connected by a double bond. But no such isomerism seemed to appear in nature. To save the theory, one could simply suggest, reasonably, that the structural difference was too small to be noticeable in terms of chemical properties.

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[43] Kekulé, "Aromatische Verbindungen" (1866).

[44] *LB,* 2:493–744.

Kekulé himself took another route to solve this problem, using a much cleverer idea. In 1872 he outlined a new theory of valence, in which valence in general was interpreted as the number of collisions in a given time interval experienced by vibrating atoms striking neighboring atoms.[45] Picture the central carbon atom in any three-carbon portion of the aromatic ring; it is bonded singly on one side, doubly on the other, and it also holds one hydrogen atom out to the side, for a total of four valences. But Kekulé pictured the carbon atom at the center of this picture as actually rapidly oscillating between its three neighboring atoms, and what we *perceive* as valences are really only collisions in rapid sequence. Each carbon atom of the benzene ring actually makes, on average in any given time interval, *an equal number of collisions with each of its two carbon neighbors*. It is as if the carbons were connected together not by single or by double bonds, but uniformly by one-and-a-half bonds all the way around the ring.

There is the required complete symmetry. In a footnote, Kekulé commented: "This conception of the motion of the atoms in the molecule can be visually portrayed very beautifully with phenakistoscopic pictures." It does seem that Kekulé conceived this hypothesis after the model of a phenakistoscope (a mid-nineteenth-century optical animation device using continuously varied photographs or drawings shown in rapid succession to simulate motion), for he also mentioned the phenakistoscope simile in a contemporaneous letter to Erlenmeyer.[46] Now, this valence hypothesis of Kekulé's was poorly received, partly because of its almost completely hypothetical character and partly because it had internal contradictions. But it does illustrate how apparent anomalies could be rather easily accommodated, at least in principle. It also illustrates, once more, Kekulé's inclination toward kinetic models, and the *visually* inventive character of his scientific imagination.

Indeed, in addition to the phenakistoscope trope, Kekulé's thought was associated with other optical metaphors. His former student J. H. van't Hoff wrote in his obituary of his mentor that Kekulé had "created the model for the ultimate clarification of his views, gradually elaborated in detail, concerning the framework, the so-called structure of matter, and showed how this matter might appear if it could be viewed through a giant microscope of fabulous power. And there was so much truth in this picture that one after the other, his deductions were verified." For example, to everyone else benzene was simply a hydrocarbon

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[45] Kekulé, "Condensationsproducte des Aldehyds" (1872).

[46] Ibid., in Anschütz, 2:657n; Kekulé to Erlenmeyer, 13 February 1872, in Anschütz, 1:410.

derived from coal tar and consisting of 92 percent carbon and 8 percent hydrogen. To Kekulé, on the other hand, benzene consisted of a ring of C's and H's; "except these C's and H's were not letters, but a *pictorial representation* of carbon and hydrogen, while the dashes express bonds that hold the whole thing together."[47]

By 1866 Kekulé's theory was well launched, and his career prospered. In June 1867 he was called to a full professorship at the University of Bonn.

Excursus: Ring around the Rosie

It was one thing for Kekulé to suggest that when similar substituents occupy different positions around a six-membered benzene ring, isomers are created that can be distinguished by their properties. It was quite another thing to hope that one might be able to deduce from chemical evidence exactly which carbon atoms held which substituents in which isomers. For instance, in salicylic acid, are the hydroxyl and carboxyl groups located on *neighboring* carbon atoms in the ring (in modern terminology, are they located on the carbon atoms numbered 1,2); or are they one carbon atom further away from each other (1,3); or are there two carbons in between, that is, are they located on opposite sides of the ring (1,4)? Modern chemists designate such isomers not just by the numbers, as indicated, but also by words: every 1,2 di-derivative of benzene is now called an "ortho" isomer, every 1,3 di-derivative is called a "meta" isomer, and every 1,4 di-derivative is called "para." (These three words began life as arbitrary coinages, derived from mere historical contingencies, that subsequently have become conventionally fixed in meaning.) But how could one hope to make such positional assignments, decades before physical instrumentation gave scientists the ability to virtually "see" into these molecules?

In his May 1865 paper Kekulé conjecturally assigned absolute orientations to two isomers of nitrobromobenzene, but did not inform his readers of the basis for this assignment. We can infer that basis from a passage in his *Annalen* paper of February 1866. Consider, Kekulé wrote, the case of a benzene ring that holds a bromine atom, being approached by a second bromine atom seeking to substitute for a second atom of hydrogen. Where would it enter? If we assume that the first bromine

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[47] Van't Hoff, obituary of Kekulé published in *Die Nation,* 13 July 1896, reproduced in Cohen, *van't Hoff* (1912), 59–62.

had entered the ring because of some unknown sort of attraction between it and the portion of the molecule it entered, then one can only assume that that attraction had been fully satisfied by the entry of the first atom; consequently, that part of the molecule would not be attractive to a second bromine atom, and could well even be repellant. The second bromine would therefore naturally incline toward the position furthest away from the first, so that the di-derivative would be the 1,4 isomer. The implication is that the first and most natural di-derivative will always be this one.

Baeyer did not like Kekulé's reasoning. We know that chlorine substitutes for hydrogen of the same atom of ethyl chloride that already holds a chlorine atom, and we know that when an oxygen atom enters into the carbon atom that already holds a hydroxyl group, the hydrogen of the hydroxyl is "loosened," that is, it becomes more acidic. Why could we not assume that a chlorine atom thus loosens a hydrogen held by the same carbon atom? If this were to be true, then a second substituent would come into the ring onto the carbon atom that is *closest,* not *furthest,* from the first substituent.[48] Given disagreements such as this between Kekulé and Baeyer, these kinds of speculative approaches probably did not appeal to the chemical community.

Even before Kekulé published this speculation, another approach was tried: not a method for *absolute* determinations of ring positions, but rather for *relative* determinations. Let us say that one of the three isomers of toluidine (methyl aniline) is shown to convert into a particular isomer of nitrobenzoic acid when it is vigorously oxidized, and that this nitrobenzoic acid can be shown to reduce to a particular one of the three isomers of aminobenzoic acid. Since all three of these isomers are mutually interconvertible, one can infer that all three molecules have the same relative positions of their two substituents, even though the absolute identity of that positional assignment remains unknown; they are all, say, "ortho" compounds (where in this case "ortho" is intended arbitrarily to express only relative and not absolute positions). Such "genetic" chains of interconversions were rapidly developed after January 1865, so that one could make a table of three different series, the compounds in each series being theoretically or actually all mutually interconvertible. These acquired the then-arbitrary names "ortho," "meta," and "para" families of aromatic isomers.[49] At first no one at-

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[48] Kekulé, "Aromatische Verbindungen," 174–75; Baeyer, "Condensation" (1867), 84–85.

[49] "Ortho" (Greek for regular or right) often designated the first or best-known isomer, such as salicylic acid for the hydroxybenzoic acids, or orthophosphoric acid. "Para" (Greek for alongside) was conventionally used upon the discovery of any additional isomer, and the Zaitsev/

tempted to map these three families onto the three possible absolute positional isomerisms (1,2, 1,3, or 1,4), because that seemed simply beyond human ability to accomplish.[50]

Gradually, methods to do this were developed. The story is complex, including more than one nomenclatural switch and many difficulties and controversies along the way, and I will not attempt to tell it here.[51] But I do want to give at least hints of how this was done. There were two basic approaches applied: one had to do with preparing new derivatives and counting the number of isomers created; the other made more specifically spatial arguments. The isomer-counting method is, in principle, as simple as it is ingenious, but it poses many practical difficulties. How might one determine the absolute positions of, say, the two bromine atoms in dibromobenzene? Try adding a third substituent, such as a nitro group. *Each different isomer of dibromobenzene will result in a different number of isomers of nitrated dibromobenzenes. Not only that, but we can easily infer, using the theory and these experimental results, which positional isomer is which.* Namely, that isomer of dibromobenzene which yields only *one* possible isomer upon nitration must be the 1,4 isomer; that isomer which yields *two* distinct nitrated versions must be the 1,2 isomer; and that isomer from which, upon nitration, one can isolate *three* different nitro isomers must be the 1,3 isomer.

These assertions may seem unmotivated, arbitrary, or mysterious when stated verbally, but not when one draws the corresponding hexagonal diagrams for these substances. The visual images make everything clear, even obvious. In fact, when even experienced contemporary chemists need to remind themselves of such details, they often turn to pencil and paper, or to private mental images, rather than a reference work. And it must also be noted that this method not only provides an experimental argument for the absolute assignment of aromatic positional isomerism, it provides powerful evidence for the truth of the benzene theory as a whole. The theory predicts that, on further substitution of each of the three isomers of *any* di-derivative, one of the "di-" isomers will yield only one isomer of a tri-derivative, a second will give two, and the third will give three. This was a true novel

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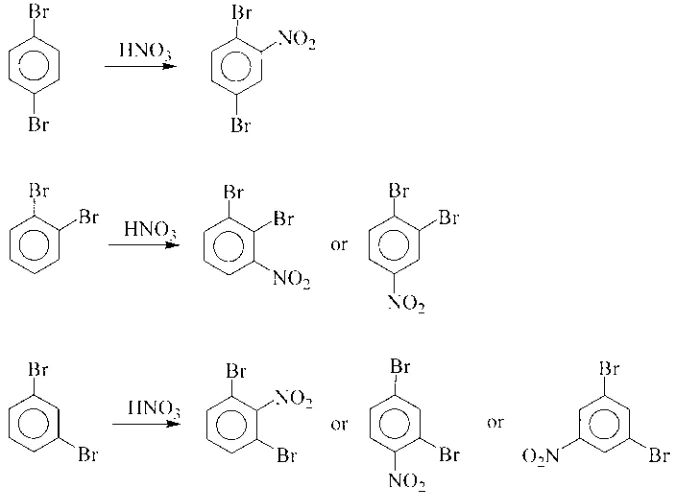
Fischer isomer of salicylic acid received this designation (paraoxybenzoic acid) upon its discovery in 1863. "Meta" (Greek for after) remained as an alternate designation for additional isomers, cf. metaphosphoric acid. The hydroxybenzoic acid model eventually and indirectly became the reason why in modern terms "ortho" indicates 1,2 placement (as for salicylic acid), "para" the 1,4 isomer (as for paraoxybenzoic acid), and "meta" the remaining option, namely, 1,3.

[50] The first such tables were developed by Körner: "Quelques dérivés" (1865) and "Synthèse de la résorcine" (1866). Kekulé summarized such genetic correlations in 1866: *LB,* 2:517–18.

[51] See Schütt, "Einführung" (1979); Meyer, *Einleitung* (1882), 46–72.



27 Koerner's absolute method of determining positions of aromatic substituents.

prediction—the experimental results could not have been suspected without the help of the theory. Moreover, had those results been uncovered empirically, before the theory was proposed, they would have been utterly mysterious.

Once one is able somehow to establish the *absolute* orientations of a very small number of di-substituted aromatics—in principle, even a single instance suffices—the extensive *genetic* tables of ortho, meta, and para families provide the orientations of all other di-derivatives of benzene that are represented in the tables. That is, suppose that a certain isomer of a di-derivative that had previously been assigned genetically (relatively) to, say, the arbitrarily named "ortho" family is now determined to have an absolute 1,2 orientation. We can then infer that *all* "ortho" isomers can be assumed to be 1,2 di-derivatives. By means of this bootstrapping strategy, the arbitrarily named classes ortho, meta, and para now acquired an absolute denotation. Tri- and tetra-derivatives were elucidated in a similar way.

The leader in this approach was Kekulé's assistant Wilhelm Körner. Körner worked in Ghent from 1864 until 1867, when he became Cannizzaro's assistant at the University of Palermo. In 1870 he was hired at the Agricultural College in Milan, and spent the rest of his career there (he is alternately known as Guglielmo Koerner). Although many others used isomer-counting as the basis for structural assignments—indeed, we have seen that isomer-counting formed one of Kekulé's principal empirical supports for the original symmetrical CHT theory of benzene—Körner brought the method to a kind of perfection. He also used the isomer-counting technique to demonstrate that the six hydrogen atoms of benzene were all chemically equivalent, as his mentor had predicted in 1865.[52] This line of argument was brought to an ultimate conclusion in an 1878 study by Beilstein, who succeeded in forming all twelve chlorobenzenes predicted by Kekulé's theory—one mono-, one penta-, and one hexa-chlorobenzene, plus three di-, three tri-, and three tetra-chlorobenzenes. Once again, this also constituted a spectacular confirmation of the benzene theory itself.

The other principal approach to the absolute determinations of positional isomers among benzene derivatives was based on spatial arguments, and it centered especially (though not exclusively) on the benzene dicarboxylic acids, i.e., the isomers of phthalic acid. Laurent had prepared phthalic acid itself by vigorously oxidizing naphthalene (he named it by subtracting the first two letters of the starting material). In an article in the March 1866 issue of the *Annalen* (one month after Kekulé's major German paper), Erlenmeyer accepted Kekulé's benzene theory, and expanded certain aspects of it. In particular, he proposed that the naphthalene molecule $C_{10}H_8$ was formed of two fused benzene rings—i.e., rings that share two atoms in common, like conjoined twins.[53] This proposal was quickly adopted by most organic chemists.

Now, it had long been known that any hydrocarbon side chain on an aromatic nucleus, no matter how short or long the chain, will oxidize to form a CO_2H side chain (that is, the hydrocarbon chain is removed, leaving an oxidized "stub" of the chain still hanging on the aromatic nucleus). So it seemed reasonable to assume, if Erlenmeyer's naphthalene structure is presumed correct, that the two CO_2H stubs that were left on the benzene ring after oxidizing naphthalene *must be next to each other,* for their respective carbon atoms had formerly belonged to that second ring. This is to say, phthalic acid must be the 1,2 isomer. This idea seemed all the more probable when one considered that only phthalic acid, and not either of its alternate isomers, was found capable of forming an internal anhydride (that is, the two acid portions of a *single* diacid molecule combining together while losing a molecule of water to form an acid anhydride). It was suggested that only if the two carboxyl groups found themselves on neighboring carbon atoms could

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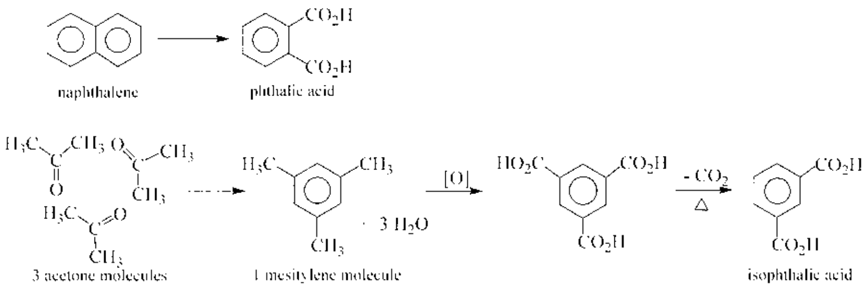
[52] Körner, "Faits" (1867); "Fatti" (1869); "Studj" (1874). For Körner's suggestions on the stereochemistry of benzene, see Paoloni, "Stereochemical Models."

[53] Erlenmeyer, "Studien" (1866).



28 Formation of phthalic and isophthalic acids.

they possibly react together to form the ringlike internal anhydride. It now seemed clear, at least to those making this spatial argument, that at least one isomer of one di-derivative could be assigned an absolute positional structure.[54]

Of course, even if this argument is accepted, it solves only part of the problem, for there are two other isomers of the dicarboxylic acid, terephthalic and isophthalic acids, with no way to determine which of these molecules had which of the two remaining possible orientations. But here too a way was found. A substance known as mesitylene had long been known as a condensation product of acetone, three molecules of acetone (C_3H_6O) combining with loss of three molecules of water to form a single hydrocarbon molecule with the formula C_9H_{12}. In 1866 Fittig showed that this compound was aromatic, proposed a non-Kekuléan notion of its structure, and reported that when oxidized it formed a benzene tricarboxylic acid. Baeyer immediately responded with a paper arguing that Fittig's oxidation to a tricarboxylic acid demonstrated that mesitylene could be nothing other than trimethylbenzene.

Moreover, since this compound had been formed by the convergence of three molecules of acetone, it was very likely that the hydrocarbon had a symmetrical molecular structure, namely, that it was 1,3,5-trimethylbenzene, the oxidized molecule being benzene 1,3,5-tricarboxylic acid. This assignment was also supported by the fact that only one isomer of any further substitution of mesitylene was known.[55] If one accepts this argument, and then removes any one of

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[54] The argument appears first to have been made by Baeyer's student Carl Graebe: Graebe and Born, "Hydrophtalsäure," (1867), 333.

[55] R. Kane, "Combinations" (1837), 100–102; Fittig, "Vorläufige Mittheilung" (1866); Baeyer, "Condensationsproducte" (1866); Fittig, "Untersuchungen" (1867).

these carboxylic acid groups—which was easily accomplished by thermal decomposition—then a new synthesis of the 1,3-dicarboxylic acid is achieved. This was found to be identical to isophthalic acid. The remaining dicarboxylic isomer, terephthalic acid, must therefore be the 1,4 isomer. One case of absolute spatial orientations on the benzene ring having been solved, it could be used (as described above) as a key for assigning all the other genetically determined ortho-, meta-, and para-derivatives known to date, and hence known in the future.

Although other models for the benzene nucleus were soon proposed, particularly Ladenburg's "prism" formula,[56] none attained the prestige and general acceptance of Kekulé's idea, and the determination of absolute positional isomers was regarded as a legitimate and viable goal for many of these aromatic studies. Almost immediately upon its first proposal, the theory began to be used as the basis for an astonishing number of investigations; A. W. Hofmann later commented, "One might say that with the idea of the benzene ring, the number of organic compounds appeared to increase to infinity at a single stroke."[57] In a wistful moment ca. 1880, Hofmann privately told Jacob Volhard, "I would give all my discoveries in exchange for this one of Kekulé's."[58]

Metachemistry?

In earlier chapters, and above, I have shown how Kekulé used his sausage formulas and models with heuristic confidence, even while disclaiming a realistic interpretation of them. He was convinced that valence was a constant rather than a variable quantity for any element; he rejected out of hand the notion that two affinities of a single atom could satisfy one another; he provided an appealing model for theories of double bonds, triple bonds, and unsaturated affinities ("gaps"), as well as a way easily to distinguish "atoms of the radical" versus "atoms of the type"; he was led to conclusions regarding certain structures (e.g., of pyrotartaric acid and of isopropyl alcohol) that other structuralists immediately jumped on as errors; and he discussed different theoretical options for the benzene nucleus. All of these are examples of positions that can be deduced or otherwise derived from contemplation of

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[56] For reviews of this subject, see Rocke, "Hypothesis and Experiment," 373–77, and Rocke, "Kekulé's Benzene Theory" (1988). Particularly important are Schelar, "Alternatives" (1966); Koeppel, "Benzene-Structure Controversies" (1973); and Koeppel, "Significance."

[57] Hofmann, "Tischrede" (1902).

[58] Volhard, *Hofmann* (1902), 166.

the particular kind of atomic symbols and models to which Kekulé was obviously attracted, from about 1857 to 1866. I suggest that they were so derived, at least in major part, and even conjecture that they constituted the "dream forms" of 1855 and 1862.

But the sausage formulas and models did have certain disadvantages that, as Kekulé confessed in 1867, "did not escape me right from the start." One of these disadvantages is that they were essentially linear, with the atoms in any molecule portrayed left to right in a horizontal row, and the bonds occurring only vertically, between the relevant atomic "bulges." Branches in a sausage chain were challenging to portray. It is no coincidence that two of Kekulé's significant missteps, pyrotartaric acid and isopropyl alcohol, had structures that Kekulé's rivals were convinced had branched chains. In the first case Kekulé erred in asserting a straight-chain structure, and in the second he erred in suggesting two different branched formulas for the same structure (they only *appeared* different because of the nature of the formulas). We have seen that Crum Brown in particular brought Kekulé up short both times and (correctly, as I believe) attributed the errors to disadvantages of the symbols that Kekulé had chosen.

The aromatic theory revealed additional problems, largely because of the complications of rings and branches that are so characteristic of aromatic substances. I have argued above, following Gillis, that Kekulé sufficiently trusted his sausage models once more, at least heuristically and provisionally, initially to propose two different possible conformations for the benzene CHT ring, awkwardly arrived at by manhandling his sausages into "rings." But as early as January 1865 he affirmed that benzene probably has a fully symmetrically structure. Although he continued to defend the sausages as superior to alternative formulas through the summer of 1866, he had in fact already begun backing away. His long German aromatic paper published in February 1866 still contained the triangle alternative, even though he rejected that option more clearly than ever in favor of the hexagon. In the aromatic *Lehrbuch* installment, published seven months later, no longer do we see any triangle, even as a rejected option. We now also see unembellished hexagons representing aromatic rings in graphic formulas, but with sausage atoms still portraying the side chains. And now we see a totally new formula style, quite similar to the Crum Brown notation, which Kekulé used only *once,* to portray a benzene ring.[59]

In March 1867 Kekulé finally abandoned his sausage formulas for-

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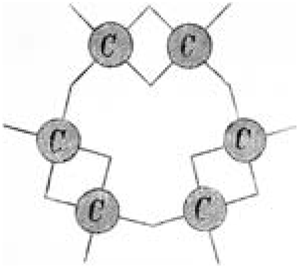
[59] *LB,* 2:496, 514, 744.



29 Kekulé's new graphic formula for benzene. Source: Kekulé, *Lehrbuch der organischen Chemie* (1866), 2:496.

ever, in favor of an alternative graphic formula style.[60] He accompanied his conversion with an explanation. It had always been his opinion that the disadvantage of Crum Brown's, Hofmann's, and Frankland's circle-and-line formulas (circles representing atoms, lines representing the joined affinity units) was that the lines have to be drawn differently (i.e., lengthened, shortened, curved, etc.) for double bonds than for single bonds. Not so for the sausages, which only need to be shoved closer together to go from a single to a double bond, and which (he noted) had often been used pedagogically by chemical colleagues. The glyptic (ball-and-stick) models based on the Crum Brown graphic formulas share the same disadvantage; moreover, such models had always been constructed in a planar fashion, thereby forgoing any advantage of the third dimension. To be sure, he wrote, the sausage formulas have their own problems. But the best features of both styles could be combined by the novel formulas that he was now proposing. Using a modified circle-and-line graphic style, Kekulé depicted three molecules of acetone approaching one another, then the same array after loss of three molecules of water and formation of three new carbon-carbon double bonds to form a single molecule of symmetrical mesitylene (1,3,5-trimethylbenzene). Kekulé remarked that this was exactly the same idea that had recently been proposed by Baeyer (discussed above), but the concept was much clearer when illustrated as he had just done.

These new two-dimensional circle-and-line graphic formulas, Kekulé revealed, had in fact been drawn from actual three-dimensional ball-and-rod models that he had had constructed for his Ghent laboratory. One of the new features here was that the lengths and angles of the lines (or in the model, the metal rods) joining the circles (wooden

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[60] Kekulé, "Mesitylen" (1867); Anschütz, 2:527.

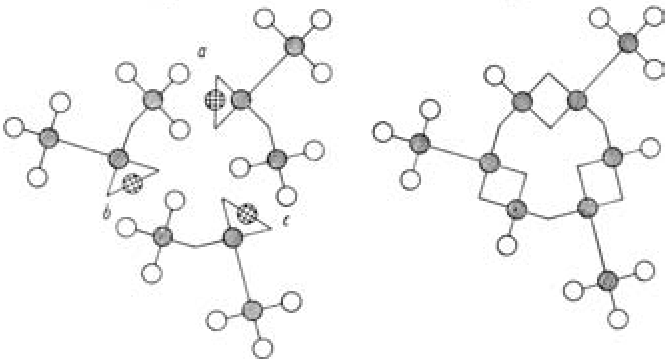
Fig. 1. Fig. 2.

30 Formation of mesitylene from three molecules of acetone. Source: Kekulé, *Zeitschrift für Chemie* 10 (1867): 215.

balls) were cleverly chosen so that one did not need to arbitrarily bend or lengthen them to depict double bonds; the same lines/rods could serve both functions without alteration. Triple bonds were still not possible without change, but one could indeed accomplish even this, with one additional modification: one can array the four affinity-rods for the carbon-atom wooden model in a *tetrahedral* fashion. A simple mechanical arrangement, he explained, had made it possible to attach the affinity-rods to each other at any angle, thus producing a molecular model kit "that accomplishes, it seems to me, everything that a model is in principal capable of accomplishing."

Kekulé presented the advantages of the same tetrahedral molecular models in a paper at the Naturforscherversammlung in Frankfurt in September 1867, and used them regularly in his classes in Bonn from summer semester 1868 (he had requested and been granted no teaching duties for winter 1867–68). Anschütz was familiar with these models from his own education at Bonn, and described them minutely; some examples are preserved at the Science Museum in Ghent.[61] Baeyer used these models in his teaching from 1867 on, and explicitly mentioned them as leading to his "strain theory" of 1885.[62] But despite the implications of his models, Kekulé always explicitly denied that the *actual* bonds of *actual* carbon atoms were tetrahedrally arrayed. As had been the case for his sausage formulas, indeed for all formulas, he regarded

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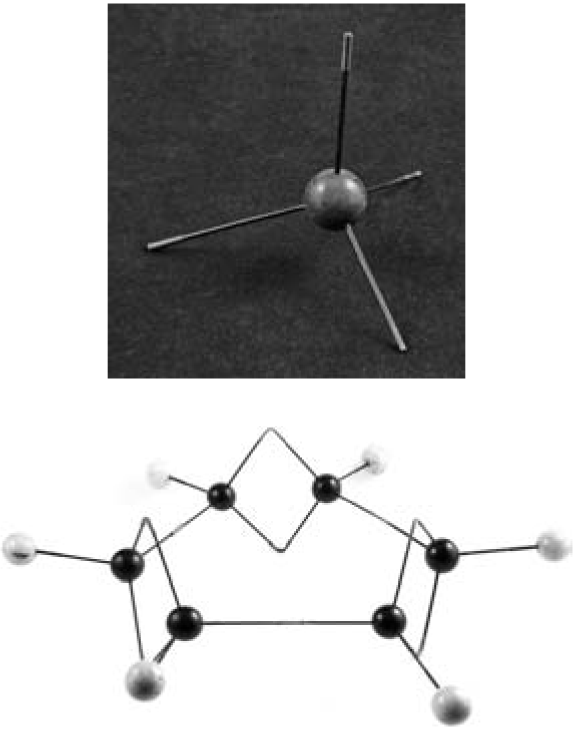
[61] Anschütz, 1:356n. See also Ramsay, "Molecules" (1974); and Ramsay, "Molecular Models" (1975).

[62] Baeyer, *Werke* (1905), 1:xxxiii–xxxiv.



31 Kekulé's tetrahedral carbon atom model; his new model for benzene. Source: Museum for the History of Sciences, University of Ghent.

them as conventional heuristic devices only, not realistic stereospatial representations.

The year 1867 seems to have been a sort of nodal point for atomistic representations, for it was then that the first molecular model kits, fashioned after the example of Hofmann's glyptic models of 1865, were commercially marketed in England (see the end of chapter 5). It was also the year of backlash against them. In June, Benjamin Brodie provided the London Chemical Society a summary of his new anti-atomistic "calculus of chemical operations," the first part of which had recently appeared in the *Philosophical Transactions of the Royal Society.* Brodie came equipped with an advertisement for the new models, and ridiculed them so effectively that his audience was moved to laughter. Chemical philosophy, he said, had gotten thoroughly "upon a wrong track," indeed "altogether off the rules of philosophy" to have produced "such a bathos as this." In the discussion, Frankland protested Brodie's position, while William Odling defended it.[63] The anti-atomists appear to have won this round of the "atomic debates."[64]

Kekulé read a transcript of this discussion that appeared in the *Chemical News*. "I will probably need to criticize [Brodie's] nonsense," he wrote to Baeyer; "I have in fact promised *The Laboratory* a couple of articles on theory and atomicity, & naturally cannot speak of atomicity without first having touched upon the various attacks on the atomic theory itself."[65] This proved to be only the second (and the last) English-language paper of his life. Kekulé had carefully studied Brodie's "chemical calculus," and he demolished central elements of it with great effectiveness. It was, he concluded, hyper-hypothetical, arbitrary, inconsistent, and "based on pure caprice." He declared his own position on the matter:

> The question whether atoms exist or not has but little significance in a chemical point of view: its discussion belongs rather to metaphysics. In chemistry we have only to decide whether the assumption of atoms is an hypothesis adapted to the explanation of chemical phenomena. . . . I have no hesitation in saying that, from a philosophical point of view, I do not believe in the actual existence of atoms, taking the word in its literal signification of indivisible particles of matter. I rather expect that we shall some day find, for what we now call atoms, a mathematico-mechanical explanation, which will render an account of atomic weight, of atomicity, and of numerous other properties of the so-called atoms. As a chemist, however, I regard the assumption of atoms, not only as advisable, but as absolutely necessary in chemistry. I will even go further, and declare my belief that *chemical atoms exist,* provided the term be understood to denote those particles of matter which undergo no further division in chemical metamorphoses.[66]

In the secondary literature, one often encounters citations of a portion of this passage, particularly the third sentence above cited alone, which has misled some into thinking that Kekulé's position was that of an atomic skeptic. His purpose, of course, was just the opposite: a vigorous

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[63] Brodie, "Chemical Calculus" (1867).

[64] Brock, *Atomic Debates* (1967).

[65] "Ich werde wahrscheinlich den Schwindel kritisiren müssen; ich habe nämlich dem *Laboratory* ein paar Artikel über Theorie u. Atomigkeit versprochen, & kann natürlich nicht von Atomigkeit reden ohne zunächst die verschiedenen Angriffe auf die Atomtheorie selbst berührt zu haben." Kekulé to Baeyer, 3 July 1867, AKS.

[66] Kekulé, "Chemical Philosophy" (1867).

defense of the utility, indeed the necessity of atomic theory, and of the reality of chemical atoms. His position reflected that of most of his colleagues. Chemical atoms may well not be irreducible bits of matter, like Dalton's tiny hard spheres; but they *behave chemically* as if they were, Kekulé was saying, and the chemist is perfectly justified in using this empirically supported concept. Indeed, if he did not use the concept he could not be a chemist.

Hermann Kolbe was clearly more of Odling's mind, at least as regards the accessibility of atomic details. The problem was not so much with Kekulé himself, Kolbe publicly opined in early 1875, for he believed that Kekulé considered the benzene ring as nothing more than a useful hypothesis. The problem was that for those who blindly followed Kekulé, the benzene theory had become an "infallible dogma," believed in just as unthinkingly as Catholics believed in the "infallibility of the old man in Rome." They were true fanatics, "looking down with pity in imagined superiority on those who do not agree with the modern methods of the newer direction of chemistry, which in reality often dispenses with any method at all."[67]

> The modern chemist, who knows exactly what a chemical compound looks like in its middle and its end, how the six carbon atoms of benzene are symmetrically linked together in a plane, who then further purports with this hypothesis (which calls itself theory) to have a clear conception of the spatial arrangement of the atoms, of their ortho, meta, and para positions, who determines the positions of all of the atoms in the compound, has long since abandoned the solid ground of exact science; the scientist has become a metaphysician.[68]

Kolbe hit upon a clever piece of mocking satire in naming true physicists "orthophysicists," in contrast to "paraphysicists," who construct hypotheses on the basis of experimental work of others, and "metaphysicists," that is, metaphysicians, who believe that they can dispense entirely with empirical evidence.[69] But as the years went by, he increasingly believed that even the term "parachemist" was too kind; his opponents were metachemists, "to whom chemical theories are as cheap as blackberries."[70] The year before his death he wrote, as always for publication in his proprietary journal:

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[67] Kolbe, "Rückblick auf 1874" (1875), 449–50.

[68] Kolbe, "Rückblick auf 1873" (1874), 419–20.

[69] Kolbe, "Chemischer Traum" (1878), 440n.

[70] " . . . deren chemische Theorien so billig sind wie Brombeeren." Kolbe to Volhard, 16 December 1874, ADM 3676. He named here Kekulé, Baeyer, Graebe, Hlasiwetz, and Fittig.

> Questions regarding the *spatial arrangement* and *disposition* of the atoms in a molecule, whether they are at the end or in the middle of the molecule, regarding the *sequential order* in which they are deployed in the molecule, regarding the manner of their chemical bonding, and finally regarding their leisure-time hobbies, whether they are sitting, hanging, sticking, more or less near to each other (Wislicenus), hooking each other, throwing out fish-hooks (Baeyer), etc.—these are not and *never* will be the subject of scientific research for sober chemists, whose investigations take place in the field of *positive* chemistry, and who lack the sixth sense which is required to pursue *transcendental* chemistry.[71]

Here Kolbe was mixing his criticism of positional isomerism in aromatic chemistry with his detestation of a new subfield of chemistry that had opened up in the 1870s, which we will consider in the next chapter.

But Kolbe's rhetorical efforts were in vain. Kekulé's benzene theory steadily gained prestige, even though many made suggestions for more or less insubstantial modification. Edvard Hjelt summarized the impact of the theory: "It made sense of existing knowledge, while also throwing a flood of light into the future. But among the most remarkable circumstances is the fact that this theory, although largely intuitively derived, has shown itself to be essentially correct and has permanently proven itself."[72] And in his memorial lecture for his mentor, Francis Japp wrote, referring particularly to the benzene theory: "The accuracy of Kekulé's predictions has done more to inspire a belief in the utility of legitimate hypotheses in chemistry, and has therefore done more for the deductive side of the science, than that of almost any other investigator. His work stands pre-eminent as an example of the power of ideas."[73] One might add: . . . and the power of visual images.

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[71] Kolbe, "Reale Typen" (1883), 441n.

[72] Hjelt, *Geschichte* (1916), 300.

[73] Japp, "Kekulé" (1898), 138.

EIGHT

Dimensional Molecules

Your [Liebig's] natural intellectual predisposition, poetic and rich in the power of the imagination, showed you how to achieve new and unexpected routes to results. . . . The poetic inclination of your mind, combined with a great facility of diction, soon led you to the unlimited field of theories, where precisely the poetic talent is the most dangerous companion. It has dictated brilliant dreams of imagination to you, which you have given to us with the expression of your complete conviction. JACOB BERZELIUS[1]

I don't want to say that it is a mistake, but it would have been an advantage if [Berzelius] had been somewhat more receptive to creation through thought, what I call the poetry of scientific research. JUSTUS LIEBIG[2]

If atoms are real material entities, they must exist in real space, and space has three dimensions. This truism was not lost on any perceptive atomist, ancient or modern, though most recognized serious difficulties in operationalizing it. This chapter traces the evolution of certain theories from Dalton to van't Hoff, which eventually constituted a new field called "stereochemistry," or the chemistry of three-dimensional molecules. The final section of the chapter broadens the scene to include physicists and the incipient kinetic theory of gases.

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[1] Berzelius to Liebig, 14 November 1843, *BLB,* 250. The original German begins: "Deine natürliche Geistesanlage, dichterisch und reich an Einbildungsvermögen (Imagination)." It was the last letter of their correspondence.

[2] Liebig to Wöhler, 26 June 1848, *BLB,* 265.

Early Stereospatial Speculations

John Dalton paid considerable attention to the spatial aspects of his novel theory of chemical atoms. As W. V. Farrar commented, "there was never anything shadowy or metaphysical about his atoms; they were (in Newton's phrase, which he often quoted) 'solid, massy, and hard'; too small to see, but very real."[3] Indeed, Dalton thought deeply about the ultimate atoms of matter long before he developed his chemical theory. On a day hike with a younger friend about the year 1820, he spoke of those early ideas of his. Picking up a lump of limestone from the road to illustrate them, he led his companion Socratically down to the world of the invisibly small, retracing his own mental steps from many years earlier. Finally they reached in thought the ultimate particles composing the limestone, and could go no further; Dalton concluded, "thou knows it must be so, for no man can split an atom."[4]

About 1810 Dalton had atomic models made to assist in his teaching. These were gumball-sized wooden balls connected by pins—not to represent Crum-Brownian valence bonds, but rather to enable them to be arrayed contiguously, in close-packing fashion. Some of these models survive at the London Science Museum. In his laboratory notebook, in placards prepared for his various public lectures between 1805 and 1811, and in one late published paper, Dalton proposed molecular structures for at least twenty-two organic substances, some of them in three-dimensional space-filling representations.[5] After Dalton's death, his friend Angus Smith wrote, "We find no scientific man holding the idea [of atoms] with such firmness; to others it was a theory, to Dalton it was a fact, which he could not conceive otherwise. . . . We appear to be entirely removed from the region of speculation when reading his words."[6]

Dalton was not the only early chemical atomist to indulge in stereospatial thinking. In the article in which he first proclaimed his adherence to Dalton's atomic theory (1808), William Wollaston stated that he was "inclined to think . . . that we shall be obliged to acquire a geometric conception of [the] relative arrangement [of the atoms in a

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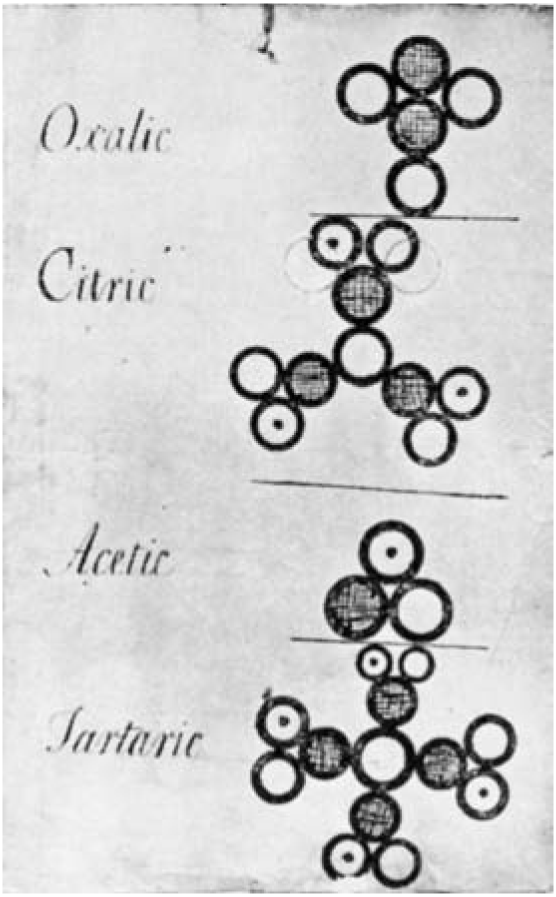
[3] Farrar, "Dalton" (1968), 290.

[4] The younger friend was Joseph Ransome, who related the story in a letter to Dalton's biographer W. C. Henry (Henry, *Memoirs* [1854], 220–22).

[5] Namely: methane, ethylene, butylene, ethanol, methanol, ether, acetone, acetic acid, oxalic acid, tartaric acid, racemic acid, citric acid, oxamide, sugar, oil, tannin, albumin, gelatin, fibrin, indigo, cheese, and wood. See Farrar, "Dalton"; also Coward and Harden, "Lecture Sheets" (1915).

[6] Smith, *Dalton* (1856), 231–32.



32 One of Dalton's lecture placards. Source: Dalton, *Manchester Memoirs,* 59:12 (1915), plate VII, sheet 24 (ca. 1811).

molecule] in all the three dimensions of solid extension."[7] That this was not simply a passing fancy for Wollaston is shown by his return to similar considerations in 1812, when he argued that the different cleavage planes of crystals were a function of the pattern of close-packing of the atoms that composed the crystals. Like Dalton, he even developed three-dimensional wooden models to illustrate these ideas.[8]

Beginning in the late 1820s, about the time that the chemical atomic

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[7] Wollaston, "Salts" (1808), 101–2.

[8] Wollaston, "Elementary Particles" (1813); Goodman, "Wollaston" (1969).

theory began really to take off, we find evidence of another spurt of spatial atomistic thinking. In his 1830 textbook Mitscherlich provided a diagram of the locations of the six atoms, referred to as "balls," comprising the molecule of potassium sulfate, and the ten atoms comprising potassium dichromate. He commented, "At the time of the first proposal of the atomic theory, the atoms of simple bodies were imagined as balls that lay touching each other in a chemical compound." This original concept, he continued, suffices to explain most phenomena today and requires few changes to apply to all cases.[9] When Thomas Graham visited Germany for the first time in September 1836, he was much impressed by Mitscherlich. He wrote his brother:

> I was particularly struck by the beautiful simplicity of some hints which he diffidently threw out as to the effect of a base, such as water or potash, on the corpuscular arrangement of particles which cannot subsist without a base. . . . This idea of Mitscherlich is, of course, altogether hypothetic, and he by no means pressed it, but it is certainly a *very little* assumption, and we can observe in it the great secret of correct philosophizing, namely, to advance by the shortest possible steps. In these corpuscular speculations it was interesting to observe how naturally he fell into the simple but philosophic views of Dalton in regard to atomic arrangements.[10]

Berzelius also at least occasionally indulged in this manner of thinking. In a volume of his monumental textbook published in 1837, he provided an example of how the same set of atoms can come together, or come apart, in different ways. He illustrated this with a diagram showing an arbitrary combination of seven atoms (represented by seven contiguous circles), namely, three metal atoms and four oxygens. Such a compound, he pointed out, could be considered MO combined with M_2O_3, or alternatively 2MO combined with MO_2. He did, of course, caution that the figure was "in no way intended to provide an idea of how the atoms in nature are positioned next to one another." It nonetheless suggests something of the pattern of his thought.[11]

It was just at this time that Berzelius and Liebig began to quarrel (by letter) over the new theories of polybasic organic acids and of organic hydracids that Liebig played such an important role in promoting. Berzelius had been an immensely labile theoretician in his youth,

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[9] Mitscherlich, *Lehrbuch* (1843–47), 1:605–6. Hermann Kopp cited the same passage and diagram from the third edition of 1830 (1:368), which was not available to me: Kopp, *Entwickelung* (1873), 830.

[10] Thomas Graham to John Graham, 27 September 1836, in Smith, *Graham* (1884), 38.

[11] Berzelius, *Lehrbuch* (1837), 6:16–18.

but by the 1830s had largely withdrawn from creative theorizing, and adamantly rejected Liebig's ideas. As the epigraphs above indicate, Berzelius castigated Liebig for what he regarded as an overdeveloped poetic and visual imagination, while Liebig privately opined that Berzelius's principal failing in maturity was to have neglected the same faculty.

In his autobiographical notes, Liebig stated that his passionate boyhood immersion in practical chemistry had developed in him the ability to "think in phenomena," using a kind of visual memory of substances and their reactions. Heinrich Debus ascribed the same mental facility to Bunsen, contrasting this "concrete" manner of thinking with a more abstract and subtle mode, and agreeing, citing Liebig, that the former was of much greater utility to the chemist.[12] Ironically, at the very time Liebig was writing these encomia to imaginative theorization he was also withdrawing from theoretical chemical discussions and returning to the safe (putatively empirical) haven of conventional chemical equivalents.

Those who tried to imagine the molecular world in the first half of the nineteenth century had to start with some basic assumptions or ground rules, beyond simple atomism. As we saw in chapter 1, a number of chemists, following Claude-Louis Berthollet at the very beginning of the century and including Graham, Williamson, and Frankland, speculated according to a kinetic or gravitational model, often patterned after the solar system.[13] This was a natural concomitant to Newton's well-known hope someday to be able successfully to apply classical mechanics to the microworld. Dumas, who idolized Berthollet, wrote in 1837: "We will perhaps someday boast, and not without reason, of successfully exploring the insides of bodies, of revealing the nature of their organs, of discovering the movements of the little systems in which they consist. We will believe it possible to submit these molecular movements to calculation, as Newton did for the celestial bodies."[14] Dumas developed this image more thoroughly three years later. In his "first memoir on chemical types" he suggested that molecules could be viewed as "so many planetary systems, formed from particles that are maintained by the diverse molecular forces whose resultant is affinity." These particles, he added, "would play the same role in the constitution of bodies which the planets play in our solar

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[12] Liebig, "Biographische Aufzeichnungen" (1963), 13–17; Debus, *Bunsen* (1901), 145.

[13] For excellent and broad discussions on this subject, see, for the nineteenth century, Levere, *Affinity and Matter* (1971), and for the eighteenth century, Thackray, *Atoms and Powers* (1970), and Kim, *Affinity* (2003).

