PHILOSOPHERS OF FIRE

An Illustrated Survey of 600 Years of Chemical History for Students of Chemistry

William B. Jensen
University of Cincinnati

Oesper Collections
Cincinnati
2003

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Dedicated to

RALPH E. OESPER
AARON J. IHDE
DEREK A. DAVENPORT

Each of whom made this possible after their own fashion

There is no question that we can train a chemical technologist without teaching him any history of chemistry and he may be a very good technologist indeed. I would argue with equal vehemence that we cannot educate a chemist without history of chemistry. I am interested in, and I believe most of us are, in the education rather than the training of chemists. The person who is merely trained to carry out analyses or syntheses can do his job quite satisfactorily without much chemical theory or any history of chemistry. On the other hand, the chemist who is in a position of responsibility for the planning of investigations needs to know something about the past history of chemical investigation and the development of chemical thought. Without such knowledge he is merely a technologist.

Aaron J. Ihde 1971

A retrospect of the past, especially in the exact sciences, alone affords a proper comprehension of what is accepted today. It is only when we are acquainted with the theories which preceded those accepted at present, that the latter can be fully understood; because there is almost always an intimate connection between them ... But quite apart from this real advantage of history, which thus, in my opinion, leads to a clearer understanding of our present position, yet another advantage may be adduced which is perhaps of still greater value to the student: namely the accurate estimation of the value of theories. An examination of the past shows the mutability of opinions; it enables us to recognize how hypotheses, apparently the most securely established, must in the course of time be abandoned. It leads us to the conviction that we live in a state of continuous transition; that our ideas of today are merely the precursors of others; and that even they cannot, for any length of time, satisfy the requirements of science ... Further, by the study of history, our faith in authority is diminished – a faith which produces pernicious effects by obstructing the way for any original development of the individual.

Albert Ladenburg 1900

Introduction

Beware the historian in search of a novel interpretive thesis. His propensity to elevate what is in reality an historical footnote into a major revisionist theme means that there is no greater corruptor of historical fact and common sense.
Wallace L. Selleck

This textbook has evolved out of the one-quarter survey course in the history of chemistry which I have been offering to the seniors and graduate students in the Department of Chemistry at the University of Cincinnati for the last 20 years. The purpose of this course is to provide a brief historical outline of the evolution of modern chemistry for students of chemistry. Since the intent is to sketch this evolution in the broadest possible manner, neither the individual development of specific theories and experimental techniques, the larger political and social context of these discoveries, nor the various philosophical issues that were involved, are discussed in great detail. Rather the goal is to provide a skeleton framework of significant names, dates, and key historical transitions on which this detail can be arranged at a later date, whether acquired through the independent reading of specialist monographs on the history of chemistry or the taking of more advanced courses.

Like a reference work, a good textbook should be tightly organized in order to facilitate rapid access to significant names, events, and dates. Unlike a reference work, however, it must be selective, rather than comprehensive, in its coverage. This selectivity is constrained not only by the comparative importance of the various topics but also by the fact that few chemistry departments are willing to devote more than a single quarter or semester to a history of chemistry course.

Like a specialist monograph, a good textbook should also provide context for these names, events, and, dates by pointing out significant trends and summarizing interpretive conclusions. Unlike a specialist monograph, however, it cannot present the detailed arguments supporting these trends and conclusions nor indulge in nuanced discussions of subtle distinctions or qualifications. In the interests of clarity and brevity, these summarized, albeit often oversimplified, conclusions and characterizations must stand on their own.

Like a popular history intended for the lay public, a good textbook should be readable. Unlike a popular history, however, it does not shy away from using technical terminology, equations, and formulas or from employing various organizational and scholarly devices, such as sectional headers, summary tables, graphs, and footnotes.

I point out these obvious distinctions between a textbook, on the one hand, and a reference book or specialist monograph, on the other, because the textbook appears to be a literary form that has apparently disappeared from the repertoire of the modern historian of science, and I want to make certain that there is no misunderstanding as to the nature and purpose of this book. Not only is it a textbook, rather than a reference book or an interpretative essay, it is also an outline or survey which takes a traditional internalist approach to the history of chemistry, and is explicitly intended for readers having a basic understanding of the fundamental concepts and techniques of modern chemistry rather than for the lay public.

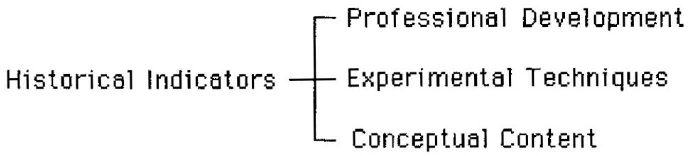
This neglect of the textbook is undoubtedly connected with the kinds of historical questions that are of most interest to professional historians of science. An introductory survey deals with only the most rudimentary of these – namely with the questions of when certain concepts and techniques became dominant in science and which scientists played a prominent role in that rise to dominance. If the historian asks the further question of how these concepts and techniques were discovered, then the situation rapidly becomes more complex and topics, which in an introductory outline consume only a paragraph and which make mention of only one or two names, suddenly expand to the size of chapters or entire books. Further complications arise from the fact that modern historians are seldom content to base their accounts of discovery on the published record but rather seek to discover unpublished correspondence, personal journals, and laboratory notes which might shed further light on these questions. These unpublished documents are frequently fragmentary, lacking a proper context, and chronologically ambiguous, thus tempting the historian to unrestrained speculation. In addition, they frequently contradict the final published accounts. Though common sense would dictate that the published accounts represent the author's final and considered opinion on the subject in question, whereas the unpublished documents are preliminary drafts or paths subsequently rejected, recent historians have tended to invert this conclusion and to claim that the unpublished documents represent the true picture, whereas the published accounts are little more than intentional misrepresentations. As a result, the recent literature in the history of science has been deluged with highly speculative, and often quite questionable, revisionist accounts of major scientific discoveries.

If one moves beyond these questions to the further question of why a given concept triumphed over its competitors and became dominant at a particular time and place, rather than earlier, later, or elsewhere, then things move from the realm of speculation into the realm of acrimony. Attempts to answer such questions range from those who believe in the scientific method and that certain concepts triumph because of their superior explanatory powers, to those who advocate a strict social constructionist approach and maintain that the dominance of one concept versus another is merely a matter of intellectual fads dictated by the larger cultural milieu. Though common sense would suggest that the true reasons probably involve a mixture of these various factors, the proponents of these extremes have again generated a vast and problematic literature that often tells us more about the individual political and philosophical biases of the authors than about the nature of science itself.

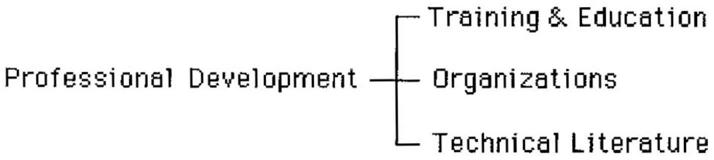
Though indulging in speculation and controversy certainly makes for a more interesting approach to history of chemistry than does plodding through the introductory basics, I seriously question their use with students who lack the necessary background to independently evaluate the cogency of the arguments being offered. Consequently, in keeping with the purpose of this textbook, I have kept largely to the more rudimentary introductory questions appropriate to an introductory survey course and have employed a simple century by century chronological approach.

Of course, every historian knows that the start and finish of significant historical eras seldom coincide with the turn of a decade, a century, or even a millennium. Yet there is something in the human psyche which endows these arbitrary dates with a special significance and which makes us want to pause and evaluate where we have been and where we are going. In addition, use of these purely conventional time divisions seems to facilitate the mastery of the names and dates required to construct our basic historical framework.

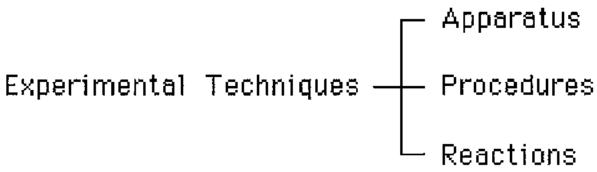
For each 100-year snapshot we will evaluate three historical indicators or indices: the state of chemistry's professional development, the state of its experimental techniques, and the state of its conceptual content:



The category of professional development is intended to subsume the state of chemical education, the existence of scientific societies and other professional organizations, and the development of a distinct chemical literature, including textbooks, monographs, journals, abstracting services, etc:

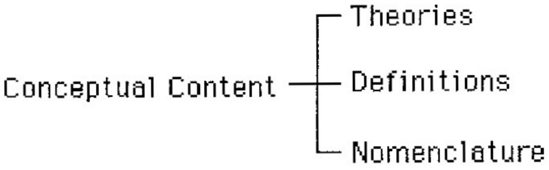


The category of experimental techniques is intended to subsume advances in instrumentation and apparatus, the development of new experimental procedures, and the discovery of new classes of reactions and compounds:

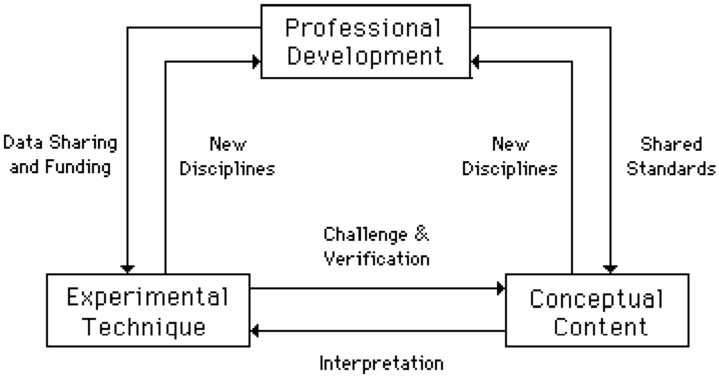


It might seem odd, at first glance, to include reactions and compounds in this category. However, the discovery of a new reaction or synthetic procedure can be as productive of new experimental results as the invention of a new instrument, and new classes of compounds may challenge existing theories of bonding and structure as effectively as quantitative data measurements.

Lastly, the category of conceptual content is intended to subsume not only theories proper, but also definitions and nomenclature – in short, all those aspects that contribute to the organization and interpretation of the experimental facts:



As suggested by the following diagram, these three indices are not completely independent of one another:



New experimental techniques and theories often lead to the development of new specialties at the professional level, whereas professionalization leads to the sharing of experimental data, provides much of the driving force for funding basic research, and streamlines theory by enforcing shared standards of vocabulary and symbolism. Likewise, theory often suggests new instruments and aids in the interpretation of experimental results, whereas experiment, in turn, both confirms and challenges current theory. This interdependence means that, as one approaches the 20th century, it becomes increasingly difficult to avoid some degree of repetition when separately discussing each indicator.

In my opinion, most older histories of chemistry suffer from three defects:

a. They are heavily biographical in nature, thus often sacrificing conceptual, technical, and sociological insights for anecdotal trivia.

b. They seldom provide any substantive coverage of events after 1920, thus ignoring most of the history of 20th-century chemistry.

c. They focus almost exclusively on the historical development of concepts related to the composition and structure of the discrete, stoichiometric, molecular species typical of organic chemistry, thus ignoring or trivializing the equally important advances made by such fields as solid-state chemistry, phase science, quantum chemistry, chemical thermodynamics, and chemical kinetics – many of which clearly reveal that the traditional molecular mind-set of the organic chemist and the introductory chemistry textbook actually correspond to special cases of a far more general set of chemical and physical concepts.

Anyone who has attempted to write a short overview history of chemistry, or has glanced through James Partington's comprehensive multivolume reference work (weighing in at four volumes and over 3000 pages) soon becomes painfully aware of the reasons for the first two of these defects. By the second half of the 19th-century, the cast of characters and topics becomes overwhelming and, by the 20th-century, almost impossible to deal with. Consequently the level of coverage becomes increasingly abbreviated, especially if the author attempts to provide biographical information, however brief, on the chemists and physicists that are mentioned. Ruthless selectivity becomes essential, though this process automatically produces an historical distortion by associating experimental and conceptual advances with only one or two selected names or dates, when in fact they were really the result of a long evolutionary discovery process and an equally long post-discovery refinement process, each of which involved the cooperative efforts of many chemists and physicists.

A closely related consequence of this selectivity is that it also produces a distorted impression of the day to day activities of the average chemist. Only a small fraction of the chemical community is privileged to have made a significant conceptual or methodological contribution to chemistry. The vast majority spend their careers applying and refining the concepts and methods discovered by others – a characterization that even includes many activities that were later honored by a Nobel prize. Work of this sort is absolutely essential to the progress of science and often involves great skill, persistence, and brilliance, though, in the end, it is often condemned to historical anonymity by the larger picture.

Both the necessity of ruthless selectivity and the focus on conceptual advances create the false illusion that chemists, like theoretical physicists, arrive at these concepts by a pen and paper process of abstract reasoning and mathematical deduction, when in fact they are often embedded in highly detailed experimental and synthetic studies of specific chemical compounds and are arrived at by a slow iterative process heavily tinged with empiricism. The simplification and clarity which we demand of historical perspective automatically belies the complexity and indirectness of the original literature.

Last, but not least, this selectivity requires that we largely ignore the history of such applied areas as industrial chemistry, geochemistry, biochemistry, medicinal chemistry, etc., most of which are the subject of an historical literature of their own.

The most natural way of applying the requisite selection process is to let time itself act as the ultimate arbiter of what is to be included and what is to be ignored – in other words, one focuses on the origins of only those advances which still have significance to modern chemistry. This criterion has long been an anathema to professional historians of science, who claim that all events – even those that were dead ends or which qualify as crank science – should be given equal and impartial treatment. To do otherwise is to commit the deadly historical sin of "whig history." I need hardly point out the incredible naivete of such a position when it comes to the reasons which motivate most people to either write or read history, let alone the overwhelming impracticality of truly putting such a plan into practice when dealing with a broad range of topics and time periods – an impracticality which no doubt accounts for the failure of said historians to provide any comprehensive histories of chemistry themselves.

Using the present to select the past also has the shortcoming that the selection process is highly dependent on the author's understanding of the present. What I or some other chemist might deem as historically important will vary with our current understanding of chemistry and with what we consider to be its most fundamental achievements. Indeed, it has been my personal experience that it is virtually impossible to get any two chemists to agree on just what constitutes the most important and most basic principles of chemistry and that often they mistake their areas of specialization or practical industrial applications for fundamental generalizations. This lack of consensus is largely responsible for the third of the defects listed above, as most past histories of chemistry have been written by organic chemists with a limited appreciation of the achievements of phase science and solid-state inorganic chemistry.

Consequently, in order to aid in this selection process, I have made a much a more explicit use of the monograph and textbook literature than is common in most histories of chemistry. The reason for this is quite simple. Whereas vast numbers of transient concepts and models live and die in the literature of the research journal, only those deemed worthy of passing on to the next generation of chemists generally make it into the textbooks or are made the subject of detailed specialist monographs.

Not only have I committed the historical sin of using the present to select the past, I have also violated the injunction of said historical theorists against using our current knowledge of chemistry to help clarify and evaluate older theories. If possible, this taboo is even more unrealistic than the first. Even a rudimentary knowledge of educational psychology shows that people do not assimilate new information in a vacuum, rather they attempt to integrate that information with their previous knowledge. Historians may have the luxury of assuming that their readers or students are blissfully ignorant of modern chemical theory, but I do not. It is simply impossible to present outdated chemical theories and terminology to an audience of trained chemists without them automatically asking "but what is really going on here?" and attempting to evaluate that theory or terminology in terms of their current knowledge of chemistry. Either the teacher can attempt to control this integration process by explicitly pointing out the differences and similarities with our current views or allow each individual to do so on their own – a process which can lead to some very bizarre distortions and misinterpretations, as repeated studies by science educators have shown.

In the end, it all boils down to the question of just how seriously one should take historians who are so naive as to claim that there is only one legitimate set of historical interests (which for them reduces largely to the political or sociological context of scientific discovery) and one legitimate method of writing history, and who further base these claims on the highly dubious proposition that the writing of political history can serve as a legitimate model for the writing of history of science. Despite their strident claims to the contrary, science, unlike politics, really does progress and we really do know more about the nature of the physical universe in the 21st century than we did in the 15th century, even if we are no wiser when it comes to the motives of the human heart. Historical hindsight is simply not the culprit it is made out to be. Indeed, it can be plausibly argued that hindsight is the only thing that differentiates history from mere chronology.

These considerations are also reflected in my rather perfunctory treatment of the subject of alchemy. Despite the recent fad in history of science, which purports to find the origins of virtually everything from Newton's physics to Boyle's atomism in the alchemical literature, I do not believe that alchemy is an important progenitor of modern chemistry, which instead clearly evolved out of metallurgy and pharmacy. As mentioned earlier, much of this revisionist literature is based on so-called “imaginative reconstructions” of manuscripts, personal interactions, and chronologies, as well as on the indiscriminate use of the terms “alchemist” and “alchemy” to describe any chemical activity that serves the thesis at hand.

While it is true that, etymologically speaking, the words chemistry and alchemy are one and the same, it has been established historical practice for almost 300 years now to employ the Arabic form only when describing those chemical activities dealing with the improvement or transmutation of metals, along with the term iatrochemistry when describing early medical and pharmaceutical applications, and the term chemistry either when describing chemical practice in general or when specifically describing the modern rationalistic approach to chemistry. While it is true that these various terms were often not employed by the actual practitioners during a given historical period (as must necessarily be the case for both the pre-Islamic and nonwestern forms of alchemy) or were often used in a far looser sense than is the case today, the recent suggestion that we should abandon our current distinctions and revert once more to the ambiguities of the past, would, in my opinion, only result in historical chaos.

Indeed, I feel that what is needed for historical clarity is a further sharpening rather than a further blurring of boundaries. In keeping with this, I have followed the opinion of Cyril Stanley Smith that the Stockholm papyrus and Leyden papyrus X are really part of a continuous tradition of practical recipe books intended for metal workers and artisans, rather than proto-alchemical documents, as they have been traditionally portrayed since the work of Berthelot at the end of the 19th century, and I have made a similar distinction between the true alchemical literature and both the ancient and medieval encyclopedia literature. In contrast to these two genres, as well as to the earlier technical and philosophical writings of the Greeks and Romans, the genuine alchemical literature is, aside from its subject matter, most easily characterized by its rampant use of allegory, its intentional obfuscation, and its pervasive forgery of dates and names. In keeping with these tendencies, it clearly has more in common with the occult and religious literature than with the literature of secular philosophy, technology, or science. It is alchemy's commitment to these practices, rather than its belief in the transmutation of metals or the elixir of life (both of which are ultimately issues of empirical falsification rather than theoretical commitment), which clearly place it outside the history of science proper.

As for the often repeated claim that the alchemists, despite their obscure writing and questionable theories, developed important pieces of equipment and accidentally stumbled on many new substances, it is, in my opinion, far more likely that they either borrowed or adapted these from the pharmaceutical and metallurgical practices of their day. Though occasional consultation of the alchemical literature is useful for descriptions of common apparatus and chemicals when filling in the gaps in the technical and pharmaceutical literature, the necessity for this increasingly disappears after the 15th century.

Finally, it should also be noted that, since these lectures are a summary or survey intended for students and not a scholarly monograph directed at specialists in the history of chemistry, the selected references which appear at the end of each lecture are exactly that. In each case I could have multiplied them tenfold. Generally, however, I have restricted them, whenever possible, to books rather than journal articles, to English rather than French or German sources, and to modern reprints of older pre-1800 books, which, unlike the originals, are likely to still be available through interlibrary loan. In addition, I have often selected books on the basis of readability and accessibility rather than currency, especially when the latter are vitiated by extensive speculation and conformity to current historical fads. Whenever possible, dates and the spelling of names and book titles have been standardized relative to Partington's multivolume *History of Chemistry*. When necessary, for purposes of clarity, I have also altered the symbols in older equations to conform with modern usage.

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Lecture I

The Fifteenth Century

(1401-1500)

Our Protochemical Heritage

> Concerning alchemy, it is more difficult to discover the actual state of things, in that historians who specialize in this field ... seem to become tinctured with the kind of lunacy they set out to describe.
>
> *Herbert Butterfield 1951*

1.1 Why Start in 1400?

Though the list of relevant manuscripts and authors would be shorter, there is little to be gained in starting our survey of the history of chemistry at a date earlier than 1400, since any earlier choice, extending back at least as far as the Roman Empire, would, with few exceptions, yield essentially the same picture relative to the actual state of chemical knowledge and technique. It is only in the 16th century that we begin to detect the first signs of significant change in this otherwise flat chemical landscape. Consequently, the 15th century and the start of the so-called Renaissance form the most convenient point for summarizing the chemical heritage of the preceding centuries.

1.2 Chemical Training

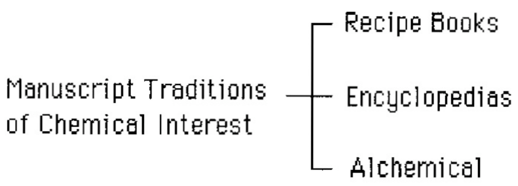
Almost 71 European universities exist by 1500, the earliest of which date from the 9th century, but chemical training is not part of the curriculum. These universities evolved out of medieval cathedral schools and ideally consisted of four faculties or schools specializing in the arts, theology, law and medicine. Though some mathematics and astronomy were taught within the school of arts as part of the traditional quadrivium, instruction was quite elementary. Likewise, though pharmacy or *materia medica* was certainly part of the curriculum within the schools of medicine, it was at this period essentially botanical rather than chemical in content. Active pursuit of what would today be thought of as chemical technology and/or chemical philosophy was largely in the hands of uneducated artisans, priests with technical interests, and a group of "philosophers" who practiced a form of metallurgical mysticism known as alchemy.

1.3 Professional Organizations

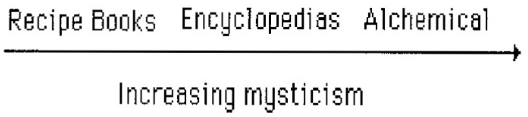
Though there are guilds of scholars connected with the universities and a tradition of scholarship and teaching within the Catholic priesthood, there are no explicit scientific societies.

1.4 Technical Literature

Likewise, there are no scientific journals and, prior to the 1450s, no printed books. However there are manuscript sources containing information of chemical interest. These include medieval recipe books, so-called encyclopedias or natural histories, and alchemical works in Greek, Arabic, and Latin:



These three manuscript traditions may be placed on a continuum relative to the amount of superstition and/or mysticism they contain and while the transition from one tradition to another naturally involves certain ambiguities at their boundaries, there is generally no problem in identifying characteristic specimens of each type:



Examples of the most straightforward of these three genres – the recipe books – are shown in Table 4.1. Intended as technical guides for metal workers, jewelers, and other artisans (and, in the case of Marcus Graecus, for military engineers), they are almost totally devoid of superstitious folklore and mystical obfuscation, even though, by modern standards, many of the recipes contain unessential ingredients and needlessly complex instructions. Aside from direct archaeological evidence, they are perhaps our most trustworthy guide to the chemical repertoire of mankind in the period between the classical Greeks and the end of the middle ages.

Table 1.1 Examples of Early Recipe Books

Date *	*Author*	*Title*
250	unknown	*Stockholm & Leyden papyri*
790	unknown	*Compositiones variae*
810	unknown	*Mappae clavicula*
1100	Theophilus	*De diversis artibus*
1150	Eraclius	*De coloribus et artibus Romanorum*
1150	Joannes	*Liber sacerdotum*
1200	Marcus Graecus	*Liber ignium*

* All dates are approximate

Though this tradition can arguably be traced back to surviving Mesopotamian cuneiform tablets dealing with recipes for glass making (some dating back as far as the 7th century BC), detailed discussions generally begin with the two late 3rd or early 4th century AD Greco-Egyptian manuscripts known as the Stockholm papyrus and Leyden papyrus X, respectively (which, despite their separate names and current locations, were, in all probability, originally made by the same scribe). The Leyden papyrus X consists largely of short recipes for the preparation of metal alloys, many of which are intended to imitate the appearance of either gold or silver; recipes for gilding and various forms of metallic writing; and a few recipes dealing with dyes. The Stockholm papyrus has the same form, but deals largely with dying and the imitation of precious stones and gems. Both papyri explicitly recognized that the alloys and gems they describe were imitations and not the real thing.

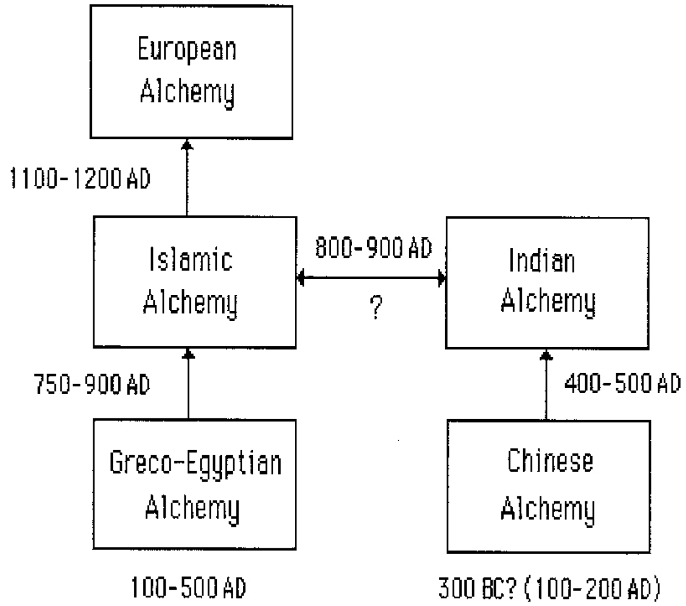
Next in order come the natural histories or encyclopedias (Table 1.2). Traceable to the works of the Roman writers Seneca and Pliny the Elder in the 1st century AD, these compilations often contain information about contemporary metallurgy, chemical technology, and (later) alchemy, though it is intermixed with a great deal of superstitious folklore and commentary. Characterized by one historian as "purely derivative compilations which observed little distinction between the factual and the fanciful, the significant and the merely curious," these works were, nonetheless, written in a straight forward manner and are lacking the esoteric symbolism and allegory so typical of the true alchemical literature.

Table 1.2 Examples of Early Encyclopedias

Date *	*Author*	*Title*
50	Lucius Annaeus Seneca	*Quaestiones naturales*
77	Gaius Plinius Secondus	*Naturalis historiae*
450	Martianus Capella	*Satyricon*
620	Isidore of Seville	*Etymologiarum libri XX*
847	Hrabanus Maurus	*De universali natura*
1240	Barthalomaeus Anglicus	*Liber de proprietatibus rerum*
1250	Vincent de Beauvais	*Speculum majus*
1260	Albertus Magnus	*De rebus metallicus et mineralibus*
1266	Roger Bacon	*Opus majus, minus, and tertium*

* All dates are approximate

The final genre – the alchemical manuscripts – are the most difficult to interpret as they are generally allegorical in nature and heavily tinged with hylozoic and hylomorphic symbolism (see Section 1.9). Begun as a sort of metallurgical mysticism in 2nd-century Alexandria, the practice of *chemeia*, *chymia* or *alchemy*, as it came to be called in the Islamic literature, spread first to Islam in the 8th century and then to Europe in the 12th century.



Known in its three western reincarnations as Greek, Arabic and Latin alchemy, respectively, after the principal languages used in the manuscripts, it also has clear parallels with similar chemical-mystical practices in both ancient China and India, though the exact historical relationship between the oriental and occidental forms of alchemy remains obscure. The most distinctive feature of oriental alchemy, however, was its emphasis on the preparation of inorganically based elixirs and medicines – a theme that does not appear in occidental alchemy until the emergence of the iatrochemical movement in the 16th century (see Lecture II). The earliest surviving copies of western alchemical manuscripts are written in Greek and Syrian and date from the 10th or 11th century, though many claim to be copies of works written as early as the 3rd or 4th centuries.

Not only does the allegorical-mystical content of most true alchemical manuscripts make their interpretation difficult, many of the actual authors are unknown. To make matters worse, these anonymous authors would often falsely claim that their effusions were actually the work of some famous personage even though the personage in question never actually practiced or even believed in alchemy. These forgeries were attributed to, among others, ancient philosophers (e.g., Democritus, Leucippus), mythical religious figures (e.g., Hermes, Moses, Miriam), famous Islamic medical writers (e.g., Avicenna, Rhazes), and recently deceased Catholic theologians and philosophers (e.g., Ramond Lull, Albert the Great, Roger Bacon, etc.) – a practice which accounts for the pervasive use of the euphemistic prefix "pseudo" among historians of the subject (see Table 1.3).

Table 1.3 Examples of Early Western Alchemical Writers

Date *	*Author*
200-500	pseudo-Democritus (Bolos of Mendes), Zosimus, Synesius, Olymiodorus
630	Stephanos of Alexandria
700	Heliodorus
1300	pseudo-Geber, pseudo-Avicenna, pseudo-Rhazes
1330	Petrus Bonis
late 1300s	pseudo-Arnaldus Villanova, pseudo-Raymond Lullis, pseudo-Roger Bacon

*All dates are approximate

Perhaps the worst example of this practice involves the 8th-century Arab scholar, Jabir ibn Hayyan (c. 721-815). Around 1300 various alchemical manuscripts attributed to him under the Latinized name of "Geber" began to appear in Europe, almost all of which are now thought to be 13th-century European forgeries, since no Arabic originals have ever been found. But even if the Arabic originals were discovered, they would probably prove little about the real Jabir, since the few surviving Arabic works attributed to him (none of which correspond to the European forgeries) are thought, in turn, to be forgeries written by members of an Islamic religious cult some time in the 10th century. In short, the European manuscripts may be nothing more than forgeries built on earlier Arabic forgeries. Regrettably, uncritical acceptance of these forgeries by cultural historians unfamiliar with the literature dealing with the history of chemistry continues to form the basis of vastly exaggerated claims concerning the so-called advanced state of Islamic chemical knowledge during the early middle ages.

1.5 Printed Books

As already briefly noted, this century also sees the introduction of printing in Europe – an innovation usually attributed to the German, Johann Gutenberg (1400-1468), some time in the period between 1440 and 1450 (the earliest surviving example of western printing dates from 1454). Though a large number of books were printed in the period 1450-1500, most dealt with either classical literature, law, or theology, and, to a lesser degree, with medicine and botanical pharmacy. The full impact of printing on the literature of alchemy and chemical technology will not occur until the 16th century.

Nevertheless, two important publications on the art of distillation deserve brief mention – a small booklet (15 pages) by Michael Puff von Schrick (1400-1473) on the distillation of alcoholic ferments, published in 1474; and a full book, *Liber de arte distillandi de simplicibus*, by the German physician, Hieronymus Brunschwig (c. 1430-1512), on the distillation ofherbs and plants, published in 1500. However, it is important to note that the chemical relevance of these publications is incidental rather than intentional. Puff von Schrick's pamphlet was, in fact, little more than a recipe book for the distillation of flavored brandies and Brunschwig's book was intended primarily for the use of apothecaries and doctors.

1.6 Experimental Apparatus and Technique

Despite the lack of explicit chemical training and an explicit literature, by 1500 there already existed an impressive array of fundamental apparatus and techniques that would eventually serve as the foundation of chemical laboratory practice – most of it originally developed for use in metallurgy, pharmacy, and everyday business. Some typical examples are summarized in Table 1.4. The only major energy sources were wood or charcoal furnaces. These would remain central to chemical practice well into the first half of the 19th century. Indeed, so

Table 1.4 Example 15th-Century Chemical Apparatus

Name	*Word Origin*
aludel	Ar *al* + *uthal*, the + utensil
alembic	Ar *al* + *anbiq*, the + still
balance	L *bi* + *lanx*, two plates or scales
bath (sand and water)	OE *baeth*, bath
beaker	L *bacarium*, basin, pitcher or jug
bellows	OE *belg*, bag or skin
blowpipe	OE *balwan* + L *pipare*, to peep
circulatory	L *circulus*, circle
crucible	L *crucibulum*, to subject to a test or crisis
cucurbit	L *cucurbita*, gourd
cupel	LL *cuppa*, small cup
filter	L *filtrum* or *feltrum*, felt or fulled wool
flask	LL *flasco*, wine bottle
funnel	L *infundibulum*, to pour in
furnace	L *fornax* or *furnus*, oven
ladle	OE *halden*, to dip
mortar	L *mortarium*, a trough used to mix mortar
muffle	ME *muflen*, to envelope
pelican	Imaginative name based on its shape
pestle	L *pistillum*, to grind or crush
retort	L *retortus*, to twist back
sieve	OHG *sib*, to drizzle
sublimator	L *sublimis*, to elevate
tripod	Gk *tripous*, three-footed
tongs	ME *tonges*, to bite
weights	OE *wegan* to weigh

important was the furnace to both industrial and laboratory technique that it would briefly give rise to an alternative name for chemistry – *pyrotechnica* or the "art of the fire" (from the Greek *pyr*, meaning "fire," and *techne*, meaning "art"). Thus, in the 16th century Biringuccio (1540) would entitle his volume on chemical technology *De la pyrotechnica*; and a century later William Davisson (1633) would entitle his popular textbook of chemistry *Philosophia pyrotechnica*, whereas Johann Barchusen (1698) would use the more concise title *Pyrosophia* or "fire wisdom." Likewise, Boyle would name one of the characters in his chemical dialogues *Pyrophilus* or "lover of fire," and the American alchemist, George Starkey, would entitle one of his iatrochemical polemics *Pyrotechny Asserted and Illustrated* (1658). In the end, however, the more traditional name of *chymia* or chemistry (whose origins and meaning are still being debated by historians) would triumph instead and the term "pyrotechnics" would become restricted to the art of manufacturing and displaying fireworks.

Table 1.5 Typical 15th-Century Laboratory Techniques

Procedure	*Word Origin*
cupellation	LL *cuppa*, small cup
decantation	L *de* + *cantus*, from the ring
digestion	L *digestus*, to distribute
distillation	L *de* + *stillare*, to remove dropwise
extraction	L *ex* + *trahere*, to draw out
filtration	L *filtrum* or *feltrum*, felt or fulled wool
fractionation	L *fractus*, to break
percolation	L *per* + *colare*, through a sieve
refluxing	L *re* + *fluxus*, to flow again
scorification	Gr *skor*, excrement
sublimation	L *sublimis*, to elevate
trituration	L *tritura*, to rub

Likewise, some typical laboratory procedures are summarized above in Table 1.5. It is of interest to note that all but two of these procedures (refluxing and trituration) are separation techniques and that the two exceptions are both methods for enhancing and prolonging contact between reacting substances.