[14] Dumas, *Leçons* (1837), 234.

system, either that of simple planets like Mars or Venus, or compound planets such as the earth with its moon, or Jupiter with its satellites."[15]

This was an undeniably appealing image, but problems arose in multitudes when one tried to develop a more specific and usable theory. The gravitational model simply could not be made to work chemically, on any detailed level. William Whewell put the point well in 1840:

> Yet this view [that chemical attraction is of the same kind as gravitational] has never, so far as I am aware, been worked out into a system of chemical theory; nor even applied with any distinctness as an explanation of any particular chemical phenomena. Any such attempt, indeed, could only tend to bring more clearly into view the entire inadequacy of such a mode of explanation. For the leading phenomena of chemistry are all of such a nature that no mechanical combination can serve to express them, without an immense accumulation of additional hypotheses.[16]

It was partly for this reason that another conceptual model for the molecular world arose in the early years of the century, one that imagined more or less stationary atoms in molecular lattices, often thought to be held together by electrical polarities. This was the crystallographic tradition that was developed initially by René Just Haüy in 1784, supplemented by chemical atomism and electrochemical dualism after 1800, and that we saw reflected in some measure in Wollaston's 1812 paper. Haüy's model, modified by the ideas of Berzelius, Avogadro, and Ampère, led to the molecular theories of M. A. Gaudin and of Alexandre Baudrimont in the 1830s, which were influential on Auguste Laurent. But by this time the chemical world was already moving away from ideas that invoked coulombic attractions between atoms; this model increasingly seemed to be just as discordant with the accumulating chemical evidence as the gravitational paradigm was. The electrochemical school was in decline in the 1840s, and by the 1850s it was on life support.[17]

By midcentury, it was understood by most perceptive scientists that neither of the two best-known physical forces, gravity and electricity, had proven usable in any detailed development of chemical theory. This realization surely must have helped to reinforce the more

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15. Dumas, "Premier mémoire" (1840), 73–74. Dumas offered no way to reconcile this image with his structural-mechanical metaphor for types, which he had propounded just the previous year.

16. Whewell, *Philosophy* (1840), 1:372.

17. Mauskopf, "Ampère and Gaudin" (1969); Mauskopf, *Crystals and Compounds* (1976); Miller, "Gaudin" (1975).

positivistic (or the more pragmatic) stance toward molecular assumptions that most chemists were then adopting.

The Spiral Staircase[18]

Haüy, Wollaston, and some others had thought that they could learn about the ultimate particles of substances by studying the shapes and cleavage planes of the crystals that the particles formed in the aggregate. In the first quarter of the nineteenth century another more or less direct physical route to the molecular level emerged, namely in the interactions of matter with light. The phenomenon that in 1811 Étienne-Louis Malus named "polarization" of light was exhibited by light that was either reflected at a surface or had passed through certain transparent minerals. In 1815 Jean-Baptiste Biot discovered that solutions of certain organic substances such as oil of turpentine rotated the plane of polarized light, similarly as had already been noticed for quartz. The amount of rotation differed for each active substance, but was always directly proportional to the amount of the organic substance through which the light passed. Turpentine *vapors* exhibited the same optical activity. Since optical rotation is an asymmetric phenomenon—that is, it shows right-handed (clockwise) or left-handed (counterclockwise) character—and since molecules of liquids and gases cannot have fixed orientations in space (as opposed to crystal lattices), Biot reasoned that such rotations could only derive from some asymmetry *in the molecules themselves* of every optically active organic substance. In 1832, and in more detail in 1836, Biot showed that tartaric acid was also optically active in the same way as he had already shown for turpentine, sugar, lemon oil, and camphor, rotating the plane of polarized light to the right (that is, clockwise as one looks in a polarimeter, through the transparent sample at the source of polarized light).

Dibasic tartaric acid ($C_4H_6O_6$) was a particularly important case, not just because its salts exhibited beautifully formed crystals, but also because it had become a crucial early instance of isomerism, which Berzelius had first discussed, defined, and named in 1830. Tartaric acid was derived from the pink tartar deposited by fermenting red wine, and the substance had been characterized chemically for almost seventy years, but a distinct substance with the same formula, also derived from wine

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[18] On the history of stereochemistry, see especially Ramsay, *Stereochemistry* (1981), and Ramberg, *Stereochemistry* (2003).

tartar, was a relatively recent discovery. Between 1820 and the 1850s this second substance was known solely from a single large stock derived from a certain wine factory in Alsace. Gay-Lussac published an analysis of it in 1826, establishing the isomerism with tartaric acid; he called it "racemic acid," but it had other names as well.[19] Biot noted that despite possessing the same formula as tartaric acid, in addition to other variant properties it was also optically *inactive.*

In 1844 Mitscherlich drew attention to facts that seemed inconsistent with the well-established isomerism between tartaric acid and racemic acid. Namely, the sodium-ammonium salts of each of the two acids have the same crystal form, in fact they possess identical physical and crystallographic properties right down the line, with the single exception that the first is optically active and the second is not. In following up this curious observation, in late April 1848 a twenty-five-year-old préparateur at the École Normale named Louis Pasteur made a monumental discovery. He noted that the tiny crystals of the tartaric salt possessed facets that gave them an asymmetric form (analogous to a human hand or a spiral staircase). The crystals of the racemic salt also looked, even on close inspection, to be identical to each other as well as to the tartaric crystals. But they were not *all* identical. About half the racemic crystals were, in fact, indistinguishable from the tartaric crystals, but the other half were exact mirror images of the first. The asymmetric facets of the latter crystals faced the opposite direction, and the two sorts of crystals could not be superimposed, even in one's imagination—just as a right hand cannot superpose onto an otherwise identical mate, or a right-hand spiral onto an otherwise identical left-hand spiral.[20]

What Pasteur had discovered was that there are two distinct mirror-image varieties of tartaric acid, which we can symbolize here as T_R and T_L. The tartaric acid known for decades was pure T_R, the acid that rotated polarized light to the right. T_L was completely unknown until Pasteur's discovery; other than optically, it has *precisely identical* physical and chemical properties to T_R. Pasteur showed that racemic acid was nothing other than an equal mixture of the two, namely, T_R+T_L. Since T_L rotated light equally but in the opposite direction as T_R (being its mirror image), the two activities exactly canceled, and that was why racemic acid exhibited no optical activity. It turns out, for complicated

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[19] Acide racémique, vinic acid, and Traubensäure all refer to an acid from grapes or wine. By the 1840s most French and English chemists were calling it paratartaric acid.

[20] Pasteur, "Mémoire" (1848).

reasons, that a mixture of two such mirror-image isomers (today called enantiomers) often results in an alteration of physical and chemical properties vis-à-vis either pure isomer, which was why racemic acid was so long considered an isomer of tartaric acid.[21] But for equally complicated reasons, the particular salt that Mitscherlich and Pasteur worked on happened not to exhibit these distinctive properties, hence producing the anomaly that drew Pasteur's attention to the problem. This particular racemic salt also atypically crystallizes out under certain physical conditions in separate mirror-image (enantiomeric) crystals.

In the previous paragraph I wrote loosely of T_R and T_L being mirror images. What I meant, in the first analysis, is that the *crystals* of the substance form nonsuperposable mirror images, but Pasteur and many other chemists immediately inferred that there also must be a corresponding kind of mirror-image asymmetry to the *molecules* that composed the crystals—for why else would the free-flowing liquid (or even gaseous) versions of these substances exhibit the same behavior of "handedness" (now called "chirality") by producing opposite optical rotations? Using a hand lens and tweezers, Pasteur laboriously separated the two kinds of mirror-image crystals of racemic acid. After the discovery he called Biot, now an old man, to his laboratory, and Biot witnessed such a separation. Biot then took the last step. He placed a solution of the novel left-handed crystals in a polarimeter and looked through the tube. The rotation was exactly equal and opposite to the known rotation of tartaric acid, proving Pasteur's point. Biot was deeply moved. According to Pasteur's later reminiscence, Biot took him by the arm, saying, "My dear child, I have loved science so much throughout my life that this makes my heart throb."[22]

In the retrospective account from the year 1860 in which this anecdote is found, Pasteur carefully and correctly distinguished between superposable mirror images, which constitute symmetrical (molecularly identical) objects, and nonsuperposable mirror images, which are asymmetric (and molecularly distinct, hence isomeric). The first material discovered to be optically active, quartz, was found to lose its

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[21] Racemic acid, having now been shown to be nothing more than a mixture of two kinds of tartaric acid, thus vanished from science as a fictitious compound; but today chemists refer to a "racemic mixture" as an equal mixture of any enantiomeric pair. The original stock of racemic acid must have come from tartar which had aged long enough that the tartaric acid had gradually and naturally racemized.

[22] This anecdote derives from Pasteur's lectures to the Société Chimique de Paris on 20 January and 3 February 1860: "Recherches," in *Leçons* (1861), translated in Pasteur, *Researches* (1905), 21. For detailed and illuminating contextual studies of these events, see Mauskopf, *Crystals and Compounds,* and Geison, *Pasteur* (1995), 53–89.

activity if dissolved or fused. This indicated that the asymmetry must inhere in the mode of aggregation of its particles. This was not true of any active organic substance, whose activity, Pasteur thus claimed, must inhere in the molecules themselves, proving Biot's speculation of many years earlier.

> Are the atoms of the right-handed acid grouped on the spirals of a right-handed helix, or placed at the summits of an irregular tetrahedron, or disposed according to some particular asymmetric grouping or other? We cannot answer these questions. But it cannot be doubted that the atoms are grouped in some asymmetric order having a non-superposable mirror image. It is no less certain that the atoms of the left-handed acid have precisely the opposite asymmetric grouping.[23]

In making this discovery, Pasteur drew deeply from the French molecular-crystallographic tradition, and also, as both Mauskopf and Geison have rightly emphasized, from the work of Auguste Laurent. Pasteur soon forgot his debt to Laurent, giving generous retrospective credit only to Biot and to Antoine Balard, in whose laboratory the work was done. But this is not surprising, and perhaps it is even forgivable. The moment of discovery happened during one of the most difficult and disturbing years in modern French history, positioned at the precise midpoint between the two bloody insurrections in Paris of February and June 1848. Laurent was an ardent republican who came to a bad end, being shut out of the power structure and dying young, in 1853. After a brief period of republican optimism after the initial revolution of late February 1848, the authoritarian empire of Napoleon III became established in France. By the time of Pasteur's retrospective account, many considered it professionally unhealthy to signal leftist leanings, and Pasteur's own youthful flirtations with republicanism were long in the past.

This chaotic political context partially explains not only Pasteur's neglect of one of his most important mentors, but also, perhaps, why this major discovery had so little immediate effect on the science of his day. But there are other factors, as well. Considering the multiple atomic-weight systems contending at that time, no one could have made progress in understanding the three-dimensional orientations of the atoms in organic molecules until the chemical community could come together in agreeing how many atoms of which types were present in any molecule; this became possible only after the formula re-

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[23] Pasteur, *Researches,* 24 (with my slight revisions to the Alembic Club translation).

forms of the "quiet revolution" of the 1850s and the Karlsruhe Congress of 1860. Even thereafter, these reforms did not much penetrate into one particular European country, namely, Pasteur's motherland.

Added to this was the fact that the tradition out of which Pasteur's contribution had grown, the model-building crystallographic tradition, was increasingly out of favor in the 1850s and 1860s, in preference to the rise of "atomicity," a.k.a. valence. The rise of ideas regarding atomic valence and molecular structure required, at least for a time, a suspension of belief in the foundational importance of *either* gravitational *or* electrical force in the construction of molecular reality. And finally, the ascendancy at this time of more positivistic styles of rhetoric and of thought, particularly in France, worked against any explicit structural molecular model-building, whether in the form of mental images or physical forms. Stereospatial speculations were particularly anathema, as they carried the implication of a realist depiction of the true nature of the unseen microworld.

The Pyramid

In 1904 the University of Utrecht named their new laboratory for physical chemistry after their native son Jacobus Henricus (Henry) van't Hoff (1852–1911). The great scientist, winner three years earlier of the first Nobel Prize for chemistry and the leading figure in the early history of stereochemistry, spoke at the grand opening, telling a tale from his youth, thirty years earlier. Van't Hoff said, "I would like to give you students a recipe for making discoveries. [Libraries] . . . have always had a mind-deadening effect on me. So when I was studying Wislicenus's just-published paper on lactic acid in the Utrecht library, I interrupted my reading half-way through to take a walk, and it was on this walk, under the influence of the fresh air, that the thought of the asymmetric carbon atom first occurred to me."[24]

The backstory of this "just-published paper on lactic acid" ($C_3H_6O_3$) is important. We have already encountered lactic acid in the third section of chapter 4. Its constitution—formulable according to the dictates of the Kekulé-Couper theory as either methyl glycolic acid or, what is the same thing, hydroxy propionic acid—was understood by

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[24] Van't Hoff spoke on 16 May 1904, describing an event that probably occurred in the late summer or fall of 1873, when he was preparing for his doctoral exams at the University of Utrecht. See Cohen, *van't Hoff* (1912), 85, 514, 519.

1861, through the efforts especially of Kolbe, Wurtz, and Kekulé. These chemists all worked with what was known as "ordinary" lactic acid, derived from fermented (spoiled) milk. There was, however, a second kind of lactic acid, which had been isolated from muscle tissue. Since the two substances had the same formula but were unquestionably distinct, everyone looked for differences in their molecular constitutions. There were good evidentiary reasons to believe that "milk" lactic possessed a methyl group, hence had to be $CH_3CH(OH)CO_2H$. Most chemists therefore guessed, without additional evidence, that "meat" lactic was probably $CH_2(OH)CH_2CO_2H$.

However, in 1869 the Zurich chemist Johannes Wislicenus synthesized a new compound, a third distinct isomer of lactic acid, and showed that it had to have the constitution that had hypothetically been imputed to "meat" lactic acid. According to a secondhand report, Wislicenus inferred that "meat" lactic therefore had to have exactly the same constitution as that which had already firmly been established for "milk" lactic. The two distinct lactic acids derived respectively from meat and from milk were thus henceforth known as what were called "absolute" isomers—that is, isomers that possessed exactly the same structures, as far as one could tell, the source of whose isomerism therefore remaining mysterious. Wislicenus concluded that the isomerism must somehow be explained by "the different arrangements of their atoms in space." For instance, perhaps density measurements would show that the arrangements of the atoms of the different isomers fill space more or less efficiently, even though the formulas are identical.[25]

Wislicenus's habit of thinking spatially is shown by a passage in an article that he had published six years earlier on lactic acid (chapter 4, fig. 7). There he cited three apparently distinct "type" formulas that had recently been proposed for "milk" lactic acid, but he added that the differences were entirely superficial and not substantive. "[E]ven if we could ever learn the actual *spatial arrangement* of atoms in a compound," the same representational problem would persist, " . . . because our formulas can at best represent *pictures of bodies drawn in a plane.* But if one wishes to represent all the perceptible properties of a body, *several pictures drawn from different standpoints* are required."[26] This was a close paraphrase of a passage in Kekulé's *Lehrbuch.*[27]

In a published secondhand account of related research described in

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[25] Wislicenus, as reported by O. Meister in *Berichte* 2 (1869): 619–21. For a discussion of this and the following material, see Fisher, "Wislicenus," 33–54.

[26] Wislicenus, "Studien" (1863), 46.

[27] *LB,* 1:157–58.

an oral presentation two months earlier than the 1869 report we just cited, the correspondent, who was none other than Kekulé himself, reported: "The speaker [Wislicenus] drew our attention to the fact that the existence of three [lactic] acids demonstrated the limitations of the structural formulas in general use, as also of the views that are usually expressed in these formulas. Such subtler cases of isomerism might perhaps best be interpreted using a spatial representation of the grouping of the atoms, that is, by using [molecular] models."[28] It was in this work that Wislicenus first mentioned one long-known (but long-neglected) difference between "milk" and "meat" lactic acid: the latter was optically active, the former was not. In fact, chemists had not given much attention to the phenomenon of optical activity, in lactic acid or anywhere else, despite Pasteur's dramatic work. It seemed to be more a domain of optics, that is to say physics, and few chemists at this time thought that optical activity could be correlated to any interesting or important chemistry. (It would eventually be established that "meat" lactic acid is a pure enantiomer, and that "milk" lactic acid is an equal mixture of the two mirror-image molecules—a precise analogy to tartaric and racemic acids.)

Wislicenus returned to the same subject once more in 1873, reviewing all that was then known about the various isomers of lactic acid, including the now-well-established identity in structural formulas of "milk" and "meat" lactic acid. Once again he wrote that the difference in the two isomers must somehow relate to a "different spatial arrangement of the atoms which are bound together in the same order." It will be necessary in the future, Wislicenus opined, to look to the "*geometric* arrangement of chemically structurally-identical molecules."[29] It was this article that van't Hoff pondered on his walk outside the Utrecht University library, in the late summer or fall of 1873.

Van't Hoff had studied science and mathematics at the Delft Polytechnic, then the University of Leiden.[30] Eager for the best chemical education possible, he entered Kekulé's lab in Bonn in October 1872 and worked there until June 1873. He must have become acquainted there with Kekulé's tetrahedral carbon models, which Kekulé was using regularly in his lectures. In summer and fall 1873 van't Hoff studied at Utrecht, passing his doctoral exams a few days before the end of the calendar year. He then spent from January until June 1874 with Wurtz

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[28] Wislicenus, as reported by Kekulé in *Berichte* 2 (1869): 550–51.

[29] Wislicenus, "Optisch-active Milchsäure" (1873), 343–44.

[30] The definitive biography is Cohen, *van't Hoff;* see also the valuable discussion of van't Hoff in Root-Bernstein, *The Ionists* (1980), and the sources cited in the following footnote.

in Paris, where he became well acquainted with an Alsatian student named Joseph Achille LeBel. Returning once more to Utrecht, he submitted a conventional experimental doctoral thesis in organic chemistry, receiving his degree in December 1874.

In September 1874 van't Hoff announced his theory of what he called the "asymmetric carbon atom" (a misleading phrase, since it is not the carbon atom itself but rather its chemical environment that van't Hoff conceived as asymmetric). Since this history has recently been well treated, I will provide only a brief account.[31] First, van't Hoff drew attention to an empirical rule. He demonstrated that evidence known at that time was consistent with the thesis that whenever *four different* atoms or radicals are attached to *any single* carbon atom through its four valence units, a new kind of isomerism presents itself, one that is associated empirically with optical activity. He called any such carbon atom "asymmetric." In particular, there was no recognized case of an optically active organic compound that was known *not* to have an asymmetric carbon atom by this definition, somewhere in its structural formula.

To be sure, by no means all optically active compounds had been structurally elucidated. However, enough was already known about the structures of such optically active compounds as lactic acid, tartaric acid, aspartic acid, malic acid, asparagine, borneol, camphor, and various sugars, that one could say with confidence, van't Hoff averred, that each of these had at least one asymmetric carbon atom in its formula. To take the two cases treated in this chapter: "meat" and "milk" lactic acid could both be represented as $C(H)(OH)(CO_2H)(CH_3)$ to highlight the single asymmetric carbon atom in this formula (i.e., the first "C," to which the four different groups in parentheses are all attached). Similarly, the formula of both forms of tartaric acid could be written $C(H)(OH)(CO_2H)(C_2H_3O_3)$. By contrast, glycolic acid was $C(H)(H)(OH)(CO_2H)$. It did not have four *different* groups around any of its carbons, so it did not possess an asymmetric carbon atom, and therefore was not optically active. The same was true, for instance, of succinic acid, $C(H)(H)(CO_2H)(C_2H_3O_2)$. Moreover, one could show that when an asymmetric carbon atom is chemically altered to a non-asymmetric condition, the optical activity of the substance vanishes.

But why did this curious rule subsist? In van't Hoff's theory, every carbon atom in every organic molecule can be conceived as occupying

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[31] Ramberg, *Stereochemistry;* Ramberg and Somsen, "Young van't Hoff" (2001); and van der Spek, "Selling a Theory" (2006).

the exact center of a regular tetrahedron (a triangular pyramid), the four vertices of which are occupied by the four atoms or radicals satisfying the four "affinities" of the carbon atom. The tetrahedron, known since the pre-Socratics, is a regular polyhedron; its vertices are equally positioned as far from each other as is geometrically possible, distributing these four points in three-dimensional space with optimal symmetry. But as can be easily demonstrated by simple model-building, any regular tetrahedral array, all four of whose vertices are *mutually distinguishable,* possesses mirror-image asymmetry; that is, it is not superposable on its mirror image. (But it is important to remember that in a purely spatial-geometric sense such a tetrahedral array is still perfectly regular.) By contrast, whenever *two or more* of the vertices are indistinguishable from each other, the model forms an object that *is* superposable on its mirror image, thus excluding the possibility of a stereospatial isomer—or, as we say today, of a stereoisomer.[32] Whenever a molecule contains an asymmetric carbon atom, it raises the possibility for optical activity and for the kind of isomerism exhibited by the two tartaric or by the two lactic acids, because, in contrast to a symmetrical carbon atom, asymmetric carbons always have two distinguishable (mirror-image) versions.

Van't Hoff's theory offered an explanation for many hitherto mysterious cases of "absolute isomerism," including that of the two acids from wine tartar and the two lactic acids. The theory also validated and made sense of Pasteur's work of 1848 and his speculative notions of 1860. The first publication of the theory was in a self-published twelve-page Dutch pamphlet, dated 5 September 1874 and printed immediately thereafter; a French translation of the pamphlet appeared almost simultaneously in a relatively obscure Dutch journal.[33] Two months later (5 November 1874), van't Hoff's former labmate in Wurtz's research group, LeBel, published a substantially similar theory in the *Bulletin de la Société Chimique*. There has never been any evidence that either man knew of the other's work in advance of his own publication. Since van't Hoff had published his theory so obscurely, it was in LeBel's paper that most chemists first read of these ideas. But because LeBel's

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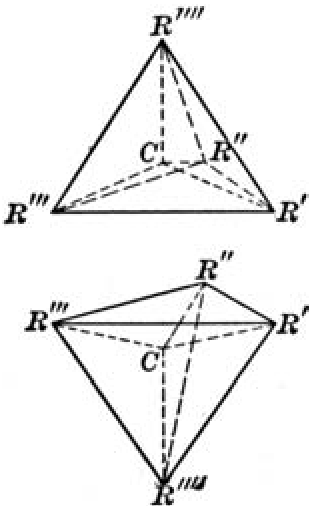
[32] If the reader needs convincing, try the following. Take two tetrahedral blocks (regular triangular pyramids). Put a dot of a different color on each of the four vertices of one of the tetrahedra—say, red, yellow, green, and blue. Prepare the second tetrahedron so that it looks like a mirror image of the first. Then, in your mind, try to superimpose the two; it will not be possible. However, whenever at least two colors are the same, then a superposition can always readily be imagined.

[33] Van't Hoff, *Voorstel* (1874); van't Hoff, "Formules" (1874).



33 Van't Hoff's first diagrams of the asymmetric tetrahedral carbon atom. Source: van't Hoff, *La chimie dans l'espace* (1875), planche I.

theory was far less influential than van't Hoff's in the late 1870s and the 1880s, and because the subject has been well treated elsewhere, we will not pursue LeBel's ideas further.[34]

In March 1875 van't Hoff published an abstract of his Dutch pamphlet in the *Bulletin de la Société Chimique,* remarking in a concluding paragraph that the foregoing abstract summarized his "note" that had appeared in Holland "at the very moment" as the November 1874 paper by LeBel. (This was a generous gesture, since his first publication was two months earlier than LeBel's.) In May 1875 he issued a full (forty-three-page) monographic treatment of his theory in French, once again published at his own expense, entitled *La chimie dans l'espace.*[35] The epigraph on the title page was Wislicenus's 1869 prediction, cited in the original German, which proclaimed that only by looking to the "arrangement of atoms in space" will one ever find an explanation of the case of the lactic acids. In his preface to the French monograph, van't Hoff mentioned his disappointment to have had so little reaction to his theory, good or bad, eight months after its first publication—hence the present publication (van't Hoff was still without a profes-

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[34] LeBel, "Sur les relations" (1874). See Delépine, *LeBel* (1947); Snelders, "LeBel's Ideas" (1975); and Ramberg, *Stereochemistry,* 59–65.

[35] Van't Hoff, "Sur les formules de structure" (1875); van't Hoff, *La chimie dans l'espace* (1875).

34 Van't Hoff's first models of the tetrahedral carbon atom. Source: Boerhaave Museum, Leiden.

sional position).[36] Immediately upon introducing the "asymmetric carbon atom," van't Hoff remarked in a footnote:

> One may perhaps find some difficulty in following my argument. I have felt this difficulty myself, and I have made use of cardboard [tetrahedral atomic] models to facilitate the representation. Not wanting to demand too much of the reader, I will gladly send anyone a complete collection of all these objects, such as already are in the possession of MM. Baeyer (Strasbourg), Butlerov (St. Petersburg), [Louis] Henry (Louvain), Hofmann (Berlin), Kekulé (Bonn), Frankland (London), Wislicenus (Würzburg), Wurtz, and Berthelot (Paris). For this purpose, write to M. J. H. van't Hoff, Ph.D. chemist, Rotterdam (Holland).[37]

The problem, of course, was not that his argument was so exceedingly complex or arcane, but following it required one to manipulate mental geometric images in an unusual way. Van't Hoff had taken the initiative to send complimentary sets of these models to the indicated personages, together with copies of his booklet; it is clear that he thought that the models would assist the favorable reception of his theory. Three such sets survive today in museums, one set in the Deutsches

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[36] On the reception of van't Hoff's theory, see Ramberg, *Stereochemistry;* Cohen, *van't Hoff,* 82–138; and Snelders, "Reception" (1974).

[37] Van't Hoff, *Chimie dans l'espace,* 7n. On van't Hoff's models, see especially van der Spek, "Selling a Theory." The larger context is drawn by Meinel, "Molecules and Croquet Balls" (2004).

Museum in Munich (donated by van't Hoff directly) and two sets in the Museum Boerhaave in Leiden. If van't Hoff was reporting accurately, he had used these models himself to help clarify the implications of the theory. He may even have used the models from the very start of the construction of his theory, for it is in fact difficult for most people, even those with labile imaginations, to form mental images of asymmetric (nonsuperposable mirror-image) tetrahedra without the help of such models—as van't Hoff rightly recognized, and as every instructor of organic chemistry has confirmed in his or her own classroom.[38]

Imagination in Science: Point/Counterpoint

With the publication of *La chimie dans l'espace* and its distribution to leading European chemists, van't Hoff finally got a response from the chemical community. Baeyer told his students in Strasbourg (this according to the "very clear" recollection of Emil Fischer, studying with Baeyer in summer 1875) that here was a "new good idea" that was likely to prove very fruitful. To his former student Victor Meyer, Baeyer commented in a letter of September 1875 that he was "enchanted" by van't Hoff's "very beautiful idea" and that the theory seemed to work exceedingly well for all except possibly aromatic compounds.[39] More importantly, Wislicenus wrote directly to van't Hoff, proclaiming his high regard for the new theory, which he predicted would be "epoch-making in its significance." He proposed the idea of preparing a German edition of *La chimie dans l'espace,* translated by his assistant Felix Herrmann and equipped with a preface written by himself. Van't Hoff concurred, and *Die Lagerung der Atome im Raume* appeared at the beginning of 1877.[40] By this time van't Hoff had finally found at least minimal gainful employment, teaching chemistry and physics at the Veterinary School of Utrecht.

This German edition of van't Hoff's small book was published by

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[38] For a perspective on mental rotations from cognitive psychology, see Shepard and Cooper, *Mental Images* (1982).

[39] Baeyer said to Fischer, "Da ist wirklich mal wieder ein neuer guter Gedanke in unsere Wissenschaft gekommen, der reiche Früchte tragen wird," in "Gedächtnisrede auf Jacobus Henricus van't Hoff," in Fischer, *Gesammelte Werke* (1924), 4:893; Baeyer to Meyer, 27 September 1875, ADM 7027: "Von van't Hoff's Arbeit bin ich entzückt, ob es wahr ist wer weiss es? Ich finde die Idee aber sehr schön, sie hat mir sehr eingeleuchtet d. in der fetten Gruppe stimmt ja eigentlich alles."

[40] Van't Hoff, *Lagerung* (1877).

Heinrich Vieweg's press, the leading imprint in Germany for scientific textbooks and monographs, and so many chemists now could read what until then few had seen. Vieweg, as a company as well as a family, had a close relationship to Hermann Kolbe, and it was certain that Kolbe would take notice; with his own journal at his disposal and the sharpest pen in the business, it was not long in coming. Under the title "Signs of the Times," Kolbe let loose in May 1877 with the kind of vitriol that one rarely reads in scientific journals. He expressed dismay that this total unknown with the odd name working at a veterinary school could arrogantly purport to have solved puzzles, using the idlest of fantasies, that had hitherto confounded the most distinguished scientists of Europe: "A certain Dr. J. H. van't Hoff, of the Veterinary School of Utrecht, finds, it seems, no taste for exact chemical research. He has considered it more convenient to mount Pegasus (apparently on loan from the Veterinary School) and to proclaim in his 'La chimie dans l'espace' how, during his bold flight to the top of the chemical Parnassus, the atoms appeared to him to be arranged in cosmic space."

None of this nonsense would have gotten the least attention, Kolbe opined, had a chemist of reputation, namely Wislicenus, not taken the author under his wing and given the book some visibility and scientific cover by writing an approving preface. Kolbe concluded: "Wislicenus has thereby declared that he has abandoned the ranks of the exact scientists, and gone over to the camp of *Naturphilosophen* of ominous memory, which is distinguished from the spiritists by only a thin 'medium.'"[41]

Wislicenus, one of the kindliest men of his collegial circle, was understandably upset. He wrote Kolbe a long, moving letter, searching for some kind of common ground.

> I have never doubted that it is a holy zeal for the truth that guides your critical pen; but on the other hand I regret that you do not seem to concede any possibility of your own fallibility, which everyone must grant. . . . I know that I can err, but I also know that I have no cause to allow myself to be struck from the ranks of exact scientists, for I as well as you have the will to serve the truth.[42]

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[41] Kolbe, "Zeichen der Zeit" (1877).

[42] "Ich habe nie daran gezweifelt, dass es der heilige Eifer für die Wahrheit sei, der Ihnen die Feder bei Ihren Kritiken führt, andrerseits aber bedaure ich, dass Sie dabei die Möglichkeit eigenen Irrthums, welche ja Jeder zugeben muss, durchaus nicht zuzugeben scheinen. . . . Ich weiss, dass ich mich irren kann, aber ich weiss auch dass ich keine Ursache habe, mich aus der Reihe exacter Forscher ausstreichen zu lassen, denn ich habe so gut wie Sie den Willen, der Wahrheit zu dienen." Wislicenus to Kolbe, 24 November 1877, ADM 3550.

Van't Hoff was deeply shaken by the attack, at least temporarily, but he did not let it show. His response to Kolbe was much shorter, more factual, and more public than that of Wislicenus; but it had a bite.

> A theory that so far is not contradicted by a single fact can only be further examined experimentally. Thus when someone, even so fine a chemist as Kolbe, avers that a chemist who is not yet well known and who is employed at a veterinary school should not bother himself with theories . . . I can only say that such behavior fortunately is not a sign of the times, but rather must be regarded as a contribution to understanding a single individual.[43]

Although Kolbe's tirade was well beyond the bounds of propriety, he did have van't Hoff accurately pegged as a man of profound imaginative powers. Van't Hoff deeply admired Shakespeare and the British Romantic poets, especially Robert Burns and Lord Byron; indeed, van't Hoff was a poet himself, often composing in English. A few months before his fateful walk outside the Utrecht library, while working in August Kekulé's research group in Bonn, he wrote a revealing letter to his father, from whom he had derived his poetic passion: "Facts are the basis, the foundation; imagination is the building material, hypothesis the plan to be investigated, truth the [resulting] building. . . . Imagination and scientific judgment create truth, imagination and taste create beauty."[44] He later wrote, in a letter to Kekulé, that "you and Lord Byron were the gods of my youthful scientific-poetic dream, towards which I still strive today."[45]

A little more than a year after Kolbe's attack (11 October 1878), van't Hoff treated this theme in a very public way, in his inaugural lecture at the University of Amsterdam, entitled "Imagination in Science." Here he argued forcefully for the essential role that imagination plays in all aspects of scientific investigation. He then brought history to bear on the question. After a careful study of more than two hundred scientific lives, he concluded that a sizeable percentage of especially the most creative and famous scientists also exhibited a manifest development of the creative exercise of the imagination in fields other than science, such as in literature, art, or music. His concluding words were borrowed from the English historian Henry Thomas Buckle: "There is a spiritual, a poetic, and for aught we know a spontaneous and uncaused

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[43] Van't Hoff, "Zusammenhang" (1877), 1620.

[44] Undated letter from van't Hoff to his father, ca. early 1873, in Cohen, *van't Hoff,* 54.

[45] Weyer, "Van't Hoff" (1977), 218.

element in the human mind, which ever and anon, suddenly and without warning, gives us a glimpse and a forecast of the future, and urges us to seize the truth, as it were by anticipation."[46]

It was just about the time of his inaugural lecture at Amsterdam that van't Hoff published his one larger work on organic chemistry, a two-volume treatise curiously entitled *Ansichten über die organische Chemie* (Views on Organic Chemistry). Once again the publisher was Vieweg, and this time Kolbe really went off the deep end. "I could not believe my eyes when I looked through it," he wrote to his friend Heinrich Vieweg. "This work contains the *greatest nonsense* that I've ever read. The author is definitely out of his mind, fit for the madhouse."[47] One must make allowances for the source of this judgment, but Kolbe did not have it completely wrong. Most readers, indeed probably *all* readers, found the book—which was something like a textbook but also something like a set of essays on mathematical chemistry—hard slogging. Here are two short examples. Van't Hoff set as his goal "to derive the most diverse processes of organic chemistry from the simplest transformations of carbon, and from the most unitary view possible . . . [I]t seems not unlikely to make oneself an image [Bild] of the effect of form and motion [of molecules] on the attraction at small distance which represents in a general way the external change that gravitation experiences when it becomes chemical attraction."[48]

Ansichten über die organische Chemie sold few copies; van't Hoff himself later suggested that its obscurity was well deserved, and that it was scarcely worth reading.[49] This work continues a pattern we have already seen, namely van't Hoff's propensity not only for imaginative theorizing, but also for the use of actual images as productive tools. Van't Hoff also characterized his mentor Kekulé as having the same proclivity. Kekulé was a "grandmaster of the pictorial representation," which grew out of his personal need to create "easily-grasped representations," possibly, van't Hoff said, because of his early training as an architect.[50] The book marked the end of van't Hoff's activities in the field of organic

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[46] Van't Hoff, *Verbeeldingskracht* (1878); German tr. ("Die Phantasie in der Wissenschaft") in Cohen, *van't Hoff,* 20, 149–65; English tr. from the German by G. F. Springer, *Imagination in Science* (1967). The quotation is my translation from Cohen's German.

[47] "Ich traute meinen Augen nicht, als ich darin blätterte. Dieses Heft enthält den grössten Blödsinn, den ich je gelesen. Der Verfasser ist entschieden unzurechnungsfähig, reif für das Irrenhaus." Kolbe to H. Vieweg, 30 January 1878, VA.

[48] Van't Hoff, *Ansichten* (1878, 1881), 1:1 and 2:240.

[49] Cohen, *van't Hoff,* 142. See also Root-Bernstein, *Ionists,* 217–32; Ramberg and Somsen, "Young van't Hoff."

[50] Van't Hoff, obituary of Kekulé published in *Die Nation,* 13 July 1896, reproduced in Cohen, *van't Hoff,* 59–62.

chemistry; from this point on he would move to equally fundamental work in physical chemistry and physics.

About this same time, Kekulé himself reflected on theory construction in chemistry, in a lecture designed for a lay audience. It was his rectoral (presidential) address at the University of Bonn (18 October 1877) on the "scientific goals and accomplishments of chemistry."[51] Kekulé began by declaring that only the atomic theory was presently able to account for the totality of phenomena in physics and chemistry. A more fundamental and purely dynamical theory might someday be constructed that could dispense with material atoms, but no such theory was yet in sight—certainly not William Thomson's recent hypothesis of vortex atoms. As he had declared eleven years earlier (discussed in the last section of the previous chapter), Kekulé pointed out that the possible divisibility of the atom had no operational relevance for the chemist, since chemistry was unaffected whether or not atoms were, ontologically considered, *ultimate* particles of matter; as he aphoristically put it, "chemistry has need of atoms *first,* but not *last.*" He then summarized the development over the previous twenty years of the theories of valence and structure. He pictured atoms as having some sort of (probably vibratory) movement inside the molecule, but chemical science had shown that any such movement had to be restricted. Possibly the number of vibrations in a given time interval was directly correlated with the property that chemists empirically perceived as valence; in any case, the valence had to be *constant,* not variable. (This conjecture constitutes a generalization of Kekulé's phenakistoscopic theory of benzene.)

Of course, Kekulé continued, structure theory specifies only the bonding *sequences* of the atoms, not their *spatial positions* inside the molecule. Of two isomeric hydrocarbons, one possessing a highly branched structure and the other a straight-chain structure, the former is always found to be more volatile; this must obviously have to do with the differing centers of gravity and moments of inertia of the two molecules. This is one example of many ways that we can indirectly learn about the average spatial positions of the atoms and the molecules.

> Thus the hypothesis of the *asymmetric carbon,* expressed by LeBel and further developed by van't Hoff, according to which the four affinities of the carbon atom, which already had previously been depicted [schematically] as tetrahedral, are considered to be even *spatially* in a tetrahedral position, becomes more probable. [This is] a hy-

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[51] Kekulé, *Wissenschaftliche Ziele* (1878); reprinted in Anschütz, 2:903–17.

> pothesis which to be sure does not perhaps deserve the unqualified praise accorded to it by Wislicenus, but in any case still less merits the bitter ridicule poured over it by Kolbe.[52]

Now, as we have seen, van't Hoff idolized Kekulé from first to last, but he had been disappointed with how Kekulé had treated him during his semester in Bonn; Kekulé had provided him a good but not outstanding reference in June 1873, and in the summer of 1877 had failed to respond to his request for a letter supporting his bid for the position in Amsterdam.[53] Now came this carefully worded statement, which was half-hearted in its praise, and seemed to award priority for the initial discovery to LeBel. Kekulé must have gotten better information at some point after his rectoral address, for ten years later he wrote to van't Hoff, asking, for historical purposes, about the exact timing of initial publication of the theory of the asymmetric carbon atom—a theory, he now declared to van't Hoff, that "right from the start was very plausible [einleuchtend] to me." He wrote that with van't Hoff's permission he would like to publish a "small historical notice" on this point in the *Berichte.* Van't Hoff responded that he had indeed been "a little hurt" by Kekulé's comment ten years earlier, but "what was that compared to the extraordinary stimulation that you, my great teacher, have been to me!"[54]

If Kekulé thought he could escape a rant from Kolbe's poison pen by the restrained nature of his praise of van't Hoff in his rectoral address, he was sadly mistaken. Kolbe wrote that Kekulé's stated "goals for chemistry" were "wild fantasies without any real basis"; Kekulé had simply never learned the vital necessity for any serious scientist of "reining in his imagination." It particularly galled Kolbe that Kekulé had declared his structural theory a "law of nature." Kolbe expressed his perplexity at the influence that Kekulé appeared to exert among most chemists, especially the young and impressionable.

> With the theory of chaining of atoms and especially with the theory of the benzene ring Kekulé promised to explain numerous cases of isomerism, especially in aromatic compounds. . . . [But this theory] has contributed not a thing to the explanation of

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[52] Anschütz, 2:912.

[53] Weyer, "Van't Hoff."

[54] Ibid.; Cohen, *van't Hoff,* 47–57, 133–38. The letter from Kekulé to van't Hoff and the response were dated 20 and 22 February 1887. Weyer demonstrated that Cohen had misdated Kekulé's letter as 20 February 1877, making Kekulé's misstatement in his rectoral address mysterious in Cohen's account.

> the causes of those isomerisms, for what Kekulé and his crowd consider to be explanations are nothing but pictures, clever and artfully drawn figures, compounded of symbols of the elementary atoms considered as lying in a plane, more or less symmetrically ordered, and chained together with lines. One lets these symbols assume various positions, the ortho, meta, and para positions, like extras on a stage, and considers this an explanation for isomerism.

At first Kolbe had had the impression that Kekulé had wanted to satirize van't Hoff's nonsense of the asymmetric carbon atom in his rectoral address. But then he had understood that Kekulé was entirely serious in considering van't Hoff's "chemical dreams as an actual *accomplishment,* and his incomprehensible content as a 'scientific goal of chemistry.'") "It is very tempting," Kolbe concluded, "to ascribe scientific value to dreams," but it is certainly not science.[55]

Kolbe died in 1884. In 1894, van't Hoff published a revised edition of *Die Lagerung der Atome im Raume* (an updated French edition, entitled *Dix années dans l'histoire d'une théorie,* had already appeared in 1887). Wislicenus wrote a new preface, pondering the enormous changes regarding the reception of van't Hoff's theory over the preceding seventeen years. In 1877 van't Hoff had been an unknown novice who was propounding a brave new idea, and now he was a world-famous elder, his theory part of the lifeblood of the science. Wislicenus was proud, he wrote, to have been the "godfather" of van't Hoff's masterpiece.[56] Van't Hoff's preface was even more interesting. Every time he had edited a new edition, he wrote, new names had been discovered in the prehistory of "stereochemistry" that he needed to mention. (The word had been coined in 1888 by Victor Meyer, following the etymological example established by the naming of the stereoscope.) There was Gaudin, there was Pasteur, and now an Italian paper from 1869 had been noted in which Emmanuele Paternò had used the concept of a tetrahedral carbon atom for the explanation of a case of isomerism.[57]

> So, in any case, we were not being premature when we, LeBel and I (November and September 1874, respectively) . . . communicated our views. It was probably a coincidence that we had worked together shortly before that in Wurtz's laboratory; we

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[55] Kolbe, "Kritik" (1878), 140, 145, 148–51, 156.

[56] Wislicenus, in van't Hoff, *Lagerung,* 2nd ed. (1894), vii–ix.

[57] Paternò, "Intorno" (1869), 117–22. Körner and Havrez also pursued stereochemical ideas about benzene before 1874. See Meinel, "Molecules and Croquet Balls," 262–64; Ramsay, *Stereochemistry,* 65–67; Heilbronner and Jacques, "Havrez" (1998); and Paoloni, "Stereochemical Models" (1992).

> never exchanged a word there about the tetrahedron, even though both of us perhaps were secretly harboring the thought. The idea had come to me the previous year in Utrecht, after reading Wislicenus's paper on lactic acid. . . . LeBel's and my papers are in substantial agreement; however, the conceptions are not entirely the same, and this has been emphasized especially in recent days, perhaps too strongly. Historically, the difference is that LeBel started from the basis of Pasteur's work, and I from that of Kekulé.[58]

This is the strongest public statement that van't Hoff made regarding Kekulé's influence on him in the formulation of his theory of asymmetric carbon. He was certainly referring to carbon tetravalence, and possibly also to Kekulé's tetrahedral atomic models for carbon compounds. It is curious that Kekulé invented and made use of these tetrahedral physical models for years without exploring the consequences that would ensue if the model were assumed to be a realistic representation of the microworld. It seems clear that Kekulé trusted some of the implications of his sausage models during the period 1857–67, at least for provisional heuristic purposes (as I argued especially in chapter 7), but I know of no evidence that he ever did so for his tetrahedral models after 1867. Moreover, at least four other chemists explicitly invoked the carbon tetrahedron during the 1860s: Pasteur in 1860 (discussed in the second section of the present chapter), Butlerov in 1862,[59] Gaudin in 1865,[60] and Paternò in 1869. Wislicenus stressed the need to consider three-dimensional spatial considerations for certain molecules at least three times before 1874. Why did it take so long for someone to seriously explore the chemical consequences of the idea?

Other historians have asked this question, and most have offered the answer that there was a psychological barrier between conventionalist theoretical approaches to the microworld for purely heuristic purposes, and a putatively realistic depiction of how atoms and molecules might look if they were of a size suitable for direct sensual perception. The first was regarded by most nineteenth-century scientists as professionally acceptable within the ambit of proper scientific method; the second was not. Even if a scientist might cherish the latter kind of speculative thought in the privacy of his study, there was sufficient peer pressure that few proceeded far in that direction: Laurent, Gaudin, and Baudrimont were exceptions to the general rule. I agree that such pres-

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[58] Van't Hoff, *Lagerung,* 2nd ed. (1894), 1–2. The first sentence is a subtle and gentlemanly way to point out that he (van't Hoff) really was first in print.