1.7 Distillation

One of the few techniques listed in Table 1.5 having a traceable history is the art of distillation (for cupellation and scorification, however, see Lecture II). Writing in 1945, the historian, R. J. Forbes, in his monograph, *A Short History of Distillation*, claimed that there was no firm evidence for true distillation prior to the introduction of the alembic by the Alexandrian alchemists some time in the first or second century AD. However, the American archaeologist and chemical historian, Martin Levey, published evidence in the 1950s of crude Babylonian and Sumerian apparatus (c. 3500 BC) for distillation and extraction, and the remains of what appears to be some form of crude distillation apparatus (c. 90 BC - 25 AD) have since been uncovered in the Indus valley region by archaeologists.

Though the cooling ability of the alembic was poor, its use had led to the discovery of alcohol (via distillation of wine) by the 11th or early 12th century, and to the discovery of sulfuric acid (via the distillation of green or blue vitriol), nitric acid (via the distillation of salt petre and vitriol), and aqua regia (via the distillation of salt petre, sal ammoniac, and vitriol) by the 13th century.

Examination of manuscript sources and the books by Puff von Schrick and Brunschwig also show that several important improvements in distillation apparatus had come into use by the 15th century:

a. *The Retort:* An all-glass distillation apparatus that eliminated the necessity of luting the still head (alembic) to the still base (cucurbit). This feature made it especially useful for the distillation of corrosive mineral acids.

b. *The Rosenhut:* A tall conical still head or alembic originally made of copper (whence its name), but later also from pewter and other materials. Though metal provides better heat exchange than either glass or ceramic, this benefit was probably not recognized at the time and the use of metal was probably motivated instead by the fact that it provided an easier and less expensive way of making large industrial-scale stills.

c. *The Moor's Head:* A water-cooled alembic head, initially in the form of a wet towel wrapped around the still head (whence its resemblance to a turban or Moor's head) and later in the form of a open basin of water with a drain valve.

d. *The Serpentine or Worm:* An elongated, coiled alembic beak cooled in a water basin or trough.

This latter device was actually first described by the Italian, Taddeo Alderotti (1223-1295), in the 13th century. Though mentioned by Ortholanus in the 14th century, it did not come into common use until the 15th century, when it is mentioned by such writers as Michael Savonardo and John Wenod (who also provided the first drawing of the apparatus in 1420).

By the 15th century these advances had led to what can only be described as a "distillation craze" in which virtually everything imaginable – whether plant, animal, mineral, or mixtures thereof – was subjected to destructive distillation in hopes of extracting its active essence or seminal principle. As distillation grew more popular, it revolutionized *materia medica* and gave medicine an increasingly chemical slant that would eventually pave the way for the entrance of chemistry into the university curriculum in the 17th century. Likewise, as the products of distillation grew in importance, they began to challenge the ability of the traditional four Aristotelian elements (see Section 1.9) to rationalize and classify the range of textures being discovered, and thus laid the foundations for the development of alternative systems of chemical elements and principles in the 16th and 17th centuries.

1.8 Substances

Tables 1.6-1.9 provide a survey of some of the more important chemical substances known to alchemy, metallurgy and pharmacy prior to 1400 (with their modern formulas appended for greater clarity). In the case of the metals and alloys listed in Table 1.6 there is some ambiguity relative to Zn, As, Sb and Bi. Thus while there is little evidence that Zn metal was recognized in Europe prior to this date, recent archeological work has definitely established that it was well-known in both India and China. The paradox that brass was long known even though Zn metal was not is explained by the fact that the Zn used in brass manufacture was produced *in situ* during the smelting process via reduction of an appropriate ore and not added in the form of the pure metal. Further complications result from the fact that there was often a confusion of one substance with another, for example, of Sb with Pb. In addition

Table 1.6 Example Metals & Alloys Known Prior to the Renaissance

gold	tin	zinc*	tertiarium (Pb/Sn)
silver	mercury	bronze (Cu/Sn)	chrysocolla (Au/Cu)
copper	arsenic*	aurichalcum or brass (Cu/Zn)	Ag/Cu
iron	antimony*	electrum or asem (Au/Ag)	Ag/Sn
lead	bismuth*	stannum (Ag/Pb)	

* Some debate about exact dates of recognition

Table 1.7 Example Acids, Alkalis, & Salts Known Prior to the Renaissance

oil of vitriol (H_2SO_4)	potash (K_2CO_3)	rock salt (NaCl)
spirit of salt (HCl)	nitron or soda (Na_2CO_3)	nitre or salt petre (KNO_3)
aqua fortis (HNO_3)	volatile alkali (NH_3)	sal ammoniac (NH_4Cl)
aqua regia (HCl/HNO_3)	lime ($CaO/Ca(OH)_2$)	sal tartari ($KHC_4H_4O_6$)
vinegar (CH_3COOH)	caustic soda (NaOH)	liver of sulfur (CaS_x)
blue vitriol ($CuSO_4 \bullet 5H_2O$)		green vitriol ($FeSO_4 \bullet 7H_2O$)
alum ($K_2Al_2(SO_4)_4 \bullet 24H_2O$		white vitriol ($ZnSO_4 \bullet 7H_2O$))

Table 1.8 Example Minerals & Pigments Known Prior to the Renaissance

realgar (As_4S_4)	hematite or red orchre (Fe_2O_3)	azurite ($Cu_3(CO_3)_2(OH)_2$)
orpiment (As_2S_3)	yellow orchre ($Fe_2O_3 \bullet H_2O$)	malachite ($Cu_2CO_3(OH)_2$)
cinnabar (HgS)	litharge (PbO)	verdigris ($Cu_3O(CH_3COO)_2$)
stibnite (Sb_2S_3)	minium or red lead (Pb_3O_4)	gypsum ($CaSO_4 \bullet 2H_2O$)
pyrite (FeS_2)	tutia (ZnO)	chalk ($CaCO_3$)
galena (PbS)	flos aeris (Cu_2O)	borax ($Na_2B_4O_7 \bullet 10H_2O$)
		ceruse ($Pb_4(CO_3)_3(OH)_2$)

Table 1.9 Example Combustibles Known Prior to the Renaissance

carbon (charcoal, graphite, diamond)	asphalt (pitch or bitumen)
brimestone or sulfur	alcohol
petroleum (naphtha)	

to the organic substances listed in Table 1.9, a wide variety of plant materials, dyes, and extracts were also known, though poorly characterized from a chemical point of view.

1.9 Conceptual Content

To the extent that we can talk of so-called "chemical theory" during both this period and the preceding centuries, it is based on two primary sources of ideas concerning those transformations that we currently identify as chemical:

a. The hylozoic (from the Greek *hyle*, meaning "matter" and *zoos*, meaning "alive") folklore of primitive metallurgy.

b. The hylomorphic (from the Greek *hyle*, meaning "matter" and *morphe*, meaning "shape") theory of generation and corruption (substantial change) inherited from the writings of Plato (427-347 BC), via neoplatonism and St. Augustine (354-430 AD), and the writings of Aristotle (384-322 BC), via Thomas Aquinas (1225-1274 AD) and medieval scholasticism.

Both sources are animistic, the first explicitly and the second implicitly:

form = essence or active masculine seminal principle (semen)
matter = inert matrix or passive female womb

In terms of concrete laboratory practice these assumptions translate into:

form = volatile vapors, especially those having pungent odors
matter = inert solids (earths) or distillation residues (caput mortem)

Thus most laboratory operations involved the production, via distillation or sublimation, of volatile and/or pungent vaporsknown as essences or quintessences and the exposure of metals and other solids to these vapors in an attempt to induce a change in substantial form (insemination), followed by long periods of heating (incubation) in order to insure the growth or maturation of the desired product (embryo).

The underlying logic was the belief that, in nature itself, metals, like plants and animals, were produced from seeds buried within the womb or matrix of the earth, where they gradually matured or grew. Soft, easily oxidizable metals, such as lead or tin, were thought to be the early immature stages of this growth process, whereas the not easily oxidizable noble metals, such as silver and gold, were the final or mature stages. The alchemist sought to assist or accelerate this natural growth process in the laboratory by first stripping an immature metal of its outer forms or properties by reducing it to a black propertyless powder or *caput mortem* and then implanting or impregnating a new metallic seed within the dead body by exposure to various volatile vapors or essences as described above, followed by acceleration of the incubation and maturation processes.

Unfortunately not only were most alchemical writings allegorical, they were also, by modern standards, hopelessly vague. As aptly summarized by one early 20th-century commentator:

The directions the alchemist was able to give to those who sought *to effect the change of one thing into another were these. Firstly remove those properties which characterized the thing to be changed, and leave only the properties it shared with other things like it; secondly, to destroy the properties which the thing possessed in common with certain other things; thirdly, to commingle the Essence of the thing with the Essence of the something else, in due proportion and under proper conditions; and finally, to hope for the best, keep a clear head, and maintain a sense of virtue.*

If he who was about to attempt the transmutation inquired how he was to destroy the specific properties, and the class properties, of the thing he proposed to change, and by what method he was to obtain its Essence, and cause that Essence to produce the new thing, he would be told to travel along "the road which was followed by the Great Architect of the Universe in the Creation of the world." And if he demanded more detailed directions, he would be informed that the substance wherewith his experiments began must first be mortified, then dissolved, then conjoined, then putrefied, then congealed, then cibated, then sublimed, and fermented, and, finally, exhalted. He would, moreover, be warned that in all these operations he must use, not things which he could touch, handle, and weigh, but the virtues, the lives, and the souls, of such things.

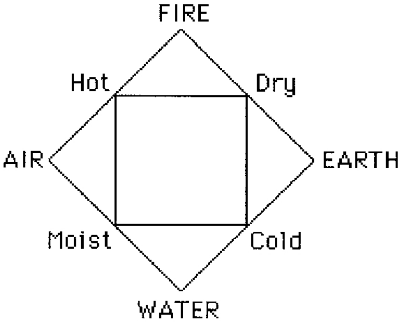
The animistic view of matter underlying these procedures is quite explicit in the description of copper metal provided by the 7th-century alchemical commentator, Stephanos of Alexandria:

> *It is necessary to deprive matter of its qualities in order to draw out its soul ... Copper is like a man; it has a soul and a body ... the soul is the most subtle part ... that is to say, the tinctorial spirit. The body is the ponderable, material, terrestrial thing endowed with a shadow ... After a series of suitable treatments, copper becomes without shadow and better than gold.*

As noted by Schumaker in his classic study of alchemy as one of the occult sciences, its underlying theoretical principles were "animistic, voluntaristic, and even dramatic" in nature, thus accounting for the fact that, “except in the most primitive fashion, the alchemist did not analyze but rather analogized.”

The writings of Aristotle also provided a second, more intellectualized, conceptual component in the form of the so-called “four elements” of earth, air, fire, and water:

		Texture	
		Moist	Dry
Temperature	Hot	AIR	FIRE
	Cold	WATER	EARTH



Amplifications of the elements originally introduced by the Greek philosopher-poet, Empedocles (c. 5th century BC), these four exemplars were intended to approximate the most primitive substances possible – substances that had been stripped of all qualities or forms other than the minimal “universal” forms of texture (dry or moist) and temperature (hot or cold) common to all substances. The criterion for simplicity or elemental character was not compositional simplicity, in the sense of the presence or absence of certain material components, but rather sensual simplicity, based in turn, on the criterion of universality.

Within the context of these universal qualities, analysis of a material into its “elements” did not mean to chemically decompose it into its simplest material components, but rather to describe the degree to which it partook of the primitive universal forms or qualities of texture and temperature exemplified by each of the four Aristotelian elements. As the 19th-century British philosopher of science, William Whewell, succinctly put it, analysis was, in effect, the decomposition of a substance into “adjectives” rather than “substantives.”

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OUR PROTOCHEMICAL HERITAGE

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Lecture II

The Sixteenth Century

(1501-1600)

The Impact of Medicine and Metallurgy

> How long has medicine been practiced in the world? Yet it is said that the
> newcomer Paracelsus has overthrown all the old rules and maintains
> they were only fit to kill men with. That much I believe ... but I
> would not think it wise to risk my life on his new experiments.
> *Michel de Montaigne 1580*

2.1 Chemical Training

The number of European universities now stands at 108. Though chemistry and technology are still excluded from the curriculum, the medical schools will come under increasing attack in the 16th century as a result of the activities of the Swiss-German activist, Philippus Aureolus Theophrastus Bombast von Hohenheim (1493-1541), better known as Paracelsus. Paracelsus and his followers give rise to a movement known as iatrochemistry (from the Greek *iatros*, meaning "healer"), which advocated the introduction of mineral substances (e.g., As and Hg) and alchemical concepts into the practice of *materia medica* and physiology in opposition to the traditional botanically based pharmacology of the Roman physician, Galen of Pergamum (c. 129-199 AD), advocated by most medical schools of the period. While one is hard pressed to argue that Paracelsus ever made a significant contribution to either scientific knowledge or theory, there is no doubt that his extreme advocacy of alchemical models in medicine and pharmacy would have a profound effect on the future professional development of chemistry, as will be seen in greater detailin the next lecture.

2.2 Professional Organizations

This century sees the formation of the first tentative scientific societies, such as the short-lived Italian examples of the *Accademia degli Affati* (1548) and the *Academia Secretorum Naturae* (1560). These beginnings, however, are very sporadic, and the heyday for the formation of scientific societies will not come until the 17th century.

2.3 Technical Literature

The impact of printing on the technological literature, whose first beginnings were already noted in the early books on distillation by Puff von Schrick and Brunschwig, now takes off (Table 2.1) and produces a veritable flood of classic volumes (including yet a second volume by Brunschwig):

Table 2.1 Example 16th-Century Technical Books of Chemical Interest

Date	*Author*	*Title*
1507	Hieronymus Brunschwig	*Liber de arte distillandi de composita*
1520	Anonymous	*Probierbüchlein*
1540	Vanoccio Biringuccio	*De la pyrotechnica*
1540	Giovanni Plictho	*De l'arte de tentori*
1548	Cipriano Piccolpasso	*Le tre libri dell' arte del vasaio*
1556	Georg Agricola	*De re metallica*
1574	Lazarus Ercker	*Mineralischen Erzt und Berg Werck ...*
1580	Bernard Palissy	*Discours admirables*

These books are in some ways an elaboration of the earlier traditions of the recipe book and the encyclopedia. Nevertheless, they are incomparably richer and more detailed in their presentation and, for this reason, are deserving of a separate designation. For lack of a better term, we will refer to this new genre as the “didactic technical literature.” While various traditional folklore beliefs are often taken seriously by the authors of these books, their intent, unlike that of the alchemical literature, is to summarize and instruct in clear language rather than to obfuscate and mystify.

Though all of the titles listed in the above table are of great interest to the history of chemistry for the information they contain on the various chemical substances and techniques used in distillation, metallurgy, assaying, dying, enameling, and the manufacture of pigments, glass, explosives, and pottery, none of them were intended to be self-consciously chemical in content. Indeed, it is not known to what extent the individual renaissance craftsmen engaged in metallurgy, distilling, etc. considered themselves to be chemists, as distinct from brewers, dyers, apothecaries, or assayers, though there is little evidence that they identified their crafts in any way with the practice of alchemy.

Thus Ercker, Agricola, and Biringuccio were all careful toclearly distinguish between the practice of metallurgy and assaying, on the one hand, and the practice of alchemy, on the other, and were all highly critical of the alchemist's claim to have successfully transmuted base metals into gold. Ercker disposed of the subject in a few sentences and Agricola in a couple of paragraphs. Biringuccio devoted several pages to his critique of alchemy. Though he clearly believed that metals were naturally transmuted via a hylozoic growth process within the bowels of the earth, he did not believe that the alchemist had been successful in artificially duplicating the process in the laboratory, and contrasts their vain and fanciful claims with those of the metallurgist, who humbly makes use of that which nature has already provided.

With the exception of Palissy, most of those who wrote books on these subjects in the 16th century were not craftsmen themselves. Thus Agricola was a physician, Piccolpasso was a military architect, Ercker was a mining official, and Biringuccio managed an arsenal and salt petre works.

An argument can be made that, like the recipe books and encyclopedias, the didactic technical literature has a separate tradition reaching back to the 1st century BC and the book *De architectura* by the Roman writer, Pollio Vitruvius (c. 100-40 BC), which contains valuable information on chemical substances used in the construction and decoration of Roman buildings. However, unlike the other genres, there seems to be no manuscript tradition spanning the gap between Vitruvius and the 16th century. Though printed versions of the traditional recipe books also begin to appear, as well as editions of early alchemical writings, they have little to tell us from this point on. The contents of the typical recipe book remain relatively static and the alchemical literature becomes increasingly mystical. From here on the didactic technical literature provides us with a far more reliable source of information on chemical substances and processes.

After the death of Paracelsus in 1541, a new genre of iatrochemical literature gradually appears (Paracelsus' own collected works were not published until 1589). In its less extreme forms, this literature is a curious blend of relatively straightforward instructions for the practical preparation of chemical medicines, abusive polemics, mystical allegory, and rampant occultism. This was in part because the assault of Paracelsus and his followers on the medical establishment was more than just an argument over alternative theories of pharmacology and physiology. In many ways a child of the reformation, Paracelsianism was also an assault on established authority in general – whether of the Catholic church, the priesthood, traditional scholarship, or the university establishment. Its ultimate success created something of an intellectual vacuum that would eventually be filled by an eclectic mix of not only alchemy but also of neoplatonism, theosophy, astrology, magic, cabalism, rosicrucianism, numerology, and other assorted forms of occultism.

Previous historians have picked through the practical recipe portions of much of this literature in order to extract what little it can tell us about chemical apparatus, preparative techniques, and known chemical substances, though, as with the traditional recipe books and alchemical literature, there is little beyond what can already be found in the didactic technical literature.

There are, however, some important exceptions. Though technically falling outside the time frame of this lecture, a work bearing the curious title of *Triumph Wagen Antimonii* (usually translated as *The Triumphant Chariot of Antimony*) deserves brief mention. First published in 1604 and reputedly written by a 15th-century Benedictine monk by the name of Basilius Valentinus or Basil Valentine, it provided a fairly readable summary of the known compounds and uses of antimony and was strongly iatrochemical in its advocacy of these dangerous substances in medicine. It is now thought that the book was probably written in the late 16th century by its publisher and supposed translator, Johann Thölde, who is known to have been strongly influenced by Paracelsus and his writings.

Perhaps the most notable thing about both the alchemical and early iatrochemical literature is the disjunction between practice and theory, with little or no interaction between the practical recipes, on the one hand, and the fanciful mystical speculations, on the other. While it is true that these books often contain polemics on the importance of submitting nature to the test of personal experience, these are more a reflection of the inherent anti-authoritarianism of Paracelsianism than they are of a true scientific skepticism. What is really being tested is not the validity of the hylozoic or mystical model, but rather the purity and understanding of the alchemist or iatrochemist. While certain modern historians have naively interpreted these polemics as evidence of a scientific mind set, contemporary observers were not always so easily fooled. As Sir Francis Bacon observed in his *Novum organum* of 1620:

> *... the Alchemist nurses eternal hope, and when the thing fails, lays the blame upon some error of his own; fearing either that he has not sufficiently understood the words of his art or authors (whereupon he turns to tradition and auricular whispers), or else that in his manipulations he has made some slip of a scruple in weight or a moment in time (where upon he repeats his trials to infinity).*

2.4 Experimental Technique

The separation and testing procedures described in the didactic technical literature dealing with metallurgy and assaying represent the beginnings of modern analytical chemistry. Many of them were probably in use for centuries prior to their written description in the 16th century, and many continued to be used well into the first half of the 20th century. Thus in the second century BC, the Greek historian and geographer Agatharchides of Samos (181-146 BC) gave a description of the process used by Egyptian metal workers to purify gold which is essentially identical to the crucible assay method described 1600 years later by Agricola, Ercker and Biringuccio, and some of these methods are also briefly mentioned in the early European recipe and alchemical literature (e.g., Theophilus, c. 1100, and pseudo-Geber, circa1300). Indeed, it is a fascinating activity to compare these early accounts of assaying techniques with those found in the 1911 volume by Charles Fulton (*A Manual of Fire Assaying*), which was one of the first attempts, after nearly 2000 years of empirical practice, to elucidate the chemistry underlying these time-honored practices.

The term "assay" is related to the word "essay" and means "to attempt or try." The corresponding German word, *Probe* (as in *Probierbüchlein*), is related to the English word "probe" and ultimately to the Latin word *probare*, which means "to examine." Both terms reflect the fact that the purpose of a metallurgical assay was to test or try the metal content of an ore before committing time and money to its processing on an industrial scale. Though it is possible to assay for any of the various metals, in the 16th century the emphasis was, for obvious reasons, on the assaying of gold and silver, and government sponsorship of this activity because of its relevance to both the minting and counterfeiting of coins.

In a typical gold/silver assay, a weighed quantity of ore was either heated in a crucible with a mixture of litharge (lead oxide), a reducing agent (e.g. fine charcoal or sugar), and a suitable flux, or was mixed directly with metallic lead in a small clay dish and heated in an air current using a bellows and blowpipe. The first of these processes was known as a crucible assay and the second as scorification. Both produced a mixture of lead metal and lead oxide. The former alloyed with the metallic gold and silver present and the latter reacted with the silicates and oxides of the less noble metals to form an ionic slag or glass.

The alloyed lead beads from the crucible or scorification dish were then placed in small bone-ash cups called cupels (mostly composed of the carbonates and oxides of calcium and magnesium) and heated to selectively oxidize the lead. The resulting lead oxide was absorbed into the bone-ash cupel leaving behind a bead of pure gold and/or silver. The percentage of silver in the beads could be roughly determined using a streak test, done by comparing the color of the streak it left on a touchstone with that produced by a series of touch needles of known Au-Ag composition, or by determining its relative specific gravity. The silver and gold could then be further separated from one another by selectively dissolving the silver in nitric acid (parting acid), and the final yields carefully measured using delicate assay balances, which were often enclosed in glass cases to protect them from air currents and dust.

Another processes described in early assay books is the separation of alluvial gold from the surrounding gravel and dirt via amalgamation with mercury and its subsequent recovery via distillation.

Essentially all of the chemical apparatus and processes listed in Section 1.6, and in the contemporary alchemical literature, are described in detail in the didactic literature dealing with distillation and assaying, where they are also often profusely illustrated by means of woodcuts, and it is very difficult to believe that all of the apparatus and procedures used in these practical everyday crafts were somehow imported from the obscure manuscript writings of anonymous alchemists. To the extent that there is an overlap, the majority of the information flow was almost certainly in the opposite direction. Though early alchemical manuscripts do contain descriptions of apparatus, they are often vague and cloaked in allegory. The few accompanying illustrations are often highly schematic and may in fact be interpretive annotations added by later medieval copyists.

As with virtually everything connected with the true alchemical literature, one must be careful not to take things at face value. A case in point involves a famous illustration found in a late 15th-century manuscript by the British alchemist, Thomas Norton (1433?-1513), known as *The Ordinall of Alchemy*. This shows a supposed alchemist sitting in front of an enclosed balance. On the floor by the table are a series of crucibles and a crucible mold and in the foreground are two assistants, one performing fractional distillation and the other using a pelican to reflux. A second illustration shows several assistants apparently digesting silver-gold alloys in parting flasks and using alembics to distill acid. Save for the differences in the period costumes, the apparatus and procedures depicted in the illustrations are virtually indistinguishable from those found in Brunschwig and Ercker. The first of these illustrations has been cited by one recent alchemical enthusiast as evidence that the alchemists made use of delicate balances and quantitative assaying techniques in their work. Unfortunately, absolutely no mention of any of the techniques or apparatus in these illustrations is to be found in Norton’s actual manuscript, and it is far more probable that the illustrations are imaginative embellishments, based on the artist's knowledge of the techniques used by the local assayer and apothecary, rather than factual renditions of what really went on in Norton's alchemical laboratory

2.5 Conceptual Content

This continues to remain static. A minor change is the rise to prominence of the *tria prima* or three principles of Paracelsus as a supplement to the traditional four elements of Empedocles and Aristotle. These three principles of salt, mercury, and sulfur were thought to embody the qualities of solubility, volatility, and inflammability, respectively, and evolved out of the alchemical literature. Aristotle and Theophrastus thought that minerals and metals arise within the earth as a result of the action of a cold moist (i.e. active male) principle on a dry earthy (i.e. passive female) principle. In the legitimate Islamic alchemical and medical literature these two principles become associated with mercury and sulfur, respectively, (an idea which, in turn, may have come from Chinese and Indian sources), and from Islam this theory passes into the early European alchemical literature from which it is eventually adopted and amplified by Paracelsus and his followers.

Though similar in type (i.e., hylomorphic), its importance lies in its challenge to the traditional four elements and in its adoption of the chemically more relevant qualities of solubility, volatility, and inflammability. Thus, within the context of the *tria prima*, alcohol was described as a “sulfurous vegetable mercury” – in other words, as a flammable (sulfurous), volatile (mercury) liquid prepared from fermented vegetable matter.

2.6 Selected References

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* S. von Osten, *Das Alchemistenlaboratorium von Oberstockstall*, Universitätsverlag Wagner: Innsbruck, 1998. This is the official report (heavily illustrated) of the excavations of the trash pit for a late 16th-century chemical laboratory located in Castle Oberstockstall in the village of Kirchberg in Lower Austria. The recovery of over 1000 objects has allowed the reconstruction of many pieces of laboratory apparatus relating to the practice of metallurgical assaying and Paracelsian iatrochemistry, as well as alchemy. This is undoubtedly one of the most important developments in the history of chemistry in recent years.

Lecture III

The Seventeenth Century

(1601-1700)

Chymistry Institutionalized and Corpuscularized

> I observe that of late chymistry begins, as indeed it deserves, to be cultivated by learned men who before despised it; and to be pretended to by many who never cultivated it, that they may be thought not ignorant of it.
>
> *Robert Boyle 1661*

3.1 Chemical Training

With the coming of the 17th century chemistry finally finds a place in the university in the form of service courses within the medical schools – the combined result of both the distillation craze and the iatrochemical movement. Typical examples of some early university appointments of chemical interest are shown in Table 3.1.

Table 3.1 Early University Appointments of Chemical Interest

Date	*School*	*Lecturer*
1602	Wittenberg	Daniel Sennert
1609	Marburg	Johann Hartmann
1641	Jena	Werner Rolfinck
1673	Montpellier	Sebastian Matte La Faveur
1683	Altdorf	Johann Hoffmann
1683	Oxford	Robert Plot
1694	Utrecht	Johann Barchusen

In some cases, the actual lectureships were in *materia medica* (i.e., pharmacy) and the lecturer in question simply had a strong chemical slant, whereas in others (e.g., Hartmann) the appointment dealt explicitly with *chymiatria* or iatrochemistry.

3.2 Professional Organizations

This century also sees the formation of government endorsed scientific societies, beginning with the short-lived Roman *Accademi dei Lincei* (1603) and its equally short-lived Florentine successor, the *Accademia del Cimento* (1657) – the most important of which are the *Royal Society of London* (1662) and the French *Académie Royal de Sciences* (1666).

3.3 Technical Literature

Both the Royal Society and the French Academy are associated with the publication of important scientific journals (*Transactions of Royal Society* and the unofficial *Journal des savants*, respectively) soon after their formation. Though most of the papers initially appearing in these journals dealt with natural history, mathematics, and mechanics, occasional chemical papers appear as well.

Books belonging to all of the genres previously mentioned (alchemy, iatrochemistry, didactic technology, etc.) continue to be published. In addition, a new genre – that of the didactic chemistry textbook – also makes an appearance, an event linked to the rise of university lectures on chemistry. The prototype of this genre is the text, *Alchemia*, first published by Andreas Libavius (c. 1540-1616) in 1597, and followed by a century of popular didactic French iatrochemical texts, many of which were also translated into German and English (see Table 3.2 at the top of the next page).

The appearance of Libavius' text represents a fundamental bifurcation in the alchemical and iatrochemical literature. From this point on there will be both a didactic branch, represented by the above examples, and a mystical branch. The didactic branch, through its association with university curricula and the new scientific societies, will evolve into modern chemistry, whereas the mystical branch, as personified by such authors as Robert Fludd

Table 3.2 Examples of Early Didactic Chemical Textbooks

Date	*Author*	*Title*
1610	Jean Beguin	*Tryocinium chymicum*
1633	William Davisson	*Philosophia pyrotechnica*
1646	Estienne de Clave	*Cours de chimie*
1660	Nicolas Le Févre	*Traicté de la chymie*
1663	Christophle Glaser	*Traité de la chymie*
1675	Nicolas Lemery	*Cours de chymie*

(1574-1637) and Michael Maier (1568-1622), will become increasingly alienated from these organizations and, by the end of the 18th century, will have devolved into a species of "crank" occultism.

In his text Libavius does not take issue with the fundamental assumption of alchemy and iatrochemistry that the goal of the chemist is to extract and concentrate the active seminal principles of substances in the form of essences or quintessences, though he does take issue with the assumption that chemical knowledge can only be acquired through a semi-religious process of prayer, purification, and contemplation involving supposed secrets encoded as hidden mysteries and allegories. Rather, in keeping with the didactic technical literature, he argues that alchemy and iatrochemistry can be taught, like metallurgy, glass making, and dying, in straightforward, clear, expository language. In keeping with this, the first half of his text deals with the description of chemical apparatus and techniques (including a complete blueprint of a chemical laboratory), and the second half with an empirical classification of chemical products based on their method of preparation (e.g., magisteries, extracts, distillates, sublimates, etc.).

Like the original text of Libavius, most of the French texts in Table 3.2 concentrate on the description of laboratory procedures and chemical products of medicinal interest. Though the explicit treatment of so-called chemical theory in these books slowly increases throughout the century, it never plays a prominent role.

Indeed, in the 1675 edition of Lemery's book, its treatment occupies only five of the more than 300 pages of text.

This emphasis on practice rather than theory contrasts sharply with that found in Oswald Croll's *Basilica chymica* of 1609, which was widely regarded as one of the better summaries of Paracelsianism. Here roughly half of the book, in the form of a lengthy introduction and an appended treatise on the doctrine of signatures, is devoted to polemics and occultism, rather than to practical preparative recipes. But even this is moderate when compared with the later writings of Maier and Fludd.

Like Croll, all of the authors in Table 3.2 accepted the Paracelsian claim that chemistry was essential to the practice of medicine and pharmacy, and many of them also accepted such Paracelsian doctrines as the *tria prima*. As with Libavius, what is really at issue here is not a question of laboratory practice or even theory, but rather how chemical information is to be processed and communicated to others – whether to the public at large via textbooks, journals, and public lectures presented in clear expository language, or to a select group of adepts via a series of secret initiations and esoteric mysteries encoded in allegorical symbolism. It is this difference, rather than issues of animism and transmutation versus mechanical atomism, which defines the boundary between the scientific-technical mentality, on the one hand, and the alchemical-magical mentality, on the other.

3.4 Experimental Technique

As shown in Table 3.3, the 17th century sees the introduction of a number of significant scientific instruments. However, the first of these devices is irrelevant to chemistry and the remaining six will not have a major impact on chemical practice until the 18th and 19th centuries. In addition, there are some minor improvements in laboratory heating devices (the alcohol lamp, the mouth blowpipe, and the use of burning lens and mirrors), as well as the first use of an *in situ* pneumatic trough to collect chemically evolved gases (by Boyle and Mayow), though again the full impact of these innovations will not be felt until the 18th century.

Table 3.3 Important 17th-Century Advances in Instrumentation

Date	*Instrument*	*Inventor*
1608	telescope	Hans Lippershey
1609	compound microscope	Zacharias Janssen, Hans Lippershey
1612	hydrometer	Johann Thölde?
1643	barometer	Evangelista Torricelli
1654	sealed thermometer	Ferdinand II of Tuscany
1657	vacuum (air) pump	Otto von Guericke
1672	electrostatic machine	Otto von Guericke

This century also sees an increasing realization that the analytical detection of a metal doesn't always require its reduction and isolation as in a standard fire assay, but can be done indirectly through the use of characteristic color and precipitation reactions with an appropriate reagent. Examples, such as the use of vegetable dyes to detect acids, copper compounds to detect ammonia, and nut gall to detect iron, can be found in the writings of several 17th-century chemists, including Libavius, Hoffmann, Glauber, Tachenius, and especially Robert Boyle.

3.5 Conceptual Content

The undermining of the traditional four elements of Aristotle and Empedocles, begun by the *tria prima* of Paracelsus, continues throughout the 17th century as writers on iatrochemistry introduce

Table 3.4 Examples of Alternative Chemical Principles

Date	*Author*	*Principles*
1669	Becher	terra pinquis, terra lapida, terra mercurialis, water, air
1675	Lemery	oil, phlegm, spirit, salt, earth
1703	Stahl	phlogiston, universal acid, water, salt

an ever increasing array of alternative hylomorphic principles or elements (Table 3.4), in large part to account for the ever-increasing range of textures uncovered as a by-product of the distillation craze (recall Section 1.7).

3.6 The Rise of Hylomeric Theories

Of far greater importance, however, is the revival of an interest in the particulate or hylomeric (from the Greek *hyle*, meaning "matter" and *meros*, meaning "part") theories of the Greek philosophers Leucippus (c. 450 BC), Democritus (460-370 BC) and Epicurus (341-270 BC) – the first serious challenge to the hylozoic-hylomorphic concepts that had dominated chemical thought for the previous 1600 years. Only secondary and often critical accounts (e.g., in Aristotle) of the doctrines of Leucippus and Democritus have survived. In contrast, the surviving manuscript sources for Epicurus (Diogenes Laertius and Titus Lucretius Carus) were both published in book form in the 15th century, but did not attract the serious attention of scientists for another 200 years. The primary reason for this initial neglect was that Epicurean atomism was strongly naturalistic and was coupled within Epicurean philosophy with an overt attack on religion and superstition. As a consequence it was tainted with the charges of materialism and atheism.

Serious attempts to "Christianize" Epicurean atomism were undertaken in the 17th century by the French priest and scientist, Pierre Gassendi (1592-1655), and by his British imitator, Walter Charleton (1619-1707), and were based largely on rejecting the assumption that atoms (and, by implication, the universe as a whole) were self-existent, self-moving and, via random collisions, ultimately self-organizing and self-governing. All that was required was to postulate that God was both the creator of atoms and the ultimate cause of atomic motion, and that atomic collisions were merely the hidden mechanism by which he attained his desired ends.

Yet others sought to further modify Epicurean atomism by rejecting one or more of its other assumptions:

a. The only true properties are size, shape, and motion – all others are secondary physiological responses.

b. There is a lower limit to particle divisibility (i.e., true minimal particles called atoms).

c. There is an interparticle vacuum or void.

d. All interparticle interaction is due to mechanical entanglement.

e. There is no dichotomy between mind and matter, thus implying that the soul is both material and mortal.

Many early users of particulate theories, such as Daniel Sennert, rejected the first premise and instead used a kind of hybridized Aristotelian atomism, based in part on the older theory of natural minima, in which the particles acted as carriers of such secondary properties as color, taste, acidity, etc. In yet other cases (e.g., J. C. Magnenus), the individual types of atoms were directly equated with each of the four Aristotelian elements. In other words, many so-called early proponents of particulate theories were not so much using a new reductionistic mechanical approach to chemical phenomena as they were reifying and atomizing the older theories of forms and seminal principles. Perhaps the most extreme example of this approach is found in the writing of the Frenchman, Claude Berigand, who, in 1643, postulated a separate atom type for each of the basic sense qualities (taste, odor, color, etc.). These atomized qualities could become wedged in the pores of gross matter in various proportions so as to create the complex world of sensory experience.

By the end of the 17th century, these corpuscularized qualities would evolve into the imponderable fluids much beloved of the 18th- and early 19th-century theorist, of which phlogiston and caloric are the most notable examples (see Section 6.4). Indeed, particulate theories even began to creep into the alchemical literature – a fact that has led one recent historian to make the highly dubious claim that alchemy, rather than Greek atomism, is the true source of the revival of these theories in the 17th century!

The most important alternatives to pure Epicurean atomism, however, were the plenum theory of the French philosopher, René Descartes (1596-1650), which rejected the second, third and fifth premises, and the dynamical atomism of the British natural philosopher, Sir Isaac Newton (1642-1727), which rejected the fourth premise and instead postulated the existence of interparticle forces of attraction and repulsion.

Later 17th-century French chemists (e.g., Lemery) tended to pay lip service to Cartesian hylomerism, though at the level of application used in chemistry it differed little in its consequences from pure Epicurean atomism, since the particles or "molecules" (a term introduced by Gassendi) of the various chemical substances encountered in the laboratory were assumed, on the basis of either theory, to be fairly complex and thus to lie far above the true ultimate atoms of Epicurus on the particle hierarchy.

Likewise, though Newton applied his dynamical atomism in his *Principia* of 1687 to rationalize Boyle's law relating gas pressure and volume at constant temperature, its first truly chemical applications did not occur until the 18th century. Consequently, most 17th-century chemical atomism remained mechanical in nature and continued to rely on hypothetical variations in particle sizes and shapes (or texture, as it was sometimes called) in order to rationalize chemical phenomena.

In the 17th century the major advocate of the application of mechanical atomism to chemical phenomena was, without a doubt, the British natural philosopher, Robert Boyle (1627-1691). Boyle felt that the differences between one particulate theory and another were trivial compared to the differences between hylomeric theories in general and the older hylomorphic theories of Aristotle and Paracelsus. Consequently, he was rather eclectic in his use of the various versions and tended to lump all of them together under the common rubric of "corpuscular theories." However, despite his advocacy of a corpuscular approach to chemistry, neither Boyle nor any of his contemporaries were able to develop a specific form of the corpuscular theory that could be meaningfully related to quantitative chemical data.

Instead, Boyle, in true Baconian fashion, scoured the alchemical, iatrochemical, and didactic technical literature in search of experimental observations which could be used to demonstrate the superiority of the corpuscular approach to both chemical and physical phenomena. By "demonstrate," Boyle did not mean that they quantitatively proved the corpuscular theory, but rather that they showed that tentative qualitative hylomeric rationales of the observed phenomena were infinitely more plausible than those based on the competing hylomorphic principles of Aristotle and Paracelsus. As a result, the true impact of mechanical corpuscularism on 17th-century chemistry was largely indirect and is best illustrated by its application to the acid-alkali theory of salt formation.

3.7 The Acid-Alkali Theory

The reaction between acids and various alkalis (i.e., metallic carbonates) first attracted the attention of iatrochemical writers as a possible chemical model for the process of digestion. Ignoring the CO_2 gas that was evolved (which they misinterpreted as a violent churning or mechanical motion of the interacting acid and alkali particles), they viewed this reaction as a simple addition:

$$\textit{acid} + \textit{alkali} \rightarrow \textit{salt} \qquad [1]$$

From the standpoint of the corpuscular theory, acids were thought to have sharp, pointed particles (which accounted for their sour taste and ability to attack or corrode substances) and alkalis were thought have porous particles. Neutralization and salt formation consisted of the points of the acid particles becoming mechanically wedged in the pores of the alkali particles (thereby blunting or neutralizing their sharp taste and corrosive properties).

The ultimate importance of this theory for chemistry, however, does not lie in this hypothetical mechanical mechanism for neutralization, but rather in the fact that it gradually accustomed chemists to the idea of characterizing salts in terms of their component acid-alkali particles rather than in terms of abstract property-bearing principles, and to looking at acid-alkali reactions as exchanges between preexisting material parts, rather than in terms of the generation and corruption of alternative abstract forms or essences.

This approach to the description of acid-alkali reactions may be found in the writings of many late 17th-century chemists, including Glauber, Lemery, Sylvius, Tachenius, and especially John Mayow, who, in his *Tractatus quinque medico-physici* of 1674, offered a striking experimental confirmation of the concept in his description of the analysis and synthesis of various nitrate salts:

> *With regard then to the constituent elements of nitre, sal nitrium [i.e. nitrate salts] seems to be composed of an extremely fiery acid [i.e., nitric acid], and, in addition, of an alkali [i.e., either potash or soda] or of pure saline volatile salt [i.e., ammonium carbonate] taking the place of the sal alkali. And this may be ascertained not only from its analysis but also by the way in which it is produced ... If nitre is analyzed by distillation, acid spirit will pass to the receiver, while fixed nitre, closely resembling sal alkali, will be found left in the retort ... In the same way, if we look at the mode in which nitre is produced, we shall recognize clearly the same constituent elements. For if the acid spirit of nitre is poured upon any alkali, or, in place of the alkali, upon purely saline volatile salt, from the mutual strife of these two things coming together and the intense action, sal nitrum is generated, which will readily deflagrate when thrown in the fire.*

While it is true that some 17th-century iatrochemists tried to overly generalize the acid-alkali theory in an attempt to apply it to all physiological and chemical phenomena, there is no doubt that, in its more limited form, it contained a substantial amount of truth – an observation which led the British chemical historian, J. E. Marsh, to conclude many years ago that it was:

> *... the first generalization with regard the composition of substances which is appropriate to the facts ... it is, in fact, with the introduction of the theory of salt formation [in the 17th century] that chemistry first becomes a science.*

3.8 Protochemistry versus Chemical Science

Though I would not go quite as far as Marsh, I would argue that a sufficiently significant change in chemical thought occurred in the 17th century to justify a division of its history, starting about 1660 (a date which, coincidentally, roughly coincides with the end of the Renaissance), into a period of *proto*chemistry, encompassing all that preceded this date, and a period of chemical science, encompassing all that succeeds this date. This passage from *proto*chemistry to chemical science involved a significant change in attitude toward the nature and function of chemical activity more than it did a significant change in theory or practice. It was an explicit recognition that chemistry could be pursued, not just as a useful adjunct to the practice of metallurgy or medicine, or as a mystical religious system (i.e., alchemy), but also as a science of matter and its transformations.

Again, it was Robert Boyle, more than any other 17th-century scientist, who most personified this change in attitude, when he wrote:

> *... I saw that several chymists had by a laudable diligence obtain'd various productions, and hit upon many more phenomena, considerable in their kind, than could be well expected from their narrow principles; but finding the generality of those addicted to chymistry to have had scarce any view, but to the preparation of medicines, or to the improving of metals, I was tempted to consider the art, not as a physician or an alchymist, but as a philosopher. And with this view, I drew up a scheme for a chymical philosophy.*

It is the progressive changes in the content of this "scheme for a chymical philosophy" that will form the substance of our remaining lectures. Indeed, from this point on, progress will be so rapid that, for the remaining three centuries of our survey, we will have to devote separate lectures to each of our three historical indicators.

3.9 The Fate of Alchemy

As we saw in Lecture 1, both the terms *chemia* and *alchemy* were originally used to describe the art of artificially transmuting base metals into gold. We also saw that many practitioners of the chemically based arts of metallurgy and pharmaceutical distillation were at pains to distinguish their crafts from the practice of alchemy, as illustrated by the examples of Agricola, Ercker and Biringuccio in the 16th century – all three of whom insisted on differentiating between smelting and assaying, on the one hand, and alchemy, on the other. However, with the rise of Paracelsianism in the late 16th and early 17th centuries, we see an aggressive campaign to expand the terms *alchemy* and *chemia* to encompass both the metallurgical and pharmaceutical aspects of chemical practice as well, based in part on the argument that alchemy imitates nature not only through its supposed ability to artificially accelerate the maturation or transmutation of metals in the laboratory but through its ability to artificially improve and refine all things in nature via the extraction and concentration of their active essences.

As a result, one encounters a transitional period in the 17th century during which the terms *alchymy* and *chymistry*, as well as the term *pyrotechnica*, compete with one another as potential descriptors of chemical practice in general. As both the above quote from Boyle and the titles of the didactic iatrochemical texts given in Table 3.2 suggest, by the end of this century the term *chemia* or chemistry had begun to clearly emerge as the victor in this struggle. Simultaneously, the term *pyrotechnica* became more and more restricted to the practice of manufacturing and displaying fireworks, whereas the term *alchemy* was once more relegated to the art of "improving metals" and to the excesses of the more mystical branch of the iatrochemical movement.

It is of interest to note, however, that, in spite of both the appearance of the didactic chemistry textbook and the first applications of mechanical atomism in chemistry, the 17th century appears – at least at first glance – to also correspond to a flowering of European alchemy. A plot of the number of new and reissued alchemy books published per annum between 1500 and 1800 peaks in this century, and the vast number of oil paintings depicting alchemists, made by such 17th-century Dutch and Flemish artists as David Teniers the Younger, Jan Steen, David

Rychaert, and Thomas Wijk, would seem to suggest that 17th-century alchemists were literally coming out of the woodwork. The presence of two large collections of these paintings in the United States (the Bader and Fisher Collections), and the widespread distribution of prints based on their holdings, have played a major role in shaping the image which most modern chemists have of the alchemist.

Until recently, these alchemical paintings have generally been taken at face value by historians of chemistry as faithful renditions of actual alchemists and alchemical laboratories, not unlike the drawing in Norton's *Ordinall* mentioned earlier in Section 2.4. However, in an important article published in 1975, C. R. Hill conclusively demonstrated what any good art historian should have suspected from the beginning, namely that these paintings are not literal images of actual alchemists and their laboratories but imaginative artistic reconstructions of what the 17th-century public thought an alchemist should look like. As such, they are no more accurate than similar imaginative images of alchemists by 19th- or 20th-century artists. They are, in fact, genre paintings, of which literally hundreds of copies were produced (it is estimated that Teniers and his assistants alone painted nearly 400) in order to feed a growing market among the rising mercantile class for paintings of this sort, not unlike the 20th-century fad for paintings of big-eyed children or dogs playing poker. Though they tell us more about popular trends in 17th-century mass art than about alchemy, these paintings do contain relatively accurate renditions of period chemical apparatus (though not necessarily of how this apparatus was arranged and used under actual laboratory conditions), based, no doubt, on what the artist saw at the local apothecary, distiller, or assayer.

This conclusion concerning alchemical oil paintings requires that one raise a similar question concerning the publication of alchemical books. To what extent were these books produced and read by serious alchemists rather than simply being driven by a popular public demand for books dealing with the bizarre and forbidden? To the extent the books in question are really iatrochemical, rather than alchemical in the restricted sense of the word, there is also the question of how much they fed on the ever-present desire of the public for books offering medical panaceas. To any reader familiar with the vast annual output of books on pseudoscience, alternative medicine, and the occult in the 20th century, the relevance of these questions should be obvious. Like their present-day counterparts, 17th-century book publishers no doubt preferred to print what sold rather than what was necessarily original or of intellectual value.

Whatever the ultimate resolution to the above debate, there is no doubt that interest in alchemy proper steadily declined throughout the 18th century. The number of published alchemical books fell precipitously and a new form of alchemical art appeared which satirized the alchemist as a fool and a charlatan. By the end of that century, the term chemistry had become firmly established as the descriptor for the rational scientific practice of the chemical arts and the term alchemy had been reduced, as mentioned earlier, to a descriptor for a branch of crank occultism.

As already indicated in the introduction, this book is based on the premise that alchemy in the traditional sense was not a particularly important progenitor of modern chemical science, which instead clearly evolved out of Renaissance metallurgy and pharmacy. This is an opinion that is not unique to the present author but has also been previously expressed by other chemical historians, of whom Mircea Eliade may be quoted as a typical example:

> *Alchemy is one of those creations of the pre-scientific era and the historiographer who would attempt to present it as a rudimentary phase of chemistry or, indeed, as a secular science, would be treading on very shaky ground. The historian's perspective has been vitiated by his eagerness to demonstrate the beginnings of experiment and observation found in certain alchemical works and consequently he has assigned an exaggerated importance to those texts which revealed the first rough gropings toward the scientific method while ignoring others in which the alchemical perspective proper was patently more valuable.*

But if one accepts this judgment concerning the minimal scientific relevance of alchemy, why then have so many previous histories of chemistry devoted so much time and space to its discussion? A sociologist would no doubt answer this question by observing that metallurgy and pharmacy are still very much with us today as independent sciences, so acceptance of them as the primary source of modern chemical practice is equivalent to giving chemistry a set of relatively recent and nonexclusive origins, whereas adoption of the orphan child of alchemy as its most important progenitor provides chemistry with an ancient and independent (not to mention mysterious and colorful) origin of its very own. It does not take much insight into the human ego to understand why most chemists would be attracted the latter rather than the former interpretation.

Perhaps when all is said we can at least agree to the more diplomatic and balanced rendition of the above argument provided by the late Robert Multhauf in 1966, when he observed that:

> *The direct contribution of alchemy to chemistry seems to have been minimal. That it is generally been credited with considerable importance is probably due to its immense indirect importance, firstly in the fact that, through alchemy, chemistry gained some semblance of independence in the spectrum of the arts and sciences, and secondly through the fact that it evolved into "medical chemistry," which in the European Renaissance, gave chemistry a secure and significant place in science.*

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Lecture IV

The Eighteenth Century

(1701-1800)

The Chemist Individualized

> Let Miss Chemistry be your only mistress – the sole object
> of your devotion and homage.
> *James Woodhouse 1795*

4.1 Chemistry and Medical Schools

Needless to say, the close association of chemistry with medicine and pharmacy, begun in the 17th century, continued to persist in continental European universities throughout the 18th century. Thus Haufbauer, in a survey of 54 German universities andschools, found that by 1800 all but three had salaried positions in chemistry and, of these, 34 or 67% were associated with the teaching of medicine. A similar close association between the teaching of chemistry and medicine may also be found in the 18th-century Scottish medical schools at Glasgow and Edinburgh (Table 4.1):

Table 4.1 Professors of Chemistry in 18th-Century Scottish Medical Schools

	Glasgow		*Edinburgh*
1746	William Cullen	1756	William Cullen
1756	Joseph Black	1766	Joseph Black
1766	John Robinson		
1769	William Irvine		
1789	Thomas Hope		

This Scottish chemical-medical tradition evolved, in turn, from the Dutch chemical-medical tradition of the late 17th and early 18th centuries begun by Herman Boerhaave (1668-1738) and was, inturn, transmitted to the United States via doctors trained in Scotland. As a consequence, most American teachers of chemistry in the 18th and early 19th centuries also occupied chairs of chemistry connected with medical schools (Table 4.2).

Table 4.2 Early American Chairs in Chemistry Connected with Medicine

Date	*Appointee*	*School*
1765	John Morgan	Philadelphia Medical College
1767	James Smith	Columbia Medical School
1769	Benjamin Rush	Philadelphia Medical College
1783	Aaron Dexter	Harvard Medical School
1796	James Woodhouse	University of Pennsylvania Medical School
1798	Lyman Spaulding	Dartmouth Medical School

4.2 Newer Routes to Chemical Training

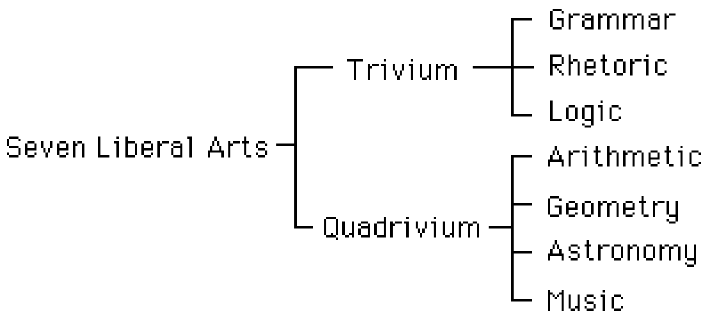
In addition to the medical school, the 18th century also saw the evolution of two additional routes to chemical training in the form of the mining academy or technical school and in the form of the expansion of the original astronomy-mathematics component within the traditional school of arts.

As noted in earlier lectures, the first explicit didactic treatments of mining, assaying, and other chemically related technologies appear in the 16th-century books by Biringuccio, Agricola, Ercker and others. The knowledge which they describe was initially acquired through apprenticeship rather than formal schooling. However, by the 18th century many countries, and especially Sweden and the various principalities of Germany and Austria, had begun to set up formal mining academies in which training in chemistry played an important role – of which the Freiburg Mining Academy in Germany was probably the most famous (Table 4.3). Thus Haufbauer, in his survey of German universities and schools, found that eight or 16% of the 51 institutions teaching chemistry by 1800 were mining academies.

Table 4.3 Early German State Mining Schools

Founding Date	*School*
1735	Schemnitz Mining Academy
1746	Vienna Teresianum
1765	Freiburg Mining Academy
1770	Berlin Mining School
1774	Heidelberg State Economics School
1777	Giessen School of Economics

Elementary mathematics and astronomy had been taught within the university schools of art from the very beginning as part of the "quadrivium" portion of the traditional liberal arts program, which dated from the early middle ages:



By the 16th century, the teaching of astronomy had been expanded to include mechanics in general, and eventually other branches of physics or "natural philosophy" as well, such as pneumatics and optics. The major impetus for also including chemistry as a branch of natural philosophy was the revival of the atomic theory in the 17th century. This tended to view chemistry as a special branch of applied mechanics – one which dealt with the specific, rather than the general, properties of bodies and with the study of the hidden or micro movements of atoms, rather than with the visible macro movements of everyday objects. As shown in Table

4.4, this coupling of the teaching of chemistry with natural philosophy persisted in many American colleges until the 1860s:

Table 4.4 Early American Chairs in Chemistry & Natural Philosophy

Date	*Professor*	*School*
1756	William Smith	College of Philadelphia
1774	James Madison	College of William and Mary
1792	Samuel L. Mitchell	Columbia
1795	John Maclean	College of New Jersey (Princeton)

Table 4.5 Chemistry as Natural Philosophy: Some Example Texts

Date	*Author*	*Title*
1680	Charles Morton	*Compendium physicae*
1790	Tiberius Cavallo	*Elements of Natural & Experimental Physics*
1867	James M'Gauley	*Lectures on Natural Philosophy*

Some example textbooks which subsumed chemistry under the rubric of natural philosophy and which span the period 1670-1870 are shown in Table 4.5. Indeed, Morton's *Compendium physicae* was used in manuscript form to teach chemistry at Harvard from 1687-1728.

4.3 The Lecture-Demonstration Method

Not unexpectedly, the teaching of chemistry was initially modeled on the teaching of medicine. Often there was both a professor, who lectured on theory, and a demonstrator, who gave practical illustrations, just as there was both a professor of anatomy and a barber or surgeon who actually dissected the bodies. This duality is well illustrated by the appointments during the 17th and 18th centuries at the Jardin du Roi in Paris (Table 4.6).

Table 4.6 Chemistry at the Jardin du Roi or Jardin des Plantes in Paris

Year	*Demonstrator*	*Year*	*Professor*
1648	W. Davisson	1743	L. C. Bourdelain
1651	N. Le Fevre	1777	P. J. Macquer
1660	C. Glaser	1784	A. F. Fourcroy
1678	M. Charas		
1694	G. F. Boulduc		
1707	E. F. Geoffroy		
1731	L. Lemery		
1742	G. F. Rouelle		
1768	H. M. Rouelle		
1779	A. L. Brongniart		

For the first 240 years (1600-1840) of its academic existence chemistry functioned primarily as an introductory service course for doctors, pharmacists, and metallurgists and was largely taught using the lecture-demonstration method rather than by means of individual student laboratory work. Thus Haufbauer found that only 18 of 54 German schools had laboratories by 1800, though all but three were teaching chemistry. In addition, most of these were really private laboratories for use of the professor rather than student teaching laboratories. Indeed, during this period the term laboratory usually referred to a small room off the front of the lecture hall in which the professor and his assistant could prepare lecture demonstrations and occasionally conduct original research.

4.4 Scientific Organizations

The founding of permanent, state-endorsed, scientific societies, pioneered by England and France in the late 17th-century, continued unabated throughout the 18th century (Table 4.7). Again, most of these societies began the publication of memoirs or transactions within a few years of their founding which occasionally published papers of chemical interest.

Table 4.7 Example 18th-Century Scientific Societies

Date	*Country*	*Organization*
1724	Russia	Academy of Sciences of St. Petersburg
1731	Ireland	Royal Society of Dublin
1739	Scotland	Royal Society of Edinburgh
1742	Denmark	Royal Danish Academy of Science and Letters
1743	United States	American Philosophical Society
1780	United States	American Academy of Arts and Sciences

4.5 Chemical Societies

In addition to these general scientific societies, the 18th century also saw the organization of the first societies devoted solely to chemistry. However, these were amateur rather than professional in nature and generally consisted of medical students having explicit chemical interests. Our best known examples (Table 4.8) involve the founding of student medical-chemical societies at the Universities of Edinburgh and Glasgow and their imitation by American medical students attending the University of Pennsylvania, many of whom had studied in Scotland as well. This is yet another example of the influence of the Scottish chemical-medical tradition on the early teaching of chemistry in the United States mentioned in Section 4.1.

Table 4.8 Some Early Student Chemical/Medical Societies

Date	*Country*	*Organization*
1785	Scotland	Chemical Society of Edinburgh
1786	Scotland	Chemical Society of Glasgow
1789	United States	The Philadelphia Chemical Society
1792	United States	The Chemical Society of Philadelphia

All of these student societies were short-lived and none of them published printed memoirs or transactions.

4.6 Early Chemical Journals

As noted in Section 4.4, the memoirs, transactions, proceedings, etc. published by scientific societies during the period 1662-1770 occasionally included papers of chemical interest. However, the late 18th century finally sees the appearance of journals which are devoted primarily, if not exclusively, to chemistry (Table 4.9) – a phenomenon which predates the rise of professional chemical societies by more than 60 years, though one which coincides with the founding of the amateur student chemical-medical societies mentioned in the previous section. All of these journals were private commercial ventures, owned and edited by a single chemist, who often exercised a great deal of influence on the chemistry of the day.

Table 4.9 Examples of Early Commercial Chemical Journals

Date	*Editor*	*Journal*
1778	Crell	*Chemisches Journal für Freunde der Naturlehre ...*
1789	Lavoisier	*Annales de chimie et physique*
1798	Scherer	*Allgemeines Journal der Chemie*
1798	Rozier	*Journal de physique, de chimie ...*
1798	Nicholson	*Journal of Natural Philosophy, Chemistry ...*

4.7 Textbooks

The tradition of the didactic textbook continued to evolve throughout the 18th century and, as shown in Table 4.10 at the top of the next page, continued to be dominated by the French. The later editions of Lemery's *Cours de chymie*, and the text, *Elementa chemiae,* first published in 1732 by the Dutch chemist/physician Herman Boerhaave, dominated the first half of the century. These were succeeded by the extremely popular texts of Pierre Macquer (1718-1784) and Antoine Baumé (1728-1804) in the period 1749-1780, and by the texts of the French chemists, Antoine Fourcroy, (1755-1809) and Antoine Lavoisier (1743-1794) in the last two decades of the century. As with their 17th-century predecessors, most of these textbooks underwent numerous editions, printings, and translations. Starting with the volume by Boerhaave, they also have less and less explicit pharmacological content and become increasingly physical and theoretical in their emphasis as the century progresses, until, in the text of Lavoisier, all traces of the iatrochemical influence have disappeared.

Table 4.10 Popular 18th-Century Chemistry Textbooks

Year	*Author*	*Title*
1732	Boerhaave	*Elementa chemiae*
1749	Macquer	*Elemens de chymie theoretique*
1751	Macquer	*Elemens de chymie practique*
1773	Baumé	*Chymie expérimentale et raisonnée*
1783	Fourcroy	*Lécons élémentaires d'histoire naturelle et de chimie*
1789	Lavoisier	*Traité élémentaire de chimie*

4.8 Specialist Monographs

The 18th century sees the addition of several new genres to the chemical literature as well, including the appearance of collections

Table 4.11 Example 18th-Century Collections of Chemical Essays

Year	*Author*	*Title*
1774	Lavoisier	*Opuscules physiques et chimiques*
1780	Bergman	*Opuscula physica et chemica*
1781	Watson	*Chemical Essays*
1786	Scheele	*Chemical Essays*

of "chemical essays" dealing with specific topics (Table 4.11), the appearance of specialist monographs dealing specifically with analytical chemistry (Table 4.12), and the appearance of chemical dictionaries (Table 4.13), though this latter genre has some late 17th-century precedents in the form of several published dictionaries of alchemical terms.

Table 4.12 Example 18th-Century Monographs on Analytical Chemistry

Year	*Author*	*Title*
1770	Engeström	*Description of a Mineralogical Pocket Laboratory*
1778	Bergman	*De analysi aquarium*
1779	Bergman	*De tubo ferruminatorio*
1780	Bergman	*De minerarum docimasia humida*
1790	Gottling	*Vollständiges chemisches Probekabinett*
1799	Vauquelin	*Manuel de l'esseyeur*

Table 4.13 Example 18th-Century Chemical Dictionaries

Year	*Author*	*Title*
1766	Macquer	*Dictionnaire de chymie*
1791	Kels	*Handbuch der Chemie*
1793	Remler	*Neues chemisches Wörterbuch*
1795	Nicholson	*A Dictionary of Chemistry*

4.9 Summary

By the end of the 18th century chemistry had become a fully recognizable profession, distinct from that of the traditional alchemist, technologist, metallurgist, physician, or pharmacist. Though it was still not possible to obtain an explicit university degree in chemistry, and medicine and pharmacy continued to serve as the dominant routes into the field, those who taught it as a service course in the medical schools and mining academies often had an explicit sense of their own specialization. Indeed, by 1789 we find Lavoisier already complaining that:

... very little of chemistry can be learned in a first course, which is hardly sufficient to make the language of the science familiar to the ears, or the apparatus familiar to the eyes. It is almost impossible to become a chemist in less than three or four years of constant application.

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Lecture V

The Eighteenth Century

(1701-1800)

The Pneumatic Revolution

> Every important step forward made by astronomy, physics, chemistry or biology
> had one essential condition – the previous existence or invention of certain
> apparatus; and as the sciences sought to extend their advances, so
> it became necessary for instrumental technique to develop
> and to expand in its delicate adjustments.
> *Louis de Broglie 1937*

5.1 Accounts of Laboratory Apparatus

As noted in earlier lectures, systematic accounts of laboratory apparatus and techniques can be traced back to the 16th-century didactic technical literature and, starting with Libavius' *Alchemia* of 1597, most 17th- and 18th-century chemistry textbooks also devoted space to descriptions of apparatus and common procedures. Indeed, the last third of Lavoisier's famous *Traité* of 1789 deals with this subject in great detail.

5.2 Energy Sources (Thermal)

Charcoal furnaces and, to a lesser degree, the burning mirrors and lens introduced in the 17th-century, continued to dominate laboratory practice throughout the 18th century. However, a number of new innovations, directly based on the improved understanding of combustion provided by the work of Antoine Lavoisier and his collaborators, make an appearance in the 1780s (Table 5.1). These include the oxygen blowtorch, first described by Lavoisier in 1782; the oxyhydrogen blowtorch developed by Jean Bochard de Saron (1730-1794) about the same time; and Argand oil lamp, developed by Ami Argand (1750-1803) around 1784.

Table 5.1 Advances in 18th-Century Heating Apparatus

Date	*Innovation*	*Innovator*
1782	oxygen blowtorch	Antoine Lavoisier
1782	oxyhydrogen blowtorch	Jean Bochard de Saron
1784	Argand oil lamp	Ami Argand

With the use of his oxygen blowtorch, Lavoisier found that he was able to fuse many previously refractory solids, and simplified versions of his apparatus, like that introduced by the German, Friederich Ehrmann, in 1785, began appearing soon afterwards. Bochard de Saron's oxyhydrogen blowtorch was, of course, capable of attaining even higher temperatures than Lavoisier's oxygen blowtorch. Though referred to by Lavoisier in his memoir of 1782, the details of this device were, however, apparently never published and it was independently rediscovered by the American chemist, Robert Hare, in 1802. Originally designed as an improved light source for homes and businesses, the Argand oil lamp made use of an adjustable hollow wick and glass shade to manipulate air currents, and was first adapted to use as a portable laboratory heat source sometime in the 1790s (e.g. Guyton de Mourveau 1798).

In addition to improved heating devices, the 18th century also made substantial advances in the quantitative measurement of heat effects, both in the form of the thermometer and the calorimeter – advances predicated, in turn, on a new theoretical understanding of the difference between the quantity of heat, on the one hand, and its intensity, on the other (see next lecture).

The earliest precursor (see figure and Table 5.2) of the modern thermometer, the so-called open-tube "barothermoscope," developed by Galileo near the end of the 16th century and modified by Rey in 1632, would have been valueless in the chemical laboratory. Only with the introduction of the sealed thermoscope or true thermometer by 1654 do we have a device with potential chemical applications. All that was lacking was a quantified temperature scale – a defect that was remedied by a number of instrument makers in the period 1702-1743 – so that, by the last half of the

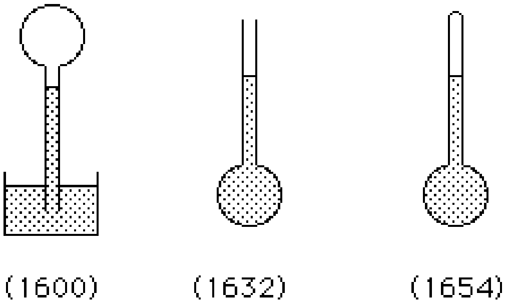

Table 5.2 Evolution of the Thermometer

Date	*Device*	*Developer*
1592-1601	barothermoscope	Galileo
1632	open liquid thermoscope	Rey
1654	sealed liquid thermometer	Ferdinand II
1702-1717	fahrenheit scale	Roemer, Fahrenheit
1710-1743	centigrade scale	Linnaeus, Elvius, Celsius, Christian of Lyons

century, more physically minded chemists, like Boerhaave, Lavoisier and Lomonosov, were routinely reporting numerical temperature values. Of course, not all practicing chemists were enamored of these instrumental advances and as late as 1779 the Swedish chemist, Torbern Bergmann (1755-1784), was embarrassed to confess that he still knew of chemists "who considered thermometers, and such instruments, as physical subtleties, superfluous and unnecessary in a laboratory."

Early experiments on heat capacities did not involve the use of a specifically designed piece of apparatus, but were rather based on the temperature changes observed on mixing various liquids. The first explicit calorimeter appears to be the famous ice calorimeter designed by Lavoisier and Laplace in 1783 for measuring heats of combustion. This was followed by the simple water calorimeter, first described by Adair Crawford in 1788.

5.3 Energy Sources (Electrical)

Though the crude electrostatic machine invented by von Guericke in the 17th century was mentioned in Section 3.4, the scientific study of static electricity did not gain momentum until the 18th-century (see Table 5.3).

Table 5.3. Evolution of 18th-Century Electrical Apparatus

Date	*Innovation*	*Innovator*
1706	glass-globe generator	Francis Haukesbee
1745-1746	Leyden jar	E. von Kleist, P. Musschenbroek
1800	Voltaic pile	Alessandro Volta

In 1706 Francis Haukesbee replaced von Guericke's hand-rubbed, rotating sulfur ball with a glass globe, and by the 1740s further improvements, such as leather rubbers, point collectors, and belt drives had also been added to electrostatic machines. Far more important, however, was the independent discovery in the period 1745-1746 of the so-called Leyden jar by Pieter van Musschenbroek and Ewald von Kleist, a kind of macro-capacitor which allowed for the storage and transfer of static electrical charge. In the chemical laboratory this device was used primarily in eudiometry to spark gas mixtures and especially those of hydrogen and oxygen.

In the 1770s Priestley and Cavendish had noted the production of nitrogen oxides when sparks were discharged in air, and there were some preliminary investigations of the effects of electrical sparking on various chemicals by the Dutch scientist, Martin van Marum, in the 1780s. The most important result, however, was the successful electrostatic decomposition of water in 1789 by Adrien Paets van Troostwijk (1752-1837) and J. R. Deimann.

Unfortunately, while it is possible to generate high-voltage, static charges, the actual quantity of charge involved is quite small and, since the amount of electrochemical change depends on this quantity rather than the voltage, the observed chemical effects are also quite small. In addition, the current during a spark discharge alternates, so that in the decomposition of water, for example, one obtains a mixture of oxygen and hydrogen rather than the spatially isolated gases obtained using direct current. Thus George Pearson, on repeating the electrostatic decomposition of water in 1799, found that he required 14,600 charging cycles of his Leyden jar in order to generate only 0.33 cubic inches of gas. All of this would radically change with the discovery of the voltaic pile by the Italian physicist, Alessandro Volta (1745-1827), in 1800. However, though this discovery chronologically falls at the very end of the 18th century, its impact lies completely within the 19th century and it will, consequently, be discussed in later lectures.

5.4 General Apparatus

Corks were supposedly introduced around 1680 by the Benedictine monk, Dom Perignon, in connection his discovery of Champagne, but apparently were not widely used by 17th-century chemists. They do not appear in 17th-century alchemical paintings or in the 17th-century distillation literature. Instead the various pieces of apparatus were connected by "luting" them together using either beeswax or egg white and lime at low temperatures or a mixture of clay and fat at higher temperatures. Storage bottles were closed with either a glass stopper, a plug of wood, or with a piece of cloth or animal bladder tied over the mouth. However, cork usage slowly increased during the 18th-century. Priestley mentions them, as does Lavoisier in his *Traité* of 1789, where he recommends their use when inserting narrow tubes into large openings, though he also suggests luting the corked joints as an extra precaution against leakage.

Yet other 18th-century innovations of note include the selective introduction, starting around 1779, of both porcelain (Wedgewood) and platinum (Achard) laboratory ware.

5.5 Separation Techniques

The 18th century sees two important improvements in the traditional art of distillation – the invention of the counter-current laboratory condenser by the German chemist, Christian Weigel (1748-1831), in 1771 (usually, but incorrectly, attributed to Liebig in the 19th century), and the introduction of the technique of vacuum distillation. Though distillation under reduced pressure had actually been described by Boyle as early as 1660, its rediscovery and first industrial application is due to the French engineer, Philippe Lebon (1760-1804), in 1796.