[59] Butlerov, "Verwandtschaft" (1862), 299.

[60] Gaudin, *Reforme* (1865), 16, cited by Miller, "Gaudin" (1975), 9.

sure existed and worked against the sort of theory that van't Hoff and LeBel eventually independently put forward. Such hesitancy would appear to cut against one of the arguments of this book, that many chemists—especially Kekulé—were thinking visually at this time and often trusted their mental images for heuristic purposes.

However, the development of stereospatial interpretations of structural theory must be seen in the light of the history of chemical semiotics. The introduction to chapter 3 discusses what I refer to as an ontological transition from chemical formulas largely viewed as arbitrary conventions to formulas now regarded by many as permanent and true, a transition that roughly coincided with the establishment of reformed atomic weights by Gerhardt, Williamson, Cannizzaro, and Kekulé. It must be cautioned, first, that this shift was neither sudden nor complete, even in its heartland of Germany and England; and that even those who believed that a single system of relative atomic weights had now been definitively established continued (quite reasonably) to caution that two-dimensional mappings of *chemical* atoms said nothing about the real stereospatial distributions of *physical* atoms. Nonetheless, a door had now been opened. Among structural chemists, the older members of this community had been professionally bred in the positivistically inclined 1840s, whereas the younger members had fewer inhibitions to surmount against a more realist interpretation. Berzelian chemical formulas had always expressed both logical and iconographic meanings;[61] in the 1860s and 1870s the iconographic psychological implications increased apace. Gradually, various kinds of formulas and models were increasingly interpretable as approximations to stereospatial arrays.

So the kind of professional inhibition referred to above may well have been waning by about 1870. However, there were two other, more technical (and hitherto unnoted) factors that may well have independently operated against taking the asymmetric carbon atom seriously. After the establishment of carbon tetravalence in the late 1850s, Pasteur in 1860 and Butlerov in 1862 both suggested the possible hypothesis of a tetrahedral arrangement of carbon valences, but both were careful to specify that the tetrahedron must be irregular or asymmetric *in shape*—a geometrically distorted rather than a regular tetrahedron. They did so presumably partly because at that time most organic chemists thought that there was good evidence that the four "affinity units" of carbon were not all equal in strength. Butlerov explicitly stated that

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[61] Klein, *Experiments, Models, Paper Tools* (2003).

this was why he was hypothetically proposing an *irregular* tetrahedral model for carbon. But in 1864 Carl Schorlemmer and Alexander Crum Brown removed the principal evidentiary basis for the belief that the valences of carbon were intrinsically distinguishable, namely, the purported existence of the two distinct isomers: "methyl" gas and "ethyl hydride" gas. Once Schorlemmer and Crum Brown had shown that these compounds were identical, the belief in any asymmetry or distinguishability of the four valences of the carbon atom collapsed.

And here is the point. I suggest that those who might, in principle, have been willing to explore a tetrahedral carbon theory may have succumbed to the natural error of assuming that one needed irregularity in the *geometric shape* of the tetrahedron, hence one required a chemical nonequivalence of carbon valences, in order to provide the theoretical basis of a stereospatial account of hitherto unexplained isomerisms, namely, nonsuperposable mirror-image structures. When the thesis of the distinguishability of the four carbon valences fell, so also (many may have falsely believed) fell the foundation for any future theory of an asymmetric tetrahedral carbon atom. On the contrary, van't Hoff proposed in 1874 that molecular asymmetry, thus nonsuperposability, is established only by the *chemical* distinguishability of the four *geometrically indistinguishable* vertices of the regular tetrahedron. Van't Hoff's correction of this error provides yet another striking example of the importance of mental images and physical models in understanding the details of new chemistry.

A final possible inhibition to the development of stereochemistry was mentioned by Baeyer. He later explained, in reference to the prehistory of van't Hoff's theory, that often in the 1860s he had made use of models using Kekulé's tetrahedral carbons for teaching and research, but he had never asked himself whether the model could be a realistic depiction of organic molecules because Kekulé had taught his students that the four affinity units of a carbon atom could readily exchange places, and he said that he had learned this incorrect lesson only too well.[62] We have no reason to doubt this testimony regarding Kekulé's oral pedagogy, but he never published such an assertion. The idea appears to be modeled after Williamson's theory of dynamic equilibrium of substitutions of hydrogens and chlorines in HCl solution, outlined in his Friday Evening Discourse in June 1851, an idea that was vigorously attacked by Kolbe (chapter 1, this volume). Kekulé's

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[62] Baeyer, *Gesammelte Werke* (1905), 1:xxxii–xxxiii; he repeated this statement in *Berichte,* 23 (1890), 1274.

reason for never having published the idea mentioned by Baeyer is obvious: if interatomic bonds in organic molecules are that labile, then it is hard to see how consistent molecular "structures" may ever persist through time.

The idea of a continual exchange of places in the four valences of carbon was surely related to Kekulé's ideas on atomic motion, bruited once more in his rectoral address of 1877, which he regarded as a ubiquitous factor in the microworld. But he also repeatedly insisted, and this in published scientific work, that the structures of organic molecules persist. How could such a master theoretician hold two such contradictory notions simultaneously? The same dialectical tension that we see in Kekulé's concepts between a dynamical world of vibrating, rotating, and translating atoms, and the staid world of atoms fixed by valence units into relatively motionless positions can be traced, as we have seen, to a similar tension in the ideas of Kekulé's most important mentor, Williamson (and also, possibly, to the diverse molecular metaphors of Dumas and Berthollet). Regardless of this tension, or perhaps because of it, both are imaginative visions of the highest order. Sometimes it is only the greatest masters who know how to use apparent contradictions for creative purposes.

Chemists, Physicists, and the Microworld

Williamson's, Graham's, Kekulé's, and van't Hoff's ideas about intramolecular atomic motions suggests that these men paid attention to what developments in the science of physics might offer for chemists. And indeed physicists, like chemists, had had some dramatic recent successes in exploring the microworld. In the 1840s obscure theorists such as John Waterston and John Herapath had argued that the gas laws would result if one supposed that gases were composed of elastic molecules in rapid random inertial motion, the pressure of a gas being the simple result of innumerable tiny transfers of momentum consequent to impacts of the molecules with all sides of the container. The hypothetical elements of this theory, its conflict with the older Newtonian-Daltonian static view of gases, and the existence of an alternative caloric explanation (which was moribund, but not yet dead) resulted in that this incipient kinetic theory of gases remained very much on the periphery of science during the 1840s.

In 1843 Waterston noted, as part of his kinetic theory, that if the theory were true then one mathematical result would be that under standard conditions equal volumes of different gases should contain equal numbers of gas molecules. The only way to reconcile this result with known chemical facts, he wrote, was to assume that these molecules could sometimes split apart in chemical reactions, for instance hydrogen and oxygen in the formation of water. This, of course, is nothing other than Avogadro's hypotheses.[63] Waterston's publication was obscure, and remained without influence. However, at the British Association meeting in Ipswich in 1851—the same meeting at which Williamson read his final ether theory paper, "On the Constitution of Salts"—Waterston presented a brief version of the theory. Five years later the German physicist August Karl Krönig published a short paper on kinetic gas theory, which was substantially identical to Waterston's; it may well have been deliberately modeled after it, without citation.[64] It was Krönig's publication that induced the Zurich theoretical physicist Rudolf Clausius to begin work that quickly led to a much more robust and sophisticated mathematical development of a theory of "the kind of motion we call heat." Clausius's 1857 paper has traditionally (and rightly) been viewed as the effective starting point for the development of the modern kinetic theory of gases and of heat.[65]

Possibly following Waterston's 1851 statement, Krönig noted the equal-volumes-equal-numbers implication of the theory, but only in passing. Clausius stressed this result, and like Waterston he also concluded that it would be necessary to assume the splitting apart of "elementary" gas molecules in order to explain well-established stoichimetric data. Curiously, he stated this conclusion as if it were a new thought. Someone may have pointed out to him (or reminded him) subsequent to the publication of this paper that he had touched on a long-disputed point in the neighboring science of chemistry, for in a paper published the following year he mentioned that many years earlier Dumas, Laurent, and Gerhardt had all suggested the idea of submolecularity of elementary gases.[66]

Thereafter, the kinetic theory experienced rapid development, with additional important papers by Clausius and by James Clerk Maxwell (who drew particular attention to the equal-volumes-equal-numbers

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[63] Waterston, *Mental Functions* (1843), cited in Brush, *Kind of Motion* (1976), 139.

[64] This thesis was plausibly argued by Edward Daub, who suggested a specific route of transmission from Waterston's BAAS abstract, through a paper by Helmholtz, to Krönig: "Waterston's Influence" (1971).

[65] Waterston, "Theory" (1851); Krönig, "Grundzüge" (1856); Clausius, "Art der Bewegung" (1857).

[66] Clausius, "Ueber die Natur des Ozons" (1858), 645n.

result), published in the period 1858–60. Details of the relationships between chemists and physicists in this period, and of the perceived support for Avogadro's hypotheses in chemistry that was provided by the kinetic theory in physics, have not been well studied. However, the possibility of mutual influence is certainly there: counting reprinted and translated publications from the scientists mentioned above, one can find no fewer than fourteen derivations of the equal-volumes-equal-numbers hypothesis from kinetic assumptions in physics journals that appeared in the years from 1856 until 1860.[67]

We can say with certainty that, among chemists, Cannizzaro and Kekulé, at least, read Clausius's 1857 paper with understanding, and noted the consequences of the new physical theory for chemistry. In his "Sketch of a Course of Chemical Philosophy," which was dated 12 March 1858, Cannizzaro argued that "all recent research, from Gay-Lussac to Clausius," supports the equal-volumes-equal-numbers hypothesis of Avogadro.[68] Fourteen years later Cannizzaro characterized the equal-volumes-equal-numbers statement as a "theory" or a "hypothesis" that forms a "solid foundation" for chemistry, due to the work of "Avogadro, Ampère, Krönig, and Clausius." In Cannizzaro's telling, it was chemistry that first perceived and proclaimed this truth, which only later "acquired great credit amongst men devoted to mathematical and physical studies," especially naming Maxwell and John Tyndall.[69]

Kekulé, too, directly cited Clausius's 1857 paper toward the end of the first fascicle of his textbook, published in June 1859.[70] In fact, within this single fascicle one can perceive a difference in tone in passages regarding gas theory that were probably written earlier (ca. 1856) versus later (ca. 1858). Early in the fascicle Kekulé expressed caution and uncertainty about the nature of physical molecules; what we can have greater confidence in, he wrote then, is the ascertainment of *chemical atoms*.

> An exact determination of even *relative* sizes of molecules is not attainable. By considering a large number of compounds and by comparing a large number of reactions, we can assume those atomic and molecular sizes that permit the properties of

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[67] All listed in Brush, *Kind of Motion* (1976), 732, 744, 747. I have relied on Brush's fine work for much of the discussion here on the history of the kinetic theory.

[68] Cannizzaro, "Sunto" (1858), 323; Cannizzaro, *Sketch* (1910), 4.

[69] Cannizzaro, "Considerations" (1872), 946–50. Cannizzaro wrote the four names "Avogadro, Ampère, Krönig, Clausius" twice (946, 948) in that order, making the point very deliberately.

[70] *LB,* 1:232n.

> compounds and the events in reactions to be conceived and explained in the most comprehensive, simplest, and clearest way, and that therefore seem probable and convenient; but for that reason that may never be *proven*.[71]

But by the end of the fascicle he had become more confident and more assertive. He now stated directly that "the chemical molecule is identical to the physical gas molecule," and equal volumes of different gases under equivalent conditions contain equal numbers of the latter.

> These simple relationships have long been overlooked by most chemists, because on the one hand they have clung too strongly to the traditional views, and assumed incorrect atomic weights for the individual elements, but more significantly because they have not sufficiently distinguished between the concepts of atom, molecule, and equivalent; they have proceeded from the erroneous conviction that the specific weight must be a function of the atoms or equivalents, whereas it is really only a function of the molecules, and so must be dependent on the size and weight of the molecules.

Since we can have confidence in the equal-volumes-equal-numbers thesis, Kekulé wrote, comparative vapor densities provide a direct measure of comparative weights of these gas molecules; and we can also have confidence that the gas molecules of physics are the same as the chemists' molecules, at least for organic compounds.[72]

It is reasonable to conjecture that Kekulé's increasing confidence was at least partly due to the support that the incipient kinetic theory of Clausius (et al.) provided to Avogadro's hypotheses. Kekulé directed that one of his twenty-five complimentary copies of his *Lehrbuch* installment be sent to Clausius, with the author's compliments. It would appear that he had had no earlier direct contact with Clausius. In Clausius's letter of thanks, he told Kekulé that he had received the gift with "great joy."[73]

All this, we note, was *before* the Karlsruhe Congress. At the congress

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[71] Ibid., 1:95–97 and 1:106 (quoted).

[72] Ibid., 1:233–40 (quote from 233–34). These were the last pages of the first fascicle.

[73] "Obwohl ich, wie Sie wissen, nicht selbst Chemiker bin, so interessire ich mich doch lebhaft für die chemische Processe, welche ganz besonderes geeignet sind, die den Körpern innewohnenden Molekularkräfte kennen zu lehren, und vor allem ist es die organische Chemie welche durch ihre grossartigen und wichtigen Umgestaltungen die Aufmerksamkeit auf sich zieht." Clausius to Kekulé, 4 July 1859, AKS. In directing a request to Kekulé eight years later, Clausius wrote that although they still had never met, "so stehen wir einander doch in wissenschaftlicher Beziehung so nahe," that he felt comfortable contacting Kekulé. Clausius to Kekulé, 4 May 1867, AKS.

itself, Kekulé and Cannizzaro had several public discussions on the question of whether the chemical molecule was always and necessarily identical to the physical molecule of the kinetic theory of gases; Cannizzaro affirmed that one could readily make this assumption, but Kekulé averred that its full generality was not yet proven.[74] Kekulé returned to this and other related questions in a long letter to his friend, the physicist/chemist Lothar Meyer, who, agreeing with Cannizzaro's position, had offered various private criticisms of Kekulé's public statements in Karlsruhe as well as of his written discourse in the published portion of his textbook. Kekulé wrote in reply:

> The admittedly rather unclear expressions on this matter [specific volumes] that are found in my book can hardly lead to further misunderstandings. I'll leave the mechanical section—motion of the atoms within the molecule, etc.—to the side; we'll surely talk or write later about this. . . . I have a particular interest at the moment in discussions of these questions, and, entre nous, I will tell you why. I am very seriously contemplating writing a small book this coming winter with the approximate title *The Atomistic Molecular Theory.*[75]

He never wrote any such book, but apparently this idea was more than a passing fancy. Kekulé told Meyer that he had formulated the first ideas for the book in Karlsruhe (early September 1860) and already had some portions written (in late October). A month later he wrote his friend Carl Weltzien:

> Even wilder than in my laboratory is what is going on in my head. My thoughts are being haunted by a great deal of diffusion and molecular magnitudes, mixed with some volumes and with specific heat. But the higher molecular theory [= a new prospective book title?] won't fully polish up, even with all this nonsense. One needs to let the thing ferment for a while. But with all of this, I think that some kind of form should emerge. If only I don't first die of boredom regarding the other parts of my life here, or if only I don't fall asleep, which is not exactly out of the question here.[76]

When Clausius was called to the University of Bonn in 1869, he and Kekulé quickly became such close friends that they used the familiar

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[74] See the compte rendu of the congress, prepared by Wurtz and published in Anschütz, 2:671–88, on 676–79.

[75] Kekulé to Meyer, 23 October 1860, in Anschütz, 1:204–8. Meyer continued politely and publicly to press Kekulé on these points; see Anschütz, 1:264–65.

[76] Kekulé to Weltzien, 19 November 1860, in ibid., 1:208–9.

"Du" with each other. Kekulé proposed to him a collaboration on molecular theory, but Clausius declined.[77]

We have seen in the immediately preceding section of this chapter that in 1877 Kekulé conjecturally generalized his phenakistoscopic theory of the benzene ring that he had propounded five years earlier. This is surprising, considering the criticism to which his 1872 paper had been subjected. Kekulé's former student Albert Ladenburg immediately published a critique suggesting that Kekulé's idea would contradict the belief in the stability of the mutual relationships of atoms within a compound, a basic principle of structural chemistry. And Arthur Michaelis argued that the physical principles that would necessarily be entailed by the idea would have absurd consequences; indeed, they would be inconsistent with any contemporary understanding of mechanics.[78]

By the 1870s, two generations had passed between the natural philosophers of Dalton's, Berzelius's, and Faraday's times, when one could still perhaps speak of a unity of investigation of the physical world. Even by the 1830s and 1840s one could perceive distinctive cultures, educations, and methodologies pursued by physicists on the one hand, and chemists, especially organic chemists, on the other. Some organic chemists—Williamson, Cannizzaro, and Kekulé were among them—paid close attention to developments in physics, even trying to think like a physicist when necessary. But specialization had proceeded to the point that such a wearing of two hats had become challenging in the extreme. Kekulé's brilliance as a theoretical organic chemist versus his naïveté as a physicist is only one measure of this divide, but it is symptomatic. So is van't Hoff's brilliant, brief excursion into organic chemistry, followed by his failure with his *Ansichten über die organische Chemie* and then his triumphant pursuit of physical chemistry. But despite these cultural differences, and differences in the conceptual routes they took, by about 1860 both communities were exploring the microworld, using creative visualization as well as the more traditional tools of their profession.

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[77] Ibid., 1:379.

[78] These papers are discussed in ibid., 1:510–13.

NINE

Kopp's World

But I thoroughly believe myself, and hope to prove to you, that science is full of beautiful pictures, of real poetry, and of wonder-working fairies; and what is more . . . though they themselves will always remain invisible, yet you will see their wonderful power at work everywhere around you. . . . There is only one gift we must have before we can learn to know them—we must have *imagination.* I do not mean mere fancy, which creates unreal images and impossible monsters, but imagination, the power of making pictures or *images* in our mind, of that which *is,* though it is invisible to us. ARABELLA BUCKLEY[1]

Despite his high contemporary reputation, Hermann Kopp (1817–92) has drawn little attention from historians, partly because of his cautious and retiring personality and his willingness to allow more assertive colleagues to take the spotlight. All of Kopp's important scientific and historical contributions deserve greater study, but for our purposes there is particular interest in a different sort of book he authored, a fanciful ground-level exploration of atoms and molecules that appeared in 1882. An examination of this fantasy will also provide further insight into the imaginative world of the nineteenth-century chemist. The last section of this chapter explores a chemical parody that has some parallels to Kopp's fantasy, and that appeared four years later, in the same year in which the third (and the major) edition of Kopp's work was published. I want to suggest that what appears at first impression to be merely playful banter may have significance for the pursuit of

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[1] Buckley, *Fairyland* (1879), 10–11.

serious scientific inquiry and for a historical understanding of the nature of that inquiry. Just as recent historians have rightly argued for the importance of understanding the gestural ("body-knowledge") aspects of doing science, we can also make a similar argument for what might be called jestural approaches.[2]

The Making of a Chemist-Historian

Born in Hanau (in Electoral Hesse), Kopp was the son of a cultured physician who had strong interests in the sciences.[3] After concluding his secondary education at the Hanau Gymnasium, Kopp spent three semesters at the University of Heidelberg (Baden), where he initially studied classical philology, but was then attracted to chemistry by the lectures of Leopold Gmelin. After two additional semesters at his home-state University of Marburg, Kopp passed examinations for the doctoral degree and habilitation in the fall of 1838. In fall 1839 he traveled to Giessen (in the Grand Duchy of Hesse), where Liebig welcomed him into his just-renovated and expanded laboratory. In spring 1841 he became Privatdozent for both physics and chemistry there, teaching crystallography and theoretical chemistry. In 1843 he was named ausserordentlicher Professor, although a meager salary was attached to this position only from 1846.

When Liebig left Giessen in 1852, his junior colleagues Kopp and Heinrich Will were named his joint successors, but a year later Kopp chose to become professor of theoretical chemistry, leaving the more general professorial title and direction of the chemical institute to his colleague. Kopp transferred to the University of Heidelberg in 1864, where he remained until his retirement in 1890. Articulate, diligent, judicious, and possessed of an attractive personality, Kopp was universally respected; he and his closest friend Robert Bunsen were probably the most widely admired colleagues of their generation. T. E. Thorpe wrote that "to know Kopp was to love him, and to love him was . . . a liberal education."[4]

For Kopp was not just one of the leading chemists of his generation, but was a universal scholar, equally at home with Greek and Latin

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[2] See Gilbert and Mulkay, *Opening Pandora's Box* (1984); Paradis, "Satire and Science" (1997); and Beller, "Jocular Commemorations" (1999). This is a topic in need of further inquiry.

[3] The following sketch of Kopp's life is based on Hofmann, "Kopp" (1892); Thorpe, "Kopp" (1893); and Speter, "'Vater Kopp'" (1938).

[4] Thorpe, "Kopp," 776.

35 Hermann Franz Moritz Kopp. Source: Photo Deutsches Museum.

manuscripts as with chemical apparatus. As a twenty-four-year-old Privatdozent he spurned an easier road to career success by choosing to lecture on the history of chemistry, even though student interest in the subject was tepid. He then compounded the apparent folly by squandering his valuable time writing a monumental history of chemistry, all four volumes of which were published before his thirtieth birthday.[5] He boldly—rashly?—carried his story up to his day (ca. 1840), discussing in the last chapter of the first volume, inter alia, the work of his boss, the already world-famous Justus Liebig; the work of Liebig's greatest rival, Dumas; and the work of Liebig's greatest friend, Wöhler. And he did so in measured terms, without sycophancy.[6] Although there existed a few other histories of chemistry before Kopp's, the subject had never been treated with such detail, scholarship, and circumspection. The work quickly sold out, and the youthful Kopp became famous in his collegial circle. For the next forty years he intended to produce a second edition of this history, of which he published several large pieces, but he never was able to complete the job.[7]

Soon after his arrival in Heidelberg, the Bavarian Academy of Sci-

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[5] Kopp, *Geschichte* (1843–47).

[6] Ibid., 1:421–46.

[7] Kopp, *Beiträge* (1869, 1875), 840 pages; *Entwickelung* (1873), 854 pages; *Alchemie* (1886), 396 pages.

ences asked Kopp to write a history of modern chemistry in Germany, in the series *Geschichte der Wissenschaften in Deutschland.* The leading figure behind this ambitious project was none other than Leopold von Ranke, the reputed founder of objective historical method based on careful study of primary sources. And indeed we can see the influence of this objectivist historiography on Kopp as early as the 1840s. But Kopp was never able to write history from a purely nationalist basis. His preface to *Die Entwickelung der Chemie in der neueren Zeit,* his contribution to the Rankean project, aggressively defended the international perspective that he there adopted.[8]

In his generation, no one understood the history of his field better than Kopp, nor was anyone a more complete master of the emerging new scientific literature. Upon the death of Berzelius in 1848, Liebig took over responsibility for the annual reports that had made Berzelius the "law-giver of chemistry" for so many years—"if only," as Liebig commented to Wöhler, "that it not end up in other and worse hands."[9] But Liebig did not do much of the immense work of reading and summarizing the chemical literature of each preceding year; he persuaded Kopp to do it. Kopp enlisted several of his Giessen colleagues as contributors, but continued as the principal author-editor of this important series until 1862. In contrast to Berzelius's disputatious and judgmental prose, Kopp's annual reports successfully sought a neutral, factual tone.

Liebig did not stop there. In 1851 he wrote to Wöhler, "By the way, I have decided to bring Kopp into the *Annalen* [*der Chemie*]. His talent, his orderly mind, his good judgment, and the breadth of his knowledge are unique, and his participation as an editor would be of great benefit to the journal. What do you think?" Wöhler responded, "I can only express my pleasure that you wish to give over the editing of the *Annalen* to Kopp. There could be no better editor than he. I have enormous respect for his quite exceptional mind; I only regret that he will in the end come to grief with all the correspondence and printer's ink."[10] For the next twenty years, "Liebig's" *Annalen* was really Kopp's *Annalen.*

We see that Kopp enjoyed the total confidence of the two leading

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[8] Ruska, "Kopp" (1937); Weyer, *Chemiegeschichtsschreibung* (1974), 83–84, 90–92; Strube, "Geschichtsauffassung" (1963); Rocke, "'Between Two Stools'" (1990); and Rocke, "History and Science" (1993), 23.

[9] Liebig to Wöhler, 29 August 1848, *LWB,* 1:320. The series was *Jahresberichte über die Fortschritte der Chemie* (Giessen: Ricker, from 1848).

[10] Liebig to Wöhler, 8 February 1851; Wöhler to Liebig, 14 February 1851; both in *LWB,* 1:361.

German chemists of his day, Liebig and Wöhler, but his circle extended much further than that. Kopp's alma mater, Marburg, although located in another German state, was only about thirty kilometers distance from Giessen, so collegial visits between the two university towns could be frequent. Kopp became personally and professionally close to his colleagues there—including Bunsen, who taught at Marburg for twelve years, and Kolbe, who was there for seventeen years (sixteen while Kopp was in Giessen). And Kopp obviously knew all who went through the chemical mecca of Giessen in those crucial years of the 1840s, including especially his colleague and close friend August Wilhelm Hofmann (until 1845), Alexander Williamson (whom he taught 1844–46), and August Kekulé (whom he taught 1847–51). With his extended collegial circle of friends, his total mastery of the literature and history of the field, his important editing duties, and his exceptional memory, judgment, and work ethic, there was no more central chemical personality in the middle decades of the nineteenth century than Hermann Kopp.

In his scientific work Kopp concentrated on the relationship between macroscopic physical and chemical properties of substances and the invisible microworld of the atoms and molecules that compose them.[11] Investigations of this type were not new, of course. Two crucial and nearly simultaneous physical-chemical discoveries deserve particular notice. The first of these, announced in April 1819 by A. T. Petit and P. L. Dulong, was the empirical and purely numerical correlation that revealed an approximate inverse proportionality between the presumed relative weights of many atoms and the specific heat capacities of macroscopic quantities of the elements that they compose. If this relationship were true in the general case, it would suggest that all atoms have about the same heat capacity. Assuming the Petit-Dulong "law of atomic heats" to be general, one could use it to provide evidence to favor one of the various possible atomic-weight multiples of a given element, thus pointing to one particular choice in the case of a disputed molecular formula. The second discovery, publicly announced in December 1819 by Eilhard Mitscherlich, was that chemically distinct substances can sometimes crystallize in the same form (isomorphically). As Petit and Dulong had done, Mitscherlich drew inferences from this to the microworld. Isomorphism can be the result, he thought, of a close analogy in the molecular formulas of two different compounds.

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[11] The most thorough and perceptive analyses of Kopp's scientific work are Thorpe, "Kopp," 782–815, and Bessmertny, "Kopp" (1932).

And again one could use the law of isomorphism to deduce that one particular atomistic formula is more likely than another, when other data on the question were equivocal.

The laws of atomic heats and of isomorphism demonstrated that apparently unexciting empirical correlations of physical properties could have dramatic inferential applications to the microworld. Berzelius and others regularly used such tools in the construction of chemical atomism. And in fact, if one is interested in inference to the microworld, the study of physical properties has one important epistemological advantage over the study of chemical reactions. Namely, these properties reflect a stable substance being observed statically, rather than a substance in a dynamic state, undergoing a chemical transformation into another substance.

There are reasons to believe that these were the considerations that led Kopp to this field of research. A hallmark of his career was epistemological caution, but one can see, half-concealed below the surface, a continuous deep concern with theory, including and especially atomic-molecular theory. It should not be forgotten that throughout his career Kopp's major teaching field was theoretical chemistry. Moreover, many of Kopp's own empirical physical-chemical generalizations were regularly enlisted in the aid of atomic-molecular conceptions, analogous to the Petit-Dulong and Mitscherlich methods, though Kopp was often hesitant to do so himself. For instance, his boiling-point series for various organic compounds, determined with the greatest care over several years, proved crucial in refuting the dualists' assertion that "methyl" and "ethyl" were monomeric radicals, and in supporting Gerhardt's and Williamson's unitary theories. And in earlier chapters we have seen Kopp's significant influence on Kekulé, both in the latter's respect for the study of physical properties of organic compounds, and (possibly) in the epistemological caution with which he made theoretical assertions. Kopp's views on these matters were perhaps best reflected in the final pages of the first volume of his history of chemistry, published in 1843, in which he indicated his belief that the next great period in the history of the science would occur when purely chemical endeavors were thoroughly united with mathematical and physical approaches. Early signs of such a unification were already in evidence, he thought, and only the future would reveal the nature of the more encompassing and more powerful science that would be created.[12]

Given Liebig's theoretically agnostic stance after about 1840, the cli-

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[12] Kopp, *Geschichte,* 1:447–55.

mate in Giessen was not friendly toward modernist theory, which may have given certain junior colleagues pause. Still, we have seen some indications in chapter 2 that Kopp and especially Will were more open than Liebig was to the new ideas emerging in the science ca. 1850; Kopp's contemporaneous summaries of Williamson's papers demonstrate that he was at least paying close attention.[13] After Liebig was called to Munich in 1852, the two new full professors of chemistry in Giessen declared themselves publicly for the new ideas, though Will did this more clearly than Kopp. Kolbe noted the change immediately, and with alarm. Jacob Volhard, a student in Giessen at this time, noticed the same shift.[14] Kopp's annual reports, though neutral in tone, indicated respect for the new ideas of Wurtz, Kekulé, Couper, and others, and suggested that Kolbe's theories were not as distinctive as Kolbe himself thought they were.[15] Kolbe's judgment, privately expressed in a letter to Erlenmeyer, summarized the situation accurately: Kopp "belongs to no party, though type theories are most comfortable for him."[16] As we noted in chapter 1, in his 1873 history Kopp retrospectively saw Williamson's first ether theory paper of 1850 as a revolutionary turning point in the modern history of the science.

In 1863 the education ministry in Berlin sought to acquire Bunsen from Heidelberg. But Bunsen had little desire to work under the Prussian regime led by Bismarck and instead extorted a concession from his home ministry to keep him in Heidelberg. His condition was that a second Ordinarius for chemistry be appointed, namely Kopp. Kopp was called from Giessen, and he accepted; he arrived in Heidelberg in March 1864.[17] The two men were already old friends. They pursued similar kinds of research, mostly physical-chemical in nature, and they had similar progressive political opinions. Having struck out with Bunsen, the Prussian ministry next selected Hofmann, who was happy to return to Germany after two decades in London. Over the next two decades, Hofmann attempted no fewer than three more times to call Kopp to

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[13] *Jahresbericht über die Fortschritte der Chemie* 3 (1850): 459–60; *Jahresbericht* 4 (1851): 510–12.

[14] Will, "Theorie" (1854), 292; Kopp, "Specifische Volume" (1854), 24–28; Kolbe to Vieweg, 23 October 1854, VA ("Selbst Will und Kopp in Giessen scheinen sich dieser moderner Richtung anzuschliessen"); Vorländer, "Volhard" (1912), 1860–61. Volhard stated directly that Will taught the doctrines of Gerhardt after Liebig's departure; the evidence for Kopp's shift is more subtle.

[15] *Jahresbericht* 7 (1854): 370–73; *Jahresbericht* 10 (1857): 268–72; *Jahresbericht* 11 (1858): 221–25; and *Jahresbericht* 13 (1860): 218–22.

[16] "Wer keiner Partei angehört wie Kopp, wenn schon ihm auch die typischen Anschauungsweisen die bequemsten sind . . . " Kolbe to Erlenmeyer, 17 December 1863, HDN 11.

[17] This chronology is often misdated in Kopp biographies, but is established by documents in Kopp's Personalakte, PA 1868, Universitätsarchiv Heidelberg, 1, 3.

Berlin, but each time Kopp refused. “Bunsen alone,” he told Hofmann, “holds me fast in Heidelberg.”[18] Bunsen and Kopp became exceedingly close, especially after Bunsen’s other great friend Gustav Kirchhoff left Heidelberg in 1874. Bunsen’s tall, handsome figure contrasted with that of the short, corpulent Kopp; in the 1870s and 1880s the curious pair was a common sight walking in the parks and hills of Heidelberg.[19]

In amongst the Molecules

In the fall of 1876 Kopp pursued an idea concerning the theory of solutions that would not, in the end, lead to publishable results.[20] Namely, he hypothesized that certain salts in aqueous solution actually might float around as anhydrous molecules, dissociated from the water molecule(s) that they attract to themselves only when they crystallize and separate out of the solution. “Then I imagined,” he wrote, “ . . . how the molecules of the salt and of water would knock about there. From that point the play of my thoughts then turned to gaseous bodies.” After all, one could imagine atomic-molecular appearances in the gaseous state more accurately than in the liquid state, since so much more was known about the physical nature of gases than liquids.[21]

His experiments to attempt to substantiate his hypothesis about solutions were not fruitful, but his extended thought-play was intriguing and enjoyable. For his private amusement Kopp composed a draft fantasy and entitled it “Aus der Molecular-Welt” (From the World of Molecules). But Kopp did not consider it publishable, so he consigned it to what he drolly referred to as his “dungeon,” a drawer in his desk into which he was accustomed to throw half-finished or otherwise unpublishable work. He soon forgot it existed.

A few years later, Kopp cast about for something to give his friend Bunsen in honor of his seventy-first birthday, 31 March 1882. In past years, he and Bunsen had often had occasion to spend the six-week

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[18] Hofmann, “Kopp,” 511–12.

[19] Lockemann, *Bunsen* (1949), 194–96.

[20] The information in this and the next paragraph derives from statements in Kopp’s preface to *AMW,* v–ix. The chronology, he wrote there, was established by consulting his old laboratory notebooks. The work he speaks of may be the same as that referred to in his letter to Wöhler of 15 October 1876, in which he writes that “das unchemische [?] Arbeiten, dem ich mich mit Liebe wieder einmal hingegeben habe, und das Experimentiren . . . ist mir ausgezeichnet bekommen. Es ist zunächst verschiedenes Krystallochemisches, was ich in Untersuchung habe” (BBAW, Sammlung Wachs).

[21] *AMW,* viii.

Easter semester break together in Italy, but this year Kopp could not get away, so Bunsen had gone there with their mutual friend, the physicist Georg Quincke.[22] Kopp understood that Bunsen and Quincke were planning to be in Naples on the targeted day. Short of time, and casting about for something appropriate that he might quickly adapt for the purpose, he looked in his "dungeon." He found the manuscript, remembered the circumstances of its composition, and decided that here was good material for the intended purpose. He filled out certain sections and "purified" it (removing some references that might have been taken personally by this or that colleague). He also untangled the tails of much of his "Rattenkönig" prose to make it easier to read, for (he said) he well recognized his unfortunate tendency to stuff far too much in his sentences, making each sentence resemble the Russian dolls that fit one inside another in an almost endless series.[23] (Kopp was far from successful in this simplifying endeavor.)[24] He then had the revised manuscript quickly printed up, mailed it to Naples poste restante, and secretly directed Quincke to look for it there, to present to Bunsen as a birthday surprise.[25]

A sense of the style can be had by citing in extenso the opening two paragraphs (in my translation):

> In Naples we have often visited the aquarium, and enjoyed the remarkable animals of the sea-world there, along with the fact that there are no monkeys to see there, which are among the most interesting things to see in the aquarium of a Continental metropolis. But why not? for in Munich was there not once a guild ordinance in place that made the commercial sale of suckling pigs the exclusive province of poulterers? But today we do not want to visit the aquarium, but rather an *aerarium* set up by a member of another guild, to see what goes on with the creatures of which airy things actually consist. On our way there we will discuss the question that the name of the place where we are going can perhaps be judged as incorrectly formed (one of us is actually never sure about this), and that a confusion of the place we seek with one that is devoted to the preservation of more solid matters is near to hand, which confusion however should be charged to those who commit it. But in apothecary-Latin many things happen which linguistically are not

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[22] Bunsen to Kopp, 22 April 1882, ADM 1008, which describes the trip with Quincke, just concluded.

[23] Virtually all of Kopp's biographers mention this propensity, which increased in his old age. Even his contemporary compatriots often found his writing difficult to comprehend quickly or easily.

[24] Note for instance the 165-word sentence, *AMW,* 81–82, which embraces several different subjects. This sentence may well have been one of several examples of deliberate self-parody.

[25] *AMW,* ix.

AUS DER
MOLECULAR-WELT.

EINE GRATULATIONS-SCHRIFT AN ROBERT BUNSEN
VON
HERMANN KOPP.

DRITTE AUSGABE.

HEIDELBERG.
CARL WINTER'S UNIVERSITÄTSBUCHHANDLUNG.
1886.

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entirely in the regulations, and so we will refrain from seeking a better name that could have been applied to the place where we have in fact just arrived.

Using the mind's eye, let us look at some things in the aerarium that especially excite our attention. We direct that eye to any of the variously labeled compartments: how the curious little things are teeming in them.

Look! Look! By the gallows tree,
There on the wheel's spindle,
Half visible in the moonlight,
Dances an airy mob . . .

> sang Bürger; but we can notice this sort of mob teeming around not just in one particular place in the air, but everywhere we look. Let us consider what kinds of creatures these are in the light of recent knowledge, and let us express, to those who are not as skilled in the observational art as we, what we here perceive or experience.[26]

This introductory passage exhibits many salient characteristics of the whole: serious scientific matters treated metaphorically, mixed with puns, lighthearted banter, curious asides, and tortuous (and occasionally opaque) stream-of-consciousness digressions, all interlarded with literary allusions. The premise is that an unnamed party of German friends—at times there appear to be just the first-person narrator and a single friend, presumably Bunsen, at other times there appear to be more—are touring the Naples "aerarium," stopping by each labeled exhibit in turn—generally these were large glass globes in which the atoms and molecules inside are readily visible—and pondering what one sees there. The subjects treated include atomic valence and molecular structure, the kinetic theory of gases, and solution theory, especially as regards electrolysis. Although there are no section divisions or subheads in the ca. one-hundred-page text, the reader can easily follow the action from scene to scene. But beyond all the wit and whimsy there was another side. Throughout, Kopp wrote with indirection, while at the same time anxious for his underlying messages to be taken seriously. On this deeper level, the book is a remarkably wise and perceptive interpretive tour of nineteenth-century chemical theory, but the text requires constant exegesis to be understood in that more profound sense.[27]

The first part describes the kinetic behavior of the simple gases such as hydrogen, chlorine, oxygen, and nitrogen. Hydrogen atoms each have a single "hand," oxygen atoms have two, and nitrogen atoms have three, with which each atom holds a partner atom to form molecular pairs. The random zigzag travel of the paired atoms is described as "a

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[26] Ibid., 1–2. "Another guild" is probably a sly reference to academia. "Incorrectly formed" refers to the Greek root versus the Latin ending of *aerarium,* a faux pas for a sophisticated classicist like Kopp. "Confusion of the place" is a probable reference to *terrarium.* "Bürger" is Gottfried Bürger (1748–94); the quotation is from his ballad "Lenore."

[27] Kopp was not the first to write a popular work about invisible entities in nature. Arabella Buckley's children's book *Fairyland* (1879) was immensely popular and went through innumerable editions. But Buckley did not personify her fairies, as Kopp did, and there is nothing about atoms or molecules in her fairyland. Closer to Kopp's conception was Lucy Rider Meyer's *Fairy Land* (1887). But in contrast to all of these "fairy books," Kopp was writing for adults rather than children, and so his work has a quite different tone and purpose.

refined Laendler" (an Austrian couple dance)—"respectable, but absent the courtesies." Carbon atoms are four-handed, a phenomenon that sometimes finds an analogy in the animal world. By contrast, true five-handed atoms are very rare, just as they are in the animal world; Kopp declares that the prehensile tail of a four-handed monkey should *not* be regarded as a fifth "hand."[28] There follows a discussion of the nature of gases, covering diffusion, transpiration, and effusion of mixed gases, using a variety of appealing metaphors.[29]

Atoms possess the "attractive trait" that they normally require all of their "hands" to be held—like that of a child, who before feeling ready for sleep must have one hand held by her mother, and the thumb of the other hand inserted in her mouth. Mercury atoms in the next compartment to come into view seem decidedly unfriendly; although possessing two hands each, they prefer not to associate with other atoms of their own kind, but rather each atom petulantly holds its *own* hands. The Kopp party then walks to the exhibit labeled "steam," illustrating "affinity," where the star of the show appears to have a day off and is not required to do any of the myriad tasks he is normally called upon to perform; the molecules of airy water appear to be performing a lovely allemande à trois. In another exhibit, a hydrogen couple approaches a chlorine couple in the dance move known as an en avant deux, and they form—if there is sunlight to make the reaction happen, that is—new pairings through affinity. But these new couples appear to be not very happy, but rather "desperately *sour,*" possibly because of the (let us be honest) well-known *negative* personality of chlorine. "The cowering hydrogen looks as if he is thinking, 'Affinity, ah affinity has brought me to this state.' But we can do nothing to help him."[30]

These are all simple molecules, formed of only three or fewer atoms. How are the more complicated molecules of organic substances formed? Here Kopp enters into no fewer than eight pages of hesitations, qualifications, demurs, and literary digressions, before cautiously judging the comparative merits of two different approaches to answering what he called the "constitutional" question. Both approaches utilize the four-handedness of carbon, as well as the aforementioned two- and one-handedness of oxygen and hydrogen, respectively. But there is a significant distinction between them. One viewpoint (that of Kolbe, but whose name was not mentioned) suggests that an organic mole-

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[28] *AMW,* 2–6.
[29] Ibid., 6–10.
[30] Ibid., 10–15.

cule consists of ranked carbon atoms in a hierarchical relationship. The other more democratic (structuralist) notion is one in which all carbon atoms are accorded equal chemical importance. Which viewpoint is superior? One must be careful here, since between these two theories "the sort of modus vivendi that we as a peaceable people would prefer has not developed; they exist in open warfare." Nonetheless, Kopp wrote, they have much in common; so much so, he thought that in many cases the respective schools were quibbling over mere words rather than over substance, as has happened so often in matters of religious faith.[31]

With the utmost tact, Kopp then proceeded carefully to suggest some of the difficulties with the hierarchical-radical viewpoint, especially that the objective basis for assigning certain carbon atoms to a higher rank than others often seemed rather unclear. The positive evidence for this viewpoint was also, he delicately proposed, somewhat equivocal, some of the predictions made on its foundation having been proven true, and some not. As regards the second (structuralist) viewpoint, some had objected that it is *too* simple, thus leading to incautious applications. But this objection is just as invalid as judging the Bible by the foolishness of certain misinterpreted readings from it. More positively, predictions based on the second theory have been verified in even larger numbers than for the first theory; and this theory also declares to be impossible many things that the first seems to allow, but that have never been found. Finally, the "fully justified attempt" to seek, on the basis of this second theory, to determine the arrangements of atoms in space "has recently been taken up once more, and quite noteworthy results achieved." But in the last analysis one should always remember that both conceptions have much in common, both are useful, and no theory should ever be viewed as permanent.[32]

From this point in the conversation on, Kopp wrote, "we must accommodate our mind's eye" to the second (structuralist) conception of molecular constitutions, both because it is simpler and easier and also because "the idea appeals somewhat better to a sensibility that is still (or perhaps that is once again) childlike." The next room of the aerarium is called in Italian the *Caldario* (hothouse), and indeed there are many very hot glass balloons there. Standing before the first of these, "one of us takes off his glasses, brings his face close to the uncomfortably hot glass of the balloon, and cries out, 'I see something

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[31] Ibid., 16–24 (quote on 20–21).

[32] Ibid., 24–29.

that you don't see'; the other of us puts on his pince-nez and now sees everything there is to see, much better and more completely." This is methanol, and after this important adjustment of eyewear, the six atoms of each molecule are easy to discern, the molecules themselves clearly seen dancing about. The next balloon contains molecules with a longer carbon chain, performing their characteristic "chain dance"; it is gaseous ethanol. Similar series of balloons contain vapors of organic acids, esters, and ethers.[33]

The next room of the aerarium is labeled the *Compartimento Aromatico,* where the party finds a balloon labeled "benzene." They look in.

> Oh! They're dancing Ring around the Rosie! There are six carbon atoms in the molecule, which form a molecular ring with their dark little faces looking out; each carbon gives two of its four hands to one, and one hand to the other of its neighboring atoms, and each tows a hydrogen atom behind it with the fourth hand. How quick and nimble they are, and at the "all fall down" refrain they crouch; even the tiny hydrogens do it! Look how they bow down, straighten up, and twirl rhythmically with unbelievable speed, never letting loose of their handholds right, left, and rear, even with that additional motion which the molecule as a whole executes.