Of far greater significance, however, are the experimental advances made with respect to apparatus and procedures for the generation, isolation, and study of "factitious airs" or gases, the most important of which are summarized in the following diagram:

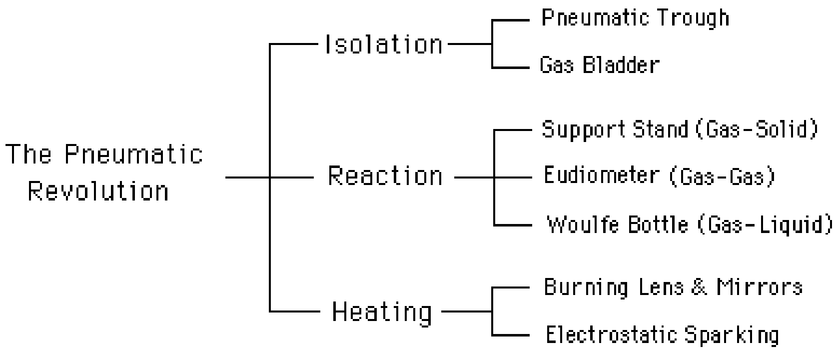

Table 5.4 Evolution of the Pneumatic Trough

Date	*Innovation*	*Innovator*
1660-1674	water collection, internal generation	Boyle, Mayow
1727	water collection, external generation	Hales
1765	nonsubmerged collection shelf	Brownriggs
1766	mercury collection	Cavendish
1774	submerged collection shelf	Priestley

As already noted in Lecture III, several of these devices, including a crude *in situ* pneumatic trough and the use of burning lens and mirrors, had already made an appearance in the late 17th century, though their full impact was not felt until this century. Often these instruments evolved over a considerable period of time, during which a variety of investigators added minor refinements and improvements, as further illustrated in Table 5.4 for the case of the pneumatic trough.

5.6 Characterization Techniques

Wet qualitative analysis based on the use of characteristic color and precipitation reactions, begun in the 17th century, continued to develop, especially in connection with the analysis of mineral waters. The German chemist, Andreas Sigismund Marggraf (1709-1782), and the Swedish chemist, Torbern Bergman, were particularly active in this regard, and in 1778 Bergman made the first attempt to codify these tests in his essay *De analysi aquarium*.

The 18th century also saw the development of blowpipe analysis, which in many ways represents an extension and miniaturization of the so-called dry methods of analysis associated with traditional fire assaying. The first systematic account of the application of this technique to the qualitative analysis of minerals was published by the Swedish chemist, Gustaf von Engeström (1738-1813), in 1770, followed by an essay on the same subject by Bergman in 1779 (recall Section 4.8).

The use of aqueous precipitation reactions also made inroads in the field of quantitative gravimetric analysis. In traditional methods of assaying, one literally reduced a sample of the ore to the metal of interest and weighed it, but with the recognition that the acid and alkali components of salts were conserved in chemical reactions and could interchange partners to form new salt combinations, came the realization that quantitative analysis did not always require the isolation of the metal of interest. The ore could be dissolved in acid and the metal precipitated as a salt, earth or calx (i.e. oxide or hydroxide). If one knew how much metal was present in the precipitated compound, one could calculate the mass of the metal in the original sample based on the mass of the precipitate formed. This method was used by Marggraf as early as 1749 to gravimetrically determine silver via its precipitation as silver chloride, and gradually grew in importance in connection with mineral analysis as the 18th century progressed.

It was again Bergman who made the first attempt to summarize this approach in his 1780 essay, *De minerarum docimasia humida*. Indeed, in an earlier essay entitled *De praecipitatis metallicis* (1779), Bergman even included a table of commonly used precipitates, along with the proper numerical conversion factors required to calculate the mass of metal present from the mass of the precipitate formed. By the end of the century, chemical journals were routinely reporting the quantitative analysis of new minerals in terms of the percentages by weight of their various component "earths" or oxides.

In the case of the newly discovered gases (see next section), the introduction of the eudiometer and its use by such chemists as Cavendish and Priestley, starting about 1774, led to the practice of reporting the composition of gaseous compounds in terms of percentage by volume.

Yet a third technique of quantitative analysis – volumetric analysis – also originated during the 18th century. It was first applied to the analysis of vinegar by the French pharmacist, Claude Joseph Geoffroy (1683-1732), in 1729. Geoffroy added powdered potash (K_2CO_3) to preweighed vinegar samples until the effervescence stopped and then reweighed the samples to obtain the weight of potash required to neutralize the vinegar. In his history of early volumetric analysis, Madsen cites at least another dozen examples of reported acid-alkali titrations during the 18th century, mostly in connection with water analysis, some of which employed tincture of violets or litmus paper to detect the end point rather than cessation of effervescence. In 1782 the French chemist, Louis-Bernard Guyton de Morveau (1737-1816), reported a volumetric determination of HCl based on precipitation of lead dichloride, and in 1795 Henri Descroizilles (1751-1825) introduced his volumetric determination of the relative strengths of chlorine bleaching solutions based on the decolorization of a standardized indigo solution.

The remarkable thing about these early applications of both quantitative gravimetric and quantitative volumetric analysis is that they show that 18th-century chemists implicitly believed in the law of definite composition long before it was articulated as an explicit chemical principle. In a sense the law was implicit in the 17th-century corpuscular mechanism for acid-alkali reactions, but it was not until 1777 that the German chemist, Carl Friedrich Wenzel (1740-1793), saw fit to explicitly state it as a fundamental assumption, albeit one that he considered to be self-evident:

That all compounds must have a definite and unchangeable composition, which can neither be smaller or larger, is self evident – otherwise nothing certain could be established from their comparison.

5.7 New Substances & The Pneumatic Revolution

A rough measure of the advance in the knowledge of specific chemical substances made between the beginning of the Renaissance and the end of the 18th century may be had by comparing the contents of the tables in Section 1.8 with the contents of Lavoisier's *Traite élémentaire de chimie* of 1789. Thus while Table 1.6 lists nine metals known with certainty by 1400, Lavoisier lists 17, with the addition of another five probable metals not yet isolated but almost certainly known in the form of their corresponding oxides. Likewise, Table 1.7 lists four inorganic and one organic (acetic) acid known by 1400, whereas Lavoisier lists 29 inorganic and 19 organic acids. But perhaps the most impressive advance involved the class of salts. Thus while Tables 1.7 and 1.8 list roughly 27 salts, Lavoisier devotes the last 81 pages of Part II of his *Traité* to these compounds and, in the form of 25 tables, enumerates over 505 specific examples. But, as Lavoisier was quick to point out, this was only a fraction of the number of theoretically possible salts:

The known salifiable bases, or substances capable of being converted into neutral salts by union with [the 48 known] acids amount to 24; viz. 3 alkalis, 4 earths and 17 metallic substances; so that in the present state of chemical knowledge, the whole possible number of neutral salts amount to 1152.

But if the greatest advance in the late 17th- and early 18th-century systematization of chemical compounds involved the study of acids, bases, and salts, it was the discovery and isolation of a hitherto unknown class of substances – the chemically active airs or gases – which would present late 18th-century chemistry with its greatest theoretical challenge. Made possible by the advances in apparatus for the manipulation and study of airs outlined in Section 5.5, such pneumatic chemists as Joseph Priestley (1733-1804), Carl Wilhelm Scheele (1742-1786), and Henry Cavendish (1731-1810) would discover more than 14 of these new gases in the ten-year period between 1766 and 1776. These are listed in Table 5.5, where their modern formula are enclosed in parentheses for greater clarity.

Table 5.5 The Discovery of Chemically Distinct Gases

*Date**	*Gas*	*Discoverer*
1766	inflammable air (H_2)	Cavendish
1770, 1772	marine acid air (HCl)	Scheele, Priestley
1770, 1774	alkaline air (NH_3)	Scheele, Priestley
1771	air of fluorspar (HF)	Scheele
1771, 1775	fluor acid air (SiF_4)	Scheele, Priestley
1772	phlogisticated air (N_2)	Rutherford, Cavendish
1772	nitrous air (NO)	Priestley
1772	phlogisticated nitrous air (NO_2)	Priestley
1772	diminished nitrous air (N_2O)	Priestley
1773, 1774	fire air, dephlogisticated air (O_2)	Scheele, Priestley
1773	dephlogisticated marine acid (Cl_2)	Scheele
1774	vitriolic acid air (SO_2)	Priestley
1775	arsenated hydrogen (AsH_3)	Scheele
1776	heavy inflammable air (CO)	Lassone

* Dates vary depending on whether one is citing laboratory notebooks or the actual date of book or journal publication.

Priestley's results were summarized in the various editions his multivolume monograph, *Experiments and Observations on Different Kinds of Air* (1774-1777), while those of Scheele were summarized in his book *Chemische Abhandlung von der Luft und dem Feuer* (1777) and in his posthumously collected *Chemical Essays* of 1786. These discoveries would, in turn, lay the empirical foundations of the first "chemical revolution" initiated by Antoine Lavoisier and his collaborators in the period 1770-1790 – an event which will form the subject of our next lecture.

Note that the list of gases in Table 5.5 could be expanded so as to also include the work of Joseph Black on fixed air or carbon dioxide, first published in 1756. Though, strictly speaking, this gas was actually discovered by van Helmont in the 17th century, it was really the work of Black in the 18th century which finally established its true chemical individuality.

5.8 Selected References

Instrumentation

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* W. E. Knowles Middleton, *A History of the Thermometer and Its Use in Meteorology* Johns Hopkins Press: Baltimore, MD, 1966.

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Methods of Analysis

* E. R. Madsen, *The Development of Titrimetric Analysis to 1806*, Gad: Copenhagen, 1956.

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Pneumatic Chemistry

- * L. Dobbin, Ed., *The Collected Papers of Carl Wilhelm Scheele*, Bell & Sons: London, 1931. This contains an English translation of Scheele's 1777 book, *Chemische Abhandlung von der Luft und dem Feuer*.
- * J. Priestley, *Experiments and Observations on Different Kinds of Air*, 3 Vols, Kraus: New York, NY, 1970. Photoreproduction of the edition of 1790.

Lecture VI

The Eighteenth Century

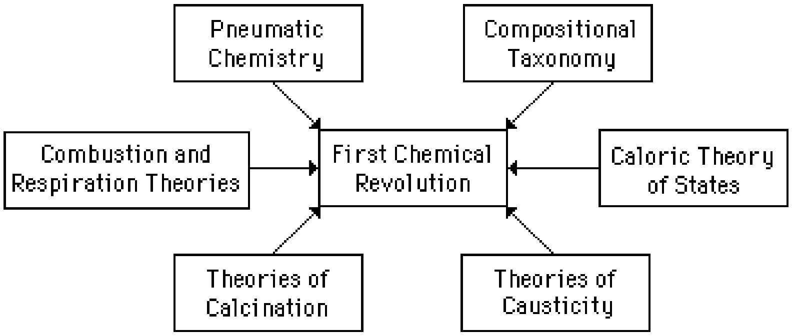
(1701-1800)

States of Matter and Chemical Composition

Revolutions in thought are steady maturations suddenly completed.
J. C. Gregory 1927

6.1 The First Chemical Revolution

The last quarter of the 18th century saw a rapid convergence of several lines of thought that had been slowing evolving since the late 17th century:



This convergence becomes particularly prominent in the period 1774-1794, and especially in the work of the French chemist, Antoine Lavoisier, and his various collaborators – so much so that this period has long been referred to by chemical historians as the “chemical revolution” and Lavoisier as the “father of modern chemistry.” Though, as we will see in later lectures, this event is but the first of three such revolutions, there is no doubt that it represents a significant watershed in chemical thought. In this lecture we want to briefly review some of the influences shown in the above diagram and their role in shaping the first of these three chemical revolutions.

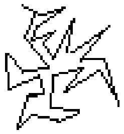
6.2 The Caloric Theory of States

That the ancient Greeks recognized the existence of solids, liquids, and gases is apparent from the nature of the four Empedoclean elements: earth (solid), water (liquid), air (gas), and fire (thermal energy). There is also no doubt that they were aware that certain materials could be reversibly melted (e.g, metals) or frozen (e.g., water), and that certain liquids (e.g., water and perfumes) could be volatilized. However, they do not appear to have generalized these observations. Rather they considered most materials to be inherently either solid or liquid in nature, and viewed evaporation as a mechanical dispersion or solution of the finely divided liquid in the surrounding air rather than as the formation of a new kind of air or gas. From this point of view, water vapor was no more a new kind of air than dissolved salt was a new kind of water or liquid. In short, there is little evidence that the Greeks thought of solids, liquids and vapors as generalized states of matter that any substance could be made to assume given the appropriate changes in temperature and pressure.

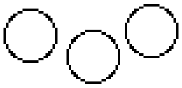
Writing in 55 BC, the Roman Epicurean, Titus Lucretius Carus, gave a rationale of solids, liquids, and vapors in terms of the atomic theory of Democritus and Epicurus:

Again things which look to us hard and dense must consist of particles more hooked together, and be held in union because welded together all through with branchlike elements ... Those things which are liquid and of fluid body ought to consist more of smooth and round elements ... All things lastly which you see disperse themselves in an instant, as smoke, mist, and flames, if they do not consist of entirely smooth and round, must yet not be held fast by closely tangled elements, so that they may be able to pierce the body and enter it with biting power, yet not stick together ...

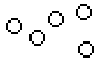
We might visualize Lucretius' description as follows:



(Solid)



(Liquid)



(Vapor)

Since the particles of solids, liquids, and vapors are pictured as differing in both size and shape, this rationale would seem to preclude their mutual interconversion or would at least require that the particles in question are complex and could only be mutually interconverted via a substantial rearrangement of their component atoms.

The term "gas" (from the Greek *chaos*, meaning "unorganized") was introduced by the Flemish iatrochemist, Joan Baptista Van Helmont (1579-1644), in the 1640s. Most of his examples (e.g., carbon dioxide or *gas sylvestre*) were prepared via the chemical decomposition of various solids and Van Helmont viewed the resulting gases as chaotic spirits (i.e., as separated "forms" or seminal essences) that had been freed from the constraints of their organizational matrices (i.e., freed from dross matter), rather than as a new state of matter analogous to air. He also distinguished between his gases and the liquid vapors and spirits produced during distillation – noting that the latter could be condensed as bulk liquids or oils whereas the former could not.

It was only with the discovery of chemically distinct kinds of "airs" in the last quarter of the 18th century, as a result of the pneumatic revolution in chemical apparatus discussed in the previous lecture, that the concept of a generalized gaseous or "aeriform" state, similar to that of the liquid and solid states, finally became established. Closely associated with this recognition was the concomitant realization that any given substance could, in principle, be reversibly transformed into the solid, liquid, and gaseous states, given the proper conditions of temperature and/or pressure, and that these transformations were, in turn, characterized both by definite transition temperatures (i.e., melting and boiling points) and by the absorption or release of fixed amounts of heat. These advances required, in turn, an ability to distinguish between the concepts of temperature and heat, as well as the experimental means to measure and quantify each of them.

As we saw in the previous lecture, crude thermometers first appeared near the end of the 16th century. They acquired their current closed-tube form by the 1650s and standardized scales by the 1740s. The development of the concept of heat capacity and the resulting quantification of the heat concept soon followed, culminating in the work of the Scottish chemist, Joseph Black (1728-1799), in the period 1759-1762 (though not published until 1770). Prior to Black, it was generally assumed that the amount of heat (ΔQ) required to raise the temperature of an object by a fixed amount (ΔT) depended only on the mass (m) of the object being heated but not on its specific nature:

heat absorbed = (mass of object)(change in temperature) [1]

or in modernized symbolism as:

$$\Delta Q = m\Delta T \qquad [2]$$

When this assumption came into conflict with the results of experiments on the mixing of hot and cold liquids, the Dutch scientists, Hermann Boerhaave and Pieter van Musschenbroeck, proposed the equally unsatisfactory hypothesis that the amount of heat required to raise the temperature of an object by a fixed amount depended instead on the volume (V) of the object being heated:

$$\Delta Q = V\Delta T \qquad [3]$$

Black's genius was to realize that the amount of heat absorbed depended not only on the quantity of matter present, as measured by its mass, but also on the kind of matter present, as indicated by its chemical character, leading to the modification of equation 2 via the introduction of a proportionality constant (σ) or material constant characteristic of the particular substance being heated:

$$\Delta Q = \sigma m\Delta T \qquad [4]$$

Black also discovered that, in the process of melting and boiling, each material absorbed, without a corresponding change in temperature, a certain fixed amount of heat (known as the latent heat of fusion and the latent heat of vaporization, respectively), and that these quantities not only differed for the melting and boiling processes, but also varied from one substance to another.

Similar concepts were developed by the Swedish physicist, Johan Wilcke (1732-1796), in the period 1772-1781 and by Lavoisier in a series of memoirs published in the period 1777-1780. Though Wilcke's work is generally thought to have been done independently of Black, it is likely that Lavoisier was aware of Black's work, though he failed to cite it in his own memoirs. It was the Portuguese scientist, J. H. de Magellan, who first used the term "specific heat" in 1780 to describe the material constant σ in equation 4 and the term was also used by Wilcke soon after.

By 1789 Lavoisier was making full use of these results in his famous *Traité élémentaire de chimie:*

The same may be affirmed of all bodies in nature: They are either solid or liquid or in a state of elastic aeriform vapor, according to the proportion which takes place between the attractive force inherent in their particles and the repulsive power of the heat acting upon these; or, what amounts to the same thing, in proportion to the degree of heat to which they are exposed ... solidity, liquidity, and aeriform elasticity are only three different states of existence of the same matter, or three particular modifications which almost all substances are susceptible of assuming successively, and which depend solely upon the degree of temperature to which they are exposed ...

Though Lavoisier was well aware that some considered heat to be a mode of motion, he explicitly adopted a material or "igneous fluid" model of heat instead because of its conceptual simplicity and ease of quantification. In 1787 he suggested the term "caloric" to describe this fluid:

Wherefore, we have distinguished the cause of heat, or that exquisitely elastic fluid which produces it, by the term of caloric.

> *Besides, that this expression fulfills our object in the system which we have adopted, it possesses this further advantage, that it accords with every species of opinion, since, strictly speaking, we are not obliged to suppose this to be a real substance; it being sufficient ... that it be considered as the repulsive cause, whatever that may be, which separates the particles of matter from each other; so that we are still at liberty to investigate its effects in an abstract and mathematical manner.*

The resulting fluid or caloric theory of heat was based on four assumptions:

a. Heat is produced by the presence of a subtle, imponderable (i.e. weightless) fluid called caloric.

b. Matter-matter interactions are attractive, matter-caloric interactions are attractive, but caloric-caloric interactions are repulsive.

c. Caloric is conserved.

d. Caloric may exist in either a combined (insensible) or free (sensible) state with respect to ponderable matter.

The qualifier "imponderable" in the first assumption accounted for the fact that the mass of an object does not change when it is heated or cooled.

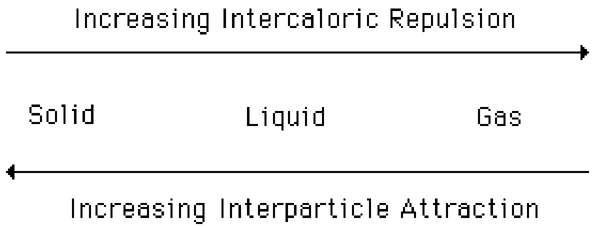
The second assumption accounted for the fact that objects expand when heated and contract when cooled and shows the pervasive influence of Newton on 18th-century chemical thought. No longer are solids, liquids, and vapors explained, as in the earlier quote from Lucretius, by differences in the sizes and shapes of their constituent particles and by their degree of mechanical entanglement, but rather by means of attractive and repulsive interparticle forces.

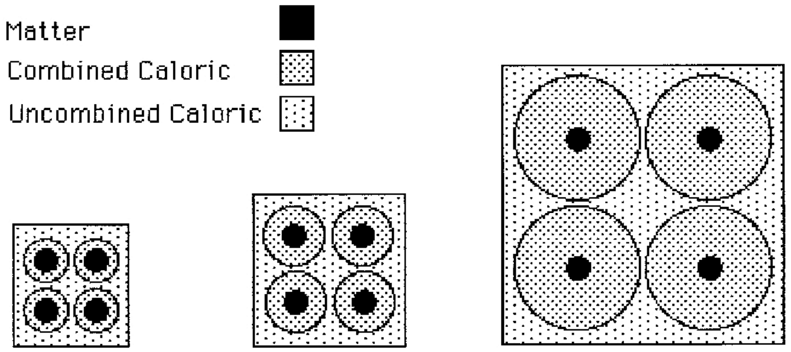
The third assumption formed the theoretical basis of calorimetry, which allowed one to quantitatively measure the caloric content of an object using the equality:

(heat lost or gained by object) =
(heat gained or lost by calorimeter) [5]

The fourth assumption accounted for the latent heats of fusion and vaporization – in other words, for why heating sometimes raised the temperature of a body (sensible or uncombined caloric) and sometimes did not (insensible or combined caloric).

As indicated in the earlier quote from Lavoisier, changes in state were viewed as a competition between interparticle attractions, on the one hand, and intercaloric repulsions, on the other, and could be engineered by altering the quantity of combined caloric:





(Solid) (Liquid) (Gas)

Thus, as shown above, solids, liquids and gases were viewed as differing, not in their degree of molecular organization and/or freedom of molecular motion, as in our modern kinetic-molecular model, but rather in terms of the relative sizes of the caloric envelopes or atmospheres surrounding their component molecules.

These atmospheres corresponded to the combined or insensible portion of the caloric responsible for the latent heats of transition, whereas the uncombined or sensible portion of the caloric content presumably resided in the spaces between the atoms. Because this portion of the caloric was not attached to the atoms, it was free to flow into the stem of a thermometer and was thus detectable as a change in temperature. This "static Newtonian model" of solids, liquids and gases would continue to dominate chemical theory well into the first half of the 19th century.

18th-century scientists also had some understanding of the role of pressure in changes of state. As early as 1724 the apparatus maker, Daniel Fahrenheit, had proposed an new type of instrument for measuring changes in atmospheric pressure, called an "hypsobarometer," which was based on the change in the boiling point of water as a function of pressure. Lavoisier was also fully aware of this effect and conducted experiments on the boiling of various liquids under reduced pressure in a vacuum jar which would inspire Lebon's later development of vacuum distillation (see previous lecture).

As a result of this work, Lavoisier became convinced that pressure was essential to the existence of the liquid state:

> *But if these two powers only existed [i.e. interparticle attractions and intercaloric repulsions], bodies would become liquid at an invisible degree of the thermometer, and would almost instantaneously pass from the solid state of aggregation to the that of aeriform elasticity ... That this does not happen, must depend upon the action of some third power. The pressure of the atmosphere prevents this separation, and causes water to remain in the liquid state until it be raised to 80° of temperature (212°) of the French thermometer, the quantity of caloric which it receives in the lowest temperatures being insufficient to overcome the pressure of the atmosphere. Whence it appears that, without this atmospheric pressure, we should not have any permanent liquid, and should only be able to see bodies in that state of existence in the very instant of melting, as the smallest additional caloric would instantly separate their particles, and dissipate them through the surrounding medium.*

6.3 The Role of Gases in Chemical Reactions: Causticity

Concomitant with these physical developments was a gradual recognition of the role of gases in chemical reactions. The first important studies along these lines were published by Black in 1756 and dealt with the origins of causticity in magnesia alba [$Mg(CO_3)$] and limestone [$Ca(CO_3)$]. At this time the carbonates of potassium, sodium, ammonium, magnesium, and calcium were known as the mild alkalis (due, as we now know, to mild hydrolysis of the carbonate anion on dissolving in water):

$$CO_3^{2-}(aq) + H_2O(l) \rightarrow HCO_3^{-}(aq) + OH^{-}(aq) \qquad [6]$$

However, when magnesia alba or limestone were strongly heated, they became extremely alkaline or caustic. For example:

limestone (mild) + heat → quicklime (caustic) [7]

and when the water solutions of the resulting products were mixed with solutions of the mild alkalis of potassium, sodium or ammonium (known as vegetable, soda, and volatile alkali, respectively), they converted these into caustic alkalis, while simultaneously reprecipitating the magnesium and calcium as the original magnesia alba or limestone respectively:

soda + quicklime → caustic soda + limestone [8]

The accepted explanation of these reactions was that the magnesia alba and limestone had absorbed a fiery or caustic principle ($\varkappa$) from the flame during the heating process in reaction 7:

limestone + $\varkappa$ → quicklime (limestone + $\varkappa$) [9]

and had lost this principle to the soda or other mild alkalis in reaction 8:

soda + quicklime (limestone + $\varkappa$) →
caustic soda (soda + $\varkappa$) + limestone [10]

Black, however, showed that, on heating, both magnesia alba and limestone actually lost rather than gained mass, as might be expected from equation 9, and that this loss was due to the evolution of a gas which he called "fixed air" (i.e., carbon dioxide) and which he further identified with the *gas sylvestre* discovered a century earlier by Van Helmont:

limestone + heat → quicklime + fixed air [11]

This fixed air was also present in the mild alkalis of potassium, sodium and ammonium, as evidenced by its release on addition of acid, and it was the transfer of this fixed air from these mild alkalis to the solutions of quicklime and calcinated magnesia alba which accounted for the precipitation of limestone or magnesia alba in equation 8:

soda (caustic soda + fixed air) + quicklime →
caustic soda + limestone (quicklime + fixed air) [12]

Black further showed that the mass gained by the quicklime in reaction 12 was equal to the mass loss in reaction 11.

In modern terms we would represent reaction 11 as:

$$Ca(CO_3)(s) + heat \rightarrow CaO(s) + CO_2(g) \qquad [13]$$

followed by hydrolysis of the resulting calcium oxide on addition of water:

$$CaO(s) + H_2O(l) \rightarrow Ca(OH)_2(aq) \qquad [14]$$

and reaction 12 as:

$$Ca(OH)_2(aq) + Na_2(CO_3)(aq) \rightarrow 2Na(OH)(aq) + Ca(CO_3)(s) \qquad [15]$$

Black's new theory of causticity was soon attacked by various critics, most of whom advocated some form of the traditional theory involving the absorption of a caustic agent from the flame. This was the case, for example, with the attacks of the German chemist, Johann Meyer, in 1764, who rather ironically called his version of the causticity principle *acidum pinque*.

6.4 The Role of Gases in Chemical Reactions: Calcination

Though the historian, Henry Guerlac, has shown that Lavoisier was originally drawn to the question of the role of airs or gases in the calcination (i.e., oxidation) of metals, starting around 1772, for reasons unrelated to Black's work, there is no doubt that he quickly became aware of it. This is apparent from the publication of his first book, *Opuscules physiques et chimiques* (*Essays Physical and Chemical*), in 1774, which contains a detailed summary and discussion of Black's work, as well as that of his various critics. Indeed, Lavoisier's own work on calcination shows some uncanny parallels with Black's earlier work on causticity.

The accepted early 18th-century rationale of calcination and combustion, due to the German chemists, Johann Becher (1635-1682) and Georg Stahl (1660-1734), was that metals contained a principle of inflammability (ϕ), called *terra pinquis* by Becher and "phlogiston" by Stahl, though in fact both were essentially nothing more than relabeled versions of the traditional Paracelsian principle of sulfur, which had functioned as a principle of inflammability for earlier generations of iatrochemists. Calcination of a metal was due to the loss of its phlogiston whereas regeneration of the metal was due to the restoration of its phlogiston via its transfer from various phlogiston-rich (i.e., flammable) reducing agents, such as charcoal or oil:

$$\textit{Calcination: metal} \rightarrow \textit{calx} + \phi \qquad [16]$$

$$\textit{Reduction: charcoal (ash} + \phi) + \text{calx} \rightarrow \textit{metal (calx} + \phi) + \text{ash} \qquad [17]$$

Lavoisier, however, discovered that metals gained mass on calcination rather than losing it, as suggested by reaction 16, and that the charcoal in reaction 17 was actually converted into fixed air, which weighed more than the charcoal from which it was formed.

Further quantitative measurements showed that the metal in reaction 16 actually combined with a gaseous component of the air, which Lavoisier initially called “vital or pure air,” because it was also necessary for the support of life, but which he later identified with the new gas discovered independently by Priestley and Scheele in 1774 and called by them “dephlogisticated air” and “fire air” respectively. Lavoisier would later rename it “oxygen gas.” Reactions 16 and 17 now became:

metal + oxygen → *calx (metal oxide)* [18]

carbon + calx (metal oxide) →
metal + fixed air (carbon dioxide) [19]

This theory was then generalized to encompass both respiration and combustion in general, including not only the calcination of metals but the burning of combustible nonmetals, such as carbon, sulfur, and phosphorus.

As with Black’s reinterpretation of causticity, Lavoisier’s new theory was widely criticized, mostly by chemists advocating slightly revised versions of the original phlogiston theory. How, for example, they argued, could one explain the appearance of flame and heat in combustion, if not by the escape of the phlogiston found in the combustible? Lavoisier countered by pointing out that combustion and calcination involved a reaction with oxygen “gas,” which, according to his new caloric theory of states (recall Section 6.2), was actually a compound of oxygen with matter of heat or caloric. When the oxygen was fixed in the form of a solid oxide product, this combined caloric was set free and thus accounted for the observed heat release:

metal + oxygen gas (oxygen + caloric) →
calx (metal + oxygen) + caloric [20]

In other words, reactions which consumed gases were predicted to be exothermic, whereas those that evolved gases were predicted to be endothermic.

Both Black's theory of causticity and Lavoisier's theory of combustion turned the traditional theories on their heads. In Black's theory the absorption of the causticity principle was replaced by the release of fixed air, whereas in Lavoisier's theory the release of phlogiston was replaced by the absorption of oxygen and the simultaneous release of caloric. Both theories also relied on a knowledge of chemically specific types of air (carbon dioxide and oxygen respectively) and on the use of conservation of mass in order to monitor their absorption and release in chemical reactions. And, finally, both theories also relied on the assumption that heat was an imponderable agent which did not alter the mass of a material when it was heated or cooled.

To the modern chemist, with his emphasis on quantification, the phlogiston theory appears inherently improbable. However, this should not blind us to the fact that it provided a perfectly adequate qualitative rationale of many chemical phenomena. Indeed, some past historians consider it to have been the first great chemical generalization – one which allowed chemists to unite under a common theoretical umbrella such apparently disparate phenomena as combustion, calcination, respiration, corrosion, reduction, and metallicity. As William Whewell observed in 1837:

> *The phlogistic theory was deposed and succeeded by the theory of oxygen. But this circumstance should not lead us to overlook the really sound and permanent part of the opinions which the founders of the phlogistic theory taught. They brought together, as processes of the same kind, a number of changes which at first appeared to have nothing in common; as acidification, combustion, and respiration. Now this classification is true; and its importance remains undiminished, whatever are the explanations which we adopt of the processes themselves ... It has been said that in the adoption of the phlogistic theory, that is, in supposing the [above] processes to be subtractions rather than additions, "of two possible roads, the wrong one was chosen, as if to prove the perversity of the human mind." But we must not forget how natural it was to suppose that some part of a body was destroyed and removed by combustion; and we may observe that*

> *the merit of Becher and Stahl did not consist in the selection of one road of two, but in advancing so far as to reach this point of separation. That, having done this, they went a little further on the wrong line was an error which detracted little from the merit or value of the progress really made.*

In the end, however, it was the qualitative nature of phlogiston which led to its ultimate downfall, not only because of its inability to rationalize the quantitative data on mass changes, but also because of an inherent vagueness in both its definition and associated properties. This conceptual flexibility led, in turn, to an ever increasing number of complex *ad hoc* rationalizations designed more to save the theory than to explain the phenomena, so that by 1783 a frustrated Lavoisier was arguing that:

> *But if in chemistry everything can be satisfactorily explained without the aid of phlogiston, it thereby becomes eminently probable that such a principle does not exist, that it is a hypothetical being, a gratuitous assumption ... the time has come when I must speak out in a more definite and formal manner concerning a view which I consider an error fatal to chemistry, and which appears to me to have considerably retarded progress by the method of false reasoning which it has engendered ... namely that chemists have turned phlogiston into a vague principle, one not rigorously defined, and which consequently adapts itself to all the explanations for which it may be required. Sometimes this principle has weight and sometimes it has not; sometimes it is free fire and sometimes it is fire combined with the earthy element; sometimes it passes through the pores of vessels, sometimes these are impervious to it; it explains both causticity and noncausticity, transparency and opacity, colors and their absence; it is a veritable Proteus changing in form at each instant.*

6.5 Analysis and the Multiplication of Elements

In his book *De caelo*, Aristotle gave a definition of an element which even a modern chemist would find acceptable:

> *An element, we take it, is a body into which other bodies may be analyzed, present in them potentially or in actuality (which of these is still disputable), and not itself divisible into bodies different in form.*

In answering the further question, "What bodies correspond to this definition?," Aristotle would, of course, argue for the four elements of Empedocles – namely, earth, air, fire, and water.

Nearly 2100 years after Aristotle, the French chemist, Pierre Macquer, in his famous textbook of 1749, would give essentially the same definition and essentially the same answer as to what bodies corresponded to the definition:

> *... analysis or decomposition of bodies is finite; for we are unable to carry it beyond a certain limit. In whatever way we attempt to go further, we are always stopped by substances in which we can produce no change, which are incapable of being resolved into others, and which stand as so many firm barriers obstructing our progress. To these substances we may, in my opinion, give the title of principles or elements: at least they really are such with regard to us. Of this kind the principal are Earth, Water, Air, and Fire.*

Forty years after Macquer, Lavoisier would repeat Aristotle's definition once more:

> *... if we apply the term elements or principles of bodies, to express our idea of the last point which analysis is capable of reaching, we must admit, as elements, all the substances into which we are capable, by any means, to reduce bodies by decomposition.*

Yet in answer to the second question, "What bodies correspond to this definition?," Lavoisier would list, not the four elements of Empedocles, as Aristotle and Macquer had, but rather 33 different substances, including metals, earths, gases, inflammable nonmetals, and even imponderable fluids such as caloric. What had happened in the 40 years separating Macquer from Lavoisier to produce such a radical change? A proper answer to this question requires, in part, that we trace the changing meaning – both conceptual and experimental – of the word "analysis" which appears in one form or another in each of the above definitions.

At the time that Aristotle was writing there was no such thing as chemical analysis. From a conceptual standpoint, the term "analysis" corresponded to an *a priori* mental analysis of what was meant by such terms as "element" and "divide," implying that any change that generated two or more product bodies differing in form or substance from the original was by definition an analysis or division of the original body and that the resulting products were therefore necessarily simpler or more elementary than the body from which they were generated. To the extent that the doctrine of the four elements had any empirical content, it was based on the observation of naturally occurring everyday changes, rather than on controlled experimentation, and reflected the fact that almost any change is likely to include among its antecedents and/or products water-like or liquid substances, earth-like or solid substances, and air-like or volatile substances, as well as involving in some manner either the generation or absorption of heat. Such an analysis was, by its very nature, far too crude and far too general to yield the kind of specificity required to generate a meaningful system of chemistry.

With the rise of the distillation craze, beginning in the 3rd century and culminating in the 17th century, one finally acquires a repeatable experimental technique that, over the course of time, is applied – albeit rather haphazardly – to an enormous variety of mineral, plant and animal substances. Since this procedure generally resulted in at least two products – one corresponding to the liquid distillate and the other to the solid residue, it was almost universally assumed that it also corresponded to a decomposition or analysis of the body being distilled. As already noted in earlier lectures, as experience with this technique grew, the number of elements or principles began to slowly increase as well. Thus, with the advent of the *tria prima* of Paracelsus, the Aristotelian element of earth bifurcated into earth proper and salt, corresponding to the categories of solid, amorphous, water-insoluble versus solid, crystalline, water-soluble distillation residues, respectively, and, by the time we reach Lemery's textbook of 1675, the Aristotelian element of water had subdivided into oil, phlegm and spirit, corresponding to liquid distillates of varying viscosity, condensability, and inflammability.

With the advent of the acid-alkali theory of salt formation in the 17th century, the element of salt further subdivided into many distinct varieties of salt, each characterized by its own unique acid-alkali combination, and, for the first time, the criterion of synthesis or combination began to explicitly supplement that of analysis or decomposition.

As mineralogy and metallurgy matured in the 18th century, more and more specific distinctions were made among the earths as well, based not only on their physical appearance, but also, to an increasing extent, on their chemical behavior – a processes driven by the development of blowpipe analysis and both qualitative and quantitative wet analysis in the last quarter of the century. This ability to distinguish one earth from another or, in other words, to distinguish between one metal ore and another, could spell the difference between economic success and economic disaster. That many European governments, hoping to more fully exploit their mineral resources, not only took these developments seriously, but also attempted to systematically support their refinement and cultivation, is indicated by the establishment of the government-sponsored mining academies discussed in Lecture IV.

Finally, with the advent of the 18th-century pneumatic revolution, the last of the Aristotelian elements – air – was also fragmented. With the recognition that there were in fact many different kinds of air, and that many of them were chemically reactive, came the realization that simple counting of the number of visible solid and/or liquid reactants and products involved in a reaction was insufficient to determine whether a combination or decomposition had occurred. The evolution or absorption of often invisible gases could only be determined with certainty by explicitly monitoring changes in mass and, with the implementation of this criterion, reactions originally thought to be decompositions (e.g., calcination) were, in fact, found to be combinations, and reactions originally thought to be combinations (e.g., the burning of limestone) were found to really be decompositions

Thus we see that it was not so much the definition of the word "element" that changed over time as it was the definition of the word "analysis" or, more accurately, the means for operationally implementing and monitoring analysis in the laboratory. As analysis was refined, the four Aristotelian elements were fragmented into more and more groups, a process that rapidly accelerated in the last quarter of the 18th century with the rise of pneumatic chemistry and systematic mineral analysis, and which partially accounts for the radical difference in the number of elements listed by Lavoisier versus Macquer. Tracing changes in the operational meaning of analysis, however, provides only part of the answer to the question of what happened in the 40 years separating Macquer from Lavoisier. In fact, as we will see in the next section, a number of important conceptual changes were also involved in this process.

6.6 Residual Concepts

To the modern chemist the concept of an "element" involves only the twin criteria of analytical simplicity and isolability. The more traditional concept of an element, however, was a good deal more complex and involved at least three additional criteria, which, for most of recorded history, took precedence over the two most valued by the modern chemist. Thus, though Aristotle identified his elements with actual material substances, it is apparent that for him their status as elements was really dependent on the qualities or forms which these materials exemplified. They were elemental because the forms of texture (dry versus moist) and temperature (hot versus cold) which they embodied, and which they supposedly imparted to more complex materials, were universal. Though one could imagine bodies lacking color, taste, or a dozen other qualities, one could not conceive of a material body that lacked either texture or temperature. In short, for Aristotle and the generations of scholastics and alchemists who followed, the primary conceptual criteria for elemental status was the presence of qualities or forms that were both universal and transferable or additive.

In addition to universality and transferability, there was yet a third conceptual component to the traditional idea of a principle or element which evolved out of hylozoism or animism and that is duality – the idea that there were both active (male or seminal) and passive (female or nutritive) principles or elements. In other words, in a chemical interaction only one of the reactants was responsible for the most outstanding characteristics of the resulting product. This dualism was the driving force behind the shared goal of both distillation and alchemy to search out and isolate the active principles or essences of things, and was even imposed by later writers on the Aristotelian elements themselves through their further division into the classes of active (fire and air) and passive (earth and water).

The revival of hylomeric or particulate theories in the 17th century would cast doubt on all three of these traditional criteria. In Epicurean atomism the ultimate or true atoms possessed only the primary properties of size, shape, and mass. However, as these primary atoms combined to create more complex particles, these particles could mechanically interact with other material particles, whether in the form of other chemical reactants, particles of light, or the atoms composing the sensory organs of man, to generate such secondary properties or qualities as taste, odor, color, acidity, etc. Since both the Aristotelian elements and the *tria prima* of Paracelsus, as well as all other substances encountered in chemical operations, possessed these secondary qualities in abundance, this could only mean that their component particles were relatively complex. As Newton succinctly put it in his *Optics*:

> *Now the smallest particles of Matter may cohere by the strongest Attractions, and compose bigger Particles of weaker Virtue; and many of these may cohere and compose bigger Particles whose Virtue is still weaker, and so on for diverse Successions, until the Progression end in the biggest Particles on which the Operations in Chymistry, and the Colours of natural Bodies depend, and which by cohering compose Bodies of sensible Magnitude.*

This is little more than a paraphrase of the particle hierarchy assumed by Epicurus, by Boyle, and by other 17th-century proponents of mechanical hylomerism, with the gradually weakening interparticle forces or virtues, as one ascends the hierarchy, taking the place of the increasing ratio of void to atom.

This particulate view undermined the universality criterion both because atomism postulated an unimaginable (but not infinite) variety of primary atoms of varying shapes and sizes and because it implied that any specific difference in the secondary properties of two substances automatically reflected a difference in the sizes and shapes of their component complex particles and thus a difference in their composition. It undermined the transferability or additivity criterion because it postulated that mechanical entanglement on combination resulted in a new size and shape for the composite particle, which, in turn, generated new secondary properties not present in either of the original reactants (or in Newtonian terms, the attraction of two particles produced a new composite particle, which, through partial saturation of the original attractions, possessed attractive forces different from its components). And, finally, it undermined the duality criterion because both interacting particles played equal roles in generating the new size and shape and/or the modified attractive forces characteristic of the product particle. Appreciation of these implications, however, was highly variable. As already noted in Section 3.6, many so-called proponents of hylomerism in the 17th century ignored them altogether and simply used corpuscularized versions of hylomorphism which fully retained the criteria of universality, additivity and duality.

The criterion of universality was first attacked from the corpuscular point of view by Boyle in his 1661 publication, *The Sceptical Chymist*. Noting that distillation did not consistently give the same products for all substances, Boyle argued that it failed to support that idea of a small set of universal elements present in all things. Moreover, since some substances (e.g., mercury) survived distillation intact, whereas others (e.g., nitre) could be reconstituted from their distillation products, and yet others (e.g., many organic materials) were irreversibly destroyed, it seemed improbable that distillation always resolved a substance into its true components.

From the standpoint of corpuscularism, this variability suggested instead that some complex particles were so stable that distillation had no effect on them (mercury), whereas in other cases it resolved the complex particles into their immediate, preexistent, component parts, as indicated by the fact that the original particles could be regenerated by combining the components (nitre), while in yet other cases it totally destroyed both the original particles and their immediate component particles, thus allowing the components of the immediate components to form entirely new complex particles not present in the original substance, as indicated by the fact they could not be combined to recreate the original (organic materials). Given this ambiguity, not only could one not be sure that a given analysis had actually uncovered the true components, rather than synthesized new materials not originally present, one could not be sure even in the case of a true decomposition that the resulting products might not be capable of yet further resolution once a stronger method of analysis was applied.

In light of these considerations, Boyle not only rejected the criterion of universality, he rejected the entire concept of property-bearing principles or elements, arguing instead for an interpretation of chemical phenomena based directly on particle sizes, shapes and motions:

> *I see not why we needs must believe that there are any primogeneal and simple bodies, of which, as of preexistent elements, nature is obliged to compound all others.*

Most chemists, however, rejected Boyle's extreme atomistic reductionism. Though willing to abandon the criterion of universality and to accept the idea that their so-called elements were composed of complex particles that were, in principle, capable of further decomposition, most were unwilling to abandon the criteria of additivity and duality and instead opted for a kind of pragmatic relativism with respect to the status of their elements. Indeed, with the demise of universality, elements began to function more and more as the generators of individual class properties. Thus, though all salts might owe their similarity to a common saline principle modified in each case by a second specific component, and all flammable substances their inflammability to a common principle of inflammability, it no longer followed that saline substances must also contain some of the principle of inflammability or flammable substances some of the saline principle.

In order to differentiate between this revised view of the property-bearing principles of the chemist and the absolute physical atoms of the physicist, Stahl suggested using the terms “chemical element” versus “physical element,” and Lemery argued for a similar distinction in his famous textbook:

> *The term Principle in Chemistry should not be taken in an entirely precise sense; for the substances so called, are not Principles except from our point of view, being so because we cannot go further in the division of bodies; but everyone knows that these principles are divisible into an infinity of parts which alone can properly be called Principles. By Chemical Principles, then, is understood substances separated and divided as far as our poor efforts are capable of doing. And as chemistry is a demonstrative science, it cannot accept as a basis things which are not real and capable of demonstration.*

Exactly the same sentiments were voiced the Scottish chemist, William Cullen, nearly a century later:

> *Elements are physical or chemical, the former are the realelements of bodies or, as they are often called, atoms, but these physical elements are rather imagined than actually known ... the strict, precise meaning of elements is that which no human art can divide, and those we call chemical elements ... All the bodies obvious to our senses are compounded through several degrees ... art never attains the ultimate degree of division, but rests in some of the intermediate stages, which we may consider as the elements, only of a higher composition; hence, however, chemical elements.*

Lavoisier would also articulate and apply the exact same distinctions 20 years after Cullen, but would do so in light of the rapid advances in chemical analysis and pneumatic chemistry that occurred after 1770 and through a rigorous application of the supplementary criteria of synthesis and mass conservation. The result was a complete reevaluation of what substances did or did not correspond to the newer relativistic concept of a chemical element as a provisionally simple substance rather than as a carrier of universal properties and would culminate in the table of 55 tentative elements published by Lavoisier and his collaborators in their *Méthode de nomenclature chimique* of 1787.

That Lavoisier was also willing to take seriously the provisional status of an element, implied by the pragmatic relativism advocated by his predecessors, is indicated by the fact that, by the time his textbook was published two years later, this list had been pruned down to 33 entries (see plate), due to the elimination of 19 organic radicals from the class of acidifiable nonmetals, which Lavoiser had subsequently shown to be composed of carbon, hydrogen and nitrogen, and the elimination of a fifth class of elements containing the three alkalis – soda, potash, and ammonia – all of which Lavoisier now suspected of being compound, though he had not yet succeeded in actually decomposing the first two. Of thisfinal list of 33 entries, six are now known to be oxides (those of B, Ca, Mg, Ba, Al and Si), two correspond to hypothetical radicals (those of Cl and F), and two (caloric and light) are now considered to be forms of energy rather than material substances. With this advance we have finally arrived at the modern concept of an element as an simple, isolable, material substance. The older defining characteristics of an element as a carrier of properties and as a universal component have been subordinated to the criteria of isolability and analytical simplicity.

Yet the transition between the older and newer definitions was not as sharp as the above account would suggest. Though the criterion of universality was abandoned, remnants of both the additivity and duality criteria lingered on. Thus close examination of Lavoisier's table reveals a curious asymmetry in its treatment of the first five entries, which were placed in a special class andlabeled as "elements" rather than as "simple substances" like the rest of the table entries. The reason for this becomes apparent from a study of Lavoisier's textbook, which quickly reveals that these five elements continued to function as the carriers of class properties in Lavoisier's scheme. Thus oxygen served as the universal principle of acidity; hydrogen as the principle of water; nitrogen as a possible principle of alkalinity; and caloric, like phlogiston before it, as the principle of heat or fire. In keeping with the assumption of additivity, these qualities were imparted to their compounds, and, in keeping with the assumption of duality, they, rather than their reaction partners, were the sole cause of these properties.

This continued use of the additivity or transferability assumption by Lavoisier is interesting, since his collaborator, Fourcroy, had explicitly attacked the concept as early as 1783, arguing that:

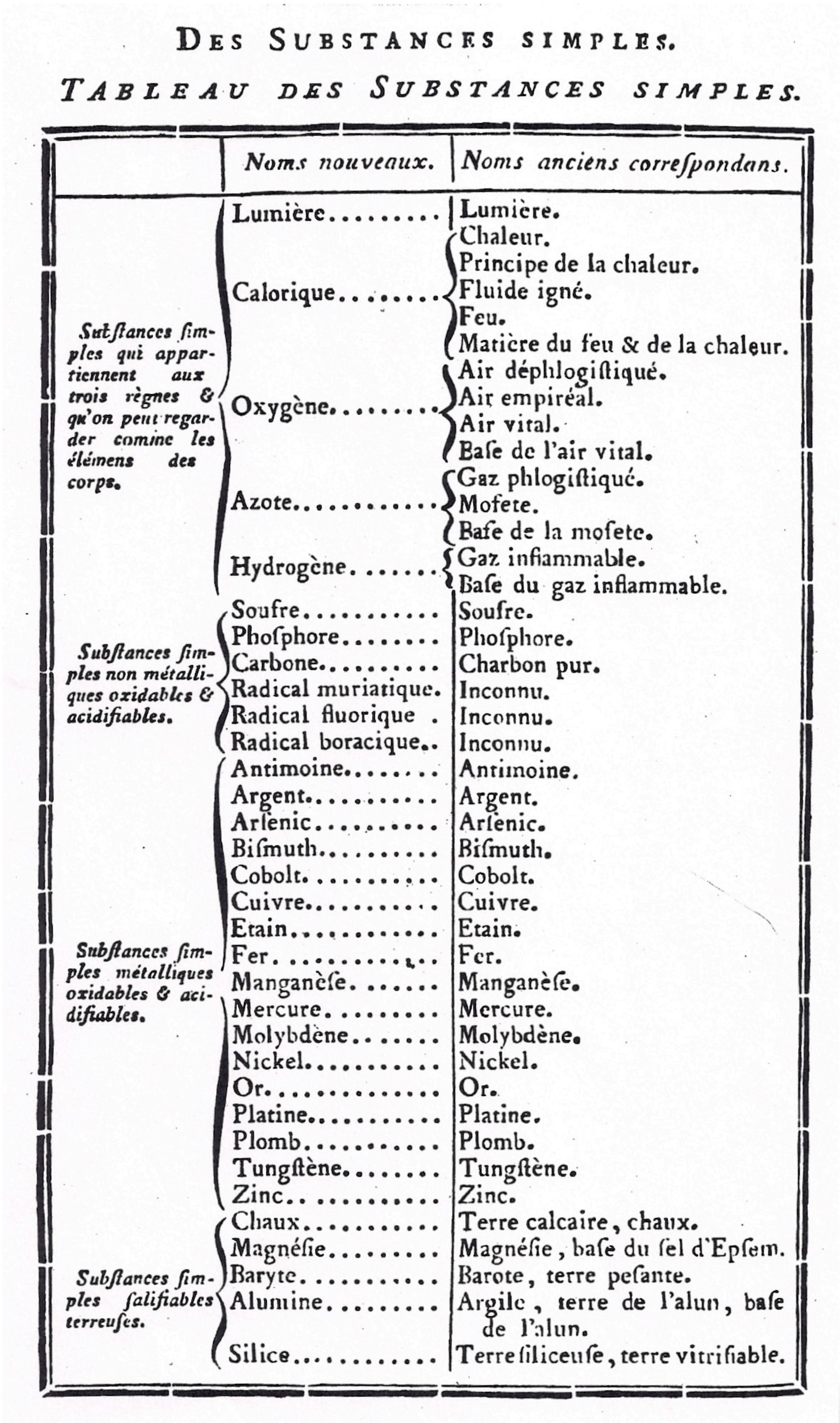
Two or more bodies united by the attraction of composition, form a substance, the properties of which are different from those which each of the bodies possessed before their union.

Not only did Fourcroy deny the additivity assumption, he fully recognized the revolutionary nature of that denial:

It is important to establish the existence of this law, because many celebrated chemists of the present age, have entertained opinions concerning the properties of compounds, which to us appear inconsistent with a great number of facts, and are directly contradictory to what we offer as one of the principle phenomena of the affinity of composition [i.e., chemical attraction].

Whether Lavoisier was numbered among Fourcroy's "celebrated chemists" is unknown, but there is no doubt that Macquer was, as he had explicitly enunciated the additivity principle in his famous textbook of 1749:

Substances that unite together lose some of their separate properties; and the compounds resulting from their union partake of the properties of those substances which serve as their principles.



DES SUBSTANCES SIMPLES.

TABLEAU DES SUBSTANCES SIMPLES.

	Noms nouveaux.	*Noms anciens correſpondans.*
Subſtances ſimples qui appartiennent aux trois règnes & qu'on peut regarder comme les élémens des corps.	Lumière	Lumière.
	Calorique	Chaleur. Principe de la chaleur. Fluide igné. Feu. Matière du feu & de la chaleur.
	Oxygène	Air déphlogiſtiqué. Air empiréal. Air vital. Baſe de l'air vital.
	Azote	Gaz phlogiſtiqué. Mofete. Baſe de la mofete.
	Hydrogène	Gaz inflammable. Baſe du gaz inflammable.
Subſtances ſimples non métalliques oxidables & acidifiables.	Soufre	Soufre.
	Phoſphore	Phoſphore.
	Carbone	Charbon pur.
	Radical muriatique.	Inconnu.
	Radical fluorique	Inconnu.
	Radical boracique	Inconnu.
Subſtances ſimples métalliques oxidables & acidifiables.	Antimoine	Antimoine.
	Argent	Argent.
	Arſenic	Arſenic.
	Biſmuth	Biſmuth.
	Cobolt	Cobolt.
	Cuivre	Cuivre.
	Etain	Etain.
	Fer	Fer.
	Manganèſe	Manganèſe.
	Mercure	Mercure.
	Molybdène	Molybdène.
	Nickel	Nickel.
	Or	Or.
	Platine	Platine.
	Plomb	Plomb.
	Tungſtène	Tungſtène.
	Zinc	Zinc.
Subſtances ſimples ſalifiables terreuſes.	Chaux	Terre calcaire, chaux.
	Magnéſie	Magnéſie, baſe du ſel d'Epſem.
	Baryte	Barote, terre peſante.
	Alumine	Argile, terre de l'alun, baſe de l'alun.
	Silice	Terre ſiliceuſe, terre vitrifiable.

Plate I
Lavoisier's 1789 table of simple substances

The more subtle assumption of duality persisted even longer and was still being attacked by the American chemist, Thomas Duché Mitchell (1791-1865), as late as 1813:

> *... what is a neutral salt, but the result of the mutual interaction of an acid and alkali, and what is combustion, but the effect of the mutual operation of oxygen gas, in some shape or other, and a combustible? ... Where was philosophy and reason when inflammability, or the power of burning, was consigned to one solitary agent? ... When we speak of the properties of bodies, as taste, smell, etc., we do not mean that any of them possesses a positive quality. They are merely sensations or effects resulting from the action of those bodies on our organs of taste, smell, etc. Inflammation, like odors, is the result of relative circumstances and not the product of a single agent.*

Mitchell's attack, though cogent, went largely unnoticed, and the last remnants of both duality and additivity appear to have gradually faded away as 19th-century chemists became preoccupied with other concerns.

6.7 Salts and Compositional Nomenclature

It is difficult to imagine how chemists would have dealt with the characterization of compounds had they accepted the extreme atomic reductionism advocated by Boyle. By opting instead for relative "chemical" rather than absolute "physical" elements, they were able to gradually develop a simple compositional nomenclature which characterized a given compound in terms of its immediate material components. As we saw in Section 3.7, this process had already begun in the 17th century with the rise of the acid-alkali theory of salt formation, and this beginning was further extended by the French chemist, Guillaume-François Rouelle (1703-1770), in the 1740s when he generalized the process of salt formation by grouping the alkalis (i.e., ammonia and the alkali metal carbonates) together with the earths (i.e., metal oxides), the metals, and some oils, under the common rubric of "bases":

$$\textit{acid} + \textit{base} \rightarrow \textit{salt} \qquad [21]$$

Again, the various by-products of this reaction (water, carbon dioxide, dihydrogen, etc.) were generally ignored. It is this generalization, as well as an increasing ability to analytically distinguish between sodium and potassium compounds, which is largely responsible for the rapid increase in the number of known salts reported by the end the 18th century, as already noted in Section 5.7.

By the second half of the 18th century, an increasing number of chemists, stimulated both by Rouelle's generalization and by the work of Linnaeus on biological classification, began explicitly arguing for a new chemical nomenclature for salts based on their component acids and bases rather than on arbitrary physical properties, such as color (e.g., butter of antimony) or taste (e.g., sugar of lead). Macquer (Table 6.1) made some sporadic suggestions along these lines in the 1760s, and Bergman proposed a systematic binary Latin nomenclature for salts in the 1770s. These were followed, in turn, by the proposals of the French chemist, Louis-Bernard Guyton de Morveau, who developed a French version of Bergman's system in the 1780s.

Table 6.1 Early Proposals for a Compositional Nomenclature

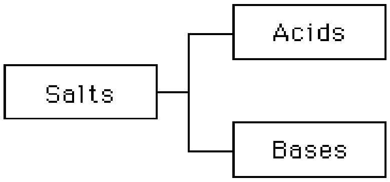
Date	*Chemist*	*Examples*
1760s	Pierre Macquer	nitre de cuivre (copper nitrate) sel d'argent (silver chloride)
1770s	Torbern Bergman	Nitrosum argentum (silver nitrate) Vitriolum potassinatum (potassium sulfate) Muriaticum ammoniacium (ammonium chloride)
1780s	Guyton de Morveau	vitriol de fer (iron sulfate) phosphate de plomb (lead phosphate) fluor ammonical (ammonium fluoride)

Thus we see that by the time Lavoisier began his work on the role of gases in chemical reactions in the 1770s, he was heir to both a well-established definition of a chemical element, and to a tradition of attempting to establish a binary compositional nomenclature for salts based on their acid-base components. Combination of these two influences should have led to the logical conclusion that acids and bases were the true material elements of salts, but before this could happen, Lavoisier's work succeeded in pushing the acid-base-salt compositional hierarchy one stage further. This occurred through Lavoisier's discovery that acids and bases were, in fact, the oxides of nonmetals and metals, respectively:

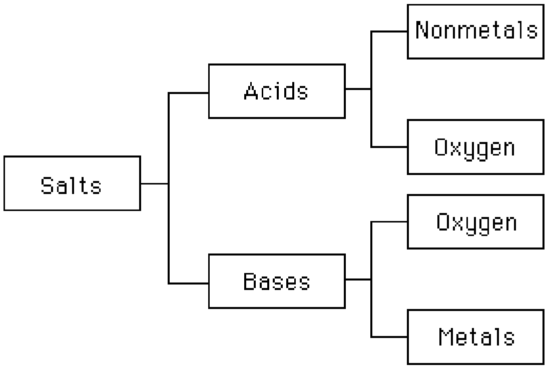
$$\textit{oxygen} + \textit{nonmetal} \rightarrow \textit{acid} \qquad [22]$$

$$\textit{oxygen} + \textit{metal} \rightarrow \textit{base} \qquad [23]$$

Thus, the original acid-base-salt hierarchy:



was now further elaborated:



and the metals, the various oxidizable nonmetals (e.g, sulfur, nitrogen, phosphorus, and carbon), and oxygen itself, rather than the original acids and bases, came to function as the true material elements of acids, bases, and salts, or at least until they, in turn, were shown to be capable of yet further decomposition. Lavoisier not only explicitly recognized the consequences of combining this compositional hierarchy with the traditional definition of an element as the last stage of analysis, in 1787 he joined forces with Guyton de Morveau, Fourcroy, and Claude-Louis Berthollet (1748-1822) in a project (the *Méthode de nomenclature chimique* mentioned earlier) to incorporate this advance into Guyton's earlier nomenclature reforms and, in so doing, laid the foundations of our current chemical nomenclature.

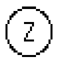
6.8 Chemical Symbolism

Not only did the *Méthode* of 1787 provide the basis of our current systematic compositional nomenclature, it also contained the first proposal for a systematic chemical symbolism. Developed by the team of Pierre Adet (1763-1832) and Jean Hassenfratz (1755-1827), it made use of specific geometric shapes to symbolize each important class of chemical substances, and differences in either orientation or inscribed letters to indicate the individual members of each class, as summarized in Table 6.2:

Table 6.2 The Chemical Symbolism of Adet and Hassenfratz

Class	*Symbol*
carriers of class properties	lines of various orientation
nonmetallic combustibles	crescents of various orientation
metals	circles containing various letters
alkalis	triangles containing various letters
earths	inverted triangles containing various letters
acidifiable compound radicals	squares containing various letters
miscellaneous	diamonds containing various letters

States were indicated by the positioning or absence of the symbol for caloric (a vertical line). Thus absence of the caloric symbol indicated the solid state, whereas its attachment to the top of another symbol indicated the liquid state for the substance in question, and its attachment to the bottom of the symbol indicated the gaseous state:

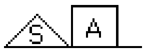


Solid Zinc Metal

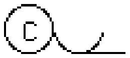
Liquid Zinc

Zinc Vapor

Likewise, compounds were indicated by the juxtaposition of the appropriate symbols for their immediate components



Acetate of Soda



Sulfate of Copper

It is important to note that the resulting formulas were merely a shorthand representation of the corresponding systematic names. They neither indicated the quantitative gravimetric composition of the substances in question nor their atomic compositions, as with our modern formulas. Unlike the nomenclature proposals of the *Méthode*, the symbolism of Adet and Hassenfratz was never widely adopted – in large part because it required the use of special fonts and/or etched plates that were unavailable to most printers.

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Lecture VII

The Eighteenth Century

(1701-1800)

Chemical Affinity

This table becomes in some degree prophetic, for if substances are mixed together, it can foretell the effect and result of the mixture, because one will see from their different relations what ought to be, so to speak, the issue of the combat.
Étienne-François Geoffroy 1718

7.1 Chemical Affinity

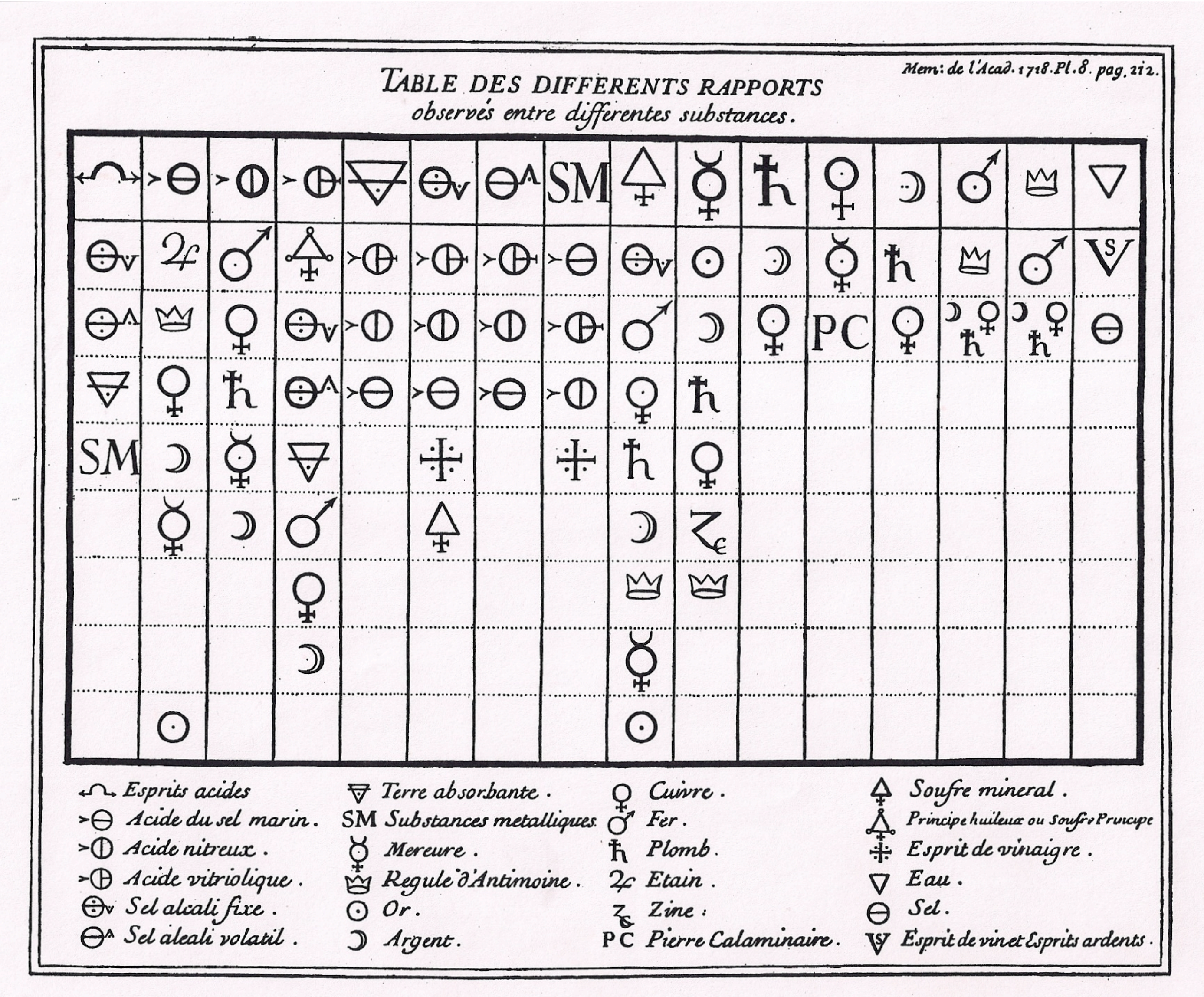
All of the issues discussed in Lecture VI, and indeed the first chemical revolution itself, centered on the two questions of states of matter and chemical composition. However, there was yet a third and, in many ways, equally important thread in 18th-century chemistry which focused instead on questions related to the theme of chemical reactivity or "chemical affinity." While acknowledging the importance of this third theme, Lavoisier had in fact intentionally excluded it from his famous *Traité* of 1789 on the grounds that the subject was still too immature and too speculative for inclusion in an introductory text:

The rigorous law from which I have never deviated, of forming no conclusions which are not fully warranted by experiment, and of never supplying the absence of facts, has prevented me from comprehending in this work that branch of chemistry which treats of affinities, although it is perhaps the best calculated of any part of chemistry for being reduced into a completely systematic body. Messrs. Geoffroy, Gellert, Bergman, Scheele, de Morveau, Kirwin, and many others have collected a number of particular facts upon this subject, which only wait for a proper arrangement; but the principle data are still wanting, or, at least, those we have are either not sufficiently defined, or not sufficiently proved, to become *the foundation upon which to build so very important a branch of chemistry. This science of affinities, or elective attractions, holds the same place with regard to the other branches of chemistry, as the higher or transcendental geometry does with respect to the simpler and elementary part, and I thought it improper to involve those simple and plain elements, which I flatter myself the greatest part of my readers will easily understand, in the obscurities and difficulties which still attend that other very useful and necessary branch of chemistry.*

7.2 Affinity Tables

As already noted in Lecture III, acceptance of a corpuscular approach to chemical phenomena not only accustomed chemists to the idea of characterizing the composition of salts in terms of their component acid-alkali particles, rather than in terms of abstract property-bearing principles, it also resulted in an interpretation of acid-alkali reactions as exchanges or competitions between preexisting material parts, rather than in terms of the generation and corruption of alternative forms or essences.

This view was soon extended to chemical reactions in general and, by the early 18th century, had led to the first attempts to systematize chemical reactions using a device known as an "affinity table." Each column of the table summarized the relative affinities of a series of reagents with regard to a common substrate placed at the head of the column in question. The higher in the column a given reagent, the greater its affinity for the substrate and the greater its ability to displace other reagents lower in the column when competing for the common substrate. The closest analogy in modern-day chemistry would be a table of electrochemical half-cell reduction potentials. This could be thought of in 18th-century terms as a column of an affinity table in which the electron functions as the common substrate and the relative the positions of the various oxidized species in the table as a measure of their relative affinities for the electron. Thus a species higher up in the table (e.g. Cu^{2+}) has a greater affinity for the electron than one lower down in the table (e.g. Zn^{2+}) and will displace the latter when competing for the common electron substrate:



Mem: de l'Acad. 1718. Pl. 8. pag. 212.

TABLE DES DIFFERENTS RAPPORTS
observés entre differentes substances.

↜	>⊖	>⦶	>⊕	🜃	⊖v	⊖^	SM	🜍	☿	♄	♀	☽	♂	♕	▽
⊖v	♃	♂	🜏	>⊕	>⊕	>⊕	>⊖	⊖v	☉	☽	☿	♄	♕	♂	🜈
⊖^	♕	♀	⊖v	>⦶	>⦶	>⦶	>⊕	♂	☽	♀	PC	♀	☽ ♀ ♄	☽ ♀ ♄	⊖
🜃	♀	♄	⊖^	>⊖	>⊖	>⊖	>⦶	♀	♄						
SM	☽	☿	🜃		🜊		🜊	♄	♀						
	☿	☽	♂		🜍			☽	Ƶ						
			♀					♕	♕						
			☽					☿							
	☉							☉							

↜ Esprits acides
>⊖ Acide du sel marin.
>⦶ Acide nitreux.
>⊕ Acide vitriolique.
⊖v Sel alcali fixe.
⊖^ Sel alcali volatil.

🜃 Terre absorbante.
SM Substances metalliques.
☿ Mercure.
♕ Regule d'Antimoine.
☉ Or.
☽ Argent.

♀ Cuivre.
♂ Fer.
♄ Plomb.
♃ Etain.
Ƶ Zinc:
PC Pierre Calaminaire.