Kopp then added a personal comment.

> As you know, dear friend, such mental pictures appeal to me, and for that reason I like the [structural] conception used here—apart from several others—and find it useful, for it lends itself to such mental pictures. But in the evening of my life, I often find it a bitter thought, that I came to this world with the unfortunate characteristic of constantly seeking my place between two stools, and this also applies to the present matter. For I like the other conception equally, among others, also because it lends itself no less to mental pictures that appeal to me, and my place is decided on neither one side nor on the other, but for the moment between the two.[34]

The party then proceeds to a cabinet in the aerarium where it appears that a kind of club has been established. "The purpose of the society: dancing. We are not allowed in; they are very exclusive here. But we can look in through the glass. They are dancing there, the molecules! . . . each as a whole, but within every molecule each atomic group—if one looks closer, even each individual atom, but we won't

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[33] Ibid., 29–33.

[34] Ibid., 33–34.

speak of that yet—is likewise dancing merrily." There is the lightest girl, Methylie, just passing by our eye, and then there is Ethylie; finally we espy the corpulent Amylie, who is actually rather disgusting, and whose compounds are in bad odor.[35] Their family name is "Alkyl," and their constant (annoyingly arrogant) partners are named "Hydroxyl." "There is always plenty of scandal in the molecular world . . . Thus it is said that Methylie along with her customary procurer lets herself be used by the authorities to denature the relationship that Ethylie is in."[36] And the unpleasant Amylie is often known to spoil the company of poor Ethylie out of simple spite, so that an evening spent in the latter's company will be rued the next morning.[37]

The next section deals with atoms of variable "handedness" (valence), and molecular compounds. If an atom uses less than its maximum number of hands, what does it do with those not being used? Perhaps we must imagine other appendages than just hands, such as occasionally used claws that can be sheathed, or thumbs in addition to fingers. All of this is highly uncertain, Kopp cautioned, and many different views are abroad.[38]

Up till now, Kopp notes, we have been concerned with atoms and molecules as individuals. But considered collectively, what about the communities and polities that they form? Molecular states (German *Staaten* = polities or nations), he assures us, are organized on a totally democratic basis, where there are no rights of birth or of class. There are no authorities that exert control over these states, but each molecule administers the law individually; indeed, there is nothing of individual *rights* in such states, only individual *obligations,* such as the obligation to move inertially until prevented by a collision with a neighbor or with the walls of the container. Moreover, "according to international agreement" each state is obligated to allow equal spaces to be occupied by equal numbers of molecules, under similar conditions.[39]

Of course, at higher pressures and/or lower temperatures, gases make

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[35] "Bad odor" = bad reputation in both languages. Several compounds of amyl do have disgusting aromas.

[36] The poisonous methyl alcohol was (and still is) used by governments to denature ethyl alcohol, in order to allow manufacture and sale of the latter for chemical purposes without beverage taxes.

[37] Amyl compounds are constituents of fusel oil, a mixture of naturally occurring substances in alcoholic beverages that many believed (and believe) cause hangovers. All this in ibid., 42–45.

[38] Ibid., 45–51.

[39] Ibid., 68–75. Since the English word "state" (in contrast to German) embraces both of the meanings "polity" and "form of matter," these puns actually work better in English than in German.

transitions to liquid, then to solid states. Kopp then begins a new section on the world of liquid substances, which is the province of a special annex to the aerarium; the party reaches this facility by walking through a darkened gate. This annex will not be as amusing to view as the aerarium itself, for "it also serves as an experiment station for the scientific mistreatment of molecules, and terrible rumors circulate in the aerarium concerning all that is done to them." After wandering aimlessly through some of the corridors of the annex, the group comes to a cabinet entitled "Electrotherapeutic Treatment of Liquid Molecules." Good, Kopp remarks, this is what we wanted to see. In common parlance, it is electrolysis.[40]

The simplest case, water, is complicated by the fact that water conducts electricity very poorly, so one needs to add a small amount of sulfuric acid. The sulfuric acid, it seems, plays a roguish game by coming entirely apart in the process but then continually reassembling itself ("rising like a phoenix, except in the wet way"); it is the water molecules that suffer the real consequences in decomposing permanently, all the way to the elements. Having tested the basic process, we proceed to more interesting demonstrations: concentrated solutions of hydrochloric acid in one case, and ammonia in the other. "We observe each of these liquids with our mind's eye: the liquid molecules within appear to be somersaulting about, they are vibrating quite gaily. We will soon see the dancing . . . of the atoms composing the gas molecules [in solution], under the influence of the electricity."[41]

The performance of the electrolysis of hydrochloric acid can begin. But what is this? The two elements separate out from each other, as expected, but the hydrogen gas bubbles out only at the negative pole, and the chlorine only at the positive pole. What happens to the free chlorine that must be liberated at the negative pole, and the free hydrogen at the positive? The answer, we note by peering carefully into the electrolyzing liquid, is that the particular dance being performed is a Scottish country dance, which is done from what is called a longways set: all the men (chlorines) in a line with their backs to us, with their partners (hydrogens) facing them and us. When the electricity begins to flow, all the atoms continually change partners down the line "at lightning speed," the chlorines moving right and the hydrogens left. Atoms become free only at either of the two ends of the set: chlorines at the right (positive) pole, and hydrogens at the left (negative) pole.

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[40] Ibid., 75–82.
[41] Ibid., 82–84.

Or perhaps, considered more accurately, the dance is actually a minuet, in which the dancers form a single line of alternating men and women (chlorines and hydrogens). In this case the action proceeds a bit differently, more like the grand chain figure in a French courtly dance.[42]

Now three electrolysis cells—concentrated hydrochloric acid, acidified water, and ammonia solution—are connected electrically in a single series, and current is applied by the attendant.

> Now it is even more important than earlier to observe not just with a sharper eye, but so to speak with a mind's eye multiplied many times over; now it is also a matter of counting in all three cells the molecules, atoms, and atomic hands in the shortest conceivable instant of time . . . It is good that there are two of us; we can check our counts against each other to see if they agree.

What the observers find, when they compare their numbers, is that the same amount of current always breaks the same absolute number of atomic handholds, hence it liberates quantities of materials proportional to their equivalent weights.[43]

The electrochemical dance over, the party begins to head through the annex back toward the main building. But they are sidetracked by a small, interesting door in the gloomy corridor through which they are walking. *What is behind the door?* they ask the attendant who is guiding them back. *Discarded salt solutions* is the answer. Here, in dusty, neglected bottles, they find various familiar solutions of salts, "the favorites of my youth and frequent companions of my maturer days." And here we find the suggestions of the nature of solutions of hydrated salts that gave rise to the earliest version of *Molecular-Welt,* as Kopp described in his preface. There is much here on hydration, on dissociation, and on the presumed motions of the atoms and molecules within the solutions, all expressed in the now-familiar personified metaphors.[44]

"But we had better retreat back into the main building of the aerarium," Kopp remarks at the end of *Molecular-Welt,* "for we cannot bear the heat in this room any longer. Now on to more interesting things! What? It's already one o'clock? Really. We wanted to be at Hassler's already at this hour. So let's go. But if it can be arranged, we certainly want to come back here again."[45]

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[42] Ibid., 84–90.
[43] Ibid., 90–94.
[44] Ibid., 94–105.
[45] Ibid., 105.

The Response

Virtually no names of chemists appear anywhere in this work.[46] The preface was introduced with the salutation "Lieber B.!" and it was dated from "H., March 1882"; Quincke (to whom the privately printed birthday present was directed in Naples) was identified as "Q.," and the author of the book was indicated only as "H.K." Bunsen, Quincke, and others who read this earliest privately printed version must have thought enough of it to persuade its author to issue a real edition for sale, which was published in late May or June in identical form, and a second unchanged edition followed before the end of the year. Four years later a third edition appeared, apparently printed in a much larger press run, and this is the version that is encountered in most libraries.[47]

Kopp sent copies of the first (private) printing to a few selected friends. On 19 April 1882 Kekulé wrote to Volhard, inter alia, "You must have been just as pleased as I was regarding the wonderful little book 'Aus der Molecularwelt,' for I assume that our friend H.K. sent you a copy too." We do not have Volhard's response, but two months later Kekulé wrote again. "You have in the meantime read H.K.'s, id est Kopp's charming little book 'Aus der Molecularwelt.' When I recently wrote you about it, I did not wish to reveal the very transparent incognito; however, immediately after receiving his package I sent our friend Kopp a thank-you letter, which, as I believe, has contributed to his decision to bring this youngest child of his fancy to commercial sale in bookshops."[48] A reasonable inference from these letters is that Volhard

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[46] 46. Of chemists, Gay-Lussac is mentioned twice in the text, J. B. van Helmont once, and a couple of others are identified by initials; that is all.

[47] 47. The exceedingly rare privately printed edition has the words "Als Manuskript gedruckt" on the title page, and the imprint is Darmstadt: Carl Winter, 1882; Kopp may well have had only a few copies printed. The title page of the first edition offered for commercial sale omits the words "Als Manuskript gedruckt" and has the imprint Heidelberg: Carl Winter, 1882. A second printing the same year adds the words "Zweiter Abdruck" to the title page. The third edition adds "3. Ausgabe"; has the imprint Heidelberg: Carl Winter, 1886; and finally names the author and dedicatee in full. The texts of the editions are otherwise identical (that is, variations between all these editions are confined solely to the front matter).

[48] 48. "Ueber das wundervolle Schriftchen 'Aus der Molecularwelt' hast Du Dich wohl ebenso gefreut wie ich, denn ich nehme an, dass Freund H.K. auch Dir ein Exemplar zugeschickt hat." Kekulé to Volhard, 19 April 1882, AKS. "H.K.'s id est Kopp's reizendes Büchlein 'Aus der Molecularwelt' hast Du inzwischen gelesen. Als ich Dir neulich davon schrieb, wollte ich das sehr durchsichtige incognito nicht enthüllen, obgleich ich an Freund Kopp direkt nach Empfang seiner Sendung einen Dank-Brief geschrieben hatte, der, wie ich glaube, mit dazu beigetragen hat, ihn zu veranlassen, dieses jüngste Kind seiner Laune in den Buchhandel zu bringen." Kekulé to Volhard, 18 June 1882, AKS.

did not in fact receive a copy of the private printing, being outside the close circle whom Kopp favored with copies. Kekulé (and presumably others in this close circle) then persuaded Kopp to issue a real edition for sale.[49] By the second half of June 1882 Kekulé could now confidently presume that Volhard had finally read the thing.

Aside from Kolbe, who was one of those to whom Kopp sent the privately printed edition and whose reaction could not have been favorable,[50] the reviews were, in fact, very positive. We have already noted Kekulé's immediate delighted reaction. Ten years later, Hofmann wrote in his obituary of Kopp, "The communications 'From the Molecular World,' with which [Kopp] surprised Bunsen on his 70th [*sic*] birthday, are delightful in the highest degree and perhaps unique of their kind. The approbation experienced by this ingenious humoresque is indicated by the number of editions that followed one another in rapid sequence."[51] Similarly, the author of another Kopp obituary characterized the work as an "unforgettable humoresque," and added, "What chemist would not follow him with pleasure into his 'aerarium'?"[52] And Thorpe remarked, "In the *Molecularwelt,* Kopp's delicate fancy and quaint humour are seen at their best; the book attracted considerable attention even beyond chemical circles, and rapidly ran through a number of editions."[53]

But what did Kopp actually intend with this little book? One should not be too quick to dismiss it *merely* as a parody or fantasy, or a simple humoresque. An earlier popular work by Kopp, *Sonst und Jetzt in der Chemie* (1867) plays the same rhetorical game with personified atoms, but without nearly the development given them in *Molecular-Welt;* this earlier work has an obviously serious historical and pedagogical intent.[54] Moverover, three passages from *Molecular-Welt* suggest that a more serious purpose lies behind it than mere fancy. Two of these pas-

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[49] Speter ("'Vater Kopp,'" 431) printed Carl Winter's letter to Kopp of 17 May 1882, with the honorarium payment and the request for authorization to proceed with printing. My guess is that by the time Kopp had finished revising the 1876 manuscript he was pleased with the result, and he may not have needed much persuading to publish it. According to this supposition, the purpose of the private printing may not have been, as he claimed in the preface, to prevent loss of a handwritten packet in the leaky Italian postal system, but rather to provide means for a trial balloon for limited distribution, expecting subsequently to have his arm twisted to publish.

[50] See Rocke, "'Between Two Stools,'" which discusses a meeting between Kopp and Kolbe within a few days of the publication of *AMW*.

[51] Hofmann, "Kopp," 519.

[52] Unsigned obituary, *Chemiker-Zeitung* 16 (1892): 271.

[53] Thorpe, "Kopp," 781.

[54] Kopp, *Sonst und Jetzt* (1867), 30–31.

sages are found in the preface, where Kopp stated explicitly that “I take seriously and consider worthwhile much of what I say here in a lighthearted way,” and where he traced the origin of the fantasy to his earlier experiments on the actual molecular state of solutes in solution.[55] The third passage occurs immediately following his discussion of structure theory, where Kopp wrote: “I have wanted to discuss all that I have just said in the very serious book with which I have so long been occupied,” but which he was now no longer certain would ever get written, because he doubted that he would ever again feel like “mentally regurgitating the thoughts of the last few minutes.”[56]

In fact, his extensive surviving correspondence with Hofmann and with Wöhler reveals that he long worked on such a book on contemporary chemical theories, particularly on the contemporary theories of “constitutions” of molecules. For at least ten years he intermittently labored over this historical-critical manuscript on theoretical chemistry, but health and money problems, overwork due to teaching and other writing commitments, and his own vacillating and cautious personality caused repeated lengthy interruptions, each of which then required extensive rewriting of what he had already drafted. He never completed this manuscript. Short of time as he was in spring 1882, it is a reasonable inference that he may have interwoven certain already written passages from this draft history of contemporary molecular theory into his 1876 draft of *Aus der Molecular-Welt* to produce the published first edition text of 1882. This supposition is consistent with statements (cited above) in the preface to the work, with the actual character of the 1882 text itself, and with various revealing passages in his private correspondence.[57] In fact, it is possible that he had now given up hopes of ever completing his draft history of molecular theory, and so he revised the *Molecular-Welt* not just to honor Bunsen, but also with the explicit intent of letting it stand in for that more serious work.

Hans Goldschmidt, a prominent student of Bunsen who was twenty-one when the first edition of *Molecular-Welt* appeared, believed that in this “extremely ingenious and witty” work Kopp was subtly try-

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[55] In my summary of the book in the second section of this chapter I have not even attempted to give the reader a full sense of the extended discussions of the details of (e.g.) kinetic gas theory and solution theory of Kopp’s day. The book can be used as a kind of primer to nineteenth-century physical chemistry.

[56] *AMW,* 29.

[57] E.g., Kopp to Hofmann, 25 January 1873, 17 July 1873, and 13 July 1882, Chemiker-Briefe 40, BBAW; Kopp to Wöhler, 11 March 1873, 7 June 1873, 8 October 1873, 3 November 1873, 30 December 1874, 15 February 1876, and 15 October 1876, Sammlung Wachs 304, BBAW.

ing to teach Bunsen about the newer theories, toward which Bunsen was known to be so cavalier, and to make them seem more attractive. Goldschmidt thought that Kopp interlarded his text with so many qualifications and skeptical remarks partly to make it more palatable to his antitheoretical friend. "This booklet," Goldschmidt concluded, "is most earnestly recommended to any chemist who has an appreciation for humor, as it shows how humor can also be carried into purely scientific questions."[58] Goldschmidt's opinion was echoed by the fine historian of chemistry Georg Lockemann (who was eleven years old when the first edition of *Molecular-Welt* appeared). Lockemann also remarked that if this was indeed Kopp's purpose it did not seem to succeed with Bunsen, but that their friendship nevertheless remained as close as ever.[59] (In fact, we know nothing about Bunsen's actual response to the booklet.)

Leaving aside the question of Kopp's underlying intent with *Molecular-Welt,* we might also inquire whether the play of imagination so prominently displayed there might suggest that Kopp used his visual imagination productively in his own scientific work. Unfortunately, we have little evidence on which to build a case for or against this supposition, other than to point to Kopp's autobiographical statement concerning his imaginative exploration of the molecular state of salt solutions and to his repeated avowals that "such mental pictures appeal to me." But to borrow Kopp's voice as my own for just a moment: "If I were to be forced to give an official opinion on the matter—and I am glad that this is not the case—it would be at even greater length than I am known for, and interlarded with 'on the one hand this' and 'on the other hand that,' and to my signature would be added a distinctly written *salvo meliori* [with due respect for a better opinion]."[60]

Having stated these qualifications, I suggest that in his charming depiction of the *World of Molecules* Kopp wanted to let his readers gain entry, in some measure and with appropriate fanciful elaboration, into his own mental world as a scientist. I believe that Goldschmidt and Lockemann were right: the humor so evident throughout the booklet was a technique to misdirect, mollify, and seduce the reader, to portray viewpoints that Kopp sincerely credited, but that he feared would be socially disfavored if presented as more serious discourse.

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[58] Goldschmidt, "Erinnerungen" (1911), 2140.

[59] Lockemann, *Bunsen,* 195.

[60] *AMW,* 24. This sentence prefaced Kopp's judgment of the relative merits of Kolbe's and Kekulé's views on the constitutions of organic molecules—without naming them, of course.

The Thirsty Chemists

In 1886 the Naturforscherversammlung—the peripatetic annual meeting of the Society of German Scientists and Physicians (GDNA)—took place in Berlin, coincident with the annual meeting of the Deutsche Chemische Gesellschaft (DCG), whose president that year was Kekulé. On Monday, September 20, there was a day session of serious chemical science at the meeting. Then, following a social excursion to the Wannsee, the DCG met at 8 p.m. in special session in the Grand Ballroom of the Hotel Kaiserhof in the Mohrenstrasse. The Kaiserhof was the first luxury hotel in the city, at that time a spectacular new facility, and ladies were specifically invited to this gala special event. This was also a rare occasion when the Berlin-based DCG could count on the attendance of chemical colleagues from across Germany, since the meeting was held in conjunction with the only truly national scientific society, the GDNA. It is unfortunate that we do not have a full record of what transpired there, but we do know that an elaborate and well-constructed lampoon of German academic chemical life was printed and issued in connection with the evening event.[61] Proceeding once more under the conviction that humor can tell us much about the actual science of that day, this subject, like Kopp's *Molecular-Welt,* is worth examining.

The ca. sixty-page booklet, entitled *Berichte der Durstigen Chemischen Gesellschaft,* was precisely modeled after a typical issue of the *Berichte der Deutschen Chemischen Gesellschaft,* right down to the standard typography and the realistic-looking (but hilariously phony) advertisements on the inside wrappers.[62] It is, in effect, an early chemical version of the *Journal of Irreproducible Results,* or of the *Harvard Lampoon*. The title page reads (in translation): "Reports of the Thirsty Chemical Society. / Unheard-of Volume. / No. 20.[63] / (Issued 20 September.) / Berlin. / Property of the Thirsty Chemical Society / Printed on Commission by R. Friedländer & Son / N.W. Carlstrasse 11 / 1886." A tongue-in-cheek extract from the bylaws was followed by a table of contents, minutes,

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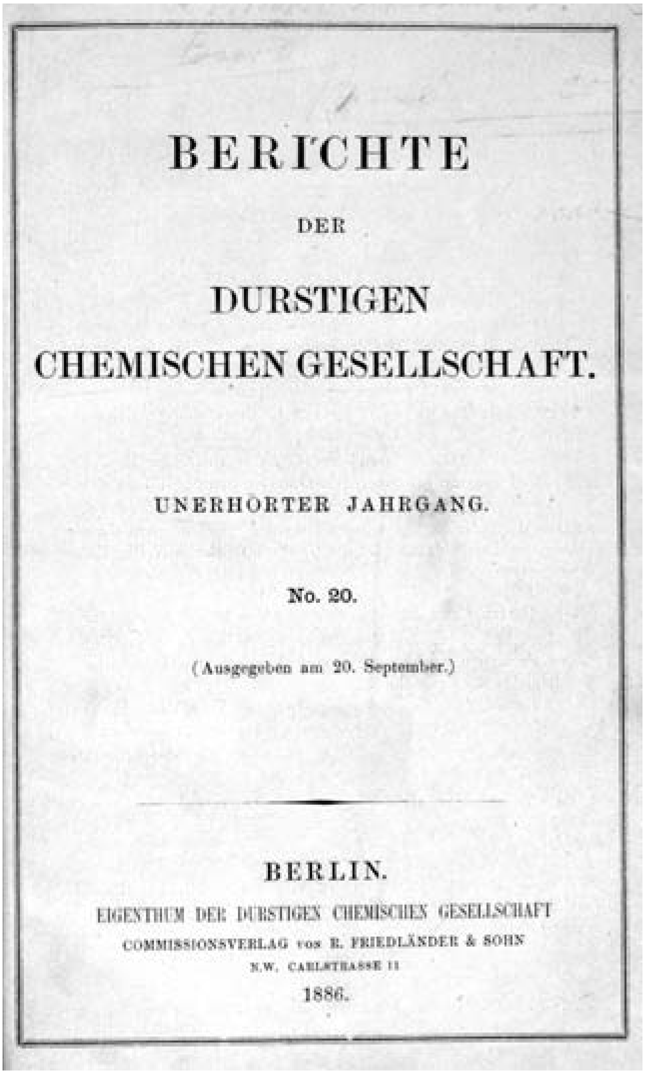
[61] *Tageblatt der 59. Versammlung Deutscher Naturforscher und Aerzte* (Berlin, 1886), 7, 106–7, 126–28.

[62] *Berichte der Durstigen Chemischen Gesellschaft* (Berlin: Friedländer, 1886); the numbered pages were 3517–68. This publication is very rare; I used the copy in Doe Library, University of California–Berkeley. Anschütz, who was present at the *Bierabend* (as he called it), commented on the evening affair and the printed lampoon: 1:609–12.

[63] There were normally nineteen issues of the *Berichte* each year.



BERICHTE
DER
DURSTIGEN
CHEMISCHEN GESELLSCHAFT.

UNERHORTER JAHRGANG.

No. 20.

(Ausgegeben am 20. September.)

BERLIN.
EIGENTHUM DER DURSTIGEN CHEMISCHEN GESELLSCHAFT
COMMISSIONSVERLAG von R. FRIEDLÄNDER & SOHN
N.W. CARLSTRASSE 11
1886.

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report of the last executive committee meeting (part of which was in verse), no fewer than sixteen parody papers, twenty-five abstracts from other journals, reports on patents, the usual page of typographical corrections (even these were witty), and author index. At the end of the volume was an eighteen-page "Poetic Supplement" consisting of eleven chemical poems, some of which indicated the melodies to which they could be sung. The last (and shortest), with my appended translation, was:

Solosang.
Ich hatt' ein schönes Thema,
Kein bess'res sag' ich Dir,
Da kamen die "Berichte,"
Es war die alte Geschichte:
Ein And'rer nahm es mir.
E.[mil] J.[acobsen][64]
Solo Song.
I had a great idea,
None better, I avow,
Then came the "Reports,"
As often happens, in short:
Another had it now.
E.[mil] J.[acobsen]

The pseudonymous authors' names signed to these fictitious pieces were sometimes recognizable parodies; for instance, the editor of the pseudo-*Berichte* was "Ferd. Thymian" (German for thyme), an obvious play on Ferdinand Tiemann, the editor of the real *Berichte,* and the president of the Gesellschaft was "Hr. Aujust Kuleké," having a little fun both with Kekulé's unusual name and with the characteristic Berlin accent that tends to substitute a soft "j" for the hard German "g."[65] At other times the names were just silly, such as Dr. Omnibus, Prof. Tieftrunck, Tiefengrund, Bierzipfel, Bierfreund, Eigelb, Practicus, Essigmutter, Luftleer, Dampfdicht, H. Armlos, A. Butterworth and James Porkins (both from Chicago), "Springfield Hopkinson aus Dancersville, Indiana," A. Speculjans (conjecturing about atoms), coauthors Tea and Totalor (on the extraction of alcohol, of course), coauthors Süffig and Stark (analyzing cognac), and Wendel Schraube (on chirality in the tails of pug dogs).[66] The only obvious hints to the real authors of the parodies were in the Poetic Supplement, where eight of the poems were

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[64] *Berichte der Durstigen Chemischen Gesellschaft,* 3551–68, on 3568.

[65] Ibid., 3517.

[66] Ibid., 3517, 3523–24, 3529–30, 3539–41. "Süffig und stark" is beer-talk; Wendel Schraube means "turning screw." "Schraube" proposed an experiment: take a right-hand screw-tailed pug and cross with a left-hand screw-tailed pug, in expectation of creating an inactive, racemic, straight-tailed pug.

signed by Emil Jacobsen (1836–1911),[67] the other three by Otto N. Witt (1853–1915).[68] Both were Berlin industrial chemists.

Much of this pamphlet reads like a good-natured roast of Kekulé, especially as regards his odd sausage formulas (long since abandoned) and his benzene theory. Some indications in this direction were small and subtle, such as the note that "Herr Dr. Octavius Sechseck [Hexagon]" was proposed for membership by "A. Benzolius and B. Theer." And might "Dr. Omnibus" have been an obscure reference to the Kekulé anecdote about the origin of structure theory during his stay in London, an anecdote that had not yet been published but was perhaps known in collegial circles by oral transmission? Other references were even more explicit. One of the abstracts was "O. Seichbeutel's" "Proof that the Hourglass Shape Consisting of Two Equilateral Triangles is Able to Explain the Benzene Ring Much Better than the Hexagon."[69] Another abstract, "Ueber Wurstgift" by S. Ch. Wein and R. Metzger, described the isolation of a poisonous substance from a pair of spoiled Vienna sausages, and the treatment of this molecule with one atom of sulfur. The resulting product molecule was "Monothiodiwurstgift," two tiny sausages linked together by a sulfur atom.[70] Again, in the paper by Tea and Totaler, the fictive authors remarked in conclusion, "We are acquainted with many, especially younger German chemists, of whom we are firmly convinced that a consistently applied extraction of alcohol would greatly increase their energy and reactivity, and would give their previously open yet unstable characters the same sort of closed and nuclear characteristics [Geschlossenheit und Kernigkeit] that we have so come to admire in Kekulé's theory of aromatic compounds."[71] And in Herr Speculjans's paper we read, "As is well known, carbon at-

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[67] Thoms, "Jacobsen" (1911); Liebermann, "Jacobsen" (1911); and Engel and Engel, *Chemie und Chemiker* (1992), 156–57, 229–31, 252, 263. Besides being a prominent member of the DCG, Jacobsen was an independently wealthy industrial chemist, a science journalist, a poet, and a parodist. He wrote, e.g., *Die Wunder der Uroscopie, oder Zumptuarium urpoëticum* (Breslau: Maruschke & Berendt, 1861); *Der Reaktionär in der Westentasche, oder, Rhythmischer Gang der qualitativen Analyse, didactisches Poëm . . . in chemische Knüttelreime gebracht* (Breslau: Maruschke & Berendt, 1861); *Die Verlobung in der Bleikammer: Chemische Verbindungs-Komödie in einem schwefelsauren Act* (Breslau: Maruschke & Berendt, 1863); and *Kosmisch-Komisches, naturkundig gereimt und geleimt für Naturforscher* (Berlin: Hofmann, 1868).

[68] See Noelting, "Witt" (1916), *Berichte der Deutschen Chemischen Gesellschaft,* 1791–93, for confirmation that Witt was one of the principal editors of the lampoon; also Noelting, "Witt" (1915), and Noelting, "Witt," *Journal of the Chemical Society* (1916). Witt was a respected dye chemist who had entered the academic world somewhat late; in September 1886 he was Privatdozent for technical chemistry at the Berlin Technische Hochschule, and five years later he was appointed professor there. Like Jacobsen, he was also a writer, poet, and humorist.

[69] *Berichte der Durstigen Chemischen Gesellschaft,* 3543.

[70] Ibid., 3545.

[71] Ibid., 3522.

oms occur in organic compounds in two different forms, the tetrahedron of van't Hoff and the sausage form of Kekulé." Indeed, Speculjans informs us, and enlightens us by diagrams, that one can explain the different forms of aldehyde by assuming that the compound consists of Kekuléan sausage carbon atoms that can be folded in different ways.[72]

Two pieces in this lampoon deserve a slightly closer look. The first is a paper by "F. W. Findig" entitled "Zur Constitution des Benzols."[73] The author begins by affirming the principle that the various sciences should be employed for the mutual benefit of each, and averring, in particular, that zoology can be of the greatest assistance to organic chemistry. For example:

> Just as carbon has four affinities [valence units], members of the four-handed [animal] family have four hands with which they can seize objects or grab on to one another. If one thus imagines a group of six individuals of this family, for instance *Macacus cynocephalus,* who form a ring together by seizing alternately one and two hands, there results a highly complete analogy to Kekulé's benzene hexagon:
>
> However, in addition to their actual four hands, the aforementioned *Macacus cynocephalus* also possess a fifth grasping member in the form of a caudal appendage [i.e., a tail]. If one takes account of the latter, as well, then six individuals in such a ring can succeed in combining together in a different fashion. Hence arises the following image:

"Findig" concludes that the monkey-ring analogy to aromatic chemistry is "highly probable," leading to the further conclusion that carbon atoms must possess an analogous entity, a "caudal residual affinity," hence that there are two different ways in which a benzene ring can be formed. These considerations thus prove the existence of "a striking case of tautomerism."[74] There is little doubt that the author of this lampoon was making allusion to Kopp's remark that five-handed animals, like five-handed atoms, are exceedingly rare—excluding from this

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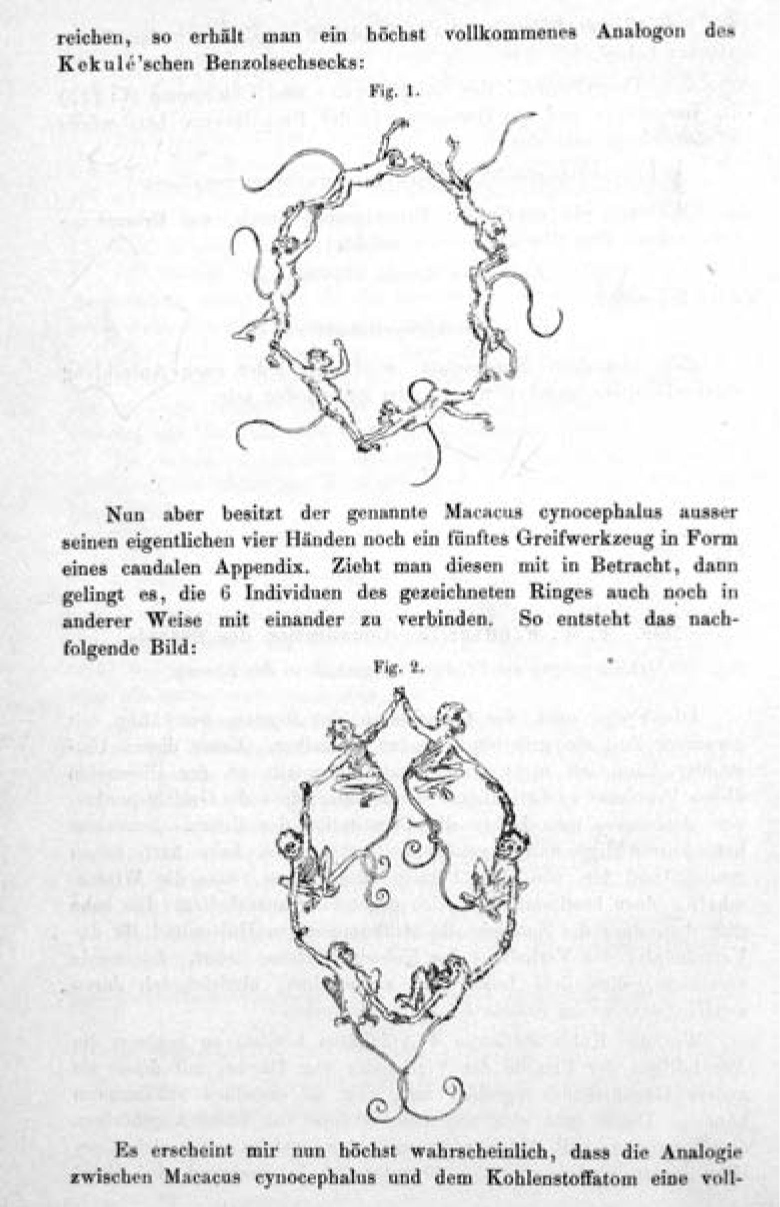
[72] Ibid., 3529–30. The paper is signed "Amsterdam, 7 September 1886," an obvious reference to van't Hoff.

[73] Ibid., 3535–37. Anschütz did not know the real author of this piece, but guessed that it was Witt (Anschütz, 1:610). This paper was "mitgetheilt in der Sitzung," the only such annotation among the sixteen parody papers; it was therefore, perhaps, the only paper presented orally at the *Bierabend* in Berlin on 20 September.

[74] "Findig" means resourceful or inventive; it was surely intended as a parody of Rudolf Fittig's name. "Tautomerism" had been defined and named by Conrad Laar in 1885, and Lothar Meyer had proposed a "centric" benzene model in 1872; probably both theories were being spoofed here.



reichen, so erhält man ein höchst vollkommenes Analogon des Kekulé'schen Benzolsechsecks:

Fig. 1.

Nun aber besitzt der genannte Macacus cynocephalus ausser seinen eigentlichen vier Händen noch ein fünftes Greifwerkzeug in Form eines caudalen Appendix. Zieht man diesen mit in Betracht, dann gelingt es, die 6 Individuen des gezeichneten Ringes auch noch in anderer Weise mit einander zu verbinden. So entsteht das nachfolgende Bild:

Fig. 2.

Es erscheint mir nun höchst wahrscheinlich, dass die Analogie zwischen Macacus cynocephalus und dem Kohlenstoffatom eine voll-

38 *Berichte der Durstigen Chemischen Gesellschaft* (1886), p. 3536.

category (as Kopp thought was appropriate) the example of a four-handed monkey with a fifth grasping member, its tail. It is also possible that the "Findig" author was spoofing Kekulé's anecdote about the origin of the benzene theory in the mental image of a snake seizing its tail in its mouth—if that anecdote was already widely known in the community by oral transmission.

My last example is a long poem (forty-one stanzas) entitled "Disputation (Frei nach Heine)" by Otto Witt, depicting the battles that had been fought during the previous dozen years, mostly in the *Berichte,* over the formula for benzene, namely between Kekulé's hexagon and Ladenburg's prism formula. Witt's extended metaphor is that of a medieval tournament.

Das ist kein gewöhnlich' Stechen
Keine Eisenwaffe blitzet,
Eine Lanze ist das Wort,
Atomistisch zugespitzet!

Und es ficht kein Paladin,
Der von Damen auserkoren,
Dieses Kampfes Ritter sind
Hochgelahrte Professoren.

Statt der Waffen tragen sie
Kolben, Becher und Büretten,
Röhrenofen und Gewichtssatz,
Off'ne und geschloss'ne Ketten. . . .

Und als Richter ob dem Streite
Thront der Schöpfer von dem Ganzen,
Dessen Blick zuerst durchschaute
Aromatische Substanzen.

Dessen grosse Denkerweisheit
Nur als Bild ein Sechseck kürte,
Jenes Bild, das, misverstanden,
Zu dem grossen Streite führte.

Sine ira, sine studio,
Wohnt er lächelnd bei dem Schisma;

Denn er weiss, dass Molecule
Weder Sechseck sind noch Prisma.

Dass die Kohlenstoffatome
Weder Wurst noch Tetraëder,
Und das Alles dies nur Schemen
Zum Gebrauch sind für's Katheder. . . .

This is not your usual joust,
No weapons of iron flashing,
Words are used instead of lances,
Atomistically sharpened!

The contestants are not paladins,
Chosen by fair damsels,
The knights of this battle are
Very learned professors.

Instead of weapons they bear
Flasks, beakers, and burettes,
Tube-still and gravimetry-law,
Open and closed chains. . . .

And as the Judge above the fray,
Reigns the creator of all of this,
He whose vision was the first to penetrate
Aromatic substances.

He who wisely, philosophically,
Chose the hexagon but as a picture,
This picture, which, misunderstood,
Resulted in this immense battle.

Sine ira, sine studio,
With a smile he observes the schism,
For he knows that molecules
Are neither hexagon nor prism,

That the carbon atoms
Are neither sausage nor tetrahedron,

And that all these are merely pictures
Meant for use in lecture and classroom. . . .

Next to the Judge (obviously Kekulé is meant) sits the lovely lady, Time, who, as the poet gradually makes clear, is the one who truly decides the winner.

"Lass den Kampf,"—so spricht sie—"toben,
"Anders wird's im Lauf der Jahre,
"Bilder werden, Bilder fallen,
"Doch bestehen bleibt das Wahre.

"Ja, bestehen bleibt das Factum,
"Das Ihr mühevoll gefunden,
"Dieses bleibt, wenn Hypothesen
"Längst vergessen und verschwunden."

"Let the battle rage," she said,
"Over the years all will change,
"Pictures rise, pictures fall,
"But what endures forever is the True.

"Yes, what endures is the Fact
"Which you have all ascertained with care,
"This endures, when hypotheses
"Are long forgotten and gone."

The battle is described in great and amusing detail, with references to specific chemical arguments. Finally the Judge tires of the endless fighting. He turns to the Lady Time and asks her for her opinion: who is right, and who is wrong? The final three stanzas are:

Und sie schaut ihn lange an,
Und wie sinnend ihre Hände
Mit verschränkten Fingern drückt sie
An die Stirn und spricht am Ende:

"An der Wissenschaften Webstuhl
"Webe Jeder, doch im Frieden!
"Jeder mehr' des Stoffes Länge,
"Doch das Muster sei verschieden!

"Wer hier Recht hat, weiss ich nicht,
"Doch es will mich schier bedünken,
"Dass das Prisma und das Sechseck,
"Dass sie alle Beide hinken."

Long she looked full at his face,
She knit her fingers in reflection,
Thoughtfully pressed them to her brow,
And at long last spoke the words:

"At the noble loom of Science
"Each worker should weave alone in peace!
"Each should add his own length to the cloth,
"Only changing there the pattern!

"I do not know who here is right,
"But it simply seems to me,
"Regarding hexagon and prism,
"That both ideas defective be."

I should not leave the impression that the *sole* targets of the *Thirsty Chemists* spoof were tetrahedra, sausages, hexagons, and Kekuléan theory. The anonymous authors of this lampoon edition took on the entire gamut of unpleasant behavior of their colleagues: too much conjecture and play of the imagination, too much concern with petty priority fights, too sensitive to perceived slights by rivals, too quick to patent unimportant innovations, silly and useless improvements of apparatus, and so on. Sometimes they wrote for pure fun, such as in the paper that demonstrated how "the small apparatus sufficiently well known to all German chemists as the 'beer coaster'" could be employed as a (paper-chromatographic) instrument, using flies as detectors, for measuring the molecular weights of liquids.[75] Clearly the authors had Kopp's *Molecular-Welt* in their sights, certainly as a positive model but perhaps for implied criticism as well.

The identity of those responsible appears to have been closely held, both at the time of the event and subsequently. Anschütz was present at the evening public session on 20 September 1886—he was thirty-four years old at the time, serving as Kekulé's assistant—and judging from

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[75] *Berichte der Durstigen Chemischen Gesellschaft,* 3532. The contribution was dated "Tiefschluckhausen, im Januar 1886."

his discussion of it, he obviously enjoyed both the show and reading the printed booklet. However, despite his strong interest in the question, he never determined—or at least he never revealed—who contributed to the lampoon, other than Jacobsen and Witt who signed their names to the poems. Although I have not been able to confirm this, it is probable that Jacobsen and Witt were authors of the entire lampoon booklet. Both were well known at the time as prolific composers of poems, lampoons, and literary spoofs; one obituarist stated that Jacobsen often placed his satirical wit as well as his organizational talents at the disposal of the Deutsche Chemische Gesellschaft.[76] At any rate, we have no other suspects.

This authorial conjecture, if true, may assist us in evaluating the obvious messages that lay in the humor, such as the antitheoretical tone—the folly of bandying hypotheses, as contrasted with the wisdom of relying only on empirically determined facts. It would not be surprising to see a certain distance from the theoretical realm from two chemists who chose to devote their lives to practical and technological endeavors, and we should be cautious in assuming that they reflected the center-of-gravity opinion of the entire German chemical community of their day. In this work one also often senses, intermixed with the banter, a measure of affectionate *self*-parody, for one of the many advantages of the satirical mode is the ambivalent or subversive meanings that it can safely communicate.[77] In any case, it is ironic that a major theme of this impressive celebration of the poetic and parodic imagination was the danger of excessive emphasis on the scientific imagination. In that regard the *Thirsty Chemists* stands in contrast to Kopp's molecular world.

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[76] Thoms, "Jacobsen," 155.

[77] Beller, "Jocular Commemorations," 253.

TEN

Kekulé's "Dreams"

What Wöhler and I imagined thirty years ago in a dream, that is, in our imaginations, you are now on the road to realizing all of it. JUSTUS LIEBIG[1]

It is very tempting to ascribe scientific value to dreams. HERMANN KOLBE[2]

Few anecdotes from the history of science are better known than the "dream stories" that Kekulé told on 11 March 1890 at a celebration in his honor in Berlin; Arthur Koestler called the benzene story "probably the most important dream in history since Joseph's seven fat and seven lean cows."[3] There has been debate in recent years whether Kekulé was sincere in telling these tales, and what broader implications the case might bear depending on whether the answer to this question is affirmative or negative. I have already woven material from these stories into chapters 2, 3, and 7, proceeding from the premises that he was speaking the truth as he remembered it and that the recounted episodes may suggest something important about the nature of scientific creativity (a subject that will be further explored in the final section of this chapter and in the final chapter of this book). Of course, the issue can never be settled with certainty, for the events in question—if real—occurred to one person only, in the

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1. "Was Wöhler und ich vor 30 Jahren im Traume d.h. in der Phantasie uns vorstellten diess alles sind Sie auf dem Wege zu realisiren." Liebig to Frankland, 28 January 1866, BSB.

2. "Es hat grossen Reiz, Träumen wissenschaftlichen Werth beizulegen." Kolbe, "Kritik" (1878), 156.

3. Koestler, *Act of Creation* (1964), 170–71.

absence of any witnesses: we can deal here only with probabilities. But to justify even a qualified judgment of the matter, one needs to examine the context in which these stories were told.

The Festivities in Berlin

On the occasion of Kekulé's sixtieth birthday party in September 1889, Adolf Baeyer secretly proposed the idea of a birthday party for the benzene theory, to honor his former teacher. The conspirators, besides Baeyer, were Kekulé's former assistants Theodor Zincke, Carl Glaser, and Richard Anschütz. Baeyer thought that the event should happen under the auspices of the Berlin-based Deutsche Chemische Gesellschaft (DCG), so he wrote to Hofmann to explore the idea. Hofmann was enthusiastic. At the beginning of December 1889 Zincke broke the news to Kekulé by letter that a celebration in his honor was being planned, and asked him to let Baeyer know his preference for an exact date. This "Kekulé-Feier" or "Benzolfest" would mark the twenty-fifth anniversary of the publication of Kekulé's first paper on benzene theory.[4] Zincke warned Kekulé preemptively that he had no veto in the matter, nor any choice but to submit to the planning right away. In his letter to Baeyer, Kekulé said that he would have much preferred to be simply "left in peace," but he also commented that he thought Zincke was right, realistically speaking. "A negative answer [from me] would clearly be viewed as only provisional; I would be besieged left & right, & would be given no real peace. It would be viewed as mere coyness. The matter is already too far along: the lion roars and will have his victim."[5]

The literal anniversary date would have been 27 January 1890,

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[4] Commemorative practices have been the subject of much recent historical work. For a broad review as these pertain to science, see Abir-Am and Elliott, *Commemorative Practices* (1999). The Kekulé event is unusual in the literature on commemoration in that it was organized primarily to honor a living scientist at the end of his career, rather than to create or sustain a ritual of more distant collective remembering. In this sense it was more akin to a *Festschrift* celebration than to the more usual sort of commemoration (in 1890, the German *Festschrift* tradition was still in its earliest days). However, see Schiemenz's important analysis of the political-economic aspects of the story: "Heretical Look" (1993).