🜍 Soufre mineral.
🜏 Principe huileux ou Soufre Principe
🜊 Esprit de vinaigre.
▽ Eau.
⊖ Sel.
🜈 Esprit de vin et Esprits ardents.

Plate II
Geoffroy's affinity table of 1718

$Cu^{2+}(aq) + Zn(s) \rightarrow Zn^{2+}(aq) + Cu(s)$ [1]

The first such affinity table was constructed by the French chemist, Étienne-François Geoffroy (1672-1731), in 1718 (seeplate), and ever more complex versions appeared throughout the century, the most thorough being those given by Torbern Bergman in his monograph, *A Dissertation on Elective Attractions*, first published in Latin in 1775.

7.3 Affinity Laws

Starting with Macquer's popular textbook of 1749 (recall Section 4.7), many 18th-century chemistry texts also began to organize their theoretical sections around a series of so-called laws summarizing the effects of chemical affinity – a practice which persisted well into the 1850s. The seven laws of chemical affinity given by Macquer in 1749 are:

1. If any one substance hath any Affinity or conformity with another, the two will unite together to form one compound.

2. All similar substances have an Affinity with each other, and are consequently disposed to unite; as water with water, earth with earth, etc.

3. Substances that unite together lose some of their separate properties; and the compounds resulting from their union partake of the properties of those substances which serve as their principles.

4. The simpler any substances are, the more perceptible and considerable are their Affinities ...

5. If a body consist of two substances, and to this compound be presented a third substance that has no Affinity at all with one of the two primary substances aforesaid, but has a greater Affinity with the other than those two substances have with each other, there will ensue a decomposition, and a new union ... the third *substance will ... coalesce with that which has an Affinity with it ... and disengage the other ...*

6. Two substances, which, when apart from all others, are incapable of contracting any union, may be rendered capable of incorporating together ... by combining with a third substance with which each has an equal Affinity.

7. A body, which of itself cannot decompose a compound consisting of two substances ... becomes nevertheless capable of separating the two by uniting with one of them, when it is itself combined with another body, having a degree of affinity with that one, sufficient to compensate for its own want thereof ... and thence ensues a double decomposition ...

It is of great interest to gauge the progress made in the study of chemical affinity throughout the century by comparing these laws with the versions given by Fourcroy in his own textbook 34 years later:

1. The attraction, or affinity of composition, cannot act but between bodies of different natures.

2. The attraction of composition acts only between the minutest particles of bodies.

3. The attraction of composition can unite more bodies than two.

4. That the affinity of composition may take place between two bodies, at least one of the two must be in a fluid state.

5. When two bodies are combined by this affinity, theirtemperature suffers a change at the instant of their union.

6. Two or more bodies united by the attraction of composition, form a substance, the properties of which are different from those which each of the bodies possessed before their union.

7. The attraction of composition is measured by the difficulty of destroying the combination formed between two or more bodies.

8. Bodies have not all the same degree of chemical attraction with regard to one another; and the degrees of that force subsisting between different bodies may be determined by observation.

The contradiction between Macquer's third law and Fourcroy's sixth law was already commented on in Section 6.6. What is of more interest here, however, is the contradiction betweenMacquer's second law and Fourcroy's first law. Macquer's version reflected the original hylozoic origins of the affinity concept, which tended to view chemical combination as a phenomenon akin to marriage or sexual union, based, in turn, on the two parties sharing a common nature or "affinity" (from the Latin *affinis*, meaning "related or similar").

Fourcroy's proposed revision of this traditional view was the result of an explicit survey of the facts of chemical affinity which he and his mentor, Jean Baptiste Bucquet, had made in the 1780s, and which showed that many of the traditional concepts were not only misleading but simply wrong. Indeed, so confident was Fourcroy of the correctness of his revised law, that he was willing to further underscore his statement with the assertion that it ...

... holds so invariably, that the attraction of composition is never stronger than when the bodies between which it acts are, in nature, the most essentially different from one another.

Realizing that this new law made the use of the term "affinity" linguistically indefensible, Fourcroy attempted to replace it with the more descriptive term "attraction of composition" (originally suggested by Bergman), but without success. Though chemists would adopt Fourcroy's new law, they would persist in using the older term, even down to the present day.

The alternative versions of the affinity law given by Macquer and Fourcroy both dealt with the question of how chemical affinity varied with the similarities or dissimilarities in the chemical characters of the reacting substances:

affinity = f(chemical character) [2]

and this was also the only factor dealt with in the affinity tables. Though Bergman, in his monograph of 1775, would tentatively suggest that relative affinity orders might also be influenced by such factors as changes in temperature, or the presence or absence of a solvent, a full exploration of the role of such environmental factors would have to await the work of Berthollet in the early years of the 19th century.

The anthropomorphic implications of the original affinity concept were also undercut by an increasing tendency, as the century progressed, to equate affinities with the operation of Newtonian short-range interparticle forces at the molecular level – a view first advocated by the British chemists, John Freind (1675-1728) and John Keill (1671-1721), at the beginning of the century, and by Newton himself in the finalized version of the 31 queries appended to the 1717 edition of his famous treatise on optics,where he succinctly summarized his program:

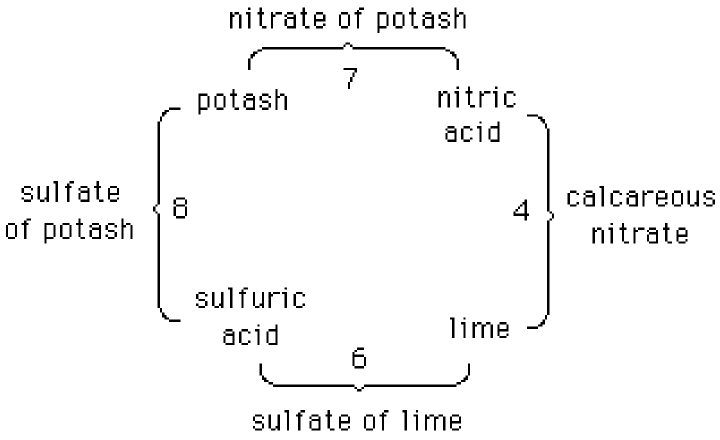
There are therefore Agents in Nature able to make the Particles of Bodies stick together by very strong Attractions. And it is the Business of experimental Philosophy to find them out.

We have already noted the application of this concept to the caloric theory of states, discussed in Section 6.2, and it would also be applied by Bergman and others to the study of affinity tables.

7.4 Affinity Diagrams

One by-product of this Newtonian interpretation was a crude precursor of the modern chemical equation known as an "affinity diagram," which attempted to graphically summarize the various competing interparticle forces or affinities at work in a given reaction. The precise form of the diagram varied from one chemist to another. The following example is taken from Fourcroy's textbook of 1789, and was intended to diagram the double decomposition reaction:

calcareous nitrate + s*ulfate of potash* →
nitrate of potash + *sulfate of lime* [3]



or in modern terms:

$$Ca(NO_3)_2(aq) + K_2(SO_4)(aq) \rightarrow 2K(NO_3)(aq) + Ca(SO_4)(s) \qquad [4]$$

Each pair of particle interactions was assigned a hypothetical numerical value for its attractive force and these values were contrived so that, for the observed direction of the reaction, the sum of the attractions within the reactants (called the *quiescent* attractions) was always less than the sum within the products (called the *divellent* attractions). Thus in the above diagram:

Sum of the quiescent forces = 8 + 4 = 12

Sum of the divellent forces = 7 + 6 = 13

Actual attempts were made to experimentally measure these interparticle forces, but little agreement was reached as to how this should be done. Thus Guyton de Morveau attempted to correlate the affinities of various metals with the force required to separate a disk of the metal in question from a mercury surface; whereas the

German chemist, Carl Wenzel, attempted to correlate them with the rate of dissolution of a cylinder of the metal in acid; and the Irish chemist, Richard Kirwin (1733-1812), with the weight of alkali or metal required to saturate a given amount of acid.

With the gift of hindsight, we now know that all of these attempts were fundamentally flawed. Guyton was actually measuring intermolecular forces (called “attractions of aggregation” by 18th-century chemists) rather than the interatomic forces (or “attractions of composition”) actually responsible for compound formation. Kirwin was conflating chemical composition with chemical affinity (he was actually measuring combining weights), and Wenzel was conflating kinetics with questions of stability.

Indeed, the purpose of Fourcroy’s seventh and eighth laws was to provide guidelines for the experimental measurement of these affinities, and he was quite explicit in his rejection of Wenzel’s kinetic criterion. In so doing, he unwittingly articulated a fundamental distinction in the study of chemical affinity that would become increasingly important as the 19th century progressed:

> *From the rapidity with which some substances combine, we are ready to imagine that their mutual attraction must be very considerable. But long experience shows that this eagerness to enter into combination, instead of indicating a perfect composition, is rather a proof that the attraction between the bodies is extremely weak, and can produce but a very imperfect compound. In order, therefore, to determine accurately the degree of affinity with which bodies unite and remain in union, we must consider instead theease or difficulty with which they are separated.*

Despite Fourcroy’s guidelines, the experimental measurement of affinity of composition remained elusive and the Newtonian program of reducing chemical affinity to quantified interparticle forces never came to successful fruition. Like the hypothetical particle sizes and shapes invoked by 17th-century mechanical corpuscularism, the interparticle forces of 18th-century dynamical corpuscularism never functioned as more than after-the-fact *ad hoc* rationalizations.

7.5 Reaction Stoichiometry

Not only did 18th-century analytical chemistry implicitly rely on the law of definite composition long before it was explicitly articulated by Wenzel (recall Section 5.6), it also implicitly assumed the law of the conservation of mass in chemical reactions, as did Black in his work on fixed air. However, it was Lavoisier, in his famous *Traité* of 1789, who first explicitly articulated the idea that chemical reactions involved not only the conservation of mass, but also the conservation of individual chemical elements:

> *We may lay it down as an incontestable axiom, that, in all the operations of art and nature, nothing is created; an equal quantity of matter exists both before and after the experiment; the quality and quantity of the elements remains precisely the same; and nothing takes place beyond changes and modifications in the combinations of these elements. Upon this principle the whole art of performing experiments depends: We must always suppose an exact equality between the elements of the body examined and those of the products of its analysis.*

In 1792 the German chemist, Jeremias Richter, would coin the word "stoichiometry" (from the Greek *stoicheion*, meaning "element," and *metron*, meaning "to measure") to describe the applications of Lavoisier's fundamental principle to both chemical reactions and to the composition of individual chemical compounds.

7.6 Summary

Chemistry in the 18th century sees the establishment of the following conceptual advances:

a. The caloric theory of the solid, liquid and gaseous states of matter based on quantified temperatures and latent heats of transition, and qualitatively interpreted at the molecular level in terms of imponderable fluids and static Newtonian interparticle forces of attraction and repulsion.

b. Recognition of the role of gases in chemical reactions and the explicit use of conservation of mass to monitor their evolution and absorption.

c. An analytical definition of a chemical element as an individualized simple substance, rather than as an universally diffused, abstract, property-bearing principle, and the use of these elements to establish a compositionally based chemical nomenclature and symbolism.

d. A systematization of chemical reactions in terms of affinity tables and the establishment of a preliminary set of qualitative rules governing the operation of chemical affinity, as well as a qualitative theoretical interpretation of these rules at the molecular level in terms of Newtonian interparticle forces and affinity diagrams.

e. The establishment of the initial stages of chemical stoichiometry based on an explicit recognition of the law of definite composition and the law that not only mass, but the chemical elements themselves, are conserved in the course of chemical reactions.

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Lecture VIII

The Nineteenth Century

(1801-1900)

The Rise of the Professional Chemist

> The modern American chemistry profession is firmly rooted to the institutional developments of the last half of the 19th century. The value system of present-day chemistry had its beginnings in that earlier period.
>
> *Edward Beardsley 1964*

8.1 Chemistry and the University

The 19th century sees three major developments in chemical education:

a. The appearance of both undergraduate and graduate-level university degrees in chemistry.

b. The appearance of student laboratory work as part of the university curriculum.

c. The transference of the bulk of chemical training from the medical schools to either the schools of arts (thereby converting them into schools of arts and sciences) or to newly founded schools of science and technology.

8.2 The Rise of Laboratory Training and Graduate Work

Beginning in the early 19th century there were some sporadic attempts to develop student teaching laboratories, some of which are summarized in Table 8.1. Most of these were privately owned affairs whose major clientele consisted of students of pharmacy seeking practical hands-on training.

Table 8.1 Early Isolated Examples of Student Laboratories

Date	*Founder*	*Location*
1800	Frederick Accum	London
1806	Friedrich Stromeyer	Göttingen
1807	Johann Fuchs	Landshut
1811	Johann Döbereiner	Jena
1817	Thomas Thomson	Glasgow
1820	Nicolaus Fischer	Breslau

in elementary chemistry. The key event, however, seems to have been the private teaching laboratory started by the German chemist, Justus Liebig (1803-1873), at Giessen in 1826. Like its predecessors, this was initially devoted largely to the training of apothecaries in practical manipulation. However, in 1833 the laboratory finally received official recognition from the university and shortly thereafter Liebig began to restructure the curriculum so as to more closely serve the needs of future chemists rather than pharmacists. Actual laboratory instruction consisted of training in both qualitative and quantitative inorganic analysis and in organic combustion analysis, followed in many cases by an advanced research project.

Despite the growing reputation of Liebig's laboratory, the Giessen model was slow in spreading to other German universities, and it was not until the 1850s that similar teaching laboratories directed at students in the arts and sciences began to appear at other schools (see Table 8.2). Interestingly, attempts to emulate Liebig were made in both Great Britain and the United States almost a decade earlier than in Germany, including:

a. The Royal College of Chemistry, founded in London in 1845 under the influence of Prince Albert and directed by the German import, August W. Hofmann (1818-1892), until 1864.

b. The Sheffield Scientific School, started at Yale in 1846 under the influence of Benjamin Silliman Sr. (1779-1864), who had taught service chemistry in the School of Arts since 1801.

c. The Lawrence Scientific School, started at Harvard in 1847, where chemistry had been taught in the Medical School since 1783.

Table 8.2 Early Student Teaching Laboratories in German Universities

Date	*Founder*	*School*
1851	Babo	Freiberg
1853	Bunsen	Heidelberg
1854	Loewig	Breslau
1855	Gorup-Besanez	Erlangen
1857	Werther	Konigsberg

Both the Sheffield and Lawrence Scientific Schools represent an attempt to introduce advanced scientific training into the traditional university setting by expanding the four traditional schools of arts, law, theology, and medicine so as to include a fifth independent school of science and technology fully empowered to grant its own independent degrees (B.S., M.S., D.Sc.). In other cases, special separate technical universities were founded – for example, the French Polytechnic and the German Technische Hochschule movements of early 19th century and, in the United States, such sporadic efforts as Rensselaer Polytechnic Institute (1824), MIT (1859), and the California Institute of Technology (1891). In yet other cases, as already noted, the natural philosophy tradition within the School of Arts was expanded in order to create a new composite School or College of Arts and Sciences.

In some universities these trends overlapped. Thus, at Harvard, chemistry was taught by the Hollis Professor of Mathematics and Natural Philosophy in the School of Arts from 1687-1783, and by the Erving Professor of Chemistry in the Medical School from 1783 until the 1850s, when the Erving Professsorship was gradually transferred to the School of Arts by Josiah Parsons Cooke, where it competed with the Rumford Professorship of Chemistry within the newly established Lawrence Scientific School.

The first German Ph.D. in chemistry granted to a German was awarded to Heinrich Rose at Kiel in 1821 and was based on work done in the private laboratory of Berzelius in Stockholm. Liebig's first British student (T. Richardson) came in 1836 and the first German Ph.D. given to a British student was awarded to Lyon Playfair in 1840. Liebig's first American student (J. L. Smith) came in 1841 and the first German Ph.D. given to an American student was awarded to Charles Wetherill in 1848 (though the Mexican student, V. Ortigiosa, had received a doctorate in 1842). From 1840-1914 nearly 800 American and British chemists received doctorate degrees in chemistry in Germany, and by the 1850s they had begun to displace the professors in their respective home countries who had come out of the earlier Scottish chemical/medical tradition. It is of interest to note that the Americans favored study at Göttingen, Freiburg, and Berlin, whereas the British favored Giessen, Würzburg, and Jena.

As of 1880, only 16, or about 5%, of American colleges teaching chemistry offered a full four-year B.S. program and 22, or about 7%, offered a three-year program. The rest simply taught introductory service courses. In the late 1860s only two American universities (Yale and Harvard) offered doctorate degrees in science. By the 1870s there were at least a dozen, including Johns Hopkins, University of Cincinnati, and University of Tennessee at Knoxville, though the latter two had no takers for the remainder of the century. Beginning in 1874, the University of Cincinnati offered both a four-year B.S. degree and a one-year M.S. degree in chemistry, as well as the option of a possible Ph.D. The first B.S. and M.S. degrees in chemistry were given in 1880, but the first Ph.D. was not awarded until 1904.

German training was not always the best, as may be seen from both the undergraduate preparation and period of graduate study of some typical American students who travelled to Germany in the 1870s:

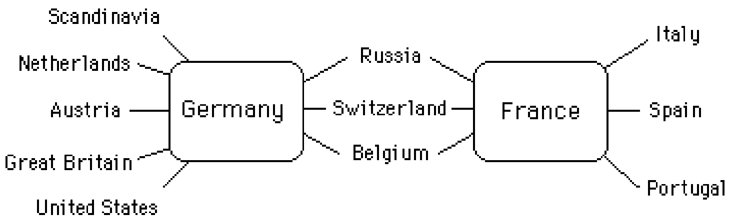
a. Thomas Norton (1851-1941), the second professor of chemistry at Cincinnati, took an introductory chemistry course his senior year at Hamilton College in New York, departed for Heidelbergupon graduation in 1873, and received his Ph.D. under Bunsen in 1875 with no thesis.

b. Alfred Springer (1854-1946), a local Cincinnati industrial chemist, graduated from high school in Cincinnati in 1870 at age 16, left for Heidelberg the same year, and received his Ph.D. under Bunsen in 1872 with no thesis.

Beginning in the late 1870s a small number of women also began to seek degrees in chemistry. Thus, for example, the first B.S. degree in chemistry at Cincinnati was awarded to Helena Stallo in 1880.

8.3 The Larger Picture

Not surprisingly, in a history course intended for American students, we have, in the previous section, largely concentrated on the development of chemical education in the United States and, to a lesser degree, in both Germany and Great Britain. Adopting a larger frame of reference, however, shows that there were really two major centers of chemical influence throughout the 18th and 19th centuries: one centered in Germany and the other in France. The development of viable chemical communities in other countries initially drew on these two sources, and they, in turn, left a lasting imprint on chemical education in the countries in question that continued to persist long after these countries had succeeded in developing their own independent chemical communities.



The spheres of influence centered on Germany and France were roughly based on language – with countries speaking Romance languages, such as Spain, Portugal and Italy, tending to gravitate more toward the French influence, and countries speaking Germanic languages, such as Holland, Austria, Scandinavia, Britain and the United States, tending to gravitate more toward Germany. On the other hand, countries and regions falling along this linguistic divide, such as Belgium, Switzerland, Alsace and Lorraine, tended to be equally divided between the two centers, the same also being true, to a lesser degree, of Russia and the Balkans.

8.4 Other Professional Trends

The 19th century sees several other important additional trends in professionalization:

a. The appearance of professional national chemical societies.

b. The appearance of specialized subdisciplines within chemistry.

With the exception of analytical chemistry, the second of these trends does not express itself in the founding of separate professional organizations until the 20th century, but is reflected in both the 19th-century journal literature and in the textbook and monograph literature.

8.5 National Chemical Societies

Most of the scientific societies organized in the 17th and 18th centuries were honorary, i.e., membership was restricted by a nomination and election process. The 19th century sees the founding of a new type of scientific society based on voluntary membership with paid dues and designed to serve the needs of the increasing numbers of professional scientists and technologists involved in educational, industrial and government work. Examples include both the *British Association for the Advancement of Science* (1831) and the *American Association for the Advancement of Science* (1847).

More germane to our purpose, however, is appearance of professional, national chemical societies, based on an open membership policy – an event coupled with the rise of the German-trained professional chemist in the 1850s (Table 8.3).

Table 8.3 Some Early Professional Chemical Societies

Date	*Country*	*Organization*
1841	England	The Chemical Society of London
1857	France	Société chimique de France
1867	Germany	Deutschen Chemischen Gesellschaft
1868	Russia	Russian Physical Chemical Society
1876	United States	American Chemical Society

8.6 Chemical Journals

The trend, begun in the late 18th century, of private commercial journals devoted to chemistry also continued to grow throughout the 19th century (Table 8.4). Added to this, however, was an increasing number of journals published by the newly founded professional chemical societies, beginning with the appearance of the *Memoirs of the Chemical Society of London*in 1841 (Table 8.5).

Table 8.4 Example 19th-Century Commercial Chemical Journals

Date	*Editor*	*Journal*
1832	Liebig	*Annalen der Chemie und Pharmacie*
1834	Erdmann	*Journal für praktische Chemie*
1843	Frances	*The Chemical Gazette*
1857	Kekulé	*Zeitschrift für Chemie*
1860	Crookes	*The Chemical News*
1870	Chandler	*The American Chemist*
1879	Remsen	*American Chemical Journal*

Table 8.5 Early Chemical Journals Published by Chemical Societies

Date	*Journal*
1841	*Memoirs of the Chemical Society of London*
1858	*Bulletin de la société chimique de France*
1868	*Berichte der Deutschen Chemischen Gesellschaft*
1869	*Journal of the Russian Physical Chemical Society*
1879	*Journal of the American Chemical Society*

8.7 The Emergence of Analytical Chemistry

The first branch of chemistry to undergo specialization was analytical chemistry. As already noted, the first specialized monographs dealing with analytical chemistry, if one discounts 16th-century works on metallurgical assaying, began to appear in the late 18th century, starting with the writings of the Swedish chemist, Torbern Bergman, and rapidly increase in number in the early 19th century, as shown in Table 8.6.

Table 8.6 Some Early 19th-Century Monographs on Analytical Chemistry

Date	*Author*	*Title*
1801	Lampadius	*Handbuch zur chemischen Analyse der Mineralkörper*
1805	Kopp	*Grundriss der chemischen Analyse mineralischer Körper*
1810	Fabricius	*Anleitung zur chemischen Analyse unorganischer Naturkörper*
1821	Pfaff	*Handbuch der analytischen Chemie*
1828	Rose	*Handbuch der analytischen Chemie*

The most important of these textbooks were those written by the German chemist, Carl Remigius Fresenius (1818-1897), while serving as an instructor in Liebig's laboratory at Giessen (1841-1845). His textbook on qualitative analysis, first published in 1841, was used until the 1960s and his textbook on quantitative analysis, first published in 1846, was in continual use until the 1930s. After his move to Wiesbaden in 1845, Fresenius took the next logical step by founding the *Zeitschrift für analytischen Chemie* in 1862. This was followed by the British journal, *The Analyst*, in 1876; the *Repertorium der analytischen Chemie* in 1881; the American *Journal of Analytical Chemistry* in 1887, and the *Annales de chimie analytique* in 1896.

This early start towards specialization meant that analytical chemistry was one of the few subdisciplines of chemistry to have its own specialized professional societies in the late 19th century, though other branches would follow suit in the 20th century. Examples include *The British Society for Analytical Chemistry*, founded in 1874; and the *American Association of Official Analytical Chemists*, founded in 1884.

8.8 The Emergence of Biochemistry

Biochemistry as a speciality has an exceedingly complex prehistory and includes contributions from many applied areas of chemistry which had specialized in terms of textbooks, journals, and even academic appointments early in the 19th century. Included are medical chemistry, agricultural chemistry, animal chemistry, physiological chemistry, pathological chemistry, forensic chemistry, and the chemistry of brewing and fermentation.

The first to differentiate was agricultural chemistry. Humphry Davy's book, *Elements of Agricultural Chemistry*, first appeared in 1813 and in the 1820s the German, Carl Sprengel (1785-1859), held chairs in agricultural chemistry at Göttingen and Brunswick. Speciality journals, often supported by government agencies, appeared about the same time and were common throughout the 19th century until much of the discipline finally merged into biochemistry between 1900-1920. An early example is the *Archiv der Agriculturchemie für denkende Landwirthe*, which was published from 1803-1818.

The traditional courses in medical chemistry began to be transformed into courses in physiological and pathological chemistry in the 1840s (see Table 8.7) and attempts were made to found several chairs of physiological chemistry in German universities during this period, the first being the appointment of Julius Schlossburger to such a chair at Tübingen in 1845. An example of an early journal in this area is the *Beiträge zur physiologische Chemie und pathologische Chemie*, which began publication in 1843. Conflicts between the Professors of Physiology, on the one hand, and the organic chemists, on the other, led to a decline in the next decade.

Table 8.7 Early 19th-Century Monographs on Physiological Chemistry

Date	*Author*	*Title*
1826	Hündefeld	*Physiologische Chemie des menchlichen Organismus*
1843	Thomson	*Chemistry of Animal Bodies*
1844	Marchand	*Lehrbuch der physiologischen Chemie*
1844	Kohlrauch	*Physiologie und Chemie*
1849	Lehmann	*Lehrbuch der physiologischen Chemie*
1856	Mialhe	*Chimie appliquée à la physiologie et la thérapeutique*

The person generally credited with merging all of these areas into the more general field of biochemistry is the German chemist, Felix Hoppe-Seyler (1825-1896), who was appointed to the chair of physiological chemistry at Tübingen in 1864. In 1871 the*Jahresberichte über die Fortschritte der Tierchemie* appeared and in 1877 Hoppe-Seyler founded the *Zeitschrift für physiologische Chemie*. Between 1877 and 1881 his famous textbook,*Physiologische Chemie*, was also published.

8.9 The Emergence of Organic Chemistry

Organic chemistry also began to split off from medical chemistry in the 1840s, and by the second half of the 19th century the use of the word chemist, without a qualifier in front, was generally synonymous with organic chemist. The first specialized textbooks began to appear during the same decade (See Table 8.8).

Table 8.8 Early Specialist Monographs on Organic Chemistry

Date	*Author*	*Title*
1839	Löwig	*Chemie der organischen Verbindungen*
1840	Liebig	*Die organische Chemie in ihrer Anwendung auf Agrikultur und Physiologie*
1844	Gerhardt	*Précis de chimie organique*
1854	Kolbe	*Ausführliches Lehrbuch der organischen Chemie*
1855	Limpricht	*Grundriss der organischen Chemie*

After the second chemical revolution of 1855-1875, (see Section 10.7) organic research took off exponentially. Jones' survey of the nearly 800 Ph.D. theses done by American and British students in Germany between 1840-1914 shows that over 90% were in the field of organic chemistry. The standard journals, such as the *Berichte*, the *Annalen*, *The American Chemical Journal*, *The Journal of the Chemical Society* etc., were almost completely dominated by organic papers in the second half of the century. Speciality journals and divisions weren't required until the 20th century. Special faculty positions in organic chemistry also began to appear in larger American universities by the 1880s and 1890s.

8.10 The Emergence of Physical Chemistry

Though earlier textbooks on "theoretical chemistry" date back to the 1860s, the first "self-conscious" textbook on physical chemistry is generally considered to be Wilhelm Ostwald's (1853-1932) massive, multivolume *Lehrbuch der allgemeinen Chemie*, published in installments between 1885 and 1887. Derivative British, American and French texts were also appearing by the end of the century (see Table 8.9). In 1887 Ostwald started the *Zeitschrift für physikalische Chemie*, and in 1896 his American student, Wilder Bancroft, began the *Journal for Physical Chemistry*.

Jones' survey shows that about 30 of the 800 American and British students who took Ph.D. degrees in Germany specialized in physical chemistry, all of them between 1892 and 1911 and mostly under the tutelage of either Ostwald or Walther Nernst. Cincinnati got it's first Professor of Physical Chemistry, Azariah Lincoln, in 1900. Lincoln was a student of Louis Kahlenberg at the University of Wisconsin, and Kahlenberg, in turn, had studied at Leipzig under Ostwald.

Table 8.9 Examples of Early Textbooks on Physical Chemistry

Date	*Author*	*Title*
1889	Ostwald	*Grundriss der allgemeinen Chemie*
1893	Nernst	*Theoretische Chemie*
1898	Morgan	*The Elements of Physical Chemistry*
1899	Walker	*Introduction to Physical Chemistry*
1902	Jones	*The Elements of Physical Chemistry*
1903	Perrin	*Traité de chimie physique, les principes*
1903	Reychler	*Les théories physio-chimique*

8.11 The Residue of Inorganic Chemistry

This speciality was late in differentiating itself from mainstream chemistry and its domination by organic chemistry. Though textbooks with inorganic in the title began to appear as soon as organic chemistry became specialized, they were really general or introductory textbooks rather than speciality texts.

Table 8.10 Early Specialist Monographs on Inorganic Chemistry

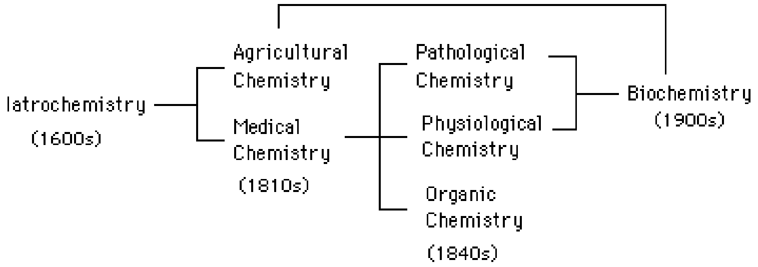
Date	*Author*	*Title*
1892	Dammer	*Handbuch der anorganische Chemie*
1904	Moissan	*Traité de chimie minéral*
1905	Werner	*Neure Anschauungen auf dem Gebiete der anorganische Chemie*
1911	Weinland	*Einfuhrung in die Chemie der Komplex-Verbindungen*

The first explicit journal, the *Zeitschrift für anorganische Chemie*, was not founded until 1892 and expanded rapidly under the stimulus of Alfred Werner's work on coordination chemistry, which finally gave inorganic chemistry an independent theoretical identity. Some early examples of speciality monographs are shown above in Table 8.10.

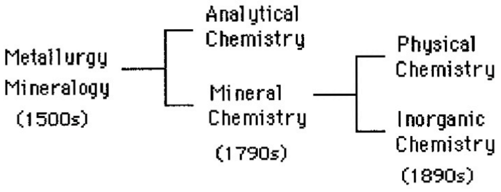
Specialities that failed to find a home in the traditional chemistry department include chemical engineering and geochemistry.

8.12 The Broader Picture

In many ways the subdisciplines of organic chemistry and biochemistry can be traced to the various splittings and fusions of the subject of iatrochemistry, first introduced into the medical schools in the 17th century:



Likewise, the origins of analytical, physical, and inorganic chemistry can be traced to the mining and mineralogical aspects of early 16th-century chemical technology and its eventual incorporation into the curriculums of early mining academies and technical schools in the late 18th century:



8.13 Yearbooks, Abstracts and Handbooks

In addition to the already established media of research journals, textbooks, monographs, and dictionaries, the 19th century sees the introduction of several new genres in the form of yearbooks, abstract journals, and handbooks or literature guides – all of them indicative of the rapid growth of chemical research and its progressive specialization.

The first to appear were annual summaries or yearbooks of chemical research, beginning with Berzelius' famous*Jahres-Bericht* of 1821-1849. As shown in Table 8.11, by the second half of the 19th century, yearbooks devoted to various special branches of chemistry, such as technology, electrochemistry, organic chemistry, etc. were also becoming common.

Table 8.11 Selected Examples of 19th-Century Chemical Yearbooks

Date	*Publication*
1821	*Jahres-Bericht der physischen Wissenschaften*
1848	*Jahresbericht für Chemie*
1855	*Jahresbericht der chemischen Technologie*
1871	*Jahresberichte uber die Fortschritte der Tierchemie*
1874	*Jahresbericht der reinen Chemie*
1892	*Jahrbuch der Chemie*
1893	*Jahrbuch der organischen Chemie*
1894	*Jahrbuch für Elektrochemie*

Though the yearbook format remained popular throughout the 19th and early 20th century, it was selective rather than comprehensive in its coverage of the literature and was soon supplemented by more detailed abstract journals. Many of the national chemical societies initially attempted to append some type of monthly summary of the chemical research appearing in other journals to their own publication, but soon found the task overwhelming. The first chemical publication devoted solely to abstracting and indexing the rapidly expanding chemical literature was the *Chemische Central-*

Blatt, which began publication in 1830 as the *Pharmaceutisches Zentralblatt*. This was eventually superseded by the American publication, *Chemical Abstracts*, which first appeared in 1907.

The earliest specialized handbook devoted to summarizing and indexing the chemical literature was Gmelin's *Handbuch der theoretischen Chemie*, which first appeared as a three-volume set in 1817. By the 1848-1872 edition, it had expanded to 18 volumes. The current edition, now retitled *Handbuch der anorganischen Chemie*, occupies over 14 shelves in the chemistry library. The organic chemist's equivalent of Gmelin, Beilstein's *Handbuch der organischen Chemie*, began publication in 1881-1883 as a three-volume set. The current edition now occupies 36 shelves in the chemistry library. The physical chemist's equivalent of Gmelin, Landolt-Börnstein's *Physikalisch-Chemischen Tabellen*, also began publication in 1883. The current edition now occupies 11 shelves in the chemistry library. Present trends suggest that these abstract journals and handbooks will probably disappear as paper-based publications in the near future and will be replaced instead by computerized on-line indices and search services.

8.14 Selected References

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Lecture IX

The Nineteenth Century

(1801-1900)

The Standardization of Laboratory Practice

> You pampered votaries of chemistry, harken back to the time when a
> combustion required the artful building and
> preserving of a charcoal fire.
> *A. J. Berry 1954*

9.1 Laboratory Training Manuals

With the explicit professionalization of chemistry in the 19thcentury, we see the earlier abbreviated textbook accounts of equipment and techniques replaced by detailed specialist monographs dealing solely with chemical apparatus and techniques or "manipulation" – accounts that were explicitly designed to serve the needs of not only students, but of practical chemists, technologists, and teachers as well (Table 9.1).

Table 9.1 Example Monographs Dealing with Laboratory Practice

Date	*Author*	*Title*
1827	Faraday	*Chemical Manipulation*
1831	Berzelius	*Chemische Operationen und Gerätschaften*
1849	Morfit	*Chemical and Pharmaceutic Manipulation*
1857	Williams	*Handbook of Chemical Manipulation*
1882	Rivière & Rivière	*Traité de manipulations de chimie*
1883	Wisser	*Chemical Manipulation*
1885	de Walque	*Manuel de manipulations chimique ou de chimie opératoire*

9.2 Energy Sources (Thermal)

The first half of the 19th century saw increased use of spirit or alcohol lamps, either in the simple wick form, in the form of adapted hollow-wick Argand lamps with metal shades, or in the form of alcohol blast lamps in which either alcohol or alcohol-kerosene mixtures were ejected under pressure from a nozzle rather than rising through a wick.

With the advent of coal-gas lighting in the larger cities of Europe and the United States in the 1820s, one sees the gradual appearance of laboratory gas burners as well. One such burner was described by Faraday as early as 1827 in his monograph *Chemical Manipulation*. The forms most commonly used in the period 1830-1855 were known as "gauze burners" because, before being lit, the gas and air were mixed in a metal cylinder having a metal screen or gauze top, in order to prevent, in keeping with the principles of the Davy safety lamp, the dangers of a flashback. Unfortunately, the resulting flame was cool and relatively diffuse. In addition, it tended to suffer from flickering and coloration due to low gas pressures and contaminants on the metal screen.

These problems were solved with the introduction of the Bunsen burner in 1855. Here the premixed air and gas are passed up a long narrow tube or barrel under positive pressure before being lit. If the length and diameter of the tube are properly chosen, the flame will not propagate down the barrel and the necessity of a wire safety screen is eliminated. The result is a hotter, more concentrated, colorless, soot-free flame. By 1870 laboratory gas burners had largely displaced the traditional charcoal furnaces that had dominated chemical laboratory practice for most of its recorded history, though introductory textbooks continued to occasionally use outdated woodcuts showing charcoal furnaces well into the first decade of the 20th century.

The pursuit of ever higher temperatures also resulted in numerous refinements of Bochard de Saron's original oxyhydrogen torch (Hare 1802, Newman 1816, Gurney 1823, Deville & Debray 1859) and in Henri Moissan's carbon arc electric resistance oven (1892), as described in his 1897 monograph, *Le four électrique*.

Significant improvements in the measurement of temperature occurred during the 19th century, including the development of the bolometer for the measurement of radiant heat (Langley 1881), the Beckmann thermometer (1888) for measuring small temperature changes, the Pt-Rh thermocouple (Seebeck 1826, Le Chatelier 1886), the Pt resistance thermometer (Siemens 1871, Callendar 1886), and the optical pyrometer (Le Chatelier 1892) for measuring high temperatures.

19th-century improvements in the design of calorimeters for the measurement of heats of transition and reaction included the mercury calorimeter (Favre & Silbermann 1844), Bunsen's redesign of the Lavoisier-Laplace ice calorimeter (1870), the introduction of the bomb calorimeter by the Irish chemist, Thomas Andrews (1848), and its later perfection by the French team of Marcellin Berthelot and Paul Vielle (1885). The enthalpy data collected by means of these instruments by such 19th-century thermochemists as Hess, Favre and Silberman, Andrews, Thomsen, and Berthelot would provide much of the foundation for the quantification of chemical thermodynamics in the opening decades of the 20th century.

A new technique for the study of the thermal behavior of matter, known as thermal analysis, also made an appearance. Based on the systematic measurement of heating and cooling curves – a practice first introduced by the French metallurgist, Floris Osmond, in 1887 – it would play, in combination with the thermocouple, the resistance thermometer, the optical pyrometer, and the technique of differential thermal analysis first introduced by Roberts-Austin in 1899, a key role in unraveling the high-temperature chemical and phase changes involved in metallurgy, geochemistry, and in the manufacture of glasses and ceramics.

The microscope also found use in this field via its application to the study of polymorphism and phase transitions by the German physicist, Moritz Frankenheim, in the 1830s. These studies were refined in the 1870s by the German physicist, Otto Lehmann, who added both a heated stage and cross polarizers to the instrument in connection with his studies of the phase behavior of liquid crystals, and were perfected in the 1950s by Kofler in Austria (Kofler & Kofler 1954) and by McCrone in the United States (McCrone1957).

The data generated by these techniques were given both a graphical representation and a theoretical interpretation, in terms of the Gibbs phase rule, by the Dutch chemist, Hendrik Bakhuis Roozeboom, beginning about 1887. The resulting “phase diagrams” proved to be a highly effective method of visually summarizing a given system’s phase structure as a function of its temperature, pressure, and chemical composition, as later illustrated in great detail in Roozeboom's massive three-volume magnum opus, *Die heterogenen Gleichgewichte von Standpunkte der Phasenlehre*, published between 1901 and 1913.

9.3 Energy Sources (Electrical)

The electrochemical limitations of electrostatic energy sources were already noted in Section 5.3, as was the discovery of the voltaic pile in 1800, which finally provided chemists with a reliable, long-lived, source of relatively constant direct current (DC) at moderate potentials, in sharp contrast to the short-lived, high-potential, low-current, alternating (AC) sources produced by 18th-century electrostatic machines and Leyden jars. The original voltaic pile (Zn/NaCl/Ag) was gradually replaced by better and more convenient electrochemical cells as the century progressed (see Table 9.2 at top of next page). These cells remained the most common sources of direct current for laboratory work (save for the Clark and Weston cells, which were used primarily as voltage standards) until their displacement by DC generators near the end of the century, though a wide variety of other chemical cells were also developed for industrial and telegraphic use, including the Planté lead storage battery in 1859 and the Leclanché cell ($C/MnO_2/(NH_4)Cl/Zn$) in 1868.

The first commercial DC and AC generators began to appear in the 1850s, their most important manufacturer being the German firm of Siemens and Halske. However, until the appearance of widespread urban electrification the 1880s, the use of these sources in laboratory work also required the installation of private power sources.

Table 9.2 Important 19th-Century Electrochemical Cells

Date	*Composition*	*Name*
1800	$Zn/(NH_4)Cl/Cu$	Cruickshank trough battery
1836	$Zn/Zn(SO_4)/Cu(SO_4)/Cu$	Daniell gravity cell
1839	$Zn/Zn(SO_4)/H(NO_3)/Pt$	Grove nitric acid cell
1841	$Zn/Zn(SO_4)/H(NO_3)/C$	Bunsen carbon cell
1842	$Zn/Zn(SO_4)/H_2(Cr_2O_7)/C$	Warington dichromate cell
1872	$Zn/Zn(SO_4)/Hg_2(SO_4)/Hg$	Clark cell
1892	$Cd/Cd(SO_4)/Hg_2(SO_4)/Hg$	Weston cell

Various instruments were also introduced for measuring the electrical parameters of charge (the voltameter: Faraday 1834), resistance (the bridge: Christie 1833, Wheatstone 1843), current (the galvanometer: Schweigger 1820, the ammeter: Ayrton & Perry 1881), and potential (the capillary electrometer: Lippmann 1873, the voltmeter: Ayrton & Perry 1881-1884).

Such electrical apparatus would play a role not only in the development of practical analytical techniques, such as electrogravimetric analysis (see Section 9.7), but also in the development of important conceptual advances, such as Faraday's laws of electrolysis, the ionic theory of dissociation, and the Nernst equation – events which would help lay the foundations of the electrical theory of the chemical bond in the next century.

Other important electrical instruments included the induction coil for the conversion of low-voltage, direct currents into high-voltage, alternating currents (Callan 1836, Ruhmkörff 1858). This device would play an important role in exciting gas discharge tubes (Plücker 1859) – a development that would, in turn, facilitate the spectroscopic study of gases and eventually lead to the discovery of the electron and the Bohr atom in the next century.

An important electrochemical procedure, predicated on the discovery and application of these instruments, was the experimental measurement of ionic conductivities, first initiated by the German physicist, Wilhelm Hittorf, in the 1850s and perfected by the German physicist, Friederich Kohlrausch, in 1880. This technique would play a significant role in the establishment of both Arrhenius' theory of ionic dissociation in 1884 and Werner's theory of inorganic coordination compounds in 1893.

9.4 Energy Sources (Electromagnetic)

As early as 1666 Newton had resolved the visible region of the electromagnetic spectrum into its component colors using a glass prism. However, it was not until the 19th century that the spectrum was extended beyond the visible with the discovery of infrared (IR) radiation by William Herschel in 1800 and ultraviolet (UV) radiation by Johann Ritter in 1801. A further extension came near the end of the century with the discovery of radiowaves by Heinrich Hertz in 1888 and X-rays by Wilhelm Roentgen in 1895. In 1802 Thomas Young published the first of his papers dealing with the wave theory of light in which he made use of a diffraction grating to assign wavelengths to the various regions of the spectrum – work that was extended and refined by many others throughout the century, but most notably by Ångström in Sweden (1868) and by Rowland in the United States (1893).

Paralleling 18th-century developments in the experimentalstudy of heat and 19th-century developments in the study of current electricity, 19th-century physicists and photochemists also developed a number of devices designed to measure both the intensity and the quantity of light. Visual photometers (e.g., the grease-spot photometer: Bunsen 1843) for measuring relative light intensities depend on the sensitivity of the human eye and made use of a split optical field that allows for the simultaneous viewing of both a reference source and the source being measured. The reference beam was then attenuated, using slits, wedges, diaphragms, rotating sectors, or changes in path length, until the two beams appeared to be of equal intensity to the human eye. In contrast, devices for measuring the quantity of light (equal to the intensity x time of exposure x area of exposure), such as the tithonometer (Draper 1843) and the actinometer (Bunsen & Roscoe 1857) were based on measuring the quantity of product formed in a standardized photochemical reaction.

Without a doubt, however, the single most important practical advance in this area during the 19th-century was the discovery of photography (Niepce 1822, Daguerre 1837, Talbot 1839) and its subsequent evolution and refinement throughout the century. Though its initial development was dominated by its everyday commercial and artistic applications, its potential as a scientific method of accurately recording and measuring light intensities and quantities was fully appreciated by the second half of the century.

Early 19th-century photographic emulsions were particularly sensitive to the blue and UV regions of the spectrum. However, in 1873 Vogel discovered that organic dyes could be used to sensitize emulsions to longer wavelengths and in 1880 William Abney succeeded in photographing spectra in the near IR region. Thus, unlike visual photometers, photography allowed one to study and quantify both the visible and nonvisible regions of the spectrum, though detection via heating effects using either bolometers, radiometers or thermocouples would remain the method of choice in the IR region until the development of IR-sensitive photocells later in the 20th century.

9.5 General Apparatus

The increased use of Argand and spirit lamps in the first half of the century, and the spread of laboratory gas burners in the second half, also affected the way in which other kinds of apparatus were used. A crucible, retort or flask heated in a charcoal furnace received its mechanical support from the furnace and the surrounding fuel. Though wooden stands, support tables, and clamps slowly came into use during the latter part of the 18th century and dominated laboratory practice during the first half of the 19th century, they were of necessity restricted to use with apparatus that was not directly exposed to the widely dispersed heat of the furnaces. In contrast, use of small portable spirit lamps and burners required metal stands, rings, and clamps to support the object being heated, and the same was true of the newer laboratory gas burners. As these heat sources gradually replaced the charcoal furnace, starting in the 1790s, this metal laboratory hardware began to gradually replace the earlier wooden versions and became dominant by the end of the 19th century.

The same is true of corks. Their inability to survive the heat of the charcoal furnace resulted in the continued practice of luting. Portable spirit lamps and gas burners, however, provided far more localized and concentrated sources of heat and thus extended the range of cork usage. Liebig, in particular, was a strong advocate of the use of unluted corks in laboratory practice as it allowed for the quick and inexpensive modular assembly of complicated apparatus from simpler interchangeable parts. He made heavy use of corks in much of his equipment design, including his apparatus for organic combustion analysis (1830) and his modification of the Weigel-Göttling counter-current condenser (1843). He praised Mohr's invention of the cork-borer (1837) and eulogized cork as one of the essential materials of the laboratory in his popular book, *Familiar Letters on Chemistry*.

Laboratory glassware also saw some important improvements during the century. Glassware subject to heating, such as retorts, flasks and beakers, should be high melting, colorless, resistant to chemical attack by water, acids, and alkalis, and be able to survive a range of thermal and mechanical stresses. Prior to the 19th century, laboratory glassware did poorly in all of these categories. It was often colored brown or green due to iron contamination, would soften in the fire, and was subject to extensive corrosion by water and alkalis, as witnessed by Lavoisier's famous experiment refuting the supposed transmutation of water into earth as a result of its prolonged refluxing in a glass pelican.

Despite the practice of coating the outside of the vessel with a mixture of clay and binder, few glass vessels survived heating in a furnace more than once, due to cracking produced by the mechanical strains induced by the uneven cooling and heating rates of the relatively thick glass walls. By the 19th century, it was understood that this latter problem was the result of the differential expansion or contraction of the outer and inner portions of the glass and that it could be minimized by making the glass as thin as possible consistent with mechanical stability. As a result, one sees the introduction in this century of thin-walled laboratory glassware made of relatively hard Bohemian glass (also called potash or lime glass because of its high K_2O and CaO content).

By the end of the century yet other important innovations in general laboratory practice had also made an appearance, including automated stirrers and shakers, gasometers, constant-temperature water baths, and vulcanized rubber tubing, stoppers, and balloons (thus replacing animal bladders).

9.6 Separation Techniques

Solid-liquid extraction or "lixiviation" is as old as recorded history and was applied to such everyday tasks as the preparation of perfumes, herbal extracts, and teas. Indeed, in the 1950s Levey published archaeological evidence of a crude Mesopotamian hot-water extraction apparatus dating from approximately 3500 BC. Within the context of laboratory practice, use of this technique centered primarily on pharmacists and chemists interested in plant and animal substances and employed a tall cylindrical or cone-shaped funnel known as a percolator or displacer. This was packed with the plant or animal matter of interest and solvent added at the top. After percolating through the organic matter, the solvent was collected at the bottom of the funnel and evaporated to isolate the extract. In the first half of the 19th-century, this process was made more efficient by various proposals for automatically evaporating the solvent from the extracted product and recirculating it back to the top of the extraction funnel for reuse (Payen 1834). By the last quarter of the century, this trend had resulted in the development of the well-known Soxhlet extractor (1879), which soon found widespread use in the fields of plant, agricultural, and food chemistry.

Liquid-liquid extraction via use of a simple separatory funnel does not seem to have been widely practiced before the 19th century, due in large part to the absence of a wide selection of water-immiscible organic solvents other than olive oil. No mention of the process or the funnel is found in either Lavoisier's 1789 account of chemical operations or in the 1827 volume by Faraday. A primitive separatory funnel, sans stopcock, was described by Berzelius in 1831, and our current version appears in a footnote to Morfit's book of 1849. By the end of the century the technique was widely used, not only among pharmacologists and biochemists, but among synthetic organic chemists as well. Indeed, in 1884 H. Schwarz proposed the first of a long-line of self-sustaining, automated liquid-liquid extractors similar in function to the Soxhlet apparatus for solid-liquid extraction mentioned above.

Renaissance distillers were aware that the more volatile a material the further it would travel in a distillation train before being condensed, and consequently they would often tap the train atvarious distances from the distillation pot in order to collect fractions of varying volatility. One such fractionation setup is shown in the 15th-century illustration to Thomas Norton's *Ordinall of Alchemy*, mentioned in earlier lectures, and a number of imaginative variations appear in the 16th- and 17th-century distillation literature. Further appreciation that this same variation occurred in time, as well as space, and that the more volatile fractions appeared first and the least volatile last, gave rise to the use of laboratory "fraction collectors" by the end of the 19th century, many of which were designed to be used in connection with vacuum distillation (Brühl 1888, Raikow 1888).

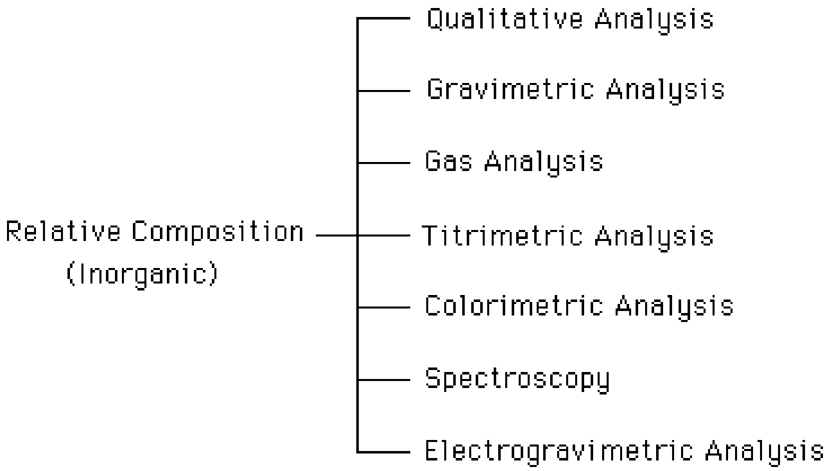
However, this collection of "fractions" of varying volatility should not be confused with the use of so-called vertical "fractionation columns" designed to enhance the degree of separation between components when distilling mixtures. This relies on extending both the time and area of contact between the liquid and gas phases using a counter-current system involving the rising vapor, on the one hand, and the descending liquid condensate, on the other, and was designed to replace the practice of repeatedly redistilling the distillate in order to concentrate a given component.

As with Lebon's vacuum distillation method, vertical fractionation columns were first developed in an industrial context and only later scaled down for laboratory use. First patented in 1818 by the French engineer, J. B. Cellier Blumenthal, these industrial distillation columns or "towers" were progressively refined throughout the century, largely by engineers concerned with the rectification of alcohol. Often referred to simply as distillation columns or continuous distillation stills, these towers were filled with a series of horizontal "bubble-cap" plates which allowed for the repeated condensation and re-distillation of increasingly volatile liquid fractions as one moved further and further up the column. By the 1870s, organic chemists were using a variety of laboratory-scale fractionation columns, the most efficient of which was the packed glass-bead column introduced by the German chemist, Walther Hempel, in 1881.

Relative to the traditional separation of solids and liquids, 19th-century innovations of note include the introduction of the chemical centrifuge by Lambert von Babo in 1852, and the technique of vacuum filtration by Jules Piccard in 1865 (using a Geissler water aspirator).

9.7 Characterization Techniques (Inorganic Composition)

Methods for determining the relative elemental composition of inorganic species multiplied rapidly throughout the century:



Their application would lead to the discovery and isolation of at least 50 new elements in the period 1800-1900, to the development of self-consistent atomic weight values, and to the establishment of reliable compositional molecular formulas.

As noted in Lecture IV, the basic assumptions of inorganic qualitative and quantitative gravimetric analysis were already understood by the end of the 18th century. What the 19th century sees, however, is their codification and standardization. This was done by Berzelius in 1820 in the case of blowpipe analysis with the publication of his monograph, *Afhandling om Blåsrörets Anwändande i Kemien och Mineralologien*; by Fresenius in 1841 and 1846 for wet qualitative analysis and gravimetric quantitative analysis, respectively, with his popular textbooks *Anleitung der qualitativen chemischen Analyse* and *Anleitung der quantitativen Analyse*; and by the German chemist, Robert Bunsen, in 1857 for eudiometry or gas analysis with the publication of his monograph *Gasometrische Methoden*. Yet further significant refinements of gas analysis techniques were made by Walther Hempel in 1880 with the publication of his monograph, *Neue Methoden zur Analyse der Gase*.

Laboratory apparatus introduced in connection with these developments included test tubes (c. 1802), the Kipp (1862) and Babo gas generators, special flasks and filters (Gooch 1880, Hirsch 1888, Büchner 1888) for vacuum filtration, desiccators and drying ovens, gas burettes and pipettes, as well as significant advances in the design of high-sensitivity analytical balances (the short-beam balance: Bunge 1867).

The 19th century also saw the first serious application of the microscope to chemistry, initially in the field of qualitative analysis. Anticipated by the work of the German chemist, Tobias Lowitz, in the period 1794-1804, interest in the analytical applications of microchemical reactions was revived by the work of the Czech chemist, Emanuel Boricky, in 1877 and finally codified by the Dutch chemist, Theodor Behrens, in 1895 with the publication of his monograph *Anleitung zur mikrochemischen Analyse*. This form of analysis would prove particularly useful in the fields of toxicology and forensic chemistry.

Building on its 18th-century origins, important advances in the technique of volumetric or titrimetric analysis continued to be made, most notably by the French chemist, Joseph-Louis Gay-Lussac, in the period 1824-1835. However, as with many of the other methods of analysis discussed above, it was a German – Friedrich Mohr – who first summarized and codified the technique in his 1855 monograph, *Lehrbuch der chemisch-analytischen Titrimethode*, though a less thorough and generally forgotten survey had been published by Karl Schwarz in 1850. Laboratory apparatus introduced in connection with this technique included liquid burettes of various kinds (Gay-Lussac 1824, Binks, Henry 1846, Mohr 1853), liquid pipettes, pinch clamps (1853), and volumetric flasks.

Even before the formal law governing the relationship between the absorption of light and solution concentration (Beer 1852, Bernard, 1852) was in place, chemists had begun to empirically explore the relationship between the intensity of a colored complex and its solution concentration as a possible method of analysis (Heine 1845, Jacquelain 1846). The introduction of the split-field comparative colorimeter by Dehm in 1864, and especially the versions produced by Duboscq in 1870 and Wolff in 1880, greatly facilitated the use of this method by eliminating the necessity of either interpolating among multiple standards (as was the case with Nessler tubes) or using progressive dilution.

Simple solution colorimetry is based on the absorption of white light by the solute and solvent in question and can only be applied with certainty to solutions containing a single solute species. Its successful extension to more complex mixtures requires use ofboth a spectroscope to select an absorption wavelength characteristic of the species of interest, and the use of either slits or polarizers to attenuate the reference beam. Known as solution spectrophotometry, this elaboration of simple colorimetry is usually attributed to the German, Carl Vierordt, as described in his 1873 monograph, *Die Anwendung des Spektralapparates zur Photometrie der Absorptionsspektren und zur quantitativen Analyse*. In 1891 both techniques were systematized by the German father and son team of Gerhard and Hugo Krüss in their monograph, *Kolorimetrie und Quantitative Spektralanalyse in ihrer Anwendung in der Chemie*, and would find their greatest application in the fields of water analysis and clinical chemistry.

The ability of certain substances to give characteristic colors when introduced into a nonluminous flame, though noted by Boyle and other early writers, was first systematically applied in chemical analysis by Marggraf in 1762, and the use of such “flame tests” soon became a standard procedure in blowpipe analysis. Though partially anticipated by the work of the British photographer, William Talbot, in 1825, it was apparently the American physician, David Alter, who first used a spectroscope in 1854 to analyze these colored flames in detail, and who first realized the potential importance of this technique in qualitative analysis. Similar results were obtained independently by the German team of Robert Bunsen and Gustav Kirchhoff in 1860, who also used the technique to discover several new elements (rubidium and cesium). Further applications of flame emission spectroscopy would eventually lead to the discovery of at least four more elements (thallium, indium, gallium, and helium) by the end of the century, and would aid in the isolation of many others (argon, neon, krypton, xenon, and many of the rare earths). Attempts (Janssen 1870, Champion *et al* 1873) were also made to quantify the technique, but with limited success, and its most significant applications during the 19th century remained in the field of qualitative analysis.

Though partially anticipated by the German industrial chemist, Carl Luckow, it is the American chemist, Wolcott Gibbs, who is generally given credit for having originated the technique of electrogravimetric analysis in 1864. Rather than isolating and weighing a metal prepared via thermal reduction, as in conventional assaying, Gibbs used the electrochemical reduction of its aqueous salt solutions instead. The technique was first summarized and codified in 1882 by the German chemist, Alexander Classen, in his monograph, *Quantitative Analyse auf electrolytischen Weg*.

9.8 Characterization Techniques (Organic Composition)

The basic tenets of organic combustion analysis were introduced by Lavoisier in the 1780s. Essentially the organic material is oxidized to carbon dioxide and water. The former is absorbed using a solution of potassium hydroxide and the latter using anhydrous calcium dichloride. From the difference in the masses of the absorbents before and after combustion, one can determine the masses of carbon dioxide and water formed and, from a knowledge of the gravimetric composition of these two compounds, one can calculate the weight of carbon and hydrogen present in the original organic sample:

$$mass\ C = 0.273\ (mass\ of\ CO_2\ \text{formed}) \qquad [1]$$

$$mass\ H = 0.112\ (mass\ of\ H_2O\ \text{formed}) \qquad [2]$$

The total mass of any oxygen and nitrogen present in the sample is assumed to be equal to the difference between the mass of the original sample and that of the carbon and hydrogen present:

$$mass\ (O\ \&\ N) = mass\ sample - mass\ (C\ \&\ H) \qquad [3]$$

Though simple in principle, the translation of these assumptions into a reliable routine laboratory procedure required many refinements (Gay-Lussac & Thenard 1810, Berzelius 1813, Döbereiner 1816, Prout 1820, 1827) until it reached its standard form with the publication in 1837 of the monograph, *Anleitung zur Analyse der organischer Körper*, by the German chemist, Justus Liebig, based on improvements he had made in the technique earlier in the decade. Additional methods for the separate determination of organic nitrogen (Dumas 1831, Kjeldahl 1883), and for the determination of sulfur (Carius 1860) and the halogens (Piria 1857, Carius 1860) soon followed. Laboratory apparatus introduced in connection with these techniques included combustion furnaces, tubes and boats; Kjeldahl flasks; and a wide variety of dryingtubes, absorption tubes and bottles, including the famous "Kali" or potash bulb of Liebig (1830), which appears on the logo of the American Chemical Society. The mass of analytical data on the composition of organic substances generated by these techniques formed the empirical basis for the various theories of organic structure and isomerism developed throughout the century.

9.9 Characterization Techniques (Molecular Mass)

All of the methods discussed above lead to the determination of a relative compositional formula. In the case of inorganic species, where a given combination of elements forms only one or two compounds of the type A_aB_b, for which a and b are clearly different, this information is usually sufficient to generate a distinct formula. However, in the case of organic species, where one has literally thousands of compounds of the type $C_cH_hN_nO_o$, many of which have identical stoichiometric coefficients (isomers) and others coefficients that differ by only small amounts, it is imperative that one determine the absolute composition of the compound as well. This is normally a whole number multiple (n) of its relative composition:

$$\textit{absolute composition} = n[\textit{relative composition}] \qquad [4]$$

a relationship that applies to their formula weights as well:

$$\begin{aligned} \textit{molecular weight} &= \textit{absolute formula weight} \\ &= n[\textit{relative formula weight}] \end{aligned}$$

Hence the determination of a molecular weight forms the final step in assigning an absolute compositional formula to a molecule.

In the early decades of the 19th century there was a vague consensus that the molecular weight of a gas correlated in some fashion with its density, but opinions differed as to just how general the correlation was. Some (e.g., Avogadro and Ampère) felt that it was universal, whereas others limited its use to only certain classes of substances (e.g., Berzelius). The result was that, during the first half of the century, chemists generally felt free to adopt whatever multiple of the relative formula happened to suit their particular theoretical fantasies concerning the structure of the molecule in question. Only with Cannizzaro's successful resolution of the atomic weight problem in 1858 (see next lecture) were gas densities finally applied as a universal criterion for molecular weight determinations.

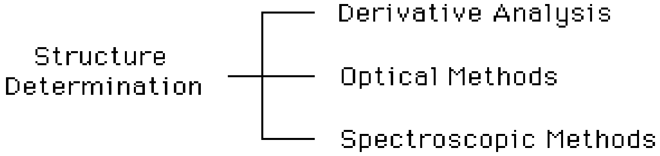
The experimental determination of molecular weights using vapor densities was pioneered by the French chemist, Jean-Baptiste Dumas, in 1826, though some of his results were called into question when they came into conflict with theoretical speculations of the day. Following Cannizzaro, the German chemist, August Hofmann, in 1863 made some improvements in an earlier technique for the measurement of gas densities first used by Gay-Lussac in 1811. But the final definitive form of the technique used for volatile organic compounds was the air-displacement method introduced by the German chemist, Victor Meyer, in 1876 and used well into the 1960s.

Correlation of solution colligative properties with solute molecular weights was first systematically studied by the French chemist, François Raoult, in the period 1878-1893. Raoult focused on the measurement of vapor-pressure depression (1878) and freezing-point depression (1882). However, perfection of the freezing-point depression technique as a routine laboratory procedure was due primarily to the German chemist, Ernst Beckmann (1888), who also introduced the use of the boiling-point elevation method (1889), as well as developing a highly sensitive thermometer for the measurement of small temperature changes (recall Section 9.2).

By the last quarter of the century, these methods were widely successful in generating accurate absolute compositional formulas for organic species – a necessary prerequisite for the further elaboration of their molecular structures. The same, however, was not true of inorganic compounds. Unknown to the 19th-century chemist, the vast majority of inorganic species form nonmolecular solids at RTP, which depolymerize on vaporization or ionically dissociate upon dissolution in a liquid solvent, and only in the case of the few molecular species, formed when the nonmetallic elements combine with one another, was one able to determine a true molecular weight.

9.10 Characterization Techniques (Molecular Structure)

19th-century techniques for the determination of molecular structure fall into three categories, all of which depend on having a prior knowledge of the absolute molecular formula:



The first of these, derivative analysis, was based on the postulate of "least structural change," first explicitly articulated by the Dutch chemist, Jacobus van't Hoff, in 1878. In other words, it is based on the assumption that it is possible to chemically substitute an atom or a group within an organic molecule without disrupting the molecule's overall structure. Thus replacement of a relatively unreactive atom or group (e.g. -H or $-CH_3$) with one (e.g., the alcohol group -OH) that shows distinctive differences in reactivity depending on whether it is bound to a primary, secondary, or tertiary carbon, or the preparation and enumeration of derivative isomers (first applied in detail by the German-Italian chemist, Wilhelm Körner, in 1874) allowed the 19th-century chemist to make important deductions concerning the original molecule's two- and three-dimensional structure.

Optical methods were based on the use of either the refractometer or the polarimeter. Used to measure refractive index, the refractometer was perfected by the Germans, Hans Landolt, Ernst Abbe, and Carl Pulfrich, in the 1870s, and was widely used for the qualitative identification of minerals and essential oils. Its application to structure determination was largely due to the efforts of Landolt and the German chemist, Julius Brühl, who developed a system of additive atomic and group refractivities in the 1880s that allowed one to approximately calculate the refractive indices of various isomers. Comparison with the experimentally measured value then allowed one to match a given absolute composition with the most probable of its possible alternative isomeric structures.

The constitutive additivity of refractivities was but one of several physical properties which could be used in this fashion to infer probable molecular connectivity. As early as the period 1839-1855, for example, Hermann Kopp had explored the constitutive additivity of molecular volumes, and by the early 20th-century these methods would become the subject of several specialist monographs, such as Samuel Smiles' *The Relations Between Chemical Constitution and Some Physical Properties* (1910), Gervaise Le Bas's *The Molecular Volumes of Liquid Compounds* (1915), and Hugo Kauffmann's *Beziehungen zwischen physikalischen Eigenschaften und chemischer Konsitution* (1920).

The polarimeter or polariscope is used to measure the interaction (known as optical activity) of a liquid or solid with polarized light. It was invented by the French physicist, Jean-Baptiste Biot, in 1810 and perfected by the German chemist, Eilhard Mitscherlich, around 1844. Widely used in the sugar industry (where it was known as a saccharimeter) to evaluate the concentrations of optically active sugar solutions, its relevance to structure determination was a result of Louis Pasteur's 1848 postulate that the optical activity of a substance was a direct indicator of an underlying dissymmetry or chirality in the three-dimensional structure of its component molecules. Its full implications for three-dimensional molecular structure determinations and the technique of isomer counting were brought out in 1874 by van't Hoff's postulate of the tetrahedral carbon atom (see next lecture).

The use of the spectroscope for purposes of structure determination was begun in 1879 by the British chemist, Walter Hartley, with his attempts to correlate the UV absorption spectra of organic compounds with the presence of certain characteristic groups in their molecules, and similar studies in the IR realm were initiated by William Abney and Edward Festing in 1881. However, these early results were too sporadic and time consuming to find widespread use, and it is not until the 20th century that structural spectroscopy finally comes to fruition.

All of the above methods, and especially that of derivative analysis, were successfully applied to the elucidation of both the two- and three-dimensional structures of organic compounds in the last quarter of the 19th century. Success in the field of inorganic chemistry, on the other hand, was decidedly more limited, as might be expected from the absence of absolute compositional formulas for most inorganic compounds. However, as we will see in the next lecture, the Swiss chemist, Alfred Werner, did have some limited success in applying these techniques to the structures of discrete complex inorganic ions during the last decade of the century.

9.11 The Theory of Analytical Chemistry

With the codification and standardization of most of the separation and characterization procedures discussed in Sections 9.7-9.10, 19th-century analytical chemistry – like fire assaying before it – became set in its ways. Authors of texts and monographs on the subject focused almost exclusively on technique and its refinement, while evidencing little or no interest in unraveling the underlying chemistry and physics. The first significant change in this attitude came with the publication in 1894 of the monograph, *Die wissenschaftlichen Grundlagen der analytischen Chemie*, by the German chemist, Wilhelm Ostwald. In this small book, Ostwald applied the newly acquired principles of the emerging field of physical chemistry – most notably the theories of chemical equilibrium and ionic dissociation – to the techniques of qualitative inorganic analysis, and to those of quantitative inorganic gravimetric, volumetric, and electrogravimetric analysis.

Ostwald also provided a brief theoretical overview of the most common methods of separation, including solid-liquid extraction, liquid-liquid extraction, liquid-gas absorption, and fractional distillation. By the end of the century there were already a number of precedents in this area. As early as 1868 Bunsen had provided a mathematical analysis of the washing of precipitates (an example of solid-liquid extraction), and in 1869 Berthelot and Jungfleisch did the same for liquid-liquid extraction (giving rise to the so-called partition coefficient). Finally, in 1893 the industrial chemists, Ernest Sorel and E. Hausbrand, each independently gave an elementary mathematical analysis of industrial fractional distillation which would eventually serve as the basis for the development of "plate theory" in the 20th century.

9.12 New Substances & the Rise of Organic Synthesis

If the elucidation of acids, alkalis and salts was the greatest triumph of 17th-century preparative chemistry and an understanding of the role of gases in chemical reactions the greatest triumph of 18th-century chemistry, it was the rise of organic chemistry and discovery of the vast number of new organic substances and reactions that formed its empirical basis, which presented 19th-century chemistry with its greatest theoretical challenge. Organic materials were, of course, known and used by man since earliest times. However, most of these were relatively complex biochemical products extracted from plants and animals rather than synthesized in the laboratory. Until the end of the 18th century characterization and classification of these products was based largely on their origins (i.e. plant or animal) and on such simple physical properties as solubility and texture (e.g., water-soluble, sticky gums; alcohol-soluble, translucent resins; water and alcohol-insoluble, viscous fats and oils, etc.).