[5] "Eine abschlägige Antwort würde offenbar für nur vorläufig gehalten werden; man würde mich von links & rechts bestürmen, & ich hätte erst recht keine Ruhe. Sie würde dabei für Ziererei gehalten werden. Die Sache ist schon zu weit gediehen: es brüllt der Leo & will sein Opfer haben." Kekulé to Baeyer, 2 December 1889, AKS. Zincke's letter, which Kekulé received on 2 December, has not been preserved, but is described in this letter. The other aspects of the early planning of the Benzolfest are described in Anschütz, 1:613.

39 Friedrich August Kekule von Stradonitz. Source: Photo Deutsches Museum.

twenty-five years to the day after Wurtz formally presented Kekulé's first benzene paper at a meeting of the Société Chimique de Paris. However, that date was less than two months away, and it was a bad time of year for prospective guests from across Germany to travel to Berlin. So Kekulé proposed Tuesday, 11 March, which was the anniversary of the approximate publication date of the relevant issue of the *Bulletin de la Société Chimique*. This date fell at the beginning of the spring academic holiday, and moreover the celebration could follow the regular Monday night meeting of the DCG already scheduled for the 10th in Berlin. The Great Hall of the Berlin city hall was immediately reserved for the event, and on 9 December a committee was formed to organize everything else.[6]

On 11 March, the Benzolfest began with a formal plenary session at 5 p.m. The "brilliantly illuminated" hall had been "richly and tastefully" decorated with wreaths of laurel and fronds of palm and was filled with hundreds of distinguished guests not only from Berlin, but

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[6] It consisted of Julius Holtz as treasurer, Emil Jacobsen and Otto Witt (who would collaborate on the humorous songs to be sung at the banquet), Carl Martius, Carl Scheibler, and Hermann Wichelhaus—all members of the executive committee of the DCG. The full report on the Benzolfest is Schultz, "Bericht" (1890). The celebration is also described in Anschütz, 1:615–41, and analyzed by Schiemenz, "Heretical Look," and by Rudofsky, "Benzolfest" (1993).

from all over Germany, with a goodly number from abroad as well.[7] Hofmann (president and effective founder of the DCG) introduced the festivities by noting that they were here celebrating an anniversary of not a hundred years, nor even fifty, but just twenty-five years. “We are thus fortunate to be able to welcome in our midst the hero of the evening, in youthful vigor of body and mind, in undiminished creative joy and power.” For the benefit of the ladies and other laypeople present Hofmann proceeded to give a brief but masterly history of aromatic compounds, from Faraday’s discovery of benzene to the recent enormous growth of the German coal-tar dye industry (tactfully saying nothing about his own part in the story).[8] He then introduced Adolf Baeyer—vice president of the society, successor of Liebig, and Kekulé’s first student—who would present the plenary address.

Baeyer’s speech has considerable interest.[9] After the expected preliminaries, he began by asking the rhetorical question: Is Kekulé’s benzene theory a true depiction of the molecule, or is it simply a heuristically useful fiction? This question evoked a consideration of molecular models. Van’t Hoff was not the first to suggest a tetrahedral shape for the carbon atom, Baeyer noted; it was Kekulé who had introduced tetrahedral carbon models in 1867. Of course, van’t Hoff had taken the idea further than Kekulé, in particular by affirming that the four valence bonds emanating from each carbon atom were relatively fixed and could therefore be studied chemically. In this sense Kekulé’s tetrahedral models were analogous to Heinrich Hertz’s famous comment about James Clerk Maxwell’s equations of the electromagnetic field: that they have almost an independent life, that they can appear wiser even than their creator and can yield more than was ever invested in them.[10]

To be sure, Baeyer said, what we are talking about are pictures or representations (Bilder), which must never be confused with real things themselves, but Hertz’s comment applies whenever our theoretical pictures approach the unseen reality. These same considerations apply to the benzene theory. Baeyer proceeded to summarize recent research on the structure of benzene. The benzene formula proposed years earlier by James Dewar had quickly been ruled out as unable to explain the

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[7] Volhard later noted that the Festsaal of the Rathaus was better noted for its impressive appearance than its acoustics. Unfamiliar with this fact, he took a seat toward the rear and regretted it deeply, for he was able to hear very little of what went on. Volhard, *Hofmann* (1902), 166.

[8] Schultz, “Bericht,” 1267–72.

[9] Ibid., 1272–87.

[10] Ibid., 1273–74.

chemical data. Albert Ladenburg's "prism" formula and Adolf Claus's "diagonal" formula were tougher nuts to crack, but Baeyer summarized research results that argued against these alternatives, as well. There could no longer be any question that the benzene molecule is indeed a symmetrical hexagon formed of six CH groups. The only question that still remained was: what to do about the fourth valence of each carbon atom? Baeyer proposed that so-called centric benzene (in which the fourth valence of each carbon atom was somehow directed toward the center of the ring) and the Kekulé structure (in which the fourth valence of each carbon atom formed a double bond with one of its two neighbors) were in a sense *both* true; they were "limiting states" of benzene. So Baeyer could now answer his initial question. Kekulé's benzene theory was, like all theories, a temporary though highly fruitful heuristic tool; but "for ordinary usage" it was also "the best expression of the facts."[11]

Baeyer concluded with some final thoughts about the relationship between Kekulé's theory of chemical structure and his aromatic theory. The crucial breakthrough, he stated, was the former, which had been published seven years earlier (in 1858). Structure theory demonstrated that "the general laws of mechanics do not suffice to explain the essence of matter, that atoms possess specific properties, a knowledge of which must precede the application of mechanics. This knowledge we owe to you [Kekulé]; it forms the content of structural chemistry, and it has reached a preliminary conclusion with the benzene theory."[12]

After the applause for Baeyer subsided, Hermann Wichelhaus, a member of the executive committee of the DCG and a former assistant of Kekulé's, arose officially to present the society's congratulations to the Jubilar. "What the bodily eye of man has never seen and never will see," Wichelhaus intoned, "has appeared to your searching mind as a picture whose features speak to us as things that are real and alive."[13] He formally presented a baroquely illustrated, calligraphic proclamation from the DCG to Kekulé, filled with effusive praise. There followed an interminable list of congratulatory testimonials, letters, and telegrams, many of them read aloud to the audience. Finally, Kekulé was given the opportunity to speak—a speech that we will treat in the next section of this chapter.

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[11] Ibid., 1275–86.

[12] Ibid., 1287.

[13] Ibid., 1288.

The formal session ended at 7:30, at which time invited (exclusively male) guests—over two hundred in number—betook themselves to the magnificent new Huster Hall of the Geselliger Verein der Gesellschaft der Freunde in the Potsdamerstrasse to enjoy an elaborate white-tie banquet in Kekulé's honor.[14] An oil portrait of Kekulé by the noted Austrian artist Heinrich von Angeli was unveiled there.[15] The meal was in nine courses, beginning with "Aromatic Soup," then "Isomeric Sea-Animals in Asymmetric Arrangement, with their Homologues," then . . . well, one quickly gets the idea. The concluding course was "Caffeine, with Production of Nicotine Vapors in the Havana Tube."[16] Interspersed with these courses was a variety of elaborate toasts, while a small orchestra played a selection of classical and popular music. Five new songs by the now notorious Jacobsen-Witt collaboration were also performed. One of these, "Die Chemie im Raume," ended with the stanza,

Doch in ein Nichts verbleicht Van't Hoffs
Asymmetrieerfindung,
Wenn man die Tetraëder zwingt
Zur holden Doppelbindung.
Es stellen Dutzenweis sich ein
Die schönsten Formationen.
Hoch, Raumchemie! Sie führet uns
In höhere Regionen.

But van't Hoff's famed asymmetry
Fades into nothingness,
Whenever the tetrahedron is forced
Into the fair double bond.
The loveliest formations then
Appear in multitudes.
Long live spatial chemistry! May she ever
Lead us to higher regions.

Another, "Weihelied" (Dedicatory Song), ended:

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[14] Most of the following details are taken from a small printed booklet entitled "Ordnung des Festes zu Ehren August Kekulé's am 11. März 1890," AKS.

[15] The principal German dye companies had financed this portrait, and another of Hofmann, both of which were donated to the Berlin Nationalgalerie.

[16] One newspaper reported that the humorous menu was composed by Jacobsen: *Apotheker-Zeitung* 5 (15 March 1890): 134; tearsheet in AKS.

Der Jahre fünfundzwanzig sind verflossen,
Die Saat, die Du dereinst uns anvertraut,
Ist stolz und schön, wie keine, aufgeschossen.
Gross ist der Bau,[17] den wir vereint gebaut.

Und wo Chemie zum Schaffen regt die Geister
Jetzt und in aller Zukunft je und je,
Bleibst unser Vorbild immer Du und Meister,
Du grosser Denker, August Kekulé.

Twenty-five years have now flown by,
The seeds you once sowed and entrusted to us
Have shot up proud and grand, like none other.
Great is the structure[17] we have together built.

And wherever chemistry moves creative minds
Now and forevermore you will stay
You, our model and our master,
The great thinker, August Kekulé.

Of the long toasts, only Hofmann's has been preserved, but it is worthy of mention. Hofmann began by proclaiming that, though eleven years older, he nonetheless counted himself (figuratively) as one of Kekulé's students. "As we all did, I too attended his school, and I hope that the master will record it on my diploma that I managed to learn a little something in his instruction." In one respect only could he claim some advantage over his fellow Kekulé-students, namely that he was older than almost any other chemist in attendance.[18] And what enormous changes had he witnessed since his student days with Liebig fifty years ago! Organic chemistry then resembled a pretty little mountain brook, studded with stones, across which one could easily walk dry-shod. But now this little brook had become a "deep, mighty river, across which one could scarcely even see; and proud, richly-laden fleets now ply its broad waters."

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[17] "Bau" and "gebaut" can also mean "Anbau" and "angebaut," paralleling "Saat." The poet is making a double metaphor to a crop that can be harvested and to a building or structure, as in structural chemistry.

[18] Hofmann was then within a month of his 72nd birthday. Liebig, Wöhler, and Kolbe were all dead; Bunsen and Kopp were slightly older, but both were by then too debilitated easily to travel to Berlin. Kopp mailed a short but generous tribute to Kekulé, which was read aloud at the fest.

> One might say that with the idea of the benzene ring, the number of organic compounds appeared to increase to infinity at a stroke. In the benzene nucleus we were given soil from which, to our astonishment, we saw the organic chemistry with which we were familiar grow tall anew, not once or twice—no: three, four, five, and six times, like so many trees. What an abundance of work had suddenly become necessary, and how quickly were found the busy hands that were required to carry it out! At first the eye traces the six trunks from which the mighty benzene-tree develops. But already the branches of the neighboring trunks have become entwined, and a canopy of leaves has formed, which is becoming ever thicker as the giant continues to soar upward to the skies; but the top of the tree towers into the clouds and is hidden from sight. . . . And in amongst the lovely flowers, what a rich abundance of fruits! Some glistening in beautiful rainbow colors, from others emanating the most stunning fragrances!

Hofmann continued in this vein at even greater length, but this will give the reader a good idea of his extended metaphor. But behind all the rhetorical devices lay an accurate characterization of chemical history of the preceding half-century, portrayed in an appealing, generous, and personally modest fashion.[19]

Hofmann was noted for habitual rhetorical excess, and (some colleagues thought) for arrogance, but it appears that this time, at least, he meant every word. Volhard reported that Hofmann often privately told close friends that despite his unmatched career success, he never considered himself a scientific genius, just a man of untiring energy, diligence, and patience. Although Kekulé had been inactive in research for close to twenty years at the time of the Benzolfest, his revolutionary work of the 1850s and 1860s had fundamentally transformed the field. Hofmann was distinctly exaggerating—and everyone knew this—when he praised the "hero of the evening" as possessing both "youthful vigor" and "undiminished creative joy and power." But taking his entire career into account, Hofmann did indeed consider Kekulé as the greatest chemical scientist in Germany—indeed, in the world.[20]

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19. Schultz, "Tischrede" (1902). Kekulé responded to Hofmann's toast with equal generosity, asserting that the real merit belonged to Hofmann, who had given the theory practical value through experimentally determined facts (*Apotheker-Zeitung* 5 ,[15 March 1890]: 134). These quoted passages are in my English translation, but the entire toast has been fully translated into English by Brock, Benfey, and Stark, "Hofmann's Benzene Tree" (1991).

20. Volhard, *Hofmann,* 165. Twice (in 1875 and 1885) Hofmann stated his opinion that Kekulé was the greatest of all living chemists, in his nominations of Kekulé to the Berlin Akademie der Wissenschaften: Greiner, *Chemiker über Chemiker* (1986), 115–17.

Kekulé's Speech

A week before the event, Kekulé had written Baeyer that he planned to say only a few words in response to the speeches and toasts; he would prepare no formal address, but would rather "leave it to the inspiration of the moment."[21] This was surely an exaggeration, but it does seem that he rose to the podium with no written text.

Nine days after the event Gustav Schultz wrote to Kekulé, informing him that he would be editing the extended report on the Benzolfest for the *Berichte*. Unfortunately, he wrote, no verbatim record had been made of the speeches. Could Kekulé please send him either the original or a copy of his speech?[22] Two days later Kekulé responded:

> Your letter rattled me more than the recent earthquake. What! The world capital of Berlin is such a backwater that no stenographer was present at the celebration of the 11th? How will you now be able to produce an accurate report? Now each person will write to you, if he writes anything at all, what he wanted to have said, not what he actually said. . . . Fortunately, not yet two weeks have passed since the 11th, and the relevant compartment of my brain has not yet been cleared out. I think that despite my increasingly dull memory I can guarantee you that I can write down what I said two weeks ago word for word, just as well and even better than a stenographer.[23]

Two weeks later Kekulé wrote again to Schultz:

> Enclosed is the manuscript of my failure of a speech and I must first say: You really made me sweat. It is certainly difficult to say something reasonable on such occasions (which is why I too did not succeed in doing so), but it is in any case even harder by far to reproduce word for word the stupid things one has said, three weeks

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[21] He "muss das endlich der Inspiration des Augenblicks überlassen." Kekulé to Baeyer, 5 March 1890, AKS.

[22] Schultz to Kekulé, 20 March 1890, AKS. Schultz, a former assistant of Kekulé's, was research director at AGFA.

[23] "Ihr Schreiben erschüttert mich mehr als das Erdbeben von neulich. Was? Die Weltstadt Berlin ist ein solches Krähwinkel, dass bei der Feier vom 11 c. kein Stenograph anwesend war? Wie wollen Sie jetzt einen wahrheitsgetreuen Bericht zu Stande bringen? Jetzt schreibt Ihnen ein Jeder, wenn er überhaupt etwas schreibt, das was er wünschte gesagt zu haben, aber nicht was er gesagt hat. . . . Zum Glück sind seit dem 11 c. noch keine 14 Tage verstrichen und das betreffende Schiebfach meines Gehirns ist noch nicht ausgeräumt. Ich glaube, trotz meines stumpf gewordenen Gedächtnisses, Ihnen jetzt noch garantiren zu können, dass ich das was ich vor 14 Tagen gesagt habe, wörtlich zu Papier bringen kann, ebensogut und besser wie ein Stenograph." Kekulé to Schultz, 22 March 1890, AKS.

> after the fact. But I think that I have succeeded in outdoing myself in the art of regurgitation, and I am doubtful whether a stenographer or a phonographer could have done it better. I believe that the speech was presented exactly in this way.[24]

He told Schultz that throughout his life, whenever he had had to give a formal speech he had always felt afterwards that he had "made a terrible fool of myself" ("habe mich grässlich blamirt"); there had always followed a three-day hangover, and so too this time. This retrospective exercise had brought the hangover back, in spades. "Today I have the feeling that it would be better to burn the whole mess and not print a thing" ("Heute habe ich das Gefühl, es wäre besser man verbrennt den ganzen Plunder und lässt nichts drücken").

Schultz gratefully received the manuscript, agreeing with Kekulé that he had succeeded in precisely reproducing the speech.[25] A few months later Kekulé reminisced to his good friend Volhard, "The esteemed learned gentlemen in the backwater of Berlin did not have stenographers at the city hall celebration, you see, which meant that, despite my great reluctance, I was forced to reconstruct my speech, which had been essentially improvised at the time, and of which absolutely nothing existed on paper. A terrible job [it was], which provided no other satisfaction than that it convinced me anew that I am a good regurgitator."[26] As we have noted in previous chapters, Kekulé had been celebrated his entire life for having an extraordinary memory. At the DCG meeting the previous evening he had given an hour-long talk without notes on the chemistry of pyridine, a talk that Anschütz and Volhard both regarded as a model of clarity, detail, and organization. (Volhard was never able to get Kekulé to write the talk up for publication in the *Annalen,* despite several pleading letters.) Anschütz was probably correct in his speculation that Kekulé had mentally worked

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[24] "Bei Uebersendung des Manuskriptes meiner verunglückten Rede muss ich zunächst sagen: Ihr habt mich weidlich schwitzen machen. Es ist gewiss schwer, bei derlei Gelegenheit etwas Vernünftiges zu sagen (weshalb es mir auch nicht gelungen ist) aber es ist jedenfalls noch weit schwerer, das Dumme, was man gesagt hat, drei Wochen nachher wörtlich zu reproduziren. Ich glaube jedoch, dass es mir gelungen ist, in der Kunst des Wiederkäuens mich selbst zu übertreffen und ich bin im Zweifel darüber, ob ein Steno- oder Phonograph es ebensogut gemacht hätte." Kekulé to Schultz, 7 April 1890, AKS.

[25] "Sie haben Ihre Rede thatsächlich so gehalten." Schultz to Kekulé, 12 April 1890, AKS.

[26] "Die geehrten und gelahrten Herrn in Krähwinkel-Berlin hatten nämlich bei der Rathausfeier keine Stenographen und nöthigten mich dann, trotz allen Sträubens, meine damals nahezu improvisirte Rede, von der absolut Nichts Schriftliches vorlag, nachträglich zu Papier zu bringen. Eine Hundearbeit, die keine andere Genugthuung gewährte, als die, dass sie mich von Neuem davon überzeugte, dass ich ein guter Wiederkäuer bin." Kekulé to Volhard, 13 August 1890, AKS. The qualification "nahezu" (which literally means "almost" but which I translated here as "essentially") suggests that Kekulé had given at least *some* thought in advance to what he would say.

out major elements of his Benzolfest speech in great detail, perhaps even the entire piece, even if he wrote nothing down—a practice for which he was well known.[27] This supposition would also explain how he was able to reproduce it so precisely. So let us assume that the text that Schultz printed as part of his published report was as accurate as both Kekulé and Schultz claimed, and turn to the speech itself.[28]

"So many honors and compliments have been heaped upon me," Kekulé began, "that not only the words, but the very thoughts fail me to thank you all. Where am I to begin? Where am I to end?" He proceeded to say all the things that one should say at a celebration in one's honor, combining expressions of gratitude with self-deprecation. "In all the speeches and in all the printed addresses I hear the same tone, a tone of the same exaggeration."[29] But whether it was justified or not, one could not ignore that the event was indeed happening, and whether justified or not, he was the guest of honor. "I am thus compelled, very much against my inclinations, to speak of my own person and to consider the question whether my small services have merited this kind of homage, or indeed any homage at all." His immediate answer to this question appeared to be negative. His hypothesis for the structure of benzene in 1865 had been nothing more than a straightforward application of structure-theoretical principles; as his friend Baeyer had noted a few minutes earlier, the benzene theory was not really an independent theory at all, only a particular example of a more encompassing theory. Moreover, it had been a simple and an obvious step: what else was he supposed to do, what else *could* he have done, with the remaining valences of carbon?[30]

Being obvious, it was by no means foreordained that he, Kekulé, would be the first to come up with the idea. At certain times, certain ideas are in the air, occurring to many people simultaneously and independently. And everyone stands on the shoulders of his predecessors anyway. Having been given the advantage of the perspective provided by the difficult labors of earlier workers, is it any wonder that one can see a bit farther than they? It is simply not true, as had been implied

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[27] Anschütz, 1:630–31. Susanna Rudofsky has published her English translation of a letter from August to Stephan, dated 24 February 1890 (in AKS), in which Kekulé wrote, "day and night the thought comes to me: How much are those gentlemen going to say, and how much will I have to answer. I would really prefer to stay away" (Rudofsky, "Benzolfest," 11).

[28] "Rede von August Kekulé," in Schultz, "Bericht," 1302–11; reprinted in Anschütz, 1:937–47. A nearly complete English translation was published by O. T. Benfey, "August Kekulé and the Birth of the Structural Theory" (1958).

[29] Anschütz, 1:937–38.

[30] Ibid., 938.

that evening, that benzene theory had arrived like a meteor from the heavens, or had emerged like Athena from the brow of a chemical Zeus. "Please, gentlemen! The human mind does not think like that. Something absolutely and totally new has never been thought; certainly not in chemistry."[31]

Progress in chemistry had been steady, gradual, and continuous, Kekulé noted, over the nearly fifty years of his experience in the field—even if it did not always seem that way. In about the year 1840, the chemical river had divided into two distinct branches, one flowing through fertile French soil, the other through a more barren channel that had been surveyed in advance by Berzelius. The two branches of this river later approached one another, but that had not at first been evident, since "a thick underbrush of misunderstandings" still divided the two groups of travelers. Suddenly, cries of triumph were heard, uttered by the type theorists and simultaneously by members of the other group, "Frankland at their head." The travelers then continued their journey on the now reunited river, "through the most fruitful fields."

There are important lessons here, Kekulé averred. Present theories do not stand on the ruins of their predecessors, but rather build from the knowledge and ideas of the past. The human mind, when awake, does not think in leaps, and total novelty in science is an illusion.[32] Nor can one recognize the truth before seeing the evidence for it. One must not gather fruit before it is ripe; otherwise it will damage the health of those who eat it, and particularly the health of younger scholars, who have not yet learned to distinguish ripe from unripe. Kekulé could vouch of all of this from his personal experience.

This is how Kekulé came to tell stories of his own development as a chemist, including the vision on the London omnibus in ca. 1855 that led to the structure theory published in 1857–58, and the vision in his study in Ghent in ca. 1862 that led to the benzene theory published in 1865, and how he had hesitated to publish each of these theories until more evidence for these ideas had accumulated.[33] I believe that these were sincere attempts at communicating real memories of events in his past,[34] a point on which some scholars have cast doubt. One of my grounds for credence is simply the impression given by a careful

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[31] Ibid., 939.

[32] Ibid., 939–41. "Meine Herren, der wachende Geist denkt nicht in Sprüngen. Das ist ihm nicht gegeben."

[33] Ibid., 941–44.

[34] To assert that the stories were probably *sincerely* told is not to assert that the stories were *objectively* told, nor that they were accurate. Memories are fallible, even so fine a one as Kekulé's.

reading of the entire speech, in context of the event being celebrated and considering the personality of the speaker. Kekulé had a lively and often irreverent wit, but in this forum there is no indication of any irony, sarcasm, or flippancy; nor would one expect any at such a highly formal occasion in his honor. This was his valedictory, not a witty or satirical riposte to a roast. Despite Hofmann's flattery, Kekulé was a tired old man with failing hearing, and no longer in good health; he was speaking solemnly for the ages, in one of his final opportunities, and he well knew it. In fact, the Benzolfest turned out to be Kekulé's very last public presentation, outside of a university lecture hall.

Moreover, the stories he chose to tell from his past fit the structure of his speech; they illustrated the themes he wanted to pursue and the advice he wanted to give about the nature of scientific progress, creativity, and career success. These themes include the continuous nature of scientific progress, the need for every scientist to become thorough master of all the details of the science before he can hope to make any advances, the importance (once one had achieved such mastery) of creative aspects of mind, especially, in his case, mental visualization, and the requirement that one must be able to develop sufficient empirical evidence for that imagined world before publishing it. And finally, the veracity of the stories is suggested by the rich amount of specific biographical detail Kekulé included in these two anecdotes (in London, e.g., the location of respective residences, the route of the omnibus, the appearance of the streets, and the cry of the conductor; in Ghent, e.g., the geographic location and the layout of his residence, the writing of his textbook, the turning of his chair to the fireplace, and so on).

The circumstance that two of his most important "eureka" experiences happened, as he reported, while in reveries or daydreams was actually a minor point in the overall context of the speech. He surely did not intend to leave the impression that one need only dream to discover. *Indeed, he carefully developed the exact opposite theme.* Progress in science can only consist in continuous, incremental small steps into the unknown. One can take that glimpse into the distance while standing on the shoulders of predecessors only after the most diligent efforts to learn, to understand, to investigate, and to ponder. This was why he made perfectly clear that each of his reveries had occurred in a state of obsessive exhaustion, and he made equally clear that it would have been a mistake for him to have published such unripe fruit at the time that they came into his mind. "Let us learn to dream, gentlemen, and then perhaps we shall find the truth:

Und wer nicht denkt,
Dem wird sie geschenkt,
Er hat sie ohne Sorgen.

And he who does not think,
To him it is given,
He has it without trouble.

But let us beware of publishing our dreams until they have been examined by the conscious understanding."[35]

The ideas of both structure theory and benzene theory were "in the air," Kekulé said, and could have occurred to any of a number of his contemporaries almost any day. But he was in fact the earliest to publish these ideas, and he posed the question why it may have happened that way. He had three answers to the question. First, he suggested (justly) that he had had the most eclectic education of any of his contemporaries, having studied intensively with leading figures in Germany, France, and England. This was vital, he stated, for it allowed him to look at questions from all sides and prevented him from being captured by any single narrow school of thought. Second, his mind had always had an "irresistible need for visualization or visualizability [Anschaulichkeit]," a quality perhaps engendered, he thought, by his early training as an architect. He made a very similar remark, in a smaller and more private forum, two years later.[36] And third, for many years in his youth and early adulthood he had faithfully followed Liebig's advice to work obsessively hard. It certainly appears that Kekulé had done just that. "Research journeys," Kekulé said, "cannot be made by express trains." But a man is no more than an expression of the circumstances of his life, and of his context, Kekulé noted; no special merit attaches to a person for such happenstance.[37]

"When I look over all of this, I find no reason that could have justified your having organized such a celebration as this. And yet you have

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35. Ibid., 942. The quotation is from Goethe, *Faust,* part I, Hexenküche, ll.286–88. The witch is speaking, and the antecedent of "sie" (it) is "die hohe Kraft der Wissenschaft" (the high power of science).

36. This was at an informal and truly extemporaneous autobiographical talk presented to a group of his present and former students at a surprise party marking the twenty-fifth anniversary of his call to Bonn (Anschütz, 1:642–43; recorded stenographically and reproduced verbatim in *Kölnische Zeitung,* 3 June 1892, and reprinted in Anschütz, 2:947–52). This talk has many similarities to the Benzolfest speech. For the quotations alluded to here, see the end of chapter 2, this volume.

37. Anschütz, 2:943–45.

indeed organized this celebration. I think I can tell you why you have done it." The chemical community had felt the need, "in our jubilee-addicted age," to have a jubilee of their own.[38] In these fast-moving times, a quarter century was the right period for such a celebration; and one could find no better symbol of the last twenty-five years than that of the benzene ring. This, even though other fields of chemistry had also flourished, and some fields had been born that would doubtless become the leading specialties in times to come. But Kekulé conceded both that the benzene ring was indeed probably the most suitable symbol of the chemical research during the past quarter century, and that he was the most visible personality associated with that subject. He concluded that although he was sure that his "meager merits have in no way earned such an homage," he gave heartfelt thanks to all his many friends for their attendance at this event, "unjustified though it may be," and to members of the Deutsche Chemische Gesellschaft for organizing it.[39]

The Aftermath

What did the audience think about Kekulé's speech and about the marvelous tales within it? Someone, probably either Kekulé himself or his son Stephan, collected twenty-two different newspaper accounts of the *Benzolfest,* and these are preserved in the Kekulé-Sammlung in Darmstadt. All of the longer reports, especially those in the *Berliner Tageblatt,* the *Apotheker-Zeitung,* the *Chemiker-Zeitung,* the *Darmstädter Zeitung,* the *Tägliche Rundschau,* the *National-Zeitung,* and the *Norddeutsche Allgemeine Zeitung,* contained descriptions or summaries of Kekulé's speech, and it is possible that Kekulé himself used some of these accounts to assist him in reconstructing what he had said in Berlin.[40] In any case, these newspaper accounts are entirely consistent

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[38] Schiemenz ("Heretical Look") is surely correct that there were political and economic motives behind the organization of the Benzolfest. By commemorating Kekulé and his benzene theory, the DCG was also promoting the entire community of chemists and celebrating the importance of chemistry in the economy of the Reich. As for all commemorations, one must look beyond "texts" to include "pretexts" and "contexts" (Abir-Am, in Abir-Am and Elliott, *Commemorative Practices,* 326). However, it would be a mistake to believe that politics and economics were the *only* motives of the organizers—especially regarding a commemoration, like this one, at which the protagonist could be physically present. The organizers surely also wanted to honor their elderly friend before it was too late to do so in person.

[39] Anschütz, 2:946.

[40] Six of these accounts were published between the 12th and the 15th of March. The seventh, that in the *Darmstädter Zeitung,* did not appear until 7 June. Kekulé prepared his manuscript for Schultz between 22 March and 7 April.

with the fully reconstructed text as it was subsequently published by Schultz in the 28 April 1890 issue[41] of the *Berichte der Deutschen Chemischen Gesellschaft.*

The newspaper reports, not surprisingly, were uniformly flattering to Kekulé. A few representative quotations will provide an impression of the press coverage of his speech. The reporter for the *Berliner Tageblatt* put in Kekulé's mouth (though not in quotation marks) the sentence: "One should consider that it is above all the imagination that acts creatively." The reporter for the *Darmstädter Zeitung* wrote: "Even in his dreams the atoms and their chaining together pursued him. The erection of the structure of the atoms, of the articulation or structure of compounds or molecules, remained his theoretical scientific task, and thus his mind's eye succeeded in penetrating the invisible world of the atoms, and in recognizing the interior arrangement of benzene." And the reporter for the *National-Zeitung* wrote: "What the Jubilar then related in a good-humored way of his years as a student and postdoc, of his youthful dreams, of the atoms gamboling around him, of the serious work pursued even to the endangerment of his health—all this cannot be reproduced in a few words."[42]

The reviews of Kekulé's speech by colleagues were mostly positive, but not universally so. The way the event may have appeared to some nonchemists is revealed by the writer and former engineer Heinrich Seidel, whom Schultz had consulted to help him with the literary grace of his report, and who commented afterwards, "I must frankly confess that I have never before heard of such an example of self-congratulation and self-satisfaction. Such a thing is probably only possible in professorial circles."[43] The apparent severity of this judgment should be tempered by the circumstances that Seidel did not know Kekulé, was neither a chemist nor an academic, and had not been present at the Benzolfest. He may also have been referring here to the behavior of the entire Berlin chemical community, and not exclusively to Kekulé's speech.

On the other side, organizer Julius Holtz wrote Schultz, "In particular, I was very happy to see that you succeeded in preserving Kekulé's magnificent speech word for word; it is a real tonic to read it again,

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[41] Wotiz and Rudofsky erred when they cited this date as 12 May.

[42] J. K., "Die Kekulé-Feier im Rathhaussaale," *Berliner Tageblatt,* 12 March 1890, 1; L. Weis, "Zur Kekuléfeier," *Darmstädter Zeitung,* 7 June 1890, 975–76; anon., "Kekulé-Feier," 2 [*sic,* for 12] March 1890, *National-Zeitung,* clipping; all in AKS.

[43] "Ich muss offen gestehen, dass mir ein solches Beispiel von Selbstbeweihräucherung und Selbstgefälligkeit bisher nicht bekannt geworden ist. Das ist wohl nur in Professorenkreisen möglich." Seidel to Schultz, 14 September 1890, AKS.

and to draw from it many lessons even for us oldsters."[44] Volhard wrote Kekulé, after reading the reconstructed text in the *Berichte,* to say that he was "very pleased" by the speech.

> I would like to know how many of the guests were clear from the start, before Baeyer and you yourself stated it, that the fundamental path-breaking thought was that of the chaining of atoms, and that the benzene ring was only one of the innumerable conclusions from that. If it were not possible to make so many dyes from benzene and base so many patents on it, one would scarcely be asking the egg to be cleverer than the chicken![45]

Anschütz later described Kekulé's speech as "perfectly formed, presented with superior energy and no evidence of fatigue" (surprising, he said, considering Kekulé's weak health), and Anschütz regarded its content as of the greatest historical importance for an understanding of Kekulé's mind, his life, and his times.[46] Another Benzolfest attendee, Francis Japp, one of Kekulé's prominent English students, used almost the same words in describing the talk.

> It was the personal utterance of a man whose utterances had hitherto been confined mainly to the exposition of the impersonal facts and theories of his science. It was modestly autobiographical; it traced the growth and training of the speaker's powers; it afforded a glimpse into his intellectual workshop. Needless to say that it produced a profound impression. . . . It should be read by every one who desires to understand Kekulé's character and influence.[47]

To summarize, although some observers surely took Kekulé's many self-deprecations as insincere, I know of no evidence to suggest that anyone present in Berlin that day thought of Kekulé's reminiscences as anything other than an attempt to offer actual recollections, or that they regarded the autobiographical anecdotes as mere tall tales concocted for the amusement of the audience.

44. "Insbesondere freue ich mich sehr, dass es Ihnen gelungen ist, die herrliche Rede Kekulé's wortgetreu zu erhalten, es ist eine wahre Herzstärkung, dieselbe nachzulesen u. manche Lehre auch für uns Alten noch daraus zu ziehen." Holtz to Schultz, 18 May 1890, AKS.

45. "Ich möchte wohl wissen, wie vielen der Festgäste es von vornherein klar war, ehe Baeyer u. Sie selbst es aussprachen, dass die bahnbrechende Grundgedanke die Atomverkettung war, und der Benzolring nur eine von unzähligen Folgerungen aus derselben. Könnte man aus dem Benzol nicht so viele Farben machen und so viele Patente gründen, man hätte schwerlich wohl das Ei gezwungen, klüger sein zu wollen als die Henne!" Meyer to Kekulé, 25 May 1890, AKS.

46. Anschütz, 1:623.

47. Japp, "Kekulé" (1898), 106.

Some historians, particularly John Wotiz, have recently argued that Kekulé was "no genius," but rather a "gifted opportunist," a "fraud," and a "cheat" who fabricated these anecdotes to create an irrefutable cover story—irrefutable because they were private mental events—in order to steal credit for cyclical benzene from those who he knew were really the first to write cyclical formulas, namely, Couper and Loschmidt. Having failed to publish before his rivals (Wotiz suggested), Kekulé falsely claimed that he had had these ideas first, in dreams, before them. He was thus guilty of "misconduct."[48]

There are problems with this scenario. It is true, in fact, that there were a few published suggestions of cyclical molecular formulas and of benzene structures before Kekulé's benzene theory (as we saw in chapter 5), but none came near to that theory. Moreover, none of these early (pre-1862) ideas could be said to have risen to the level of a scientific theory at all—they were, rather, empirically unsupported hypotheses. Not only was none later borne out; none was ever even pursued beyond its first conjectural suggestion. Indeed, the discussion in chapter 7 demonstrates that virtually *any* developed theory of aromatic substances (including Kekulé's own cyclohexatriene hypothesis) would have been premature, given the uncertain and rapidly evolving empirical foundation, before 1863 or 1864. Furthermore, Kekulé telling stories about dreams could not possibly accomplish the result that Wotiz believed Kekulé was seeking. One would be laughed off the floor if one truly intended to use the recounting of a dream as a serious priority claim against published rivals.

There is an even more fatal problem here: Kekulé could not have had the motive for prevarication that Wotiz imputes to him, for *he had no rivals to squelch*. No one had ever contested his priority for benzene theory, and none in Germany, at least, had ever contested his priority for structure theory. Before Anschütz's recuperative efforts in the early twentieth century Loschmidt's 1861 publication was completely unknown; moreover, in a paper on benzene that Loschmidt published in the same year as the Benzolfest, he himself never mentioned his own 1861 benzene conjectures.[49] Couper was even more obscure at that time, if that was possible, and was long forgotten. During Kekulé's

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[48] Wotiz and Rudofsky, "Kekulé's Dreams" (1984); anon., "Developer of Key Theory May Have Been a Fraud" (1984); Seltzer, "Influence of Kekulé Dream Disputed" (1985); Wotiz, "Unknown Kekulé" (1987); Rudofsky and Wotiz, "Psychologists" (1988); Wotiz and Rudofsky, "Herr Professor Doktor Kekulé" (1993); Borman, "Kekulé Charged with Scientific Misconduct" (1993). An early critique of these arguments is Ramsay and Rocke, "Kekulé's Dreams" (1984).

[49] Cited in Loschmidt, *Konstitutions-Formeln* (1913), 109.

lifetime no one, including Loschmidt and Couper themselves, had ever publicly (or even privately, as far as anyone knows) suggested that either Loschmidt or Couper—or anyone else, for that matter—had anticipated Kekulé's benzene theory.

It is true that Kolbe had repeatedly argued for his and Frankland's priority for carbon tetravalence, but Kolbe, now dead, had effectively written himself out of the profession in the last ten years of his life; hardly anyone credited his arguments. Frankland wished more to assert his priority for the general concept of valence, rather than carbon tetravalence, and in any case he never really cared to push the matter. (Kekulé's generous acknowledgment to Frankland's leadership in his speech must have gratified the Englishman, who then publicly returned the favor.)[50] Butlerov's relatively modest and entirely truthful claims to having played a crucial role in the further development of a consistent theory of structure could not have been a problem for Kekulé, either, in the context of 1890.

There is also the context of the material treated in chapter 9 to consider. From the perspective of 1890, in the previous eight years there had been much jollification in the German chemical community over Kopp's *Molecular-Welt* and the "Thirsty Chemists" spoof. In telling the first of his two anecdotes—the London omnibus story—Kekulé stated, "I saw what the venerable Kopp, my honored teacher and friend, so charmingly depicted for us in his 'Molekularwelt,' but I saw it long before him." Wotiz regarded this line as another bit of brazen Kekuléan thievery, but it does not need to be viewed that way. Kekulé made clear in both of his anecdotes that the two particular "dream" events he recounted were by no means unique in his mental habits, and that he had often visualized the molecular world. Other evidence is at least consistent with this suggestion, as we have seen here and there in several previous chapters of this book. If I am right in my interpretations in chapter 9 regarding Kopp's mental world, he too was in the habit of speculative molecular visualization. This would suggest a general mental phenomenon in which perhaps many chemists participated (and participate?), rather than an invention or discovery for which one might want to claim priority.

As for the "Findig" article in the Thirsty Chemists lampoon, many

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[50] In his autobiography, Frankland wrote, "The application of my theory of valence to carbon compounds, however, belongs substantially to Kekulé, whose brilliant application of this theory to carbon compounds generally, and to benzol and its congeners especially, constitutes one of the most important epochs in the history of chemical science." Frankland, *Sketches* (1901), 191. For a full and perceptive discussion, see Russell, "Kekulé and Frankland" (1993).

commentators have seen the ring of monkeys as a prelude to Kekulé's snakelike form that seizes its own tail in its mouth; indeed, some casual popular accounts have muddled this history, as we shall shortly see, and put the monkey-ring in Kekulé's story. In chapter 9 I have noted that "Findig's" monkeys must surely have been an allusion to Kopp's humorous suggestion of a zoological analogue to a pentavalent atom's fifth valence bond, provided by the grasping tail of a four-handed monkey—an analogy that Kopp then rejected with a wink to the reader. But perhaps there were other meanings. Could Kekulé have invented his snake story in 1890 with the intent to respoof the 1886 "Findig" article? Or perhaps "Findig's" monkeys had a double purpose, to parody *both* Kopp *and* Kekulé, if Kekulé's stories were already familiar to the community through oral transmission? We will probably never know.

But there is one trustworthy account that suggests that there had been oral transmission of at least the benzene "dream" story. Annoyed by the publication of a garbled popular account of the story that put the 1886 "Findig" monkeys in the mouth of his father in 1890, Kekulé's son Stephan wrote in 1927: "My father repeatedly [wiederholt] recounted the 'vision of the ring formation' in my presence, both in the narrowest circle of wife and children, as well as in front of acquaintances, and especially in front of colleagues."[51] Stephan then reprinted both "dream" stories verbatim, as they had been published in the 28 April 1890 issue of the *Berichte* (he had been present, at the age of twenty-seven, at the Benzolfest on 11 March). Stephan strongly discounted any connection whatever between the "Findig" paper in the Thirsty Chemists spoof and Kekulé's stories. Of course, Stephan claiming that Kekulé often told the stories in his presence to groups of friends and colleagues does not mean that this is necessarily true, but it is hard to imagine why he would want to prevaricate. There would be no incentive to counter skeptics, as no skeptics had yet appeared. Although some had carelessly garbled the account—hence the need for Stephan's correction—no one had ever questioned the sincerity of these stories, as far as I am aware, until a one-page paper appeared in 1975 that cast doubt on Kekulé's truthfulness.[52]

Since the publication of the article by Stephan Kekule, there has been much discussion of the possible significance of the benzene dream, if

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[51] "Mein Vater hat die 'Vision der Ringbildung' in meinem Beisein sowohl im engsten Kreise der Frau und der Kinder, wie vor Bekannten, wie namentlich vor Fachgenossen, wiederholt erzählt." S. Kekule von Stradonitz, "Zwei chemische Visionen" (1927).

[52] Vanderbilt, "Kekulé's Whirling Snake" (1975).

taken as a real event.[53] Some have suggested that Kekulé's "snake" that seized its own tail in its mouth reflects the possible unconscious influence of the well-known ancient alchemical symbol known by the Greek term "ouroboros," or tail-eater, the serpent that eats itself continuously and thus symbolizes infinity and immortality. An immediate neighbor of the Kekulé family in Darmstadt, Countess Görlitz, was murdered in 1847, and among other features in the famous trial was her ring, on which was carved such a device. Since both Kekulé and Liebig were called as witnesses in the trial, the figure may have made an impression. But whether this had an influence we will never know. Others have seen presentiments of Kekulé's ouroboros symbol in tavern signs or in devices on the title pages of old books. The tale has even received Freudian and Jungian interpretations.[54]

These ouroboros studies are probably over-interpretations. If one reads Kekulé's words carefully, it is not obvious that what he claimed to have envisioned was a snake at all. The mental images of his description were "forms" or "shapes" (Gebilde) of various kinds, especially those in long lines that twisted and turned "in snake-like fashion" (schlangenartig). The next sentence, "One of the snakes seized its own tail . . . " may not have been intended to portray a mental image of a live biological snake, but rather one of the snake*like* molecular shapes that he was describing. If one reads the two anecdotes back to back, as they were in fact recounted at the Benzolfest and published by Schultz in the *Berichte,* a much clearer impression of these molecular forms emerges than by reading either of the stories in isolation.

At the end of chapter 2, I suggested that these "dream images" may have been identical to the sausage formulas and wooden sausage models that he used in classroom, textbook, and benzene papers in Heidelberg and Ghent from 1857 until 1866; or to express the thought more precisely, that he may have modeled his formulas after these mental images. At a minimum, his descriptions of his visions in these two anecdotes are *consistent* with the formulas and models. In London he said he saw atoms in pairs, then single atoms each holding two smaller ones, others holding three at a time, still others four. In Ghent, the

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[53] Here is a sample of this extensive literature: Farber, "Dreams and Visions" (1966); Strunz, "Preconscious Mental Activity" (1993); Soldat, "Kekulés Traum" (1993); Wotiz, *Kekulé Riddle* (1993); Schaffer, "Making Up Discovery" (1994); Rothenberg, "Creative Cognitive Processes" (1995). See also the next footnote.

[54] Anschütz, 1:18–20; Fierz-David, "Kekulés Visionen" (1944); Verkade, "Kekulé" (1958); Mahdihassan, "Origin" (1960); Mahdihassan, "Kekulé's Dream" (1961); Mitscherlich, "Kekulés Traum" (1972).

snakelike lines that eventually formed rings were “often fitted together more densely.” This suggests the sort of carbon-carbon double bonds that are portrayed with sausage formulas: single bonds require a connection of one bulge per atom, but double bonds require the two atoms to be shoved more closely together so that two bulges per atom are engaged.

All of this is, of course, speculation, but there is no alternative. Those who are skeptical of the stories must also speculate. Just as for many scientific ideas, what ultimately matters to the historian is the heuristic utility of one’s speculations and the total picture of the past that one can build using them. And in this case, as in so many others, both utility and the beauty of the resulting picture are in the (mind’s) eye of the beholder.

The Eureka Experience and the Unconscious Mind

At an elite gathering around the turn of the last century, a famous scientist rose to address a general audience. He was a legendary figure in his field, but on this day he wanted to tell stories of his youth, of the time, many years ago, of his first great contribution to human knowledge. In particular, he wanted to explore the psychology of discovery by revealing something of his own inner life, secrets from his “very soul.” Speaking of his labors twenty-eight years earlier, he told of much ordinary hard work, but also of surprising elements of apparent chance, intuition, and nocturnal imagination. He related that on one overcaffeinated evening he found it difficult to sleep. He spent the night in a mental world where “ideas arose in crowds; I sensed them colliding with each other, until two of them linked up together, as it were, to form a stable combination.” The next morning he had, in this mysterious fashion, achieved the solution to the problem with which he had been struggling for two weeks; “I had only to write out the results,” he said. He then spoke of other private incidents that occurred soon thereafter, in which the keys to solve difficult, closely related problems suddenly appeared in flashes of illumination. These “eureka” episodes happened to him, he said, during seemingly *random* circumstances, unconnected with the laborious conscious preparatory work that appeared to be an invariable precondition for such events. In his public recounting he was anxious to emphasize the apparently unconscious elements of such phenomena, but he was also careful to point out that the eurekas always had to be subsequently verified in a more or less conventional fashion, for the feeling of complete certitude that normally accompanied the flashes of insight did not *always* prove justified.

Despite appearances, I am not describing Kekulé here, but another famous story of private moments of discovery, told by the great French mathematician Henri Poincaré.[55] Poincaré was speaking to an audience of psychologists in Paris in May 1908, describing events from the summer of 1880, when he was working on a theory of automorphic functions at the University of Caen. His stories bear striking similarities to Kekulé's reminiscences. There was even an omnibus in one of Poincaré's anecdotes. About to return from an excursion to Coutances, Poincaré recounted, "at the moment when I put my foot on the footboard, the idea came to me, without anything in my previous thoughts appearing to have prepared me for it." Having boarded the bus, he continued a conversation already commenced, he said, verifying his idea at his leisure once he had returned to Caen, "to satisfy my conscience."[56]

But let us pass over what are surely trivial and coincidental circumstances of Poincaré's and Kekulé's experiences—such as the omnibuses, or the fact that each man's patronymic had three syllables ending in a French acute accent—and focus instead on fundamental factors. I want now to examine some less obviously conscious and rational elements of scientific method suggested by such episodes. If their importance and generality were to be accepted, we would need to think differently about how we understand at least some species of scientific discovery to operate.

Both sets of reminiscences recount a series of eureka experiences, that is, sudden illuminations that occur on occasions that are unconnected with the hard work on the problem at hand. Such phenomena are suggestive of the existence of unconscious cognition. Poincaré mentioned that these kinds of episodes happened to him not just once, but with some regularity; he specifically noted that the kinds of episodes that he described as associated with this particular series of discoveries were repeated throughout his career. He also commented that he often had ideas "come to me in the morning or evening in my bed while in

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[55] Poincaré, "L'invention mathématique" (1908), transcript of a lecture to the Institut Général Psychologique in Paris on 23 May 1908; republished verbatim six months later as chapter 3 of his *Science et méthode* (1908), 43–63, esp. 50–55. Gray has provided an illuminating concordance between these retrospective anecdotes, Poincaré's early published works, and his private correspondence from this period: *Linear Differential Equations* (2000), 173–84, and Poincaré, *Trois suppléments* (1997), 18; see also Miller, *Imagery* (1986), 233–41 and passim. Curiously, in contrast to the Kekulé anecdotes, no one has ever cast doubt on Poincaré's sincerity in telling these eureka stories.

[56] Poincaré, *Science et méthode,* 51–52.

a semi-hypnagogic state."[57] We might well call such an event a "sleepiphany," or an "ennightenment."[58]

How general are eureka experiences? The psychologist and historian of science Howard Gruber has slyly remarked that creativity appears to require one of the three "B's"—the bed, the bath, or the bus.[59] Certainly there are many examples of this sort of thing in the literature, and we do not need to limit ourselves to the letter B. We pass over without comment the Archimedes "bathtub" legend, of which we know far too little for certain. On the other hand, there is no reason to doubt Charles Darwin's testimony of suddenly arriving at the idea of natural selection while reading Thomas Malthus, nor is that the only eureka experience he subsequently related.[60] Barbara McClintock often spoke of "so many experiences in my life of getting these signals from my subconscious that I cannot tell you necessarily where they come from, but the whole thing is solved suddenly"; she called them "unconscious integrations."[61] Wilhelm Ostwald described the moment when he conceived of energetics, early one morning while walking in the Berlin Tiergarten as he was unable to sleep, as "a real Pentecost, an outpouring of the spirit over me." William Hamilton "felt the galvanic circuit of thought close" when he first conceived of quaternions, and his sons always called the spot where it happened, on a leisurely walk with his wife, "quaternion bridge."[62] Niels Jerne famously arrived at his selection theory of antibody formation on a brief evening walk in Copenhagen.[63] We have told the story of van't Hoff's celebrated walking eureka in chapter 8.

Freeman Dyson's proof of the equivalence of the rival radiation theories of Julian Schwinger and Richard Feynman occurred to him while emerging from what he described as "a sort of semi-stupor" induced after forty-eight hours on a cross-country bus journey from Berkeley to Chicago. "Before I knew where I was," he wrote his parents shortly

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[57] Ibid., 55. Technically, "hypnagogic" is defined as the state of intermediate consciousness while going to sleep, while the state of intermediate consciousness while awakening is called "hypnopompic."

[58] These terms are not mine; they were coined by readers of Barbara Wallraff's "Word Fugitives" column in the *Atlantic Monthly,* May 2006, 157.

[59] Gruber, "On the Relation" (1981), 41.

[60] "I can remember the very spot in the road, whilst in my carriage, when to my joy the solution [to evolutionary divergence] occurred to me": *Autobiography of Charles Darwin* (New York: Appleton, 1892), 42–43.

[61] Comfort, *Tangled Field* (2001), 67–68 and passim; Keller, *Feeling for the Organism* (1983), 115 and passim.

[62] These two anecdotes are takes from Farber, "Dreams and Visions," 130, 136.

[63] Söderqvist, *Science as Autobiography* (2003), 167–72.

thereafter, "I had solved the problem that had been in the back of my mind all this year."[64] Other well-known eureka stories are told of, or by, Isaac Newton, Joseph Priestley, Carl Friedrich Gauss, Alfred Wallace, Dmitrii Mendeleev, Sigmund Freud, Hermann von Helmholtz, Svante Arrhenius, Albert Einstein, Louis de Broglie, Enrico Fermi, Otto Loewi, Linus Pauling, James Watson, John Nash, Richard Feynman, and many others.[65] The more one examines this phenomenon, the more one is impressed by the richness of available examples, even extending so far as to apply to one's own far-from-exemplary mental features.[66]

Let us therefore accept that eureka experiences are common (that is, general) to the human species, and possibly even common (that is, frequent) in the lives of many individuals. One could suggest explanations for this phenomenon that do not imply that it is the result of productive processing by the unconscious mind. It could simply be, for example, that ideas sometimes may come more readily to a mind that is in a state of relaxation; or, alternatively, that intensive directed mental work can sometimes result in the channeling of thought in an unproductive direction, so progress is made precisely when the directed character of the work ceases. But these hypotheses do not seem to match very well the circumstantial details of the best-studied cases.[67]

One need not subscribe to Freudian theories to acknowledge that research in neurology and psychology during the last quarter century has increasingly confirmed the importance of unconscious mental processes. For instance, much evidence now supports what has been called "off-line memory reprocessing," that is, memory consolidation while sleeping. More directly relevant to our subject is research that convincingly demonstrates that unconscious thought can sometimes be superior to conscious deliberation. A study recently published in *Science* magazine compared careful conscious deliberation to unconscious thought (termed "deliberation without attention"). The authors found that shoppers using conscious deliberation made the best purchasing decisions for simple items with few relevant factors, while shoppers who deliberated without attention made superior decisions when the relevant issues were very complex, such as in choosing an apartment

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[64] Dyson to his parents, 14 September 1948, cited in Kaiser, *Drawing Theories Apart* (2005), 74.

[65] Recounted, e.g., in Hadamard, *Psychology of Invention* (1945); Gruber, "On the Relation"; and Holmes, *Investigative Pathways* (2004), 172–88.

[66] Hadamard (*Psychology of Invention,* 1–20) summarized the results of questionnaires and polls on this subject, all of which support the frequency and wide distribution of eureka experiences.

[67] This was well shown in ibid., 32–37.

or a car. How can this be possible? It is now well recognized that the "bandwidth" for conscious thought is really quite narrow, while that for unconscious processes is astonishingly capacious. Think, for example, of the cocktail-party situation where the cacophony of neighboring conversations rises to consciousness only when one's own name is heard; or the now well-documented inability to drive skillfully when one is deeply engaged in a telephone conversation, even while using hands-free technology. The authors of the study in *Science* conclude that "during unconscious thought, large amounts of information can be integrated into an evaluative summary judgment" often more effectively than during conscious deliberation, when one's focused mind can sometimes inadvertently allow a single factor to assume greater importance than it deserves.[68]

Researchers in the relatively new field of cognitive science have arrived at congruent conclusions. The increasingly well accepted theory of "conceptual blending" suggests that some of the most creative moments in the life of the mind occur when disparate elements of experience are fruitfully—though often unconsciously—combined together to arrive at a thought that only *appears* to be radically new.[69] Such blended thoughts often occur, apparently, in visual images. As David Gooding has justly remarked, "The power of images consists largely in the fact that they integrate different types of knowledge and experience."[70] Along the same lines, Nancy Nersessian has explored the mutual utility of cognitive science (including the role of mental images) and history; she argues that "[t]he cognitive-historical method specifically achieves a deeper and more refined understanding of conceptual change than is possible with either approach [alone]."[71]

Howard Gruber has worked to integrate the results of psychological and historical research on eureka experiences. Following his extensive study of Darwin's thought as revealed in his scientific notebooks and correspondence, and incorporating insights from neuropsychology, Gruber offered some generalizations regarding what he called "aha experiences." He concluded that the common impressions that such

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[68] Dijksterhuis et al., "Deliberation-without-Attention Effect" (2006); the footnotes provide a useful entrée into the scientific literature on this subject. Such research has long been discussed in the trade press; see, e.g., Claxton, *Hare Brain* (1997); Nørretranders, *User Illusion* (1998); Gladwell, *Blink* (2005).

[69] Fauconnier and Turner, *Conceptual Blending* (2002).

[70] Gooding, "Picturing Experimental Practice" (1998), 306.

[71] Nersessian, "Opening the Black Box" (1994), 205. See also Nersessian, "How Do Scientists Think?" (1992), and Davies et al., "Visual Models" (2005).

sudden illuminations are rare, essentially instantaneous, and always sharp ruptures with prior thinking are all at least overstated, if not false. The evidence he presented suggests that the phenomena are not only real but surprisingly frequent; that they have an internal structure and take place over time; and that the insights of the "aha" moments usually present considerable measures of continuity with the scientist's previous thought. For example, Gruber judged that over his working life Darwin must have had an average of at least one sudden illumination per day (some of which of course were more important than others), and that his most famous one, the Malthusian "aha," is prefigured more than once in his notebooks.[72]

Immediately following Gruber's 1981 article on eureka experiences in the same issue of the journal *History of Science* appeared Frederic L. Holmes's eloquent manifesto urging the value of his own favored historical methodology, namely, the study of investigative pathways by tracing the "fine structure" of scientific activity as revealed in notebooks recorded daily over many years.[73] Holmes used this method with brilliant success in illuminating the work of Antoine Lavoisier, Claude Bernard, Hans Krebs, and others. One would imagine that in order to proceed in such a fashion Holmes must have assumed in advance the *continuity* of a scientific pathway, excluding the very possibility of discontinuous eureka experiences. On the contrary: the evidence of Holmes's work on investigative pathways, pursued aggressively over forty years, was fully concordant with the more nuanced understanding of eureka experiences as developed by Gruber.

One central aspect of this concordance is revealed by the very "fine structures" that Holmes sought out. As Gruber convincingly argued, "The more one looks at a case, the more one sees that a seemingly sudden inspiration exhibits a complex history of purposeful growth and a dense inner structure." Moreover, memories can reprocess prior mental events in unpredictable ways.

> The thinking person goes over the same ground many times. He looks at it from varying points of view—his own, his arch-enemy's, others'. He diagrams it, verbalizes it, formulates equations, constructs visual images of the whole problem, or of troublesome parts, or of what is clearly known. But he does not keep a detailed record of all this mental work, indeed could not. . . . Deep understanding of a domain

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[72] Gruber, "On the Relation"; Gruber, *Darwin on Man* (1981).

[73] Holmes, "Fine Structure" (1981).

> of knowledge requires knowing it in various ways. This multiplicity of perspectives grows slowly through hard work and sets the state for the *re*-cognition we experience as a new insight.[74]

In studying Lavoisier's evolving views on the role of the atmosphere in oxidation and respiration, Holmes showed that for several years Lavoisier effectively lived partially in two different intellectual worlds, only slowly entering a new paradigm while retaining elements of the old. In the case of the work of the contemporary molecular biologist Seymour Benzer, Holmes had the advantage of both detailed written documents *and* conversations with the living subject himself. It turns out that one of Benzer's crucial insights, which Benzer later distinctly remembered as happening in a moment and resulting in his "dropping everything" to pursue the new line, actually did not happen in a moment at all, but developed gradually over a couple of months. In agreement with Gruber, Holmes commented: "Ever simplifying, memory regularly suppresses those aspects of a complex progression of events that did not prove, in retrospect, essential to an outcome." Holmes did not at all doubt the accuracy of Benzer's memory that he had had a sudden illumination; rather, he and his subject ultimately agreed that that quite memorable experience must be placed in a broader, more complicated and diffuse mental landscape than Benzer was able at first to recall.[75]

We can find evidence for this more complex view of eureka experiences from the historical cases we have discussed. Poincaré ended his lecture to the psychologists with an interesting comment. The night of overcaffeinated mental excitement in his anecdote, he said, was by no means unique in his experience; in fact, he had often found himself in a similar state, a state that did not normally need to be triggered by a recreational drug. At such times, he said, "one becomes a witness to one's own unconscious activity, which has become partially perceptible to the over-excited consciousness, without changing its character." He suggested that during such episodes the "subliminal self" is able to sort through a much larger number of combinations of ideas than would ever be possible for the conscious self, and to select one or more particularly elegant or beautiful possibilities for presentation to the

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[74] Gruber, "On the Relation," 57–58.

[75] Holmes, *Investigative Pathways,* 175–76, 185–86; Holmes, *Lavoisier* (1985). Schaffer, in "Making Up Discovery," argues in a similar fashion, but in the process imputes to me several views that I do not hold and have not defended, including the suggestion that the earliest assertion that benzene had the cyclohexatriene structure should be credited to Adolf Claus.

conscious mind. Sometimes we are dimly aware of this unconscious work, sometimes not, he said; the results are presented to our minds as a sudden illumination. But always, Poincaré added, the conscious mind must subsequently verify the suggestion, for what is beautiful or elegant is not always true. Barbara McClintock also seemed at times to be able to bring her unconscious processing partially to consciousness. Regarding one of these "integrating" experiences, she said, "Something was going rapidly, backtracking and making sure everything was all right, because it was a very intricate process." *How do you instigate an integration?* she was asked. "You do something with yourself," she said.[76] These testimonies are entirely consistent with the recent research in neuropsychology that I have summarized.

Such phenomena may seem quite mysterious, but they needn't be, as long as one bears in mind that the phenomenon embraces a spectrum rather than a binary opposition. Everyone experiences something of this, every day. Think, for example, about the choice of words in spoken language, which is a rich mixture of conscious and unconscious elements, ranging from nearly complete unconsciousness (such as when tuning out ambient conversations, or when speaking quickly and fluently) to nearly completely conscious thought (as when painstakingly searching for the best way to say something important). The early and middle stages of learning a foreign language require particularly heavy use of conscious thought, whose narrow bandwidth provides one good reason why one speaks so slowly at first. The well-known phenomenon of the mental "invisibility" of a well-learned language is a measure of one's mastery of it, and simultaneously of the degree to which its routine operations have become unconscious. The mastery of any practice or skill, especially including complex undertakings such as scientific research, is no different.[77]

We can now return to Kekulé's mental vision of dancing atoms and molecules—trusting his sincerity, at least provisionally for the sake of this argument. How should we view these stories, in the light of all that we have just rehearsed? We are now in a position to affirm several propositions. First, eureka events of the kind related by Kekulé are well attested in the lives of many, if not most scientists. His stories follow

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[76] Poincaré, *Science et méthode,* 62; Comfort, *Tangled Field,* 68.

[77] Another example: research has demonstrated that in chess, "the expert relies not so much on an intrinsically stronger power of analysis as on a store of structured [unconscious] knowledge. When confronted with a difficult position, a weaker player may calculate for half an hour, often looking many moves ahead, yet miss the right combination, where a grandmaster sees the move immediately, without consciously analyzing anything at all." Ross, "Expert Mind" (2006), 67.

a similar pattern to many we have seen—intense labor on a difficult problem, followed by relaxation and undirected thought, then the apparently sudden illumination, followed by conscious testing and verification of the idea.

Those who are skeptical of the so-called dream stories have correctly pointed out that elements of structure theory predate Kekulé's contributions, and elements of his benzene theory, such as examples of cyclical molecular structures, were also available before Kekulé published his first paper on the subject. Skeptics suggest that the eureka stories don't make much sense if the sudden illuminations claimed by Kekulé were no novelties at the time of the respective episodes. Critics portray a Kekulé who wished to recount fictive eureka experiences that were sudden and revolutionary, sharp Dedekind cuts with the past. As I have argued, and moreover in full agreement with the skeptics, such a depiction betrays an unrealistic popular misrepresentation of the character of actual eureka phenomena. But in the skeptics' recounting we now have two factors that cast doubt on Kekulé's truthfulness: first, his adoption of a false popular misrepresentation of the eureka experience as lightning bolt (false because, as an invention, he would not know how to make this caricature true to life); and second, his incorrect implication, by his very use of that caricature, that the two theories whose geneses were being described were totally novel.

However, this characterization of Kekulé's speech is, as we have seen, the very opposite of what Kekulé intended, and the opposite of what he explicitly stated in the speech. He did not want to argue for sharp rupture and novelty; rather, he repeatedly argued for *continuity* in the history of benzene theory, including in his own discoveries. Indeed, he categorically and explicitly denied the very possibility of absolute novelty. It is assuredly possible, even likely, that Kekulé absorbed, consciously or unconsciously, one or more notions of colleagues or rivals with which he had come in contact, such as Couper's or Loschmidt's cyclical formula proposals, combining them together with the results of his own experiments and ideas, and mentally integrating (or conceptually blending) them in the so-called dreams. Such continuity can easily embrace a trajectory involving his own experimental and theoretical work, too, as I have argued conjecturally in the third section of chapter 7. If eurekas generally have more internal structure and if the resulting illuminations have more direct and perceptible relationships with what has gone before, then demonstrating that structure and those relationships does not weaken, but rather strengthens the probability that the stories were sincerely told.

John Wotiz was once quoted as saying that "[c]hemists don't operate by dreaming up things. We do experimental work and get hard facts first."[78] Actually, I believe that both Kekulé and Poincaré would have wholeheartedly agreed with at least a more nuanced version of this statement, and for three reasons. First, Kekulé's reveries, like Poincaré's—*if* they happened—were not actual nighttime dreams, but rather, apparently, mental episodes that took place somewhere between conscious and unconscious thought (which is why I have generally placed Kekulé's "dreams" in quotation marks). Second, neither man would ever have experienced such eureka episodes if he had not beforehand worked intensively, even obsessively, carefully preparing the empirical (and private psychological) groundwork. And third, like Poincaré, Kekulé insisted in his speech that it was absolutely crucial to be able to verify the ideas afterwards. We need to repeat once more the words with which he concluded his stories: "Let us learn to dream, gentlemen, then perhaps we will find the truth," Kekulé averred; "but let us beware of publishing our dreams before they have been examined by the conscious understanding."

The physicist Ludwig Boltzmann provided an appropriate coda to all of this:

> The principle that stimulates and enlivens, that which alone brings forth novelty in scientific research, is exclusively and solely the imagination, and so I might be permitted . . . to recall Schiller's verse, which, if I am not mistaken,[79] Kekulé some time ago applied in a speech on one of the oldest fields of theoretical chemistry, the molecular-theoretical visualization [Veranschaulichung] of the composition of benzene derivatives:
>
> Wage du zu hoffen und zu träumen,
> Tiefer Sinn liegt oft im kind'schen Spiel.
>
> So dare to hope and to dream:
> Profound meaning often lies in a childish game.[80]

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[78] Seltzer, "Influence of Kekulé Dream Disputed," 22–23.

[79] He was mistaken: Kekulé quoted Goethe, not Schiller.

[80] Boltzmann, *Populäre Schriften* (1905), 383–84. Boltzmann's verse is from Schiller's *Thekla, eine Geisterstimme*. The fourth word of the first line should be "irren" (to err), and the first word of the second line should be "hoher" (high), not "tiefer" (deep or profound).

ELEVEN

The Scientific Image-ination

John Dalton had a pictorial imagination. . . . This concreteness of the imagination proved to be [his] great strength as a chemist; for it so happened that chemistry in the nineteenth century thrived when it was naïve and pictorial, and languished when it tried to be abstract and subtle. W. V. FARRAR[1]

One time, we were discussing something—we must have been eleven or twelve at the time—and I said, "But thinking is nothing but talking to yourself inside." "Oh, yeah?" Bernie said. "Do you know the crazy shape of the crankshaft in a car?" "Yeah, what of it?" "Good. Now tell me: how did you describe it when you were talking to yourself?" So I learned from Bernie that thoughts can be visual as well as verbal. RICHARD FEYNMAN[2]

Mental Images and Science

In a recently published exploration of the philosophy of the imagination, the philosopher of mind Colin McGinn argues for the hitherto insufficiently appreciated importance of what one might call the image-ination (the ability to form and manipulate mental images that are not directly connected to visual perception itself). McGinn provides persuasive evidence that "[mental] images are *sui generis,* and should be added as a third great category of intentionality to the twin pillars of perception and cognition . . . Neither is it at all obvious that images necessarily carry a [conceptual] thought component . . . Images are not

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1. Farrar, "Dalton" (1968), 290.

2. Feynman, *"What Do You Care?"* (1988), 54. Feynman identified Bernie Walker as a school-friend and fellow science enthusiast in his neighborhood of Far Rockaway, New York.

just minor variations on perception and thought, of negligible theoretical interest; they are a robust mental category in need of independent investigation." One can *learn new things* from mental images, even from those that occur in not-fully-conscious mental states, McGinn persuasively argues. He concludes that the genus *visual apprehension* should be considered as having two coequal species, *percepts* and *images;* the latter is the product of a hypothesized imagistic sense he calls *mindsight* (also the title of his book)—the same referent as my more descriptive but perhaps more awkward term *image-ination*. McGinn's theory proposes that the creative imagination (an image-generating mental power) is even constitutive for understanding and generating language.[3]

McGinn's analysis suggests that images must be regarded as a far broader category than just thought-pictures of real objects, and therefore must have application not just to fields that deal with perceptions of physical things. For instance, one would scarcely be inclined to believe that Poincaré's (or anyone else's) work in the theory of differential equations, whether conscious or unconscious, could routinely involve mental imagery. One would suppose that being in the realm of pure mathematics, his theories must have arisen through pure ratiocination. It is therefore surprising to note how filled with images are Poincaré's descriptions of what happened in his mind during his eureka episodes, which, as we have seen, are surprisingly parallel to the stories that Kekulé told. The prominent contemporary American mathematician William Thurston has even averred that "[t]hinking is really the same as seeing."[4]

Other examples of visual thinking in the history of science are not hard to find. Michael Faraday had a particularly vibrant imagination; his visually inventive experimental style was desultorily explored many years ago by L. Pearce Williams, and more recently, from a more purely epistemological perspective, by Nancy Nersessian, David Gooding, and others.[5] But perhaps no one has examined the subject of visual thinking in physics more thoroughly than Arthur I. Miller. Miller's work on imagery and the visual imagination concerns, with a few exceptions, the work of twentieth-century physicists, but it also has implications

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[3] McGinn, *Mindsight* (2004), 38–39, 44.

[4] "'People don't understand how I can visualize four or five dimensions, because they don't realize how people think,' he said. 'Five-dimensional shapes are hard to visualize—but it doesn't mean you can't think about them. Thinking is really the same as seeing.'" Quoted in Kneale, "Shaping Ideas" (1983). Winner of the Fields Medal, then at Princeton, Thurston is now at Cornell University.

[5] Williams, *Faraday* (1965); Nersessian, *Faraday* (1984); Gooding, *Experiment* (1990); Gooding, "Picturing Experimental Practice" (1998).

for our study of chemistry in the nineteenth century. As Miller has noted, other nineteenth-century physicists besides Faraday, such as Maxwell, Helmholtz, and Boltzmann, are known to have been highly visual thinkers.[6]

Much of Miller's evidence for the importance of visual mental imagery in scientific thought was taken from a close study of Albert Einstein. Einstein stated many times that his thinking took place largely, often even entirely, in the form of visual imagery; some ready examples are his thought experiments of chasing a light wave, falling in an elevator, or investigating the simultaneity of events in and around moving trains.[7] David Kaiser has recently carried out an illuminating study of the reception of Feynman diagrams, which illustrates many of these same tendencies. Feynman, for one, thought of his doodles as direct and primary *intuitions,* as in some sense pictures of actual physical processes. He regarded these images as heuristically vital for his work; others who adopted the diagrams obviously thought so, too, though not all regarded them with the same visuality that their creator did.[8] The respect toward visual mental images is also found among those who pursue the biological sciences. Howard Gruber has closely studied visualization by scientists, inter alia as an essential element of Darwin's creative thought patterns, and both Evelyn Fox Keller and Nathaniel Comfort have emphasized the mental visualizations in the "unconscious integrations" of Barbara McClintock.[9]

Many theorists of science have treated themes closely related to visual thinking. Pierre Duhem famously distinguished between the "ample" and the "deep" scientific mind, seeing in the former—endemic in England, he thought—a proclivity toward the use of mechanical models to explain phenomena.[10] The utility of scientific analogies, metaphors, and models has a rich literature.[11] Thomas Kuhn suggested a relationship between Gestalt psychology and paradigm shifts, and explored

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[6] Miller, *Imagery* (1986); Miller, "Imagery and Intuition" (1989); Miller, "Imagery and Representation" (2003).

[7] Holton, "Scientific Genius," in *Thematic Origins* (1973), 353–80. "I very rarely think in words at all," Einstein wrote. "For me it is not doubtful that our thinking goes on for the most part without use of signs (words), and in addition to a considerable degree unconsciously" (quoted in ibid., 368–69). See also the important work by Holton, *Scientific Imagination* (1978).

[8] Kaiser, *Drawing Theories Apart* (2005), 175–88, 368–73.

[9] Gruber, "On the Relation" (1981), 43; Gruber and Bödeker, *Creativity* (2005), 105–91, 241–57; Keller, *Feeling for the Organism* (1983); Comfort, *Tangled Field* (2001).

[10] Duhem, *Aim and Structure* (1954), 55–104.

[11] Two recent treatments of the subject as it relates to late nineteenth-century physics are: Cat, "On Understanding" (2001); and Lützen, *Mechanistic Images* (2005).

the psychology of perception as it relates to scientific change.[12] Several other important philosophers of science have addressed the subject.[13] In the history of technology, Eugene Ferguson has explored the essential and underestimated role of the visual imagination, the "mind's eye," for inventors, artisans, and engineers.[14] The eminent Stanford psychologist Roger Shepard has collated innumerable such examples from many fields, supplemented with his own significant autobiographical commentary.[15] A classic treatment, directed especially toward the visual arts but also of much wider application, is Rudolf Arnheim's fine work on *Visual Thinking.*[16] All of this, and much more that I need not cite, leads to the conclusion that mental imagery often accompanies creative and productive scholarly work, including scientific work. Mental imagery may even be *constitutive* of creative science. Obviously, more work on this important subject needs to be done.

Mental Images and History

These facts, if I may call them such, are not well acknowledged, indeed they are sometimes vigorously disputed; historians of science, in particular, have given them far less attention than they deserve. I can suggest several reasons for such neglect. For one thing, mental images are both fleeting and very personal. They also may seem insubstantial, even unreal—and in one important sense, of course, they *are* unreal. Those whose lifework is in the arts may celebrate the vitality of their imagistic mental world, but scientists inhabit a different culture, which celebrates precision, reproducibility, universality, and materiality. For scientists, mental images may seem downright embarrassing—as Kolbe in fact repeatedly proclaimed. Perhaps for this reason, or perhaps because they do not seem directly relevant to the results of their investigations, scientists in later life rarely recount their work-related imaginative peregrinations, and virtually never do they do so at or near the time of the event.

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[12] Kuhn, *Structure* (1970), 111–15.

[13] See, for example, Giere, *Cognitive Models* (1992); Nersessian, "Opening the Black Box" (1994); and Davies et al., "Visual Models" (2005). In *Science without Laws* (1999), 121, Giere argues that studies of the role of visual images in scientific thinking can offer a salutary "middle way between philosophical positivism and sociological relativism."

[14] Ferguson, *Engineering and the Mind's Eye* (1992).

[15] Shepard, "Externalization" (1978).

[16] Arnheim, *Visual Thinking* (1969); see also Richardson, *Mental Imagery* (1969); Kosslyn, *Image and Mind* (1980); and Rollins, *Mental Imagery* (1989).

And this suggests another reason why relatively little attention has been devoted to this important subject, namely, the intrinsic difficulty for historians in investigating instances of the phenomenon. The usual sources upon which one relies, namely, the books, journal articles, laboratory records, and correspondence written by our subjects, rarely mention such mental details. In the rare instances when historians do encounter such recollections by their protagonists, the evidence must necessarily be viewed skeptically. Not only might our protagonist be shading the truth or even prevaricating for ulterior reasons, he or she also may well simply be remembering inaccurately. And it is understandably difficult—impossible, in a strict sense—for the historian to get a second source for any given mental event, in order to triangulate toward historical truth.

Of course, for one even to be in a position to report on one's mental visualizations, one must first have sufficient insight, interest, and self-reflective focus and receptiveness in order to recognize the internal phenomenon at all. Some fraction of those who report rarely or never having had active visualizations in their work may simply be unable to reflect accurately on the visual character of their own life of the mind. They may be unskilled at introspection, or psychologically unprepared to admit consciously the presence of their own imagistic thinking. It would be understandable for some scientists to unconsciously resist such self-knowledge, considering the positivist (scientistic) preconceived ideal of rigorous verbal and mathematical thinking. As a consequence, when one surveys statistically the evidence for mental visualization among scientists from self-reports, positive evidence must be taken very seriously, but negative evidence is not necessarily dispositively negative.

In one such study published many years ago, psychologist Anne Roe examined the thought patterns of sixty-one eminent American scientists by several means, especially self-reports from detailed interviews. The group included roughly equal numbers of biologists, physicists, and social scientists (psychologists and anthropologists). Interestingly, a clear majority of the biologists and physicists, but almost none of the social scientists, reported that much of their thinking was of a visual nature. But Roe commented that the raw data were "highly unsatisfactory," since none of her subjects, not even the psychologists, were trained in introspection. This required the use of leading questions during the interviews—there was no alternative, given that "there are no standardized techniques or tests by which anything in the way of objective evidence [regarding visual mental images] can be obtained." Nonetheless, Roe thought the results were suggestive.[17]

Inspired not by Roe but rather by van't Hoff, Robert Root-Bernstein carried out a study similar to van't Hoff's of 1878 (mentioned in chapter 8), using a similar historical (prosopographical) methodology. This study provided further evidence to support what Root-Bernstein calls the "hypothesis of correlative talents," namely, that the most creative scientists tend to have also pursued strong interests in the arts. Root-Bernstein proposed a second generalization: "[t]he most influential scientists have always *nonverbally* imagined a simple, new reality before they have proven its existence through complex logic, or produced evidence through complicated experiments." He suggested that these two hypotheses—the importance of the arts and the importance of the power of mental imaging for productive scientists—were connected, in that the first promoted the second. "[The] ability to imagine new realities is correlated with what are traditionally thought to be nonscientific skills—skills such as playing, modeling, abstracting, idealizing, harmonizing, analogizing, pattern forming, approximating, extrapolating, and imagining the as-yet unseen—in short, skills usually associated with the arts, music, and literature."[18]

What did Williamson's, Kopp's, and Kekulé's own contemporaries think about the questions we are attempting to answer? I will present two witnesses, one on each side of the nineteenth-century debate. In 1883 Francis Galton reported the results of a survey of one hundred men, "at least half of whom [were] distinguished in science," using a questionnaire inquiring about their ability retrospectively to form mental images of remembered scenes. He was "amazed" to find "that the great majority of the men of science to whom I first applied, protested that mental imagery was unknown to them, and they looked on me as fanciful and fantastic in supposing that the words 'mental imagery' really expressed what I believed everybody supposed them to mean." Yet when he spoke with persons in "general society," he found that "[m]any men and a yet larger number of women, and many boys and girls, declared that they habitually saw mental imagery." He reported that his interview techniques led him to have high confidence in his data, and his conclusion, that "scientific men have feeble powers

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[17] Roe, "Study of Imagery" (1951).

[18] Root-Bernstein, "Visual Thinking" (1985), 61 (my emphasis); Root-Bernstein, "Van't Hoff" (2001).

of visual representation," was subject to "no doubt whatever . . . however it may be accounted for." Curiously, however, Galton proceeded to speculate that "the highest [scientific] minds are probably those in which [this faculty] is not lost, but subordinated, and is ready for use on suitable occasions." Moreover, his data led him to the paradoxical conclusion that "men who declare themselves entirely deficient in the power of seeing mental pictures can nevertheless . . . express themselves as if they were gifted with a vivid visual imagination."[19]

Galton's ambivalence was presumably due to his own visual habits of thought, for he himself considered his finding of the rarity of visual mental imaging among scientists to be "astonishing." He had no doubt of the utility of visualization, "when it is duly subordinated to the higher intellectual operations," and his apparently discordant conclusions suggested that imagery may operate in the mental background for some unknown fraction of his subjects. At the end of his chapter he declared with regret that "[o]ur bookish and wordy education tends to repress this valuable gift of nature," which was of particular use to mechanics, engineers, and architects, but also important for the pursuit of science. He opined that the nurturing and development of this visual habit of thought was one of the most pressing desiderata of science education in his day.[20]

My other witness is the British physicist John Tyndall. On 16 September 1870 Tyndall presented a lecture to the Liverpool meeting of the British Association for the Advancement of Science extolling "The Scientific Use of the Imagination."[21] Here he affirmed broadly that "[i]n explaining sensible phenomena, we habitually form mental images of the ultra-sensible." There are, to be sure, "Tories even in science" who fear and avoid the imagination, citing its excesses; but that, Tyndall quipped, is like arguing against the use of steam power because boilers have occasionally been known to burst. Used properly, imagination is in fact the very "architect of physical theory." For instance, the "constructive imagination of Dalton" formed the atomic theory from mere stoichiometry, while the works of Newton, Davy, and Faraday provide other salient examples. "[W]ithout the exercise of this power," Tyndall remarked, "our knowledge of nature would be a mere tabulation of coexistences and sequences."[22]

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[19] Galton, *Inquiries into Human Faculty* (1883), 83–114, 378–80.

[20] Ibid., 84–89, 107, 113–14.

[21] Tyndall, *Fragments of Science* (1892), 2:101–34. The essay first appeared in the one-volume first edition of this book (1871).

[22] Ibid., 2:103–4.

Tyndall conceded that some of his contemporaries refuse to acknowledge atoms and molecules as real things, limiting the definition of "atomic theory" to the empirical law of multiple proportions. Why, then (Tyndall asked), does everyone unquestioningly accept the undulatory theory of light?—for this conception requires the existence of an imperceptible luminiferous ether. Tyndall asked his readers to follow in their imaginations a train of ether-waves of light back to their source, and to inquire what might be found there.

> Ask your imagination if it will accept a vibrating multiple proportion—a numerical ratio in a state of oscillation? I do not think it will. You cannot crown the edifice with this abstraction. The scientific imagination, which is here authoritative, demands, as the origin and cause of a series of ether-waves, a particle of vibrating matter quite as definite, though it may be excessively minute, as that which gives origin to a musical sound. Such a particle we name an atom or a molecule. I think the intellect, when focused so as to give definition without penumbral haze, is sure to realize this image at the last.[23]

Thus, the view drawn by Tyndall was that his contemporaries only needed to have greater insight and self-consistency to appreciate the leading role that imagistic mental processes actually play, and must play, in the development of science.

This is not in the end so different from what Galton concluded. And in fact there may be even more concordance than first is apparent, for Tyndall and Galton were looking at slightly different phenomena. Galton's subjects were asked to recount details and describe the vividness of remembered scenes that had actually taken place. Tyndall's comments, by contrast, relate to the evocation of mental images upon which no bodily eye has ever gazed.[24] In this regard, Tyndall was dealing with mental images more in the sense of Colin McGinn and Immanuel Kant.

In his work on the scientific imagination, Arthur Miller traces his protagonists' predilection for visual imagery partly to the influence of Kant, who placed great epistemic importance on *Anschauung* and *Anschaulichkeit*. In modern German the Kantian connotations of these words have been obscured, and the terms now normally mean, respectively, "view" or "viewpoint," and "visualizability" or perhaps some-

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[23] Ibid., 2:108–9.

[24] In initiating his investigation, Galton may even implicitly have intended to respond to and further develop Tyndall's ideas. Nor should we forget Boltzmann's vigorous support of Kekulé's visualizations, quoted at the end of the last chapter.

thing like "graphic clarity." But in Kant's technical philosophical context an *Anschauung* was, as Miller formulates it, "an intuition through pictures formed in the mind's eye from previous visualizations of physical processes in the world of perceptions." Consequently, Miller (along with many other philosophers of science) routinely translates *Anschauung* simply as "intuition."[25] However one defines it, this Kantian concept of sense-intuition was influential especially among German and German-influenced scientists of the nineteenth century; it is not hard to see Kantian elements in the work of such figures as Berzelius, Mitscherlich, Loschmidt, and even Williamson. We noted in the first section of chapter 8 the claimed predilection of Liebig and of Bunsen toward concrete visualizations, the ability to "think in [chemical] phenomena," which probably refers to something like Kantian sense-intuition. And we have also noted that Kekulé, Kopp, and members of their circle frequently used the term *anschaulich* to characterize their chemical ideas.[26]

In chapter 1 and again in chapter 5, I have explored the probable influence of the Scottish school of Common-Sense philosophy on several of our British protagonists. Other than in the case of William Hamilton, there are few obvious connections between this philosophical school and the Kantian-influenced scientists in Germany, but there are some clear parallels between the two. In neither context do I mean to suggest that these philosophical orientations led in any kind of necessary or immediate sense to a predilection for theoretical manipulation of mental images, in Germany on the one hand, and in Britain on the other. However, it is reasonable to think that a conditioned respect for intuitive *Anschaulichkeit* in the case of Kantian-influenced scientists, or for simple analogical models in a motion-filled microworld in the case of those influenced by Reid, Stewart, and Hamilton, may have promoted the ability, or at a minimum reduced any intrinsic inhibition, to think using mental images. It may have given certain scientists a kind of internal psychological permission, in the form of more receptive insight, where others might have repressed or remained unaware of what we might consider to be a common human propensity.

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[25] Miller, *Imagery,* 110, 127–29.

[26] See Gregory, "Kant, Schelling" (1989); Gregory, "Kant's Influence" (1989). Some historians have also located the inspiration for the *anschaulich* in Friedrich Fröbel's Kindergarten movement in the early nineteenth century, which itself was partially derived from the object-teaching methods of the Swiss educational philosopher Heinrich Pestalozzi. Fröbel and Pestalozzi were particularly influential in the German cultural sphere.

Transdictive Images in Physics and in Chemistry

Chemical atomists were by no means the first scientists to take the unseen microworld seriously, to imagine what might be "down there," and to reason transdictively from what Tyndall called the "ultra-sensible" realm to consequences that are accessible to experiment. Such reasoning extends back to the pre-Socratic philosophers, and in the late seventeenth and eighteenth centuries the method was well represented. Newton famously proposed that a gas consisting of stationary particles exerting a self-repulsive force that varied inversely with distance would obey Boyle's law. He publicly expressed the desire to be able in the future to extend the laws that he had shown to operate on large, visible bodies such as cannonballs and planets all the way down to the microworld of the fundamental corpuscles of solid matter and the particles of light.

Early in the nineteenth century this quest was well represented in the tradition of what some historians have called the French "mechanico-molecular" school of mathematical physics. Centered especially in the École Polytechnique in Paris, this approach was practiced with great skill and success by such savants as Pierre-Simon de Laplace, Siméon-Denis Poisson, Claude-Louis Navier, and Augustin Louis Cauchy. Following Newton's example, these men posited the existence of invisibly small particles that exerted gravity-like central forces, from which they deduced mathematically the macroscopic phenomena to be explained, such as capillarity, cohesion, or elasticity.[27] What was important for members of the French molecularist school was the rigorous mathematical derivation of their results from their assumptions and the successful matching of those results with the empirical data, but they were careful to specify that they made no representations to be seeking molecular *reality.* Their assertions were guided by epistemological rules, not ontological claims.[28] As William Whewell expressed it in 1840, describing Laplace's method of microphysical investigation, "It is a mathematical artifice of the same kind as the hypothetical division of a body into infinitesimal parts, in order to find its centre of gravity; and no more implies a physical reality than that hypothesis does."[29]

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[27] Herivel, "Aspects" (1966); Kargon, "Model and Analogy" (1969); Heilbron, *Weighing Imponderables* (1993).

[28] Heilbron, *Weighing Imponderables,* 144–45.

[29] Whewell, *Philosophy,* 1:418.

In classic essays published a generation ago, Robert Kargon and Robert Fox each examined the precipitous decline of this school in the 1810s and 1820s, and Kargon went on to trace the vigorous development of British physics toward the middle of the century. Kargon thought that it was the rise of positivistic modes of thought that initiated the decline of the Laplacian school. He also suggested that in the transfer of scientific momentum from France to Britain he could espy a determinative role of the Industrial Revolution, and of an engineering ethos. "The physical content of British theories," he wrote, "was drawn, not from astronomical analogies as with the French molecularists, but from engineering, from the characteristics of real materials."[30] This helped to explain, Kargon thought, the predilection of British physicists for analogical physical models, such as Faraday's concept of the electric or magnetic field, or Maxwell's vorticular representation of the displacement current.

By contrast, Fox did not believe that the rise of positivist rhetoric and method—for instance, in the abstract heat theory of Joseph Fourier—caused the decline of the French molecularist school. Instead, he looked to the increasing support, brief though it may have been in some cases, given to such new ideas as the undulatory theories of light and of heat, and the chemical atomic theory. These were concepts that took the microworld even more seriously than the Laplacians did, and thus represented an intellectual direction that was orthogonal to positivism. John Heilbron has recently made the even stronger assertion that physical scientists at the beginning of the nineteenth century—it appears that he was referring principally to the Laplacians—actually *eschewed* microphysical models, "apart from very general assumptions about the molecular constitution of bodies."[31] But Heilbron, consistent with Fox's suggestions, noted one major exception to this generalization: the chemical atomic theory.

A generation ago Henry Guerlac justly called Dalton's contribution the first successful example of scientifically probing the world of the invisibly small, and he characterized this as the origin point of a "Molecular Revolution" as momentous as that of Newton.[32] Indeed, Dalton's work called forth a vigorous international research program that has a continuous history from 1803 to the present—nanoscience long before the word became vogue. So notwithstanding the French molecularist

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[30] Kargon, "Model and Analogy," 430; Fox, "Rise and Fall" (1975).

[31] Heilbron, "Physics" (2003), 643.

[32] Guerlac, "Background" (1968).

school, the rise of atomic theory in chemistry must be viewed as one of the great watershed events in the history of science—*the first truly successful entry by human minds and tools into the realm of the invisibly small,* initiating a continuous investigation of the microworld that stretches in an unbroken tradition to our own day.