Only with the advances in the separation and characterization techniques outlined in the previous sections did it become possible to develop a truly chemical approach to these materials based on an understanding of their chemical composition and observed reactivities. The standard two-volume history of 19th-century organic chemistry by Graebe and Walden requires more than 1352 pages to delineate the many new organic substances and reactions discovered prior to 1900 and such detail is obviously inappropriate in an overview account. Rather our primary focus will be with the underlying logic of the approach to both organic classification and synthesis which had emerged by the end of the century.

By the second half of the 19th century organic chemists had implicitly taken the relatively inert alkanes as their reactivity reference state. Introduction of multiple bonds or substitution of one or more hydrogen atoms by oxygen, nitrogen, or the halogens resulted in enhanced reactivity relative to the parent alkane. Indeed, these substitutions imparted the ability to undergo reactions not found in the unsubstituted parent and which persisted when the size of the parent alkane was changed. These reactivity inducing modifications became known as “functional groups”, and the persistence of their characteristic reactions as the size of the parent hydrocarbon was changed became known as “homologous series.” Though both of these fundamental concepts were already present in the first volume of Gerhardt’s *Précis de chimie organique* of 1844, it was only after the rise of organic structure theory in the 1860s that the full impact of their organizational potential was finally realized.

The logic of the resulting scheme may be better visualized by abbreviating the hydrocarbon portion of a simple organic molecule as $\varkappa$, and the reactive functional group as ϕ. By further abbreviating the attacking coreactant or reagent as ϱ we can generalize a simple organic type reaction as follows:

$$\varkappa\text{-}\phi + \varrho \rightarrow \textit{products} \qquad [5]$$

where the entire $\varkappa$-ϕ complex is generally known as the reaction "substrate." Reactions in which ϕ is progressively modified, but $\varkappa$ remains unchanged (i.e., $\varkappa$-ϕ, $\varkappa$-ϕ', $\varkappa$-ϕ'' , etc.) result in a so-called derived functional sequence (originally called a heterologous series by Gerhardt), as illustrated by the series: ethanol $[CH_3(CH_2OH)]$, ethanal $[CH_3(CHO)]$, and ethanoic acid $[CH_3(COOH)]$; whereas situations in which ϕ remains unchanged but $\varkappa$ is progressively lengthened (i.e., $\varkappa$-ϕ, $\varkappa'$-ϕ, $\varkappa''$-ϕ. etc.) result in a homologous series, as illustrated by the sequence: methanol $[(CH_3)OH]$, ethanol $[(C_2H_5)OH]$, propanol $[(C_3H_7)OH]$, etc. In principle each member of a given homologous series may be elaborated into a corresponding functional sequence using the same generalized type reaction for each corresponding conversion step.

Though some of the generalized type reactions of organic chemistry have chemically specific names, such as oxidation, reduction, halogenation, etc., most are named after the chemist who first discovered them (see Table 9.3) – a practice begun in the mid-19th century and more reminiscent of the irregular naming practices of mineralogy than of the systematic nomenclature reforms of Lavoisier and his collaborators.

Table 9.3 Some Typical 19th-Century Organic Type or Name Reactions

Date	*Name*
1852	Williamson synthesis
1853	Cannizzaro reaction
1860	Kolbe reaction
1877	Friedel-Crafts reaction
1881	Hofmann degradation
1886	Beckmann rearrangement
1900	Grignard reaction

It is the creative, and often intuitive, application of these type or name reactions which came to constitute the technique or "art" of organic synthesis in the 19th century and the power not only to reproduce organic substances found in nature but to produce totally new organic species found only in the laboratory. This newly acquired creative or synthetic power, though foreshadowed in Wöhler's famous synthesis of urea in 1828, found its fullest expression in Berthelot's famous 1860 manifesto, *Chimie organique fondée sur la synthèse*, and its fullest practical development in the chemistry of the coal-tar dyes. Here not only were 19th-century organic chemists able to replicate such naturally occurring dyes as alizarin (Graebe & Liebermann 1869) and indigo (Baeyer 1883) but, beginning with Perkin's synthesis of aniline purple or mauve in 1856, to create literally hundreds of artificial dyes having no naturally occurring analogs.

9.13 Selected References

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Lecture X

The Nineteenth Century

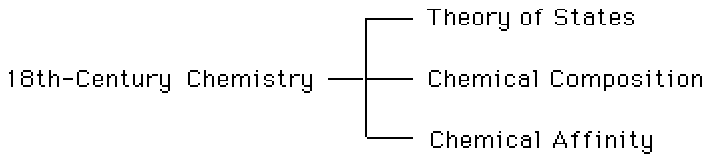
(1801-1900)

Molecular Composition and Structure

> Chemistry in the 19th century thrived when it was naive and pictorial and languished when it tried to be abstract and subtle.
>
> *W. V. Farrar 1968*

10.1 Retrospect

As indicated in Lecture VII, by the end of the 18th century at least three distinct themes had arisen in chemistry: the caloric theory of states, the problem of chemical composition, and the problem of chemical affinity:



In this and the following lecture we want to summarize how these basic themes continued to evolve and diversify throughout the 19th century.

10.2 The Theory of States

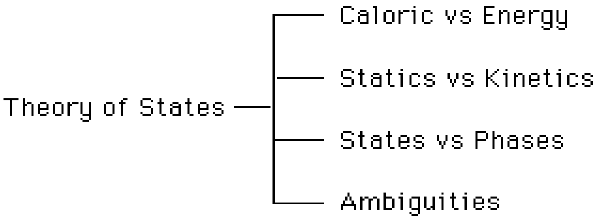
With respect to the theory of states, four important changes occurred during the 19th century:

a. The principle of conservation of heat, which served as the basis of the caloric fluid model, was subsumed under the more general principle of the conservation of energy.

b. The underlying molecular model of the three states of matter based on a static Newtonian equilibrium between attractive interparticle forces, on the one hand, and repulsive intercaloric forces, on the other, was replaced by a kinetic model in which the attractive interparticle forces competed instead with disruptive translational, rotational, and vibrational molecular motions.

c. New states of matter were added to the traditional categories of solid, liquid, and gas, and the concept of a state as a simple difference in the degree of molecular aggregation was subsumed under the more general concept of a change in "phase."

d. The discovery of colloids and nonstoichiometric compounds led to a partial recognition that the classification of materials as either heterogeneous mixtures, solutions, or pure substances was a limiting case idealization and that intermediate cases could exist as well.



10.3 Caloric versus Energy

The gradual recognition that heat was not a special conserved fluid, but rather one of several possible manifestations of the more general concept of energy, is an idea that was developed by a number of engineers, physicists and chemists during the first half of the 19th century. Stimulated by Sadi Carnot's theoretical analysis (1824) of heat engines, the idea gradually evolved in engineering circles that these engines were devices for the conversion of heat into work and that it was the sum of the heat changes (ΔQ) and work changes (ΔW), or the total energy (ΔE), that was conserved, rather than the heat and work separately:

$$\Delta E = \Delta Q + \Delta W = 0 \qquad [1]$$

The first explicit statements of the principle of the conservation of energy or the first law of thermodynamics, as it eventually came to be called, are usually credited to the German physician, Julius Mayer (1842, 1845); the English physicist, James Joule (1841, 1843); and the German physicist, Hermann von Helmholtz (1847), though the idea seems to have been in the air at the time, and there were many partial anticipations by lesser known scientists and engineers as well. While it is true that some chemists, such as Friedrich Mohr (1837), Justus Liebig (1841), William Grove (1846), and Michael Faraday (1859), took early qualitative notice of the principle, it was not until the second half of the 19th century that it began to seriously impact on chemical theory (see Section 11.5).

10.4 Statics versus Kinetics

As already noted in Section 6.2, Lavoisier was fully aware, when formulating his version of the caloric theory of heat, that many 17th-century scientists had held to the view that heat was actually a form of molecular motion rather than an imponderable fluid. Both Bacon and Descartes, for example, had attributed it to an "intestine motion" or molecular vibration of some sort – a view later supported by both the cannon-boring experiments of Rumford (1798) and and the ice-rubbing experiment of Davy (1799). The specific association of heat with the translational motion of molecules, however, rather than with just their vibrational and rotational motions, was due to the development of the kinetic theory of gases. Though its origins date back as far as the 18th century (Bernoulli 1738) and attempts were made to revive it in the first half of the 19th century (Herapath 1821, Waterston 1845), this theory did not attract widespread acceptance until the 1850s, when it was revived and developed by, among others, August Krönig (1856) and Rudolf Clausius (1857) in Germany, and by James Joule (1851) and James Clerk Maxwell (1860) in England.

Clausius referred to the new approach as the "mechanical theory of heat" and the British physicist, John Tyndall, captured its essence in the title which he gave to his popular lectures on the subject in 1862: *Heat Considered as a Mode of Motion*. Within the context of the newer view, solids, liquids, and gases no longer differed solely in terms of the distance between their statically equilibrated molecules (i.e., in terms of the sizes of their combined caloric envelopes), but now also differed in their degrees of intermolecular organization and freedom of motion. This approach also went hand and hand with the newer concept of heat as a form of energy since it reduced the interconversion of mechanical energy and heat to an issue involving the interconversion of macroscopic motion and molecular motion.

The idea that the mathematical development of the kinetic model in the case of gases and liquids required the use of statistical concepts gradually evolved as well, beginning with the work of Clausius and Maxwell and culminating in the formal development of statistical mechanics by the Austrian physicist, Ludwig Boltzmann, and the American physicist, Josiah Willard Gibbs, near the end of the century. As with the energy concept, chemists were generally slow in adopting the newer kinetic molecular models of heat and matter, and they were not widely applied to chemical theory until the last quarter of the century (see Section 11.10).

In contrast to the kinetic theory of gases and liquids, the development of structural models for the solid state took a different route. Already in the 17th century several attempts were made to rationalize the shapes of crystals in terms of the packing of spherical particles or molecules (Kepler 1611, Hooke 1665, Huygens 1690) and it was this tradition that formed the basis of the static models used by the caloric theory of states (Dalton 1808, Wollaston 1813). At the end of the 18th century, however, the French scientist, René Häuy, departed from this tradition and, in so doing, founded the independent science of crystallography. Häuy postulated that crystals were built, not from spherical particles, but from a set of primitive polyhedra known as "integrant molecules" whose shapes he attempted to deduce from a study of the cleavage properties of crystals. He further incorrectly identified these integrant molecules with the physical molecules of the chemist.

In the 1840s Hauy's integrant molecule was gradually transformed into the concept of a "unit cell" – a polyhedral arrangement of abstract points possessing certain symmetry properties, whose relationship to the actual physical molecules of the chemist and physicist became more and more problematic. As the century progressed, the development of both the unit cell concept and the resulting lattice theory of crystals, which viewed them as a series of interpenetrating point systems created by the packing of the units cells, became increasingly abstract and mathematical. In 1848 Auguste Bravais established that the known symmetries of crystals could be rationalized in terms of 14 different point lattices or units cells, and in 1891 Evgraf Federov and Artur Schoenflies each independently deduced the existence of 230 independent space groups.

Only near the end of the century was there an attempt to reestablish a link between abstract lattice theory and concrete models of molecular structure via a revival of the packed spheres model by the British scientist, William Barlow, and the chemical schools of crystallography centered around Paul von Groth in Germany and William Pope and Alfred Tutton in England. However, this reintegration into chemistry and physics became complete only with the development of the technique of X-ray diffraction analysis in the second decade of the 20th-century (see Lecture XIV).

10.5 States versus Phases

As we saw in Section 6.2, by the end of the 18th century there was a clear recognition of the three physical states of matter (solid, liquid, gas), as well as of the fact that the passage of a given substance from one state to another occurred at a fixed transition temperature and was accompanied by the absorption or evolution of a characteristic latent heat of transition. This simple picture was complicated by the discovery of crystal polymorphism by the German chemist, Eilhard Mitcherlich, in 1821. Further studies of this phenomenon, and especially those of the German physicists, Moritz Frankenheim and Otto Lehmann, in the period 1830-1880, not only multiplied the number of known cases of solid polymorphism, they also revealed that the transformation from one solid polymorph to another occurred at a fixed transition temperature analogous in every way to the melting and boiling points separating the solid, liquid, and gaseous states.

As early as 1804 Fourcroy had postulated the existence of a fourth "plastic state" separating the solid and liquid states, and starting in 1888 Reinitzer and Lehmann began to systematically study the thermal behavior of certain complex organic compounds that appeared to display a series of two or more polymorphic liquid states, each separated from the other, as in the case of solid polymorphs, by a characteristic transition temperature. Because these intermediate states displayed anisotropic optical properties similar to those of crystalline solids, but clearly had the mechanicalproperties of normal liquids, Lehmann eventually (1890) suggested that they be called "liquid crystals." Well into the 20th century, Lehmann'sinterpretation of liquid crystals as single component, liquid polymorphs or "mesophases," as they were later called by Friedel, was opposed by the German chemist, Gustav Tammann, who instead viewed them as finely dispersed multicomponent emulsions.

Yet other so-called states of matter were also proposed, though these did not appear to be characterized by definite transition temperatures. Thus the concept of the amorphous state was introduced by the German chemist, Johann von Fuchs, in 1833 to characterize noncrystalline solids or glasses, and in 1879 the British chemist, Sir William Crookes, proposed that the ionized gases found inside gaseous discharge tubes might also correspond to a new "fourth state" of matter (now known as the plasma state).

The theoretical means for unifying all of these observations were provided by Gibbs in the period 1875-1878 with the publication of his classic memoir "On the Equilibrium of Heterogeneous Substances." Gibbs coined the term "phase" to characterize any homogeneous region of matter that could be visually distinguished from neighboring regions, irrespective of whether there was or was not a difference in their composition or degree of aggregation. Though solids, liquids, and gases were, by definition, different phases, the same was also true of the various solid and liquid polymorphs. In addition, all phase changes, whether polymorphic or changes in physical state, obeyed the same laws and were characterized by both a definite transition temperature and a definite heat of transition.

Gibbs further showed that, for a heterogeneous or phase equilibrium, the variance or number of degrees of freedom (f), the number of independent chemical components (c), and the number of coexistent phases (p) were constrained by the equation:

$$f = c + 2 - p \qquad [2]$$

Known as the phase law or phase rule, this equation was first used by Bakhuis-Roozeboom in 1887 to classify various phase equilibria and to graphically summarize the experimental study of single component systems in terms of a *PT* plot or phase diagram (recall Section 9.2) – a technique that was soon extended to binary and ternary systems as well and, by the last decade of the century, the first of what would become a long line of specialist monographs dealing with the phase rule and its applications had made an appearance (Le Chatelier 1888, Meyerhoffer 1893, Bancroft 1897).

The new science of thermodynamics also provided fresh insights concerning the molecular interpretation of heats of transition and the effects of pressure on transition temperatures. The absorption or evolution of heats of transition no longer corresponded to the binding or release of combined caloric, but rather to the interconversion of heat and intermolecular potential energy resulting from the structural changes that accompanied the phase change. Though not as drastic as the structural rearrangements involved in the changes of physical state separating solids, liquids, or gases, it was understood that some change in the lattice arrangement of the component molecules was also involved in polymorphic transitions (Zincke 1876), though Lehmann's later speculations (1877) on this subject involved instead the existence of hypothetical molecular clusters and temperature-inducedchanges in either their sizes (so-called physical polymerism) or internal intermolecular arrangement (so-called physical isomerism).

It was also noted in Lecture VI that Lavoisier and other 18th-century scientists were fully aware of the effect of pressure changes on the boiling points of liquids and that by 1796 Lebon had made this phenomenon the basis of the technique of vacuum distillation. The thermodynamic rationale of this effect was provided by the French engineer, Emile Clapeyron, in 1834, when he derived an equation relating the change in the transition temperature with respect to pressure (dT/dP) to a function of the normal transition temperature (T), the change in the molar volume (ΔV) accompanying the phase change, and the heat of transition (ΔH) for the change:

$$dT/dP = T(\Delta V/\Delta H) \qquad [3]$$

Thus, since both ΔV and ΔH are positive on passing from the liquid to the gaseous phase, dT/dP must also be positive – in other words the boiling point must increase as the pressure increases and vise versa.

The first explicit use of this equation was made by the Scottish engineer, James Thomson, in 1849, when he applied it to the melting of ice under pressure. Since ΔV is negative and ΔH is positive for this change, the equation predicted that dT/dP would also be negative or that the melting point would decrease as the pressure increased – a result that was experimentally confirmed by Thomson's brother, Lord Kelvin. In 1883 the Dutch chemist, L. Th. Reicher, also applied the equation to the pressure shift in the transition temperature for a solid-solid polymorphic transition (monoclinic-rhombic sulfur).

Though Michael Faraday had successfully liquefied several gases under moderately high pressures as early as 1823, and the most important gases had all been liquefied by the end of the century using a combination of compression and adiabatic cooling, the systematic pursuit of high-pressure chemistry would not truly begin until the 20th century. However, 19th-century studies of the liquefaction of gases did lead to the discovery that each type of liquid displayed a critical temperature above which it was impossible to maintain the liquid state, however great the applied pressure. First observed for water and steam by the French engineer, Charles Cagniard de la Tour, in 1822, and again for various organic liquids by the Russian chemist, Dmitri Mendeleev, in 1860, this phenomenon was studied in detail for the case of carbon dioxide by Thomas Andrews in 1869. His results showed that, above the critical point, the distinction between the liquid and gaseous states all but disappeared.

Boyle's law (1662), relating the pressure and volume of a gas, and Gay-Lussac's law (1802), relating its temperature and volume, were apparently first combined into a single equation or "ideal gas law" by Clapeyron in 1834, though several additional changes (Clausius 1864, Horstmann 1873) in the units used to measure temperature and volume were required before the law took its current form:

$$PV = nRT \qquad [4]$$

Extensive experimental studies of the expansion and compression of gases made by the French chemist, Victor Regnault, in the 1840s revealed that gases showed increasing deviations from this law with increasing pressure and decreasing temperature. Attempts to theoretically understand both the critical temperature and the departures from ideal gas behavior observed as one approached the conditions required for liquefaction finally led to the famous modification of the ideal gas law first proposed by the Dutch physicist, Johannes Diderik van der Waals, in 1873:

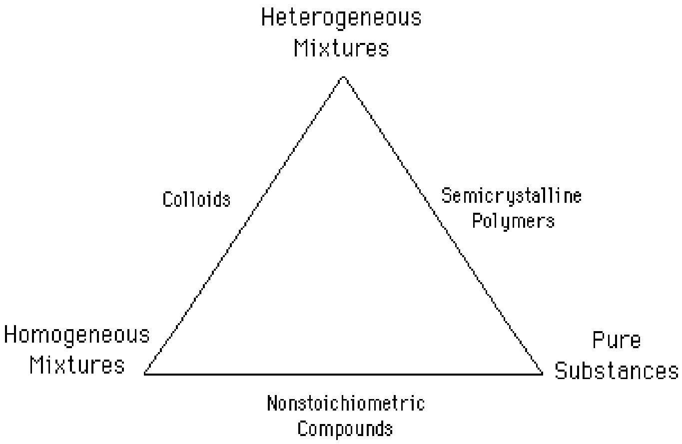
$$(P + an^2/V^2)(V - nb) = nRT \qquad [5]$$

in which both the operation of intermolecular forces (the a/V^2 term) and the finite volume of the gas molecules (the b term) were explicitly taken into account.

10.6 Ambiguities

By the end of the 18th century, chemists routinely divided the materials they worked with into the three broad categories of heterogeneous mixtures, homogeneous mixtures or solutions, and pure substances (either compound or simple). However, as with most classifications, if one looked close enough, it was possible to find borderline or intermediate cases for which the classification criteria were ambiguous (see diagram at top of next page).

In the case of heterogeneous versus homogeneous mixtures, this ambiguity centered on a class of substances known as colloids. The concept of colloidal solutions (or, more accurately,dispersions), as distinct from that of true or crystalloid solutions, was first introduced by the British chemist, Thomas Graham, in 1861. Unlike true solutions, colloidal solutions were often either opaque or



translucent in appearance, though no suspended particles were visible under even the most powerful optical microscope. In addition, they displayed unusual optical properties, such as light scattering; could be separated by dialysis through a membrane; and were often precipitated by slight changes in acidity or salt concentration. These various distinctions were refined and studied, not only by Graham, but by several other chemists throughout the century (Semi 1850-1852, Schulze 1861-1882, Linder & Picton 1892, etc.).

Graham thought of colloids as yet another state of matter, not unlike the amorphous state of von Fuchs, which a given substance could be made to assume under appropriate conditions. Just as true solutions involved a mixing of the solvent with the individual molecules found in the crystalloid state of the solute, so colloidal solutions were thought to involve the mixing of the solvent with larger clusters of these molecules apparently present in its colloidal state. These hypothetical molecular clusters were later dubbed "micelles" by the German botanist, Carl Nägeli (1879). The question of whether colloidal systems should be classified as homogeneous solutions or as finely dispersed heterogeneous mixtures remains unresolved and the consensus today is that they are best thought of as intermediate between these two limiting extremes.

In the case of solutions versus pure substances, the ambiguity centered around the question of whether solutions were simple mechanical mixtures, whose apparent homogeneity and stability were due to the fact that the mixing occurred at the molecular rather than the molar level, or whether they involved the formation of weak or transient chemical compounds between the solute and solvent. Since most solutions display an upper limit to solubility or a saturation point, this seemed to imply, in keeping with the static Newtonian model of states used throughout the first half of the century, that specific interparticle solute-solvent forces of some sort were involved whose mutual saturation set an upper limit to the degree of solubility. This was the point of view adopted by Lavoisier's colleague, Claude-Louis Berthollet, in a debate which he conducted with the French chemist, Joseph-Louis Proust, in the period 1802-1808.

Solutions, in Berthollet's opinion, differed from compounds only in degree rather than kind and were best thought of as compounds of variable composition whose components could combine in all proportions up to the saturation point. Berthollet was, of course, fully aware that compounds of constant composition also existed, but thought that they corresponded to only certain points in the continuum of allowed combining ratios where a sudden change in the forces of cohesion either caused them to precipitate from the solution as solids or to escape as gases. Proust, on the other hand, maintained that solutions were intimate molecular mixtures whose variable composition was due to the changing ratios in which the solute and solvent molecules of otherwise fixed composition were mechanically dispersed.

For a variety of reasons, most 19th-century chemists opted for Proust's point of view. This was reinforced in the second half of the century by the rise of the kinetic theory of matter, which provided an underlying mechanism (thermal motion) for the mechanical stability and homogeneity of solutions; by Raoult's studies of solution colligative properties (1878-1893), which suggested that they were simple functions of solute concentration only; and especially by van't Hoff's equation (1886) for calculating the osmotic pressures of dilute solutions, which explicitly postulated a direct analogy between dilute gases and dilute solutions.

Despite this apparent consensus, however, an increasing number of embarrassing counter-examples began to slowly accumulate in the fields of metallurgy, glass technology, and mineralogy throughout the century which suggested that many solid-state compounds were best described as non-stoichiometric or even as solid solutions. The full extent to which these examples justified Berthollet's original position, rather than that of Proust, would only become clear when the study of phase diagrams was extended to binary and ternary systems and applied to these fields by Roozeboom, van't Hoff, Tammann, Le Chatelier, Kurnakov, and others around the turn of the century. In light of these late 19th-century results, it is something of an historical irony that most histories of chemistry still report that Proust was right and Berthollet wrong, and that most modern introductory chemistry texts still present the law of definite composition as a universal chemical truth.

10.7 Extending Chemical Composition

With respect to the theory of chemical composition, three important changes occurred during the 19th century:

a. The traditional gravimetric and/or volumetric characterization of a substance's composition was expanded so as to include its atomic-molecular composition as well. Thus water could be described at the molar level not only as a compound containing 11.11% hydrogen and 88.89% oxygen by weight, or 66.67% hydrogen and 33.33% oxygen by volume, but also at the molecular level as a compound composed of molecules containing two atoms of hydrogen and one atom of oxygen – an advance based, in turn, on the successful establishment and quantification of the concepts of atomic weight and atomic equivalency or stoichiometric valence.

b. The twin parameters of atomic weight and stoichiometric valence were further used to revolutionize the classification of the chemical elements via the discovery of the periodic law and the periodic table.

c. Molecular composition was supplemented by the additional concept of molecular structure, so that, by the end of the century, it was not only possible to characterize the composition of molecules in terms of the nature and number of their component atoms, as indicated above, but their structure as well in terms of the bonding connectivity and three-dimensional arrangement of those atoms.

As we will see, the successful implementation of these changes came to a head during the years 1855-1875. Indeed, so fundamental were the advances made during this period that they may truly be said to constitute yet a second chemical revolution – one that was as fully revolutionary in its consequences as the first chemical revolution initiated by Lavoisier and his collaborators in the period 1774-1794.

10.8 Molecular Composition

As noted in previous lectures, earlier versions of the corpuscular theory, based either on speculations concerning particle shapes and sizes (17th-century mechanical atomism) or concerning interparticle forces of attraction and repulsion (18th-century dynamical atomism), had proved largely sterile for chemistry. Nevertheless, some suggestive results were obtained by the German chemist, Jeremias Richter, near the end of the 18th century, which he somewhat obscurely summarized in his book, *Anfangsgründe der Stöchyometrie oder Messkunst chymischer Elemente*, published in three volumes between 1792 and 1794.

Essentially Richter discovered that the weights of various acids and bases required for neutralization were transferable from one salt to another (the law of reciprocal proportions). Thus, if α mass units of acid A required β mass units of base B to neutralize it, and γ mass units of acid C required δ mass units of base D to neutralize it, then these same δ mass units of base D would also neutralize α mass units of acid A and the β mass units of base B would also neutralize γ mass units of acid C. In other words, α mass units of A were chemically equivalent to γ mass units of C and β mass units of B were chemically equivalent to δ mass units of D.

Though these observations would seem to suggest that the equivalent weights of the various acids and bases were somehow related to the weights of their component particles, Richter did not make this inference. Rather it is the English school master, John Dalton, who is generally given the credit for shifting the focus of corpuscular speculations from questions of atomic shapes, sizes and forces to the more fruitful questions of atomic masses and combining weights through his recognition, in the period 1803-1808, that the gravimetric composition of compounds could be used to infer information about the relative masses of their component atoms.

Dalton's theory is generally referred to as the "chemical" atomic theory, since his atoms corresponded to Lavoisier's simple substances with their manifold secondary chemical and physical properties and not to the ultimate physical atoms of Epicurus. It might well be that Daltonian atoms were conserved in chemical processes, but this did not necessarily preclude the possibility that they might be capable of yet further division under more severe conditions. Though it is questionable whether Dalton himself agreed with this distinction, it was one that was definitely made by his fellow chemists. This distinction between chemical versus physical atoms was, in effect, the particulate equivalent of the traditional distinction between chemical versus physical elements, mentioned in Lecture VI.

Assume that the analysis of a compound AB, containing a 1:1 ratio of atom A to atom B, reveals that it contains 33.33% A and 66.67% B by weight. Dalton's insight was the realization that the ratio of these weights had to directly reflect the ratio of the weights of the component atoms:

$$(66.67\,B/33.33A) = (AW_B/AW_A) = 2/1 \qquad [6]$$

In other words, the reason why AB contained twice as much B as A by weight was because the individual B atoms were twice as heavy as the individual A atoms. Hidden in this calculation, however, was the tacit assumption that one knew that the stoichiometric formula of the compound was AB and not A_2B or AB_2 or AB_3, etc. Thus, if the correct formula was really A_2B, then the ratio of the gravimetric weights reflected the ratio of one B atom to two A atoms, rather than one B atom to one A atom, and revealed that the individual B atoms were really four times heaver than the individual A atoms.

Generalizing this procedure for any binary compound, A_aB_b, gives the result:

$$(\text{mass } B/\text{mass } A) = (b/a)(AW_B/AW_A) \qquad [7]$$

and reveals that Dalton’s procedure for calculating relative atomic weights (AW_B/AW_A) requires a knowledge of both the gravimetric composition of a compound (*mass B*/*mass A*) and the ratio (*b*/*a*) in which the atoms are combined (i.e., the relative compositional formula), only the first of which can be determined by experiment. In order to obtain the second parameter (*b*/*a*), Dalton formulated a series of rules for guessing the atomic combining ratios, known as his rules of simplicity. However, these were quickly recognized to be both arbitrary and ambiguous (Bostock 1811) and, as a result, most of Dalton’s original atomic weight values are now known to be incorrect.

What followed was almost 50 years of chaos. Some chemists (Davy, Wollaston, Faraday, Gmelin) rejected the chemical atomic theory and attempted to substitute an empirical theory of “combining weights” or “mass equivalents” based on the original ideas of Richter. Yet others attempted to find a solution to Dalton’s dilemma (i.e., atomic weights require a knowledge of both gravimetric composition and the relative molecular formula but determination of the relative molecular formula requires a knowledge of atomic weights and gravimetric composition) by uncovering additional independent correlations between atomic weights and measurable experimental data. Proposals included the use of gas densities and the volumetric stoichiometry of gas-phase reactions (Avogadro 1811), the use of specific heats (Petit & Dulong 1819), and the use of crystal isomorphism (Mitcherlich 1820). Between 1814 and1848 the Swedish chemist, Jöns Jakob Berzelius, selectively applied these various suggestions, as well as his own rules governing the oxygen content of salts, as part of a one-man program to determine a complete table of atomic weights for all of the then-known elements. However, despite the high quality of his analytical work, some portion of the various tables issued by Berzelius always contained weights that are now known to be either multiples or fractions of our current values.

Our current method of writing compositional formulas, using letter abbreviations for the elements and subscripted numerical coefficients for the relative or absolute numbers of atoms present, evolved from proposals originally introduced by Berzelius in the period 1813-1814, though it was not until the 1820s and 1830s that such formulas began to appear in introductory textbooks. Often these formulas varied from author to author, depending on what set of atomic or equivalent weights the author preferred. And, of course, the resulting formulas often contained multiples or fractions of our current atom counts due to the fact that the selected set of atomic weights often contained values corresponding to fractions or multiples of our current values.

In 1858 the Italian chemist, Stanislao Cannizzaro, finally produced the definitive resolution of Dalton's dilemma by showing how to extract atomic weights from a combination of both gravimetric and gas density data for an element's volatile compounds. Cannizarro summarized his results in the form of a small pamphlet entitled *A Sketch of a Course of Chemical Philosophy*, which he distributed at a conference of chemists held at Karlruhe Germany in 1860 for the express purpose of resolving the problem of establishing a system of self-consistent atomic weights and agreeing upon the proper use of such terms as "atom," "molecule" and "equivalent." After the Karlsruhe Conference, a reliable and standardized table of atomic weights, based on the H = 1 scale, came into general use, which, when coupled with the technical advances (recall Section 9.9) in the determination of molecular weights using gas densities and (later) solution colligative properties, finally allowed for the determination of reliable and universally accepted relative and absolute compositional formulas.

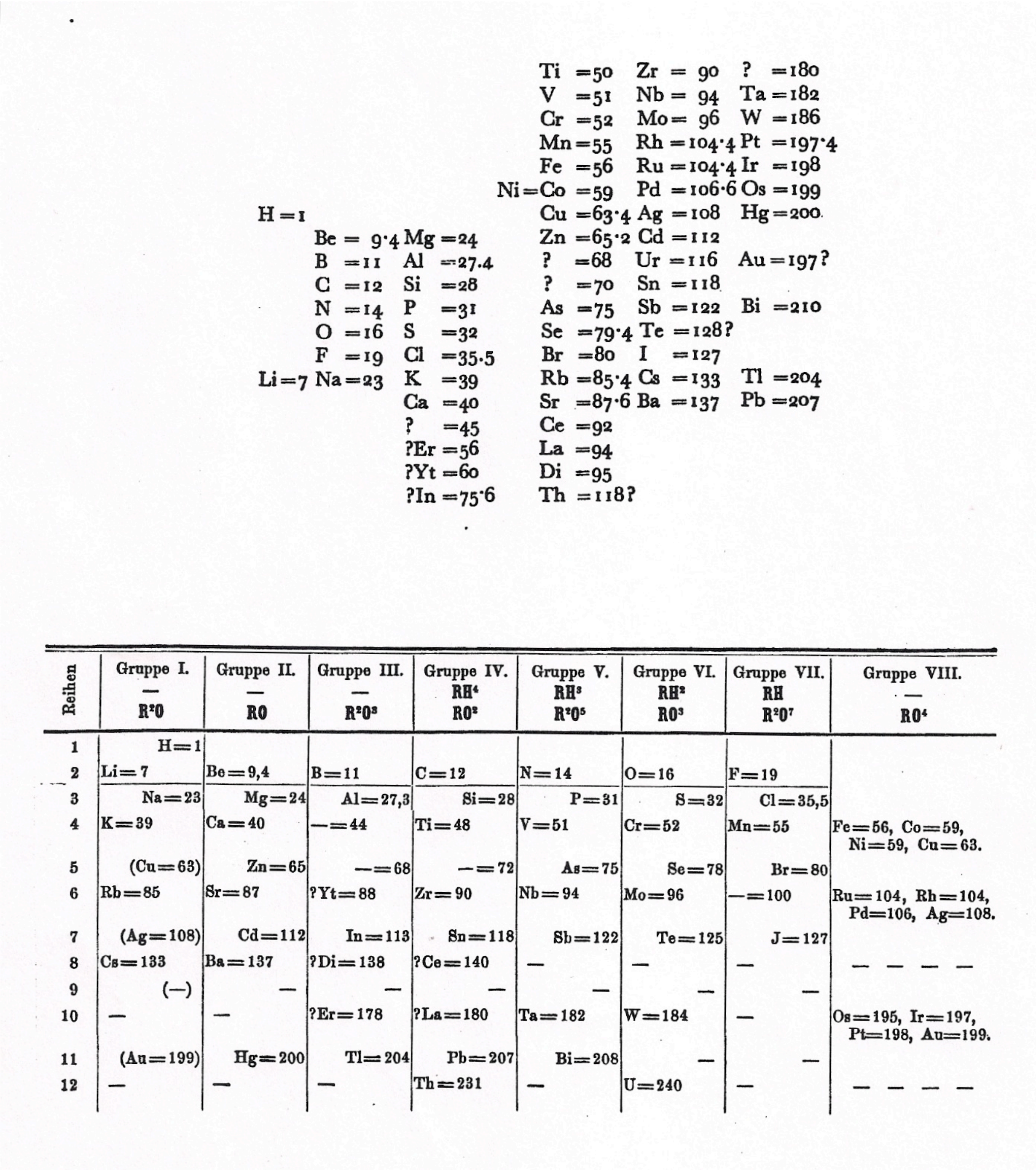
Even before these resolutions were in place, the examination of type formulas had uncovered a pattern for atom and radical substitution which allowed chemists to assign to each atom or radical a numerical value which indicated the number of hydrogen atoms it could replace in a substitution reaction (Williamson 1851,Frankland 1852, Odling 1854, Kekulé 1857). Variously referred to as the atomic "substitution value," "equivalency," "basicity