We need to qualify Guerlac's claim, but only slightly. Daltonian atomic theory in the early decades of the century did not exactly take on the appearance of a triumphal chariot, and many early atomists adopted a position reminiscent of the nice epistemological distinctions of the Laplacians. Anti-atomism was alive and well through all of the nineteenth century.[33] But there are few more unequivocal examples of visual stereospatial images of the microworld applied to unquestioning ontological conviction than in the work of John Dalton himself,[34] and he was not alone in this predilection, even early on; at the beginning of chapter 8 we saw the same tendency in the putative skeptic William Wollaston. As Ursula Klein has well argued, Berzelius's alphanumeric chemical formulas, even in their earliest incarnation of 1813–14, were not merely convenient summaries of analytical data, but were graphically suggestive of real molecular pieces. This, even though the absolute physical scale for those tiny "portions" was not yet known, and even though no one professed to know whether such portions might have internal structures.[35]

In the early chapters of this book we have traced some of these events, focusing especially on the molecular ideas of such figures as Williamson, Graham, Berzelius, Mitscherlich, Laurent, Dumas, and Liebig. By 1840, the unitary substitutionist type theory allied with the concept of polybasic organic hydracids spelled the end of dualistic electrochemistry and the starting point for an ultimately successful campaign toward the goal of determining molecular structures. But suddenly the two leaders of the field, Liebig and Dumas, simultaneously retreated from theory, and the 1840s saw a temporary return to the explicit conventionalism of what were called "equivalents." Then, starting from the "chemical springtime" paper of 1850, Williamson and those influenced by him—especially Kekulé—began their ultimately successful assault on organic molecules. This book has told the story of that assault, and at every point I have attempted to follow what I believe to have been a guiding influence of mental images.

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[33] See Brock, *Atomic Debates* (1967).

[34] Farrar, "Dalton" (1968); Rocke, "El Dorado" (2005).

[35] Klein, *Experiments, Models, Paper Tools* (2003).

And what of the physicists? A sustained and community-wide reentry of physicists into the microworld took place only beginning in the year 1857, with the rise of the kinetic theory of gases and of heat, which accelerated a generation later with the initial steps toward exploration of atomic structure. To be sure, Tyndall's evocation of ether theories, cited above, might seem to argue for an earlier transition for the physicists, for such theories began to be developed as early as the 1810s. Jed Buchwald recently examined this question and concluded that ether microphysics "first became pragmatically real" only after ca. 1893. The community constructed a new vision for their science in the 1890s, for "the microworld . . . had *not* been a major preoccupation of the working physicist throughout the century."[36]

There is also, of course, the question of the interactions between the communities of physicists and chemists. At the end of chapter 8 we traced some of these interactions in the 1850s, but much more needs to be known about these contacts and influences. It would appear that many early kinetic theorists appealed to preexistent chemical science when it supported what their mathematics suggested—referring, for instance, to Avogadro's chemical hypotheses as one satisfying consequence of their physical equations. It appears that chemists were also happy to reap harvests from the physicists' garden. But it is too little remarked that it had been the chemists who had been the first to blaze a scientifically robust pathway down to the world of the invisibly small.

Nonetheless, during the first half of the century the utility of the theory of chemical atoms, which few chemists doubted, failed to compel explicit agreement regarding its ontological status. A reasonable position taken by several leading figures was to distinguish between ontological claims versus epistemological criteria for molecular reality. One might readily admit in principle that atoms and molecules could well exist, but how certain could one be? And what means were available to increase that certainty and provide additional details of the microworld? The presumed dynamical condition of reacting molecules was another complicating factor. And the multiplicity of atomic-weight systems clearly reduced the attractiveness of any vigorous ontological claims regarding the microworld.

However, when we consider not only our protagonists' explicit programmatic or rhetorical pronouncements, but also analyze the manner

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[36] Buchwald, "How the Ether Spawned the Microworld" (2000), 221; Buchwald and Schweber, "Conclusion" (1995), 351. Buchwald writes that the microphysical model of the ether used by Fresnel was "immensely important," but was never incorporated into a research tradition, since his lattice image was very difficult to manipulate mathematically.

in which they actually constructed their atomistic theories, the situation looks somewhat different. In fact, the chemical-atomistic world of the first half of the nineteenth century exhibits good examples of what philosopher Rom Harré has called reticular theories: complex and tightly interconnected inferential webs of thought and action, consisting not just of hypotheses but also of testable consequences branching in many directions.[37] Even in the early nineteenth-century context, these reticular atomic theories, imperfect and incomplete though they may have been, still provided robust and heuristically important tools for the scientific construction of the chemical microworld, well beyond the reach of the Laplacian school of mathematical physics. The transdictive visualizations of the generation of physicists that followed Laplace—such as Ampère's imagined molecular electrical vortices as an explanation of the magnetic effects of electric currents, or Faraday's imagined chains of contiguous particles as an explanation of action at a distance—were, to be sure, heuristically invaluable to the individuals who conjured with them. However, they did not exhibit the high degree of reticulation that characterized contemporary theories of chemical atomism,[38] nor were any of these visions of the microworld widely shared across the specialist community, as was the case for the chemists.

Another significant watershed—essentially an acceleration of the intellectual movement that had begun with Dalton—arrived with the rise of the theories of valence and structure, which has been the particular focus of this book. We have seen that in the early 1850s, a (mostly) close-knit group of chemists developed a set of ideas that opened the door to an even more robust access to molecular reality, first by just a crack (with Williamson's ether theory of 1850–51), then a bit wider (with Frankland's, Kekulé's, Odling's, and Wurtz's broader suggestions, ca. 1852–55, concerning what became known as valence). To borrow Tyndall's phraseology, oxygen (for instance) was in the process transformed from the "penumbral haze" of a "numerical ratio" into the "image" of a "particle," more particularly into an existential (chemical) atom. Then, by the spring of 1858 we find brave explorations of atomic linkages of not just oxygen, but of carbon, hydrogen, nitrogen, chlorine, and sulfur atoms in the papers of Kekulé and Couper.

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[37] Harré, *Matter and Method* (1964), 9–18, 57–58; Klein, *Tools and Modes of Representation* (2001), esp. chaps. 1 and 2; *CA,* chap. 1.

[38] I do not want to imply a binary judgment here. Imagine a linear scale of ad-hoc-ness such that the extreme left is utterly ad hoc, and the extreme right is completely reticulated. I simply suggest that early nineteenth-century theories of chemical atomism can be placed significantly further to the right on this scale than the contemporary visual transdictions of physicists.

The chemical community closed ranks behind these innovators with surprisingly little hesitation, and within a few years many chemists were boldly and productively drawing detailed paper pictures of the microworld, corresponding roughly to the ideas and images of the molecular world that were buzzing around in their heads. To speak in Christopher Ritter's fine metaphor, paper provides a two-dimensional window through which the mind's eye can gaze on the microworld. The window-glass is by no means transparent, but neither is it opaque; what we can achieve is conditioned both by the window itself and by what our imagination can discern through it.[39] Guided by those mental images, in a few short years Hofmann's pretty little mountain brook of organic chemistry became a mighty river, and our world has never been the same since.

Ritter's metaphor raises a final point that should be clarified. The evidence that I have presented here suggests the importance of mental images for the science of chemistry in the nineteenth century, but in exploring this aspect of scientific thought I do not underestimate the significance of purely logical heuristics, such as the use of symbolic systems that may not necessarily be accompanied by mental images—for instance, chemical formulas manipulated in the style of mathematical equations. When chemists, then and now, look at (and through) their paper images, I believe that they use their imaginations, as well as what Klein and others have investigated as "paper tools" in a more purely logical sense.[40] Chemists used (and use) either, or both, depending on context, circumstances, and individual predilection. I have not made a systematic attempt to disentangle the two, although at many points in this book one can clearly see one or the other of these two methods in operation. At least for this subject matter, such a systematic separation is in principle a daunting task when one examines specific historical personalities in specific historical moments. My efforts were directed primarily at the first phenomenon, the heurism of mental images, which I believe has hitherto escaped appropriate scholarly attention.

A similar opposition has been examined in the history of physics. John Norton, for example, has studied Einstein's shift from a more physical-intuitive to a more mathematical-formalist cognitive strategy in the course of his investigative pathway from special to general

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[39] Ritter, "Early History" (2001), 43. Stephen Weininger has employed an equally attractive metaphor in making a persuasive argument for the cognitive importance of visually relevant symbolic language in chemistry: "Contemplating the Finger" (1998).

[40] Klein, *Experiments, Models, Paper Tools;* Chadarevian and Hopwood, *Models* (2004). I thank Dr. Klein for a helpful and stimulating discussion on this point.

relativity, and then in pursuit of a unified field theory. Both strategies played positive heuristic roles at different historical moments, though Norton showed that there were times when one or the other would prove distinctly more productive. And the two strategies form a nice parallel with the "mental images" versus "paper tools" approaches that apply in the case of chemistry. But the sources that allow the historian at least partially to disentangle the intuitive from the formalist approaches are surely richer for theoretical physics, since as a mathematical discipline its purely cognitive development can be followed in greater detail than for chemistry.[41]

In his battle with the defenders of "energetics" in 1895, when the physicist Boltzmann cast about for a decisive example to demonstrate the fruitfulness of atomic theory against the aridity of a sterile positivism, he could find no better example than that provided by organic chemists, "who deduce the possible number of isomeric compounds, or the property of rotating the plane of polarized light, directly from the picture that they make for themselves of the arrangements of the atoms."[42] The epigraph by Wilfred Farrar at the head of this chapter states the matter baldly, but not unfairly. The naïvely pictorial propensity of some Cartesians in the early eighteenth century was scorned by leading chemists of Lavoisier's generation; no wonder there was resistance in the nineteenth century to the revival of such a tradition. However, by the latter part of that century chemists no longer blushed to draw their pretty pictures and build their pretty models of the unseen entities upon which they routinely operated. There is irony in the circumstance that a long-abandoned and putatively naïve approach to chemical philosophy had once more become the theoretical lifeblood of the science.

I hope that this examination of the use of the visual imagination by chemists in the nineteenth century has suggested something of the importance of the subject. Although the methodological problem of historical access is a challenging one, the topic richly deserves further investigation in concrete phenomenal terms, which is a call for careful history. Such a fuller investigation may reveal that the "linguistic turn" that twentieth-century philosophy and humanistic theory experienced might stand in need of a new course correction—an "imagistic turn." If so, there can be no better subject from which to extract concrete examples of productive use of the interconnected world of images,

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[41] Norton, "Nature Is the Realization" (2000), 151–52.

[42] Boltzmann, *Populäre Schriften* (1905), 140.

models, and “paper tools” than the crucial period in the history of science when chemists first began to be convinced of the reality of their mental representations, and charted a path to show all scientists how best to explore the world beyond the immediate reach of the senses. In this way, the history of chemistry might contribute to a fuller understanding of the creative powers of the human mind.

Bibliography

ARCHIVAL LOCATIONS

Aschaffenburg: Erlenmeyer-Nachlass, Hugo-Dingler-Archiv, Hofbibliothek Schloss Johannisburg
Berlin: Archiv, Berlin-Brandenburgische Akademie der Wissenschaften
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Göttingen: Wöhler Nachlass, Niedersächsische Staats- und Universitätsbibliothek
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Leipzig: Universitätsarchiv
London: Archives, D.M.S. Watson Library, University College London
London: H. E. Roscoe Collection, Royal Society of Chemistry
Milton Keynes: Edward Frankland Archive, Open University
Munich: Archiv, Deutsches Museum
Munich: Sammlung Liebigiana, Bayerische Staatsbibliothek

BIBLIOGRAPHY OF PRIMARY SOURCES

Anonymous. *Berichte der Durstigen Chemischen Gesellschaft.* Berlin: Friedländer, 1886.

Baeyer, Adolf. “Ueber die Condensationsproducte des Acetons.” *Annalen der Chemie* 140 (1866): 297–306.

———. “Ueber Condensation und Polymerie.” *Annalen der Chemie,* suppl. 5 (1867): 79–95.

———. *Ueber die chemische Synthese, Festrede . . .* Munich, 1878.

———. "Vorfeier des 70. Geburtstages von Adolf von Baeyer." *Zeitschrift für angewandte Chemie* 18 (1905): 1617–22.

———. *Erinnerungen aus meinem Leben*. Braunschweig: Vieweg, 1905.

———. *Gesammelte Werke*. 2 vols. Braunschweig: Vieweg, 1905.

Beilstein, Friedrich. Review of Kekulé, *Lehrbuch der organischen Chemie,* vol. 1. *Göttingische Gelehrte Anzeigen* 13 (1863): 493–506.

Beilstein, Friedrich, and F. Schlun. "Vierte Abhandlung: Ueber die isomeren Chlorbenzoësäuren." *Annalen der Chemie* 133 (1865): 239–52.

Berthollet, Claude-Louis. *Essai de statique chimique*. 2 vols. Paris: Didot, 1803.

Berzelius, Jacob. *Lehrbuch der Chemie*. 3rd ed. 10 vols. Dresden: Arnold, 1833–41.

———. *Berzelius und Liebig: Ihre Briefe von 1831–1845*. 2nd ed. Edited by J. Carrière. Munich: Lehmann, 1898.

———. *Briefwechsel zwischen J. Berzelius und F. Wöhler,* 2 vols. Edited by O. Wallach. Leipzig: Engelmann, 1901.

———. *Jac. Berzelius bref*. 6 vols. Edited by H. G. Söderbaum. Uppsala: Almqvist & Wiksell, 1912–61.

Boltzmann, Ludwig. *Populäre Schriften*. Leipzig: Barth, 1905.

Brock, W. H., ed. *Justus von Liebig und August Wilhelm Hofmann in ihren Briefen (1841–1873)*. Weinheim: Verlag Chemie, 1984.

Brodie, Benjamin C., Jr. "Observations on the Constitution of the Alchohol-Radicals." *Journal of the Chemical Society* 3 (1850): 405–11.

———. "On the Mode of Representation Afforded by the Chemical Calculus, as Contrasted with the Atomic Theory." *Chemical News* 15 (1867): 295–305.

Brodie, Benjamin C., Sr. Address by the president. *Proceedings of the Royal Society* 10 (1859): 161–70.

Butlerov, Aleksandr M. "Bemerkungen über A. S. Couper's neue chemische Theorie." *Annalen der Chemie* 110 (1859): 51–66.

———. "Einiges über die chemische Structur der Körper." *Zeitschrift für Chemie* 4 (1861): 549–60.

———. "Ueber die Verwandtschaft der mehraffinen Atome." *Zeitschrift für Chemie* 5 (1862): 297–304.

———. "Studien über die einfachsten Verbindungen der organischen Chemie." *Zeitschrift für Chemie* 6 (1863): 484–97.

———. "Ueber die verschiedenen Erklärungsweisen einiger Fälle von Isomerie." *Zeitschrift für Chemie* 6 (1863): 500–534.

———. "Ueber den tertiären Pseudobutylalkohol." *Zeitschrift für Chemie* 7 (1864): 385–402.

———. "Ueber die systematische Anwendung des Princips der Atomigkeit zur Prognose von Isomerie- und Metameriefällen." *Zeitschrift für Chemie* 7 (1864): 513–32.

———. *Vvedenie k polnomu izucheniiu organicheskoi khimii*. Kazan, 1864–66. Translated as *Lehrbuch der organischen Chemie* (Leipzig: Quandt & Händel, 1868).

———. “Ueber die Derivate von Trimethylcarbinol.” *Annalen der Chemie* 144 (1867): 1–32.

———. “Eine Antwort.” *Annalen der Chemie* 146 (1868): 260–63.

———. “Istoricheskii ocherk razvitiia khimii v poslednie 40 let” [“Historical Sketch of the Development of Chemistry in the last 40 Years,” written 1879]. In *A. M. Butlerov: Sochineniia [Collected Works],* edited by B. A. Kazanskii et al., 3:167–280. Moscow: Akademiia Nauk SSSR, 1958.

———. *A. M. Butlerov: Izbrannye raboty po organicheskoi khimii [Selected Works on Organic Chemistry].* Edited by G. V. Bykov et al. Moscow: Akademiia Nauk SSSR, 1951.

———. *A. M. Butlerov: Sochineniia [Collected Works].* 3 vols. Edited by B. A. Kazanskii et al. Moscow: Akademiia Nauk SSSR, 1953–58.

Cannizzaro, Stanislao. “Sunto di un corso di filosofia chimica.” *Il nuovo cimento* 7 (1858): 321–66. Translated as *Sketch of a Course of Chemical Philosophy* (Edinburgh: Alembic Club, 1910).

———. “Considerations on Some Points of the Theoretic Teaching of Chemistry.” *Journal of the Chemical Society* 25 (1872): 941–67.

Chapman, Ernest, and William Thorp. “On the Relation between the Products of Gradual Oxidation and the Molecular Constitution of the Bodies Oxidised.” *Journal of the Chemical Society* 19 (1866): 477–99.

Clausius, Rudolf. “Ueber die Art der Bewegung, welche wir Wärme nennen.” *Annalen der Physik* [2] 100 (1857): 353–80.

———. “Ueber die Natur des Ozons.” *Annalen der Physik* [2] 103 (1858): 644–52.

Couper, Archibald S. “Recherches sur la benzine.” *Comptes rendus de l’Académie des Sciences* 45 (1857): 230–32.

———. “Recherches sur l’acide salicylique.” *Comptes rendus de l’Académie des Sciences* 46 (1858): 1107–10.

———. “Sur une nouvelle théorie chimique.” *Comptes rendus de l’Académie des Sciences* 46 (1858): 1157–60.

———. “Sur une nouvelle théorie chimique.” *Annales de chimie et de physique* [3] 53 (1858): 469–89.

———. “On a New Chemical Theory.” *Philosophical Magazine* [4] 16 (1858): 104–16.

Crum Brown, Alexander. *On the Theory of Chemical Combination.* M.D. thesis, University of Edinburgh, 1861. Published verbatim by Edinburgh: Neill, 1879.

———. “On the Theory of Isomeric Compounds.” *Transactions of the Royal Society of Edinburgh* 23 (1864): 707–19.

———. “On the Use of Graphic Representations of Chemical Formulae.” *Proceedings of the Royal Society of Edinburgh* 5 (3 April 1865): 429–31.

———, ed. *Testimonials in favour of Alexander Crum Brown.* Edinburgh: Muir and Paterson, 1869.

Curtius, Theodor. *Robert Bunsen als Lehrer in Heidelberg.* Heidelberg: Hörning, 1906.

Darwin, Charles. *Autobiography of Charles Darwin.* New York: Appleton, 1892.

Dumas, Jean-Baptiste. *Leçons de philosophie chimique.* Paris: Bechet, 1837.

———. “Mémoire sur la constitution de quelques corps organiques et sur la théorie des substitutions.” *Comptes rendus de l’Académie des Sciences* 8 (1839): 609–22.

———. “Note sur la constitution de l’acide acétique et de l’acide chloracétique.” *Comptes rendus de l’Académie des Sciences* 9 (1839): 813–15.

———. “Premier mémoire sur les types chimiques.” *Annales de chimie et de physique* [2] 73 (1840): 73–100.

———. “Mémoire sur la loi des substitutions et la théorie des types.” *Comptes rendus de l’Académie des Sciences* 10 (1840): 149–78.

Erlenmeyer, Emil. “Vorläufige Notiz über eine etwas abgeänderte Betrachtungsweise der Alkohole und ihrer Derivate.” *Zeitschrift für Chemie* 4 (1861): 202–4.

———. “Die Theorie.” *Zeitschrift für Chemie* 5 (1862): 18–32.

———. “Bemerkungen zu der vorstehenden Abhandlung.” *Zeitschrift für Chemie* 5 (1862): 218–23.

———. “Bemerkungen zu den beiden vorstehenden Abhandlungen.” *Zeitschrift für Chemie* 6 (1863): 21–22.

———. “Betrachtungen über Aequivalent, Atom, Molekül und Volum.” *Zeitschrift für Chemie* 6 (1863): 65–75, 97–104, 609–20.

———. “Vorläufige Notiz über das Verhältniss der Kolbe’schen Betrachtungsweise zu der sog. Typentheorie.” *Zeitschrift für Chemie* 6 (1863): 728–35.

———. “Hypothesen über chemische Isomerie und chemische Constitution.” *Zeitschrift für Chemie* 7 (1864): 1–30.

———. “Ueber die Sättigungscapacität (Atomigkeit) der Elemente, Vorläufige Notiz.” *Zeitschrift für Chemie* 7 (1864): 628–35.

———. “Studien über die s.g. aromatischen Säuren.” *Annalen der Chemie* 137 (March 1866): 327–59.

———. “Studien über den Process der Einwirkung von Jodwasserstoff auf Glycerin.” *Annalen der Chemie* 139 (August 1866): 211–34.

———. *Die Aufgabe des chemischen Unterrichts gegenüber den Anforderungen der Wissenschaft und Technik.* Munich: Bayerische Akademie der Wissenschaften, 1871.

Fischer, Emil. *Gesammelte Werke.* 4 vols. Berlin: Springer, 1924.

Fischer, G. “Ueber Paranitrobenzoësäure.” *Annalen der Chemie* 127 (1863): 137–49.

Fittig, Rudolf. “Vorläufige Mittheilung über die Oxydationsproducte des Mesitylens.” *Zeitschrift für Chemie* 9 (1866): 518–21.

———. “Untersuchungen über das Mesitylen.” *Annalen der Chemie* 141 (1867): 129–58.

Foster, George Carey. “Preliminary Report on the Recent Progress and Present State of Organic Chemistry.” *Report of the British Association for the Advancement of Science* 29 (1859): 1–22.

Frankland, Edward. “On the Isolation of the Organic Radicals.” *Journal of the Chemical Society* 2 (1849): 263–96.

———. “On a New Series of Organic Bodies Containing Metals and Phosphorus.” *Journal of the Chemical Society* 2 (1849): 297–99.

———. “Researches on the Organic Radicals.” *Journal of the Chemical Society* 3 (1850): 30–52, 322–47.

———. “On a New Series of Organic Bodies Containing Metals.” *Philosophical Transactions of the Royal Society* 142 (1852): 417–44.

———. “Contributions to the Notation of Organic and Inorganic Compounds.” *Journal of the Chemical Society* 19 (1866): 372–95.

———. *Lecture Notes for Chemical Students.* London: Van Voorst, 1866. 2nd ed., 2 vols., 1870–72.

———. *Experimental Researches in Pure and Applied Chemistry.* London: Van Voorst, 1877.

———. *Sketches from the Life of Edward Frankland.* London: Spottiswoode, 1901.

Frankland, Edward, and B. F. Duppa. “Researches on Acids of the Lactic Series.” *Philosophical Transactions of the Royal Society* 156 (1866): 309–59.

———. “Synthetical Researches on Ethers.” *Journal of the Chemical Society* 20 (1867): 102–16.

Friedel, Charles. “Transformation des aldéhydes et des acétones en alcools.” *Comptes rendus de l’Académie des Sciences* 55 (1862): 53–58.

———. “Sur l’alcool dérivé de l’acétone par l’action de l’hydrogène naissant.” *Bulletin de la Société Chimique* 2 (1863): 247–48.

Gerhardt, Charles. “Recherches sur les acides organiques anhydres.” *Comptes rendus de l’Académie des Sciences* 34 (1852): 755–58, 902–5. Also appeared in *Annales de chimie et de physique* [3] 37 (1853): 285–342.

———. “Note sur la théorie des amides.” *Comptes rendus de l’Académie des Sciences* 37 (1853): 281–84.

———. *Traité de chimie organique.* 4 vols. Paris: Didot, 1853–56.

Gerhardt, Charles, and L. Chiozza. “Addition aux recherches sur les acides anhydres.” *Comptes rendus de l’Académie des Sciences* 36 (1853): 1050–54.

———. “Recherches sur les amides.” *Comptes rendues de l’Académie des Sciences* 37 (1853): 86–90.

Graebe, Carl, and O. Born. “Ueber Hydrophtalsäure.” *Annalen der Chemie* 142 (1867): 330–45.

Graham, Thomas. “On the Law of the Diffusion of Gases.” *Philosophical Magazine* 2 (1833): 175–90, 269–76, 351–58.

———. “Researches on the Arseniates, Phosphates, and Modifications of Phosphoric Acid.” *Philosophical Transactions of the Royal Society,* 1833, 253–84.

———. “Observations on Etherification.” *Journal of the Chemical Society* 3 (1850): 24–28.

———. “Speculative Ideas Respecting the Constitution of Matter.” *Philosophical Magazine* [4] 27 (1864): 81–84.

———. *Chemical and Physical Researches.* Edited by R. A. Smith. Edinburgh: University Press, 1876.

Greiner, A., ed. *Chemiker über Chemiker: Wahlvorschläge zur Aufnahme von Chemikern in die Berliner Akademie.* Berlin: Akademie-Verlag, 1986.

Herschel, John. *Preliminary Discourse on the Study of Natural Philosophy.* London: Longman Green, 1830.

Hlasiwetz, H., and L. Barth. "Ueber einen neuen, dem Orcin homologen Körper." *Sitzungsberichte der Kaiserlichen Akademie der Wissenschaften, Wien* 49, no. 2 (1864): 203–7.

Hoff, J. H. van't. *Voorstel tot uitbreiding der tegenwoordig in de scheikunde gebruikte structuur-formules in de ruimte.* Utrecht: Greven, 1874.

———. "Sur les formules de structure dans l'espace." *Archives néerlandaises des sciences exactes et naturelles* 9 (1874): 445–54.

———. "Sur les formules de structure dans l'espace." *Bulletin de la Société Chimique* [2] 23 (1875): 295–301.

———. *La chimie dans l'espace.* Rotterdam: Bazendijk, 1875.

———. *Die Lagerung der Atome im Raume.* Braunschweig: Vieweg, 1877. 2nd ed., 1894.

———. "Über den Zusammenhang zwischen optischer Aktivität und Constitution." *Berichte der Deutschen Chemischen Gesellschaft* 10 (1877): 1620–23.

———. *De Verbeeldingskracht in de Wetenschap.* Rotterdam: Bazendijk, 1878. Translated by G. F. Springer as *Imagination in Science* (New York: Springer, 1967).

———. *Ansichten über die organische Chemie.* 2 vols. Braunschweig: Vieweg, 1878, 1881.

Hoffmann, Reinhold. "Ueber Monochloressigsäure." *Annalen der Chemie* 102 (1857): 1–20.

Hofmann, August Wilhelm. "Chemische Untersuchung der organischen Basen im Steinkohlen-Theeröl." *Annalen der Chemie* 47 (1843): 37–87.

———. "Note on the Action of Heat upon Valeric Acid." *Journal of the Chemical Society* 3 (1850): 121–34.

———. "On the Combining Power of Atoms." *Proceedings of the Royal Institution* 4 (1865): 401–30.

———. "Tischrede bei der Kekuléfeier." *Zeitschrift für Farben- und Textil-Chemie* 1 (1902): 1–2.

Kane, Robert. "On a Series of Combinations derived from Pyroacetic Spirit." *Transactions of the Royal Irish Academy* 18 (1837): 99–125.

Kekulé, August. "On a New Series of Suphuretted Acids." *Proceedings of the Royal Society* 7 (1854): 37–40.

———. "Notiz über eine neue Reihe schwefelhaltiger organischer Säuren." *Annalen der Chemie* 90 (1854): 309–16.

———. "Bildung von Glycolsäure aus Essigsäure." *Verhandlungen des naturhistorisch-medizinhistorischen Vereins Heidelberg* 1 (1857): 105–7.

———. “Ueber die Constitution des Knallquecksilbers.” *Annalen der Chemie* 101 (1857): 200–213.

———. “Ueber die s.g. gepaarten Verbindungen und die Theorie der mehratomigen Radicale.” *Annalen der Chemie* 104 (1857): 129–50.

———. “Ueber die Constitution des Knallquecksilbers.” *Annalen der Chemie* 105 (1858): 279–86.

———. “Ueber die Constitution und die Metamorphosen der chemischen Verbindungen und über die chemische Natur des Kohlenstoffs.” *Annalen der Chemie* 106 (1858): 129–59.

———. “Remarques de M. A. Kekulé à l’occasion d’une note de M. Couper sur une nouvelle théorie chimique.” *Comptes rendus de l’Académie des Sciences* 47 (1858): 378–80.

———. *Lehrbuch der organischen Chemie*. 2 vols. Erlangen: Enke. Fascicles of vol. 1 published in 1859, 1860, 1861; fascicles of vol. 2 published in 1863, 1864, 1866.

———. “Note sur l’action du brome sur l’acide succinique.” *Bulletin de l’Académie Royale de Belgique* [2] 10 (1860): 63–70.

———. “Faits pour compléter l’histoire de l’acide salicylique et de l’acide benzoique.” *Bulletin de l’Académie Royale de Belgique* [2] 10 (1860): 337–50.

———. “Beiträge zur Kenntniss der Salicylsäure und der Benzoësäure.” *Annalen der Chemie* 117 (1861): 145–64.

———. “Note sur les acides itaconique et pyrotartrique.” *Bulletin de l’Académie Royale de Belgique* [2] 11 (1861): 662–77.

———. “Untersuchungen über organische Säuren.” *Annalen der Chemie,* suppl. 2 (1862): 85–116.

———. “Betrachtungen über einige Fälle von Isomerie.” *Zeitschrift für Chemie* 6 (1863): 9–13.

———. “Sur l’atomicité des éléments.” *Comptes rendus de l’Académie des Sciences* 58 (1864): 510–14. Translated with editorial notes in *Zeitschrift für Chemie* 7 (1864): 689–94.

———. “Sur la constitution des substances aromatiques.” *Bulletin de la Société Chimique* [2] 3 (1865): 98–110.

———. “Note sur quelques produits de substitution de la benzine.” *Bulletin de l’Académie Royale de Belgique* [2] 19 (1865): 551–63.

———. “Untersuchungen über aromatische Verbindungen.” *Annalen der Chemie* 137 (1866): 129–96.

———. “On Some Points of Chemical Philosophy.” *Laboratory* 1 (July 1867): 303–6.

———. “Ueber die Constitution des Mesitylens.” *Zeitschrift für Chemie* 10 (1867): 214–18.

———. “Ueber einige Condensationsproducte des Aldehyds.” *Annalen der Chemie* 162 (1872): 77–123.

———. *Die wissenschaftlichen Ziele und Leistungen der Chemie*. Bonn: Cohen, 1878.

Kolbe, Hermann. "Untersuchungen über die Elektrolyse organischer Verbindungen." *Annalen der Chemie* 69 (1849): 257–94.

———. "Ueber die chemische Natur und Constitution der organischen Radicale." *Annalen der Chemie* 75 (1850): 211–39; and *Annalen der Chemie* 76 (1850): 1–73.

———. "On the Chemical Constitution and Nature of Organic Radicals." *Journal of the Chemical Society* 3 (1850): 369–405; and *Journal of the Chemical Society* 4 (1851): 41–79.

———. *Ausführliches Lehrbuch der organischen Chemie.* 3 vols. Braunschweig: Vieweg, 1854–78.

———. "Ueber die rationelle Zusammensetzung der fetten und aromatischen Säuren." *Annalen der Chemie* 101 (1857): 257–65.

———. "Ueber die Constitution und Basicität der Milchsäure." *Annalen der Chemie* 113 (1860): 223–38.

———. "Ueber den natürlichen Zusammenhang der organischen mit den unorganischen Verbindungen." *Annalen der Chemie* 113 (1860): 293–332.

———. "Ueber die chemische Constitution des aus dem Aceton durch nascirenden Wasserstoff erzeugten Alkohols." *Zeitschrift für Chemie* 5 (1862): 687–90.

———. "Ueber die Isomerie der Fumarsäure und Maleinsäure, sowie der Itaconsäure, Citraconsäure, und Mesaconsäure." *Zeitschrift für Chemie* 6 (1863): 13–21.

———. "Ueber die realen Typen der organischen Chemie." In *Das chemische Laboratorium der Universität Marburg,* 515–19. Braunschweig: Vieweg, 1865.

———. "Ueber einige Abkömmlinge des Cyanamids." *Journal für praktische Chemie* 109 (1870): 288–306.

———. "Ueber die Structurformeln und die Lehre von der Bindung der Atome." *Journal für praktische Chemie* 111 (1871): 127–36.

———. "Chemischer Rückblick auf das Jahr 1873." *Journal für praktische Chemie* 116 (1874): 417–25.

———. "Chemischer Rückblick auf das Jahr 1874." *Journal für praktische Chemie* 118 (1875): 449–56.

———. "Zeichen der Zeit: II." *Journal für praktische Chemie* 123 (1877): 473–77.

———. "Kritik der Rectoratsrede von August Kekulé." *Journal für praktische Chemie* 125 (1878): 139–56.

———. "Die chemische Synthese, ein chemischer Traum." *Journal für praktische Chemie* 126 (1878): 432–55.

———. "Meine Betheiligung an der Entwickelung der theoretischen Chemie." *Journal für praktische Chemie* 131 (1881): 305–23, 353–79, 497–517; *Journal für praktische Chemie* 132 (1881): 374–425.

———. "Kritisch-chemische Gänge IV." *Journal für praktische Chemie* 136 (1883): 356–82.

———. "Die realen Typen der organischen Verbindungen." *Journal für praktische Chemie* 136 (1883): 440–47.

———. *Kurzes Lehrbuch der organischen Chemie*. Braunschweig: Vieweg, 1883.

Kolbe, Hermann, and E. Lautemann. “Ueber die Constitution und Basicität der Salicylsäure.” *Annalen der Chemie* 115 (1860): 157–206.

Kopp, Hermann. *Geschichte der Chemie*. 4 vols. Braunschweig: Vieweg, 1843–47.

———. “Ueber die specifischen Volume flüssiger Verbindungen.” *Annalen der Chemie* 92 (1854): 1–32.

———. *Sonst und Jetzt in der Chemie: Ein populär-wissenschaftlicher Vortrag*. Braunschweig: Vieweg, 1867.

———. *Beiträge zur Geschichte der Chemie*. Braunschweig: Vieweg, 1869, 1875.

———. *Entwickelung der Chemie in der neueren Zeit*. Munich: Oldenbourg, 1873.

———. *Die Alchemie in älterer und neuerer Zeit*. Heidelberg: Winter, 1886.

———. *Aus der Molecular-Welt*. Heidelberg: Winter, 1882. 3rd ed., 1886.

Körner, Wilhelm. “Sur quelques dérivés de l’acide phénique.” *Bulletin de l’Académie Royale de Belgique* [2] 20 (1865): 135–48.

———. “Synthèse de la résorcine.” *Comptes rendus de l’Académie des Sciences* 63 (1866): 564–66.

———. “Faits pour servir à la détermination du lieu chimique dans la série aromatique.” *Bulletin de l’Académie des Sciences de Belgique* [2] 24 (1867): 166–85.

———. “Fatti per servire alla determinazione del luogo chimico nelle sostanze aromatiche.” *Giornale de scienze naturali ed economiche* 5 (1869): 208–56.

———. “Studj sull’isomeriea delle cosi dette sostanze aromatiche.” *Gazzetta chimica italiana* 4 (1874): 305–446.

Krönig, A. “Grundzüge einer Theorie der Gase.” *Annalen der Physik* [2] 99 (1856): 315–22.

Laurent, Auguste. “Sur la série naphthalique.” *Revue scientifique* 14 (1843): 74–113.

———. *Méthode de chimie*. Paris: Mallet-Bachelier, 1854.

LeBel, Joseph Achille. “Sur les relations qui existent entre les formules atomiques des corps organiques et le pouvoir rotatoire de leurs dissolutions.” *Bulletin de la Société Chimique* [2] 22 (1874): 337–47.

Liebig, Justus. *Aus Justus Liebig’s und Friedrich Wöhler’s Briefwechsel in den Jahren 1829–1873*. Edited by A. W. Hofmann. 2 vols. Braunschweig: Vieweg, 1888.

———. *Experimentalchemie . . . aufgeschrieben seitens A. Kekulé, stud. chem., 1848*. [Berlin]: [AGFA], [1927].

———. “Eigenhändige biographische Aufzeichnungen.” In *Justus von Liebig in eigenen Zeugnissen,* edited by H. von Dechend. 2nd ed. Weinheim: Verlag Chemie, 1963.

Limpricht, Heinrich. “Einige Bemerkungen zu der von A. Kekulé veröffentlichten Abhandlung ‘Ueber die s.g. gepaarten Verbindungen und die Theorie der mehratomigen Radicale.’” *Annalen der Chemie* 105 (1858): 177–86.

Limpricht, Heinrich, and L. von Uslar. “Ueber die Sulfobenzoësäure.” *Annalen der Chemie* 102 (1857): 239–59.

Loschmidt, Joseph. *Chemische Studien I: A. Constitutions-Formeln der organischen Chemie in graphischer Darstellung.* Vienna, 1861. Reprinted as *Konstitutions-Formeln der organischen Chemie in graphischer Darstellung.* Edited by R. Anschütz. Leipzig: Engelmann, 1913. Facsimile edition of the latter: Milwaukee: Aldrich Chemical Co., 1989.

Mansfield, Charles. "Researches on Coal Tar." *Journal of the Chemical Society* 1 (1848): 244–68.

Markovnikov, V. V. "Zur Geschichte der Lehre über die chemische Structur." *Zeitschrift für Chemie* 8 (1865): 280–87.

Mendius, Otto. "Ueber gepaarte Säuren und insbesondere über Sulfosalicylsäure." *Annalen der Chemie* 103 (1857): 39–80.

Meyer, Lothar. "Zur Abwehr." *Annalen der Chemie* 145 (1868): 124–27.

Meyer, Richard. *Einleitung in das Studium der aromatischen Verbindungen.* Heidelberg: Winter, 1882.

Mitscherlich, Eilhard. *Lehrbuch der Chemie.* 4th ed. 2 vols. Berlin: Mittler, 1843–47.

Naquet, Alfred. "Sur l'atomicité de l'oxigène, du soufre, du sélénium et du tellure." *Comptes rendus de l'Académie des Sciences* 58 (1864): 381–83.

———. "Sur l'atomicité des éléments." *Comptes rendus de l'Académie des Sciences* 58 (1864): 675–78.

Odling, William. "On the Constitution of Acids and Salts." *Journal of the Chemical Society* 7 (1854): 1–22.

———. "On the Constitution of the Hydro-carbons." *Proceedings of the Royal Institution* 2 (1855): 63–66.

———. Comment. *Chemical News* 78 (1898): 286.

Pasteur, Louis. "Mémoire sur la relation qui peut exister contre la forme crystalline et la composition chimique, et sur la cause de la polarisation rotatoire." *Comptes rendus de l'Académie des Sciences* 26 (1848): 535–38.

———. "Recherches sur la dissymétrie moléculaire des produits organiques naturels." In *Leçons de chimie professées en 1860.* Paris: Hachette, 1861.

———. *Researches on the Molecular Asymmetry of Natural Organic Products.* Edinburgh: Alembic Club, 1905.

Paternò, E. "Intorno all'azione del percloruro di fosforo sul clorale." *Giornale di scienze naturali ed economiche de Palermo* 5 (1869): 117–22.

Reichenbach, E., and F. Beilstein. "Dritte Abhandlung: Ueber die Natur der sogenannten Salylsäure." *Annalen der Chemie* 132 (1864): 309–21.

Schmitt, Rudolf. "Ueber die Umwandlung der Weinsäure und Apfelsäure in Bernsteinsäure." *Annalen der Chemie* 114 (1860): 106–11.

Schultz, Gustav. "Bericht über die Feier der Deutschen Chemischen Gesellschaft zu Ehren August Kekulé's." *Berichte der Deutschen Chemischen Gesellschaft* 23 (1890): 1265–1312.

———. "A.W. v. Hofmanns Tischrede bei der Kekuléfeier." *Zeitschrift für Farben- und Textil-Chemie* 1 (1902).

Simpson, Maxwell. “On the Synthesis of Succinic and Pyrotartaric Acids.” *Proceedings of the Royal Society* 11 (1861): 190–92.

Strecker, Adolf. “Ueber die künstliche Bildung der Milchsäure.” *Annalen der Chemie* 75 (1850): 27–45.

Tollens, B., and R. Fittig. “Ueber die Synthese der Kohlenwasserstoffe der Benzolreihe.” *Annalen der Chemie* 131 (1864): 303–23.

Tyndall, John. *Fragments of Science.* London: Longmans Green, 1871. 2nd ed. 2 vols. New York: Appleton, 1892.

Waterston, J. J. *Thoughts on the Mental Functions.* Edinburgh, 1843.

———. “On a General Theory of Gases.” *Report of the British Association for the Advancement of Science* 21 (1851): 6.

Whewell, William. *Philosophy of the Inductive Sciences.* 2 vols. London: Parker, 1840.

Wilbrand, J., and F. Beilstein. “Ueber eine neue Reihe isomerer Verbindungen der Benzoëgruppe, Nitrodracylsäure und deren Derivate.” *Annalen der Chemie* 128 (1863): 257–73.

Will, Heinrich. “Zur Theorie der Constitution organischer Verbindungen.” *Annalen der Chemie* 91 (1854): 257–92.

Williamson, Alexander. “Theory of Aetherification.” Abstract in *Report of the British Association for the Advancement of Science* 20 (1850): 2:65; full paper in *Philosophical Magazine* [3] 37 (1850): 350–56.

———. “Suggestions for the Dynamics of Chemistry derived from the Theory of Etherification.” *Proceedings of the Royal Institution* 1 (1851): 90–94.

———. “On Etherification.” *Journal of the Chemical Society* 4 (1851): 229–39.

———. “On the Constitution of Salts.” Abstract in *Report of the British Association for the Advancement of Science* 21 (1851): 2:54; full paper in *Journal of the Chemical Society* 4 (1851): 350–55.

———. “Sur la théorie de l’étherification,” *Annales de chimie et de physique* [3] 40 (1854): 98–114.

———. “On Dr. Kolbe’s Additive Formulae.” *Journal of the Chemical Society* 7 (1854): 122–39.

———. “Note on the Decomposition of Sulphuric Acid by Pentachloride of Phosphorus.” *Proceedings of the Royal Society* 7 (1856): 11–15.

———. Address to the Chemical Section, British Association for the Advancement of Science. *Chemical News* 8 (1863): 118–20.

———. *Chemistry for Students.* Oxford: Clarendon Press, 1865.

———. Presidential address. *Chemical News* 14 (1866): 17–18.

———. “The Late Professor Graham.” *Nature* 1 (1869): 20–22.

Wislicenus, Johannes. “Studien zur Geschichte der Milchsäure und ihrer Homologen.” *Annalen der Chemie* 128 (1863): 1–67.

———. “Ueber die optisch-active Milchsäure der Fleischflüssigkeit, die Paramilchsäure.” *Annalen der Chemie* 167 (1873): 302–46.

Wollaston, William H. “On Super-Acid and Sub-Acid Salts.” *Philosophical Transactions of the Royal Society* 98 (1808): 96–102.

———. “On the Elementary Particles of Certain Crystals.” *Philosophical Transactions of the Royal Society* 103 (1813): 51–63.

Wurtz, Adolphe. “Recherches sur l’acide sulfophosphorique et le chloroxyde de phosphore.” *Annales de chimie et de physique* [3] 20 (1847): 480–81.

———. “Mémoire sur une série d’alcaloïdes homologues avec l’ammoniac.” *Annales de chimie et de physique* 30 (1850): 443–507.

———. “Sur les dédoublements des éthers cyaniques.” *Comptes rendus de l’Académie des Sciences* 37 (1853): 180–83.

———. “Sur la théorie des amides.” *Comptes rendus de l’Académie des Sciences* 37 (1853): 246–50.

———. “Nouvelles observations sur la théorie des amides.” *Comptes rendus de l’Académie des Sciences* 37 (1853): 357–61.

———. “Théorie des combinaisons glycériques.” *Annales de chimie et de physique* [3] 43 (1855): 492–96.

———. “Sur une nouvelle classe de radicaux organiques.” *Comptes rendus de l’Académie des Sciences* 40 (1855): 1885–88; *Annales de chimie et de physique* [3] 44 (1855): 275–313.

———. “Sur le glycol ou alcool diatomique.” *Comptes rendus de l’Académie des Sciences* 43 (1856): 199–204.

———. “Note sur l’aldéhyde et sur le chlorure d’acétyle.” *Annales de chimie et de physique* [3] 49 (1857): 58–62.

———. “Mémoire sur la constitution et sur la vrai formule de l’acide oxalique.” *Comptes rendus de l’Académie des Sciences* 44 (1857): 1306–10.

———. “Recherches sur l’acide lactique.” *Comptes rendus de l’Académie des Sciences* 45 (1857): 1228–32.

———. “Sur un nouvel acide lactique.” *Comptes rendus de l’Académie des Sciences* 45 (1857): 1232–34.

———. “Recherches sur la constitution de l’acide lactique.” *Bulletin de la Société Chimique* 1 (1859): 36–46.

———. “Nouvelles recherches sur l’acide lactique.” *Comptes rendus de l’Académie des Sciences* 48 (1859): 1092–94.

———. “Mémoire sur les glycols ou alcools diatomiques.” *Annales de chimie et de physique* [3] 55 (1859): 400–478.

———. “Recherches sur l’acide lactique.” *Annales de chimie et de physique* [3] 59 (1860): 161–91.

———. “Sur l’atomicité des éléments.” *Bulletin de la Société Chimique* [2] 2 (1864): 247–53.

———. *Cours de philosophie chimique.* Paris: Renou et Maulde, 1864.

———. *Leçons de philosophie chimique.* Paris: Hachette, 1864. Published simultaneously as *Leçons de chimie professées en 1863* (Paris: Hachette, 1864).

———. “Histoire des doctrines chimiques depuis Lavoisier,” in *Dictionnnaire de chimie pure et appliqué,* vol. 1 (Paris: Hachette, 1868).

———. *Histoire des doctrines chimiques depuis Lavoisier jusqu’à nos jours.* Paris: Hachette, 1869.

———. *La théorie des atomes dans la conception générale du monde.* Paris: Masson, 1875.

———. *La théorie atomique.* Paris: Baillière, 1879.

Wurtz, Adolphe, and Charles Friedel. "Mémoire sur l'acide lactique." *Annales de chimie et de physique* [3] 63 (1861): 101–24.

Zaitsev, Konstantin. "Ueber Paraoxybenzoësäure." *Annalen der Chemie* 127 (1863): 129–37.

Zinin, Nikolai. "Ueber desoxydirtes Benzoin, ein Product der Einwirkung des Wasserstoffs auf Benzoin." *Annalen der Chemie* 126 (1863): 218–24.

BIBLIOGRAPHY OF SECONDARY SOURCES

Abir-Am, Pnina, and C. A. Elliott, eds. *Commemorative Practices in Science. Osiris* 14 (1999).

Anonymous. Obituary of Hermann Kopp. *Chemiker-Zeitung* 16 (1892): 271.

Anonymous. Obituary of George Carey Foster. *Journal of the Chemical Society* 115 (1919): 413–27.

Anonymous. "Developer of Key Theory May Have Been a Fraud." *Chronicle of Higher Education,* 10 October 1984, A6.

Anschütz, Richard. "Life and Chemical Work of Archibald Scott Couper." *Proceedings of the Royal Society of Edinburgh* 29 (1909): 193–273.

———. *August Kekulé.* Vol. 1, *Leben und Wirken.* Berlin: Verlag Chemie, 1929.

———, ed. *August Kekulé.* Vol. 2, *Abhandlungen, Berichte, Kritiken, Artikel, Reden.* Berlin: Verlag Chemie, 1929.

Armstrong, Henry E. "The Doctrine of Atomic Valency." *Nature* 125 (1930): 807–10.

Arnheim, Rudolf. *Visual Thinking.* University of California Press, 1969.

Bachelard, Gaston. *Les intuitions atomistiques.* 2nd ed. Paris: Vrin, 1975.

Baker, A. Albert, Jr. *Unsaturation in Organic Chemistry.* Boston: Houghton-Mifflin, 1968.

Bauer, Alexander. "Zur Erinnerung an J. Loschmidt." *Oesterreichische Chemiker-Zeitung* 16 (1913): 241–42.

———. "Erinnerungen." *Oestereichische Chemiker-Zeitung* 22 (1919): 117.

Beller, Mara. "Jocular Commemorations: The Copenhagen Spirit." *Osiris* 14 (1999): 252–73.

Benfey, O.Theodor, trans. "August Kekulé and the Birth of the Structural Theory of Organic Chemistry in 1858." *Journal of Chemical Education* 35 (1958): 21–23.

———, ed. *Classics in the Theory of Chemical Combination.* New York: Dover, 1963.

———. *From Vital Force to Structural Formulas.* Boston: Houghton-Mifflin, 1964.

———, ed. *Kekulé Centennial.* Washington, D.C.: American Chemical Society, 1966.

Bensaude-Vincent, Bernadette. "Karlsruhe, septembre 1860." *Relations internationales* 62 (1990): 149–69.

Berson, Jerome A. *Chemical Creativity: Ideas from the Work of Woodward, Hückel, Meerwein, and Others*. Weinheim: Wiley-VCH, 1999.

———. *Chemical Discovery and the Logicians' Program: A Problematic Pairing.* Weinheim: Wiley-VCH, 2003.

Bessmertny, Bertha. "Hermann Kopp als Chemiker." *Archeion* 14 (1932): 62–68.

Bhushan, Nalini, and Stuart Rosenfeld, eds. *Of Minds and Molecules: New Philosophical Perspectives on Chemistry.* Oxford: Oxford University Press, 2000.

Boden, Margaret. *The Creative Mind: Myths and Mechanisms.* New York: Basic Books, 1991.

———, ed. *Dimensions of Creativity.* Cambridge, MA: MIT Press, 1994.

Borman, Stu. "19th-Century Chemist Kekulé Charged with Scientific Misconduct." *Chemical & Engineering News,* 23 August 1993, 20–21.

Brock, William H., ed. *The Atomic Debates: Brodie and the Rejection of the Atomic Theory.* Leicester: Leicester University Press, 1967.

———. "August Kekulé (1829–96): Theoretical Chemist." *Endeavour* 20 (1996): 121–25.

———. "Alexander W. Williamson," in *Dictionary of Nineteenth-Century British Scientists,* 2168–75. Chicago: University of Chicago Press, 2004.

Brock, William H., O. T. Benfey, and S. Stark. "Hofmann's Benzene Tree at the Kekulé Festivities." *Journal of Chemical Education* 68 (1991): 887–88.

Bronowski, Jacob. *The Visionary Eye: Essays in the Arts, Literature, and Science.* Cambridge, MA: MIT Press, 1978.

Brooke, John. "Doing Down the Frenchies: How Much Credit Should Kekulé Have Given?" In *The Kekulé Riddle,* edited by John Wotiz, 59–76. Clearwater, FL: Cache River Press, 1993.

Brooks, Nathan. "Alexander Butlerov and the Professionalization of Science in Russia." *Russian Review* 57 (1998): 10–24.

Brush, Stephen. *The Kind of Motion We Call Heat.* 2 vols. Amsterdam: North Holland, 1976.

———. "Dynamics of Theory Change in Chemistry, Part 1: The Benzene Problem, 1865–1945." *Studies in History and Philosophy of Science* 30 (1999): 21–79.

Buchwald, Jed. "How the Ether Spawned the Microworld." In *Biographies of Scientific Objects,* edited by L. Daston, 203–25. University of Chicago Press, 2000.

Buchwald, Jed, and Sam Schweber. "Conclusion." In *Scientific Practice,* edited by Jed Buchwald, 345–51. University of Chicago Press, 1995.

Buckley, Arabella. *The Fairyland of Science.* New York: Hurst, [1879].

Bud, Robert F. "The Discipline of Chemistry: The Origins and Early Years of the Chemical Society of London." Ph.D. diss., University of Pennsylvania, 1980.

Bykov, G. V. "The Origin of the Theory of Chemical Structure." *Journal of Chemical Education* 39 (1962): 220–24.

———. *Istoriia organicheskoi khimii [History of Organic Chemistry].* Moscow: Izd. Khimiia, 1976.

———. "K istoriografii teorii khimicheskogo stroeniia [On the Historiography of the Theory of Chemical Structure]." *Voprosy istorii estestvoznaniia i tekhniki,* 1982, no. 4:121–30.

———, and J. Jacques. "Deux pionniers de la chimie moderne, Adolphe Wurtz et Alexandre M. Boutlerov, d'après une correspondence inédite." *Revue d'histoire des sciences* 13 (1860): 115–34.

Bykov, G. V., and L. M. Bekassova. "Beiträge zur Geschichte der Chemie der 60er Jahre des XIX. Jahrhunderts. II. F. Beilsteins Briefe an A. M. Butlerov." *Physis* 8 (1966): 267–85.

Cat, Jordi. "On Understanding: Maxwell on the Methods of Illustration and Scientific Metaphor." *Studies in History and Philosophy of Modern Physics* 32 (2001): 395–441.

Chadarevian, Sorana de, and N. Hopwood, eds. *Models: The Third Dimension of Science.* Stanford: Stanford University Press, 2004.

Clarke, F. W. "The Atomic Theory." *Manchester Memoirs* 47, no. 11 (1903): 1–32.

Claxton, G. *Hare Brain, Tortoise Mind: How Intelligence Increases When You Think Less.* New York: HarperCollins, 1997.

Cohen, Ernst. *Jacobus Henricus van't Hoff, Sein Leben und Wirken.* Leipzig: Akademische Verlagsgesellschaft, 1912.

Comfort, Nathaniel. *The Tangled Field: Barbara McClintock's Search for the Patterns of Genetic Control.* Cambridge, MA: Harvard University Press, 2001.

Conrad, M. "Emil Erlenmeyer." *Berichte der Deutschen Chemischen Gesellschaft* 43 (1910): 3645–64.

Coward, H. F., and A. Harden. "John Dalton's Lectures and Lecture Illustrations, Pt. III: The Lecture Sheets Illustrating the Atomic Theory." *Manchester Memoirs* 59, no. 12 (1915): 41–66.

Curtius, Theodor. *Geschichte des chemischen Universitäts-Laboratoriums zu Heidelberg.* Heidelberg: Rochow, 1908.

Dagognet, François. *Tableaux et langages de la chimie.* Paris: Seuil, 1969.

———. *Écriture et iconographie.* Paris: Vrin, 1973.

Daston, Lorraine, ed. *Biographies of Scientific Objects.* Chicago: University of Chicago Press, 2000.

Daub, Edward. "Waterston's Influence on Krönig's Kinetic Theory of Gases." *Isis* 62 (1971): 512–15.

Davies, J., N. Nersessian, and A. Goel. "Visual Models in Analogical Problem Solving." *Foundations of Science* 10 (2005): 133–52.

Dayan, Anthony. "The Circumstances of Kekulé's 'Molecular Dream' in London in 1854." *Bulletin for the History of Chemistry* 31, no. 1 (2006): 28–30.

Debus, Heinrich. *Erinnerungen an Robert Wilhelm Bunsen.* Kassel: Fischer, 1901.

Delépine, M. *Vie et oeuvres de Joseph-Achille LeBel.* Paris: Dupont, 1947.

Dijksterhuis, A., et al. "On Making the Right Choice: The Deliberation-without-Attention Effect." *Science* 311 (17 Feb. 2006): 935, 1005–7.

Divers, Edward. “Alexander William Williamson, 1824–1904.” *Proceedings of the Royal Society* 78A (1907): xxiv–xliv.

Dobbin, Leonard. “The Couper Quest.” *Journal of Chemical Education* 11 (1934): 331–38.

Duhem, Pierre. *The Aim and Structure of Physical Theory.* Princeton: Princeton University Press, 1954.

Engel, Michael, and Brita Engel. *Chemie und Chemiker in Berlin*. Berlin: Verlag für Wissenschafts- und Regionalgeschichte, 1992.

Farber, Eduard. “Dreams and Visions in a Century of Chemistry.” In *Kekulé Centennial,* edited by O. T. Benfey, 129–39. Washington, D.C.: American Chemical Society, 1966.

Farrar, W. V. “Dalton and Structural Chemistry.” In *John Dalton and the Progress of Science,* edited by D. S. L. Cardwell, 290–99. Manchester University Press, 1968.

Fauconnier, Gilles, and Mark Turner. *The Way We Think: Conceptual Blending and the Mind’s Hidden Complexities*. New York: Basic Books, 2002.

Feist, Gregory. *The Psychology of Science and the Origins of the Scientific Mind.* New Haven: Yale University Press, 2006.

Ferguson, Eugene. *Engineering and the Mind’s Eye.* Cambridge, MA: MIT Press, 1992.

Feynman, Richard. *“What Do You Care What Other People Think?”* New York: Norton, 1988.

Fichter, F. “Rudolph Fittig.” *Berichte der Deutschen Chemischen Gesellschaft* 44 (1911): 1339–1401.

Fierz-David, H. E. “August von Kekulés chemische Visionen.” *Gesnerus* 1 (1944): 146–51.

Finke, R. A., T. B. Ward, and S. M. Smith. *Creative Cognition: Theory, Research, and Applications.* Cambridge, MA: MIT Press, 1992.

Fisher, Nicholas W. “Organic Classification before Kekulé.” *Ambix* 20 (1973): 106–31, 209–33.

———. “Kekulé and Organic Classification.” *Ambix* 21 (1974): 29–52.

———. “Wislicenus and Lactic Acid: The Chemical Background to van’t Hoff’s Hypothesis.” In *van’t Hoff-LeBel Centennial,* edited by O. Bertrand Ramsay, 33–54. Washington, D.C.: American Chemical Society, 1975.

Fleischhacker, W., and T. Schönfeld, eds. *Pioneering Ideas for the Physical and Chemical Sciences: Josef Loschmidt’s Contributions.* New York: Plenum, 1997.

Foster, George Carey. “Alexander William Williamson.” *Journal of the Chemical Society* 87 (1905): 605–18.

Fox, Robert. “The Rise and Fall of Laplacian Physics.” *Historical Studies in the Physical Sciences* 4 (1975): 89–136.

Francoeur, Eric. “The Forgotten Tool: The Design and Use of Molecular Models.” *Social Studies of Science* 27 (1997): 27–40.

———. “Molecular Models and the Articulation of Structural Constraints in Chemistry.” In *Tools and Modes of Representation in the Laboratory Sciences,* edited by Ursula Klein, 95–115. Dordrecht: Kluwer, 2001.

Galison, Peter. *Image and Logic: A Material Culture of Microphysics.* Chicago: University of Chicago Press, 1997.

Galton, Francis. *Inquiries into Human Faculty and its Development.* New York: Macmillan, 1883.

Gardner, Howard. *Art, Mind, and Brain: A Cognitive Approach to Creativity.* New York: Basic, 1982.

Geison, Gerald R. *The Private Science of Louis Pasteur.* Princeton: Princeton University Press, 1995.

Giere, Ronald N., ed. *Cognitive Models of Science.* Minneapolis: University of Minnesota Press, 1992.

———. *Science without Laws.* Chicago: University of Chicago Press, 1999.

Gilbert, G. Nigel, and Michael Mulkay. *Opening Pandora’s Box: A Sociologial Analysis of Scientists’ Discourse.* Cambridge: Cambridge University Press, 1984.

Gillis, Jean. “Kekulé te Gent (1858–1867).” *Verhandelingen van de Koninklijke Vlaamse Academie voor Wetenschappen,* Nr. 62 (Brussels, 1959): 1–101.

———. “Auguste Kekulé et son oeuvre, réalisée à Gand.” *Mémoires de la Classe des Sciences, Académie des Sciences de Belgique* 37 (1966): 1–40.

———. “De atoom- en molecuulmodellen van Kekulé.” *Mededelingen van de Vlaamse Chemische Vereniging:* 29 (1967): 175–80.

Gladwell, Malcolm. *Blink: The Power of Thinking without Thinking.* New York: Little Brown, 2005.

Goldschmidt, H. “Erinnerungen an Robert Wilhelm Bunsen.” *Zeitschrift für angewandte Chemie* 24 (1911): 2137–40.

Göbel, Wolfgang. *Friedrich August Kekulé.* Leipzig: Teubner, 1984.

Gooding, David. *Experiment and the Making of Meaning.* Dordrecht: Kluwer, 1990.

———. “Picturing Experimental Practice.” In *Experimental Essays—Versuche zum Experiment,* edited by M. Heidelberger and F. Steinle, 298–322. Baden-Baden: Nomos, 1998.

Goodman, D. C. “Wollaston and the Atomic Theory of Dalton.” *Historical Studies in the Physical Sciences* 1 (1969): 37–59.

Graebe, Carl. *Geschichte der organischen Chemie.* Berlin: Springer, 1920.

Gray, Jeremy. *Linear Differential Equations and Group Theory from Riemann to Poincaré.* 2nd ed. Basel: Birkhäuser, 2000.

Gregory, Frederick. “Kant, Schelling, and the Administration of Science in the Romantic Era.” *Osiris* [2] 5 (1989): 17–35.

———. “Kant’s Influence on Natural Scientists in the German Romantic Era.” In *New Trends in the History of Science,* edited by R. Visser et al. Amsterdam: Rodopi, 1989.

Grimaux, Edouard, and Charles Gerhardt, Jr. *Charles Gerhardt, sa vie, son oeuvre, sa correspondence 1816–1856*. Paris: Masson, 1900.

Grosholz, Emily, and Roald Hoffmann. "How Symbolic and Iconic Languages Bridge the Two Worlds of the Chemist." In *Of Minds and Molecules: New Philosophical Perspectives on Chemistry,* edited by Nalini Bhushan and Stuart Rosenfeld, 230–47. Oxford: Oxford University Press, 2000.

Gruber, Howard. "On the Relation between 'Aha Experiences' and the Construction of Ideas." *History of Science* 19 (1981): 41–59.

———. *Darwin on Man: A Psychological Study of Scientific Creativity.* 2nd ed. Chicago: University of Chicago Press, 1981.

Gruber, Howard, and Katja Bödecker. *Creativity, Psychology and the History of Science.* Dordrecht: Springer, 2005.

Guerlac, Henry. "The Background to Dalton's Atomic Theory." In *John Dalton and the Progress of Science,* edited by Donald Cardwell, 57–91. Manchester: Manchester University Press, 1968.

Hadamard, Jacques. *The Psychology of Invention in the Mathematical Field.* Princeton: Princeton University Press, 1945.

Hafner, Klaus. *August Kekulé dem Baumeister der Chemie zum 150. Geburtstag.* Darmstadt: Justus von Liebig Verlag, 1980.

Harré, Rom. *Theories and Things.* London: Sheed and Ward, 1961.

———. *Matter and Method.* London: Macmillan, 1964.

Harris, J., and W. H. Brock. "From Giessen to Gower Street: Towards a Biography of Alexander William Williamson (1824–1904)." *Annals of Science* 31 (1974): 95–130.

Heilbron, John. *Weighing Imponderables and Other Quantitative Science around 1800.* Berkeley: University of California Press, 1993.

———. "Physics." In *The Oxford Companion to the History of Modern Science,* ed. John Heilbron, 643–46. Oxford Unversity Press, 2003.

Heilbronner, Edgar, and Klaus Hafner. "Bemerkungen zu Loschmidts Benzolformel." *Chemie in unserer Zeit* 32 (1998): 34–42.

Heilbronner, Edgar, and Jean Jacques. "Paul Havrez und seine Benzolformel." *Chemie in unserer Zeit* 32 (1998): 256–64.

Henry, W. C. *Memoirs of the Life and Scientific Researches of John Dalton.* London: Cavendish Society, 1854.

Herivel, J. "Aspects of French Theoretical Physics in the Nineteenth Century." *British Journal for the History of Science* 3 (1966): 121–24.

Hiebert, Erwin. "The Experimental Basis for Kekulé's Valence Theory." *Journal of Chemical Education* 36 (1959): 320–27.

Hjelt, Edvard. *Geschichte der organischen Chemie.* Braunschweig: Vieweg, 1916.

Hoffmann, Roald. *The Same and Not the Same.* New York: Columbia University Press, 1995.

Hoffmann, Roald, and Vivian Torrence. *Chemistry Imagined: Reflections on Science.* Washington, D.C.: Smithsonian Institution Press, 1993.

Hofmann, A. W. “Hermann Kopp.” *Berichte der Deutschen Chemischen Gesellschaft* 25 (1892): 505–21.

Holmes, Frederic Lawrence. “The Fine Structure of Scientific Creativity.” *History of Science* 19 (1981): 60–70.

———. *Lavoisier and the Chemistry of Life: An Exploration of Scientific Creativity.* Madison: University of Wisconsin Press, 1985.

———. *Investigative Pathways: Patterns and Stages in the Careers of Experimental Scientists.* New Haven: Yale University Press, 2004.

Holton, Gerald. *Thematic Origins of Scientific Thought.* Cambridge, MA: Harvard University Press, 1973.

———. *The Scientific Imagination: Case Studies.* Cambridge: Cambridge University Press, 1978.

Ihde, Aaron J. *The Development of Modern Chemistry.* New York: Harper & Row, 1964.

Jacques, Jean. “Boutlerov, Couper, et la Société chimique de Paris.” *Bulletin de la Société Chimique,* 1953, 528–30.

Japp, Francis. “Kekulé Memorial Lecture.” *Journal of the Chemical Society,* 1897, 97–138.

Jensen, William B. “Chemical Satire and Theory, 1868.” *Chemistry in Britain* 15 (1979): 132–34, 137, 141.

Kaiser, David. *Drawing Theories Apart: The Dispersion of Feynman Diagrams in Postwar Physics.* Chicago: University of Chicago Press, 2005.

Kargon, Robert. “Model and Analogy in Victorian Science: Maxwell’s Critique of the French Physicists.” *Journal of the History of Ideas* 30 (1969): 423–36.

Kekule von Stradonitz, Stephan. “Zwei chemische Visionen.” *Zeitschrift für angewandte Chemie* 40 (1927): 736–37.

Keller, Evelyn Fox. *A Feeling for the Organism.* New York: Freeman, 1983.

Kim, Mi Gyung. *Affinity, That Elusive Dream.* Cambridge, MA: MIT Press, 2003.

Klein, Ursula. “Techniques of Modelling and Paper Tools in Classical Chemistry.” In *Models as Mediators: Perspectives on Natural and Social Science,* edited by Mary S. Morgan and Margaret Morrison, 146–66. Cambridge: Cambridge University Press, 1999.

———, ed. *Tools and Modes of Representation in the Laboratory Sciences.* Dordrecht: Kluwer, 2001.

———. *Experiments, Models, Paper Tools: Cultures of Organic Chemistry in the Nineteenth Century.* Stanford: Stanford University Press, 2003.

Kneale, Dennis. “Shaping Ideas: A Research Topologist Wows World of Math by Seeing the Unseen.” *Wall Street Journal,* 18 March 1983, 1, 10.

Koeppel, Tonja. “Benzene-Structure Controversies, 1865–1920.” Ph.D. diss., University of Pennsylvania, 1973.

———. “Significance and Limitation of Stereochemical Benzene Models.” In *van’t Hoff-LeBel Centennial,* edited by O. Bertrand Ramsay, 97–113. Washington, D.C.: American Chemical Society, 1975.

Koestler, Arthur. *The Act of Creation*. London: Hutchinson, 1964.

Kosslyn, Stephen. *Image and Mind*. Cambridge, MA: Harvard University Press, 1980.

Krätz, Otto. "Emil Erlenmeyer, 1825–1909." *Chemie in unserer Zeit* 6 (1972): 52–58.

———. "Iwan Turgenyew und die russischen Chemiker in Heidelberg." *Chemie in unserer Zeit* 21 (1987): 89–99.

Krätz, Otto, and C. Priesner, eds. *Liebigs Experimentalvorlesung: Vorlesungsbuch und Kekulé's Mitschrift*. Weinheim: Verlag Chemie, 1983.

Kuhn, Thomas. *The Structure of Scientific Revolutions*. 2nd ed. Chicago: University of Chicago Press, 1970.

Kussmaul, Adolf. "Ein Dreigestirn grosser Naturforscher an der Heidelberger Universität im 19. Jahrhundert." *Deutsche Revue* 27 (1902): 173–87.

Larder, David. "Alexander Crum Brown and His Doctoral Thesis of 1861." *Ambix* 14 (1967): 112–32.

Laszlo, Pierre. *La parole des choses, ou le langage de la chimie*. Paris: Hermann, 1993.

Laudan, Larry. "Towards a Reassessment of Comte's 'Méthode Positive.'" *Philosophy of Science* 38 (1971): 35–53.

Leicester, H. M. "Kekulé, Butlerov, Markovnikov: Controversies on Chemical Structure from 1860 to 1870." In *Kekulé Centennial,* edited by O. T. Benfey, 13–23. Washington, D.C.: American Chemical Society, 1966.

Levere, Trevor. "Affinity or Structure: An Early Problem in Organic Chemistry." *Ambix* 17 (1970): 111–26.

———. *Affinity and Matter: Elements of Chemical Philosophy, 1800–1865*. Oxford: Oxford University Press, 1971.

Liebermann, Carl. "Emil Jacobsen." *Berichte der Deutschen Chemischen Gesellschaft* 44 (1911): 549–50.

Lightman, Bernard, ed. *Dictionary of Nineteenth-Century British Scientists*. 4 vols. London: Thoemmes / Chicago: University of Chicago Press, 2004.

Lockemann, Georg. *Robert Wilhelm Bunsen*. Stuttgart: Wissenschaftliche Verlagsgesellschaft, 1949.

Lützen, J. *Mechanistic Images in Geometric Form: Heinrich Hertz's Principles of Mechanics*. Oxford: Oxford University Press, 2005.

Mahdihassan, S. "The Probable Origin of Kekulé's Symbol of the Benzene Ring." *Scientia* 95 (1960): 48–53.

———. "Kekulé's Dream of the Ouroboros and the Significance of this Symbol." *Scientia* 96 (1961): 187–95.

Mandelbaum, Maurice. *Philosophy, Science, and Sense Perception*. Baltimore: Johns Hopkins University Press, 1964.

Mauskopf, Seymour H. "The Atomic Structural Theories of Ampère and Gaudin: Molecular Speculation and Avogadro's Hypothesis." *Isis* 60 (1969): 61–74.

———. *Crystals and Compounds: Molecular Structure and Composition in Nineteenth-Century French Science.* Philadelphia: American Philosophical Society, 1976.

McGinn, Colin. *Mindsight: Image, Dream, Meaning.* Cambridge, MA: Harvard University Press, 2004.

Medawar, Peter. *Induction and Intuition in Scientific Thought.* Philadelphia: American Philosophical Society, 1969.

Meinel, Christoph. "'A World out of Chaos': Anschauung, Modellbildung und chemische Synthese bei August Wilhelm Hofmann." In *Interfolia fructus: Gedenkschrift für Rudolf Schmitz (1918–1992),* edited by P. Dilg, 79–92. Frankfurt: Govi-Verlag, 1995.

———. "Molecules and Croquet Balls." In *Models: The Third Dimension of Science,* edited by Sorana de Chadarevian and N. Hopwood, 242–75. Stanford: Stanford University Press, 2004.

Meyer, Lothar. "Leopold von Pebal." *Berichte der Deutschen Chemischen Gesellschaft* 20 (1887): 997–1015.

Meyer, Lucy Rider. *Real Fairy Folks, or Fairy Land of Chemistry.* Boston: Lothrop, 1887.

Miller, Arthur I. *Imagery in Scientific Thought.* Cambridge, MA: MIT Press, 1986.

———. "Imagery, Metaphor, and Physical Reality." In *Psychology of Science: Contributions to Metascience,* edited by B. Gholson et al. Cambridge University Press, 1989.

———. "Imagery and Intuition in Creative Scientific Thought: Albert Einstein's Invention of the Special Theory of Relativity." In *Creative People at Work,* edited by Doris Wallace and Howard Gruber, 170–87. Oxford: Oxford University Press, 1989.

———. *Insights of Genius: Imagery and Creativity in Science and Art.* New York: Springer, 1996.

———. *Einstein, Picasso: Space, Time, and the Beauty that Causes Havoc.* New York: Basic Books, 2001.

———. "Imagery and Representation in Twentieth-Century Physics." In *The Cambridge History of Science,* vol. 5, edited by Mary Jo Nye, 191–215. Cambridge: Cambridge University Press, 2003.

Miller, Jane A. "M. A. Gaudin and Early Nineteenth Century Stereochemistry." In *van't Hoff-LeBel Centennial,* edited by O. Bertrand Ramsay, 1–17. Washington, D.C.: American Chemical Society, 1975.

Mitscherlich, Alexander. "Kekulés Traum: Psychologische Betrachtung einer chemischen Legende." *Psyche* 26 (1972): 649–55.

Morgan, Mary S., and Margaret Morrison, eds. *Models as Mediators: Perspectives on Natural and Social Science.* Cambridge: Cambridge University Press, 1999.

Nersessian, Nancy. *Faraday to Einstein: Constructing Meaning in Scientific Theories.* Dordrecht: Kluwer, 1984.

———. “How Do Scientists Think? Capturing the Dynamics of Conceptual Change in Science.” In *Cognitive Models of Science,* edited by Ronald N. Giere, 5–22. Minneapolis: University of Minnesota Press, 1992.

———. “Opening the Black Box: Cognitive Science and the History of Science.” *Osiris* [2] 10 (1994): 194–214.

Nesbit, J., and M. Bradford. “2006 Visualization Challenge.” *Science* 313 (22 September 2006): 1729.

Noelting, E. “O. N. Witt.” *Chemiker-Zeitung* 39 (1915): 441–49.

———. “O. N. Witt.” *Berichte der Deutschen Chemischen Gesellschaft* 49 (1916): 1751–1832.

———. “O. N. Witt.” *Journal of the Chemical Society* 109 (1916): 428–31.

Nørretranders, T. *The User Illusion: Cutting Consciousness Down to Size.* New York: Viking, 1998.

Norton, John. “Nature Is the Realization of the Simplest Conceivable Mathematical Ideas: Einstein and the Canon of Mathematical Simplicity.” *Studies in the History and Philosophy of Modern Physics* 31 (2000): 135–70.

Nye, Mary Jo. *From Chemical Philosophy to Theoretical Chemistry: Dynamics of Matter and Dynamics of Disciplines, 1800–1950.* Berkeley: University of California Press, 1993.

Olson, Richard. *Scottish Philosophy and British Physics.* Princeton: Princeton University Press, 1975.

Pang, Alex. “Visual Representation and Post-Constructivist History of Science.” *Historical Studies in the Physical and Biological Sciences* 28 (1997): 139–71.

Paoloni, Leonello. “Stereochemical Models of Benzene, 1869–1875.” *Bulletin for the History of Chemistry* 12 (1992): 10–24.

Paradis, J. G. “Satire and Science in Victorian Culture.” In *Victorian Science in Context,* edited by B. Lightman, 143–75. University of Chicago Press, 1997.

Partington, James R. *History of Chemistry.* Vol. 4. London: Macmillan, 1964.

Paul, E. R. “Alexander W. Williamson on the Atomic Theory: A Study of Nineteenth-Century British Atomism.” *Annals of Science* 35 (1978): 17–31.

Poincaré, Henri. “L’invention mathématique.” *Bulletin de l’Institut général psychologique* 8 (1908): 175–87.

———. *Science et méthode.* Paris: Flammarion, 1908.

———. *Trois suppléments sur la découverte des fonctions fuchsiennes.* Berlin: Akademie Verlag, 1997.

Ramberg, Peter. *Chemical Structure, Spatial Arrangement: The Early History of Stereochemistry, 1874–1914.* Aldershot: Ashgate, 2003.

Ramberg, Peter, and G. J. Somsen. “The Young J. H. van’t Hoff: The Background to the Publication of his 1874 Pamphlet.” *Annals of Science* 58 (2001): 51–74.

Ramsay, O. Bertrand. “Molecules in Three Dimensions.” *Chemistry* 47, nos. 1 and 2 (1974): 6–9 and 6–11.

———, ed. *van’t Hoff-LeBel Centennial.* Washington, D.C.: American Chemical Society, 1975.

———. “Molecular Models in the Early Development of Stereochemistry.” In *van’t Hoff-Lebel Centennial,* 74–96. Washington, D.C.: American Chemical Society, 1975.

———. *Stereochemistry.* London: Heyden, 1981.

Ramsay, O. Bertrand, and A. J. Rocke. “Kekulé’s Dreams: Separating the Fiction from the Fact.” *Chemistry in Britain* 20 (1984): 1093–94.

Richards, Robert. *The Romantic Conception of Life.* Chicago: University of Chicago Press, 2002.

Richardson, Alan. *Mental Imagery.* New York: Springer, 1969.

Ritter, Christopher. “An Early History of Alexander Crum Brown’s Graphical Formulas.” In *Tools and Modes of Representation in the Laboratory Sciences,* edited by Ursula Klein, 35–46. Dordrecht: Kluwer, 2001.

Rocke, Alan J. “Kekulé, Butlerov, and the Historiography of the Theory of Chemical Structure.” *British Journal for the History of Science* 14 (1981): 27–57.

———. “Subatomic Speculations and the Origin of Structure Theory.” *Ambix* 30 (1983): 1–18.

———. *Chemical Atomism in the Nineteenth Century: From Dalton to Cannizzaro.* Columbus: Ohio State University Press, 1984.

———. “Hypothesis and Experiment in the Early Development of Kekulé’s Benzene Theory.” *Annals of Science* 42 (1985): 355–81.

———. “Kekulé’s Benzene Theory and the Appraisal of Scientific Theories.” In *Scrutinizing Science: Empirical Studies of Scientific Change,* edited by A. Donovan, L. Laudan, and R. Laudan, 145–61. Boston: Kluwer, 1988.

———. “‘Between Two Stools’: Kopp, Kolbe, and the History of Chemistry.” *Bulletin for the History of Chemistry* 7 (1990): 19–24.

———. “History and Science, History of Science: Adolphe Wurtz and the Renovation of the Academic Professions in France.” *Ambix* 40 (1993): 20–32.

———. “Waking up to the Facts.” *Chemistry in Britain* 29 (1993): 401–2.

———. *The Quiet Revolution: Hermann Kolbe and the Science of Organic Chemistry.* Berkeley: University of California Press, 1993.

———. *Nationalizing Science: Adolphe Wurtz and the Battle for French Chemistry.* Cambridge, MA: MIT Press, 2001.

———. “In Search of El Dorado: John Dalton and the Origins of the Atomic Theory.” *Social Research* 72 (2005): 125–58.

Rocke, Alan J., and Emil Heuser, eds. *Justus von Liebig und Hermann Kolbe in ihren Briefen, 1846–1873.* Mannheim: Bionomica, 1994.

Roe, Anne. “A Study of Imagery in Research Scientists.” *Journal of Personality* 19 (1951): 459–70.

Rollins, Mark. *Mental Imagery.* New Haven: Yale University Press, 1989.

Root-Bernstein, Robert S. “The Ionists: Founding Physical Chemistry, 1872–1890.” Ph.D. diss., Princeton University, 1980.

———. “Visual Thinking: The Art of Imagining Reality.” *Transactions of the American Philosophical Society* 75 (1985): 50–67.

———. *Discovering: Inventing and Solving Problems at the Frontiers of Scientific Knowledge.* Cambridge, MA: Harvard University Press, 1989.

———. "Van't Hoff on Imagination and Genius." In *Van't Hoff and the Emergence of Chemical Thermodynamics,* edited by W. Hornix and S. Mannaerts, 295–307. Delft University Press, 2001.

Ross, Philip. "The Expert Mind." *Scientific American,* August 2006, 64–71.

Rothenberg, Albert. "Creative Cognitive Processes in Kekulé's Discovery of the Structure of the Benzene Molecule." *American Journal of Psychology* 108 (1995): 419–38.

Rudofsky, Susanna. "The Benzolfest." In *The Kekulé Riddle,* edited by John Wotiz, 9–20. Clearwater, FL: Cache River Press, 1993.

Rudofsky, Susanna, and John Wotiz. "Psychologists and the Dream Accounts of August Kekulé." *Ambix* 35 (1988): 31–38.

Rudwick, Martin. "The Emergence of a Visual Language for Geological Science, 1760–1840." *History of Science* 14 (1976): 149–95.

———. *Bursting the Limits of Time: The Reconstruction of Geohistory in the Age of Revolution.* Chicago: University of Chicago Press, 2005.

Ruska, J. "Hermann Kopp, Historian of Chemistry." *Journal of Chemical Education* 14 (1937): 3–12.

Russell, Colin A. *The History of Valency.* Leicester: Leicester University Press, 1971.

———. "Kekulé and Frankland: A Psychological Puzzle?" In *The Kekulé Riddle,* edited by John Wotiz, 77–101. Clearwater, FL: Cache River Press, 1993.

———. *Edward Frankland: Chemistry, Controversy, and Conspiracy in Victorian England.* Cambridge: Cambridge University Press, 1996.

Schaffer, Simon. "Making Up Discovery." In *Dimensions of Creativity,* edited by Margaret Boden, 13–51. Cambridge, MA: MIT Press, 1994

Schelar, Virginia. "Alternatives to the Kekulé Formula for Benzene: The Ladenburg Formula." In *Kekulé Centennial,* edited by O. T. Benfey, 163–93. Washington, D.C.: American Chemical Society, 1966.

Schiemenz, Günter. "Neuer Wein in alten Schläuchen? Das Hexagon, das Tetraeder und Legenden um August Kekulé." *Gesellschaft Deutscher Chemiker, Fachgruppe Geschichte der Chemie, Mitteilungen* 3 (1989): 38–52.

———. "Goodbye Kekulé? Joseph Loschmidt und die monocyclische Struktur des Benzols." *Naturwissenschaftliche Rundschau* 46 (1993): 85–88.

———. "A Heretical Look at the Benzolfest." *British Journal for the History of Science* 26 (1993): 195–205.

———. "Joseph Loschmidt und die Benzol-Formel: Über die Entstehung einer Legende." *Sudhoffs Archiv* 78 (1994): 41–58.

Schmorl, Karl. *Adolf von Baeyer, 1835–1917.* Stuttgart: Wissenschaftliche Verlagsgesellschaft, 1952.

Schummer, Joachim. *Realismus und Chemie: Philosophische Untersuchungen der Wissenschaft der Stoffen.* Würzburg: Königshausen & Neumann, 1996.

Schuster, Peter M. “From Curiosity to Passion: Loschmidt’s Route from Philosophy to Natural Science.” In *Pioneering Ideas for the Physical and Chemical Sciences: Josef Loschmidt’s Contributions,* edited by W. Fleischhacker and T. Schönfeld, 269–76. New York: Plenum, 1997.

Schütt, Hans-Werner. “Über die Einführung der Präfixe para- meta- und ortho- in die chemische Nomenklatur.” *Sudhoffs Archiv* 63 (1979): 123–35.

Seltzer, Richard. “Influence of Kekulé Dream on Benzene Structure Disputed.” *Chemical & Engineering News,* 4 November 1985, 22–23.

Shepard, R. N. “The Mental Image.” *American Psychologist* 33 (1978): 125–37.

———. “Externalization of Mental Images and the Act of Creation.” In *Visual Learning, Thinking, and Communication,* edited by B. S. Randhawa and W. E. Coffman, 133–89. New York: Academic Press, 1978.

Shepard, R. N., and L. A. Cooper. *Mental Images and Their Transformations.* Cambridge, MA: MIT Press, 1982.

Smith, Pamela H. *The Body of the Artisan: Art and Experience in the Scientific Revolution.* Chicago: University of Chicago Press, 2004.

Smith, R. Angus. *Memoir of John Dalton and History of the Atomic Theory.* London: Bailliere, 1856.

———. *Life and Works of Thomas Graham.* London: Smith, 1884.

Snelders, H. “The Reception of J. H. van’t Hoff’s Theory of the Asymmetric Carbon Atom.” *Journal of Chemical Education* 51 (1974): 2–7.

———. “J. A. LeBel’s Stereochemical Ideas Compared with those of J. H. van’t Hoff.” In *van’t Hoff-LeBel Centennial,* edited by O. Bertrand Ramsay, 66–73. Washington, D.C.: American Chemical Society, 1975.

Söderqvist, Thomas. *Science as Autobiography: The Troubled Life of Niels Jerne.* New Haven: Yale University Press, 2003.

Soldat, J. le. “Kekulés Traum: Ergänzende Betrachtungen zum ‘Benzolring.’” *Psyche* 47 (1993): 180–201.

Spek, T. M. van der. “Selling a Theory: The Role of Molecular Models in J. H. van’t Hoff’s Stereochemistry Theory.” *Annals of Science* 63 (2006): 157–77.

Speter, Max. “‘Vater Kopp’: Bio-, Biblio- und Psychographisches von und über Hermann Kopp (1817–1892).” *Osiris* 5 (1938): 392–460.

Stanley, Michael. “The Chemical Work of Thomas Graham.” Ph.D. diss., Open University, 1979.

———. “The Making of a Chemist: Thomas Graham in Scotland.” *Proceedings of the Royal Society of Glasgow,* no. 5 (1987).

Strube, W. “Zur Geschichtsauffassung J. B. Trommsdorffs und H. Kopps.” *Wissenschaftliche Zeitschrift der Technischen Hochschule für Chemie Leune-Merseburg* 5 (1963): 377–78.

Strunz, Franz. “Kekulés Traum: Zum Zusammenhang von geistiger Spontanaktivität und wissenschaftlicher Problemlösung.” *Chemie in unserer Zeit* 23 (1989): 170–76.

———. “Preconscious Mental Activity and Scientific Problem-Solving: A Critique of the Kekulé Dream Controversy.” *Dreaming* 3 (1993): 281–94.

Swords, Michael. “The Chemical Philosophy of Thomas Graham.” Ph.D. diss., Case Western Reserve University, 1973.

Thackray, Arnold. *Atoms and Powers: An Essay on Newtonian Matter-Theory and the Development of Chemistry.* Cambridge, MA: Harvard University Press, 1970.

Thoms, Hermann. “Emil Jacobsen.” *Berichte der Deutschen Pharmaceutischen Gesellschaft* 21 (1911): 152–58.

Thorpe, T. Edward. “Kopp Memorial Lecture.” *Journal of the Chemical Society* 63 (1893): 775–815.

———. *Essays in Historical Chemistry.* London: Macmillan, [1911].

Vanderbilt, Byron. “Kekulé’s Whirling Snake: Fact or Fiction.” *Journal of Chemical Education* 52 (1975): 709.

Verkade, P. E. “August Kekulé.” *Proceedings of the Chemical Society,* 1958, 205–10.

Volhard, Jacob. *August Wilhelm von Hofmann: Ein Lebensbild.* Berlin: Friedländer, 1902.

Vorländer, Daniel. “Jacob Volhard.” *Berichte der Deutschen Chemischen Gesellschaft* 45 (1912): 1855–1902.

W[alker], J. “Alexander Crum Brown.” *Journal of the Chemical Society* 123 (1923): 3422–31.

Wallace, Doris, and Howard Gruber, eds. *Creative People at Work.* Oxford: Oxford University Press, 1989.

Weininger, Stephen. “Contemplating the Finger: Visuality and the Semiotics of Chemistry.” *Hyle* 4 (1998): 3–27.

———. “Butlerov’s Vision: The Timeless, the Transient, and the Representation of Chemical Structure.” In *Of Minds and Molecules: New Philosophical Perspectives on Chemistry,* edited by Nalini Bhushan and Stuart Rosenfeld, 143–61. Oxford: Oxford University Press, 2000.

Weyer, Jost. *Chemiegeschichtsschreibung von Wiegleb (1790) bis Partington (1970).* Hildesheim: Gerstenberg, 1974.

———. “Van’t Hoff, Kekulé und die Stereochemie: Zwei unveröffentlichte Briefe von J. H. van’t Hoff an A. Kekulé.” *Janus* 64 (1977): 217–30.

Williams, L. Pearce. *Michael Faraday: A Biography.* London: Chapman and Hall, 1965.

Wise, Norton. “Making Visible.” *Isis* 97 (2006): 75–82.

Wizinger-Aust, Robert. “August Kekulé, Leben und Werk.” In *Kekulé und seine Benzolformel,* edited by Wizinger-Aust et al., 7–32. Weinheim: Verlag Chemie, 1966.

Wotiz, John. “The Unknown Kekulé.” In *Essays on the History of Organic Chemistry,* edited by J. G. Traynham, 21–34. Baton Rouge: LSU Press, 1987.

———, ed. *The Kekulé Riddle: A Challenge for Chemists and Psychologists.* Clearwater, FL: Cache River Press, 1993.

Wotiz, John, and Christian Noe. “August Kekulé and Josef Loschmidt.” In *The Kekulé Riddle,* edited by John Wotiz, 221–45. Clearwater, FL: Cache River Press, 1993.

Wotiz, John, and Susanna Rudofsky. “Kekulé’s Dreams: Fact or Fiction?” *Chemistry in Britain* 20 (1984): 720–23.

———. “Herr Professor Doktor Kekulé: Why Dreams?” In *The Kekulé Riddle,* edited by John Wotiz, 247–75. Clearwater, FL: Cache River Press, 1993.

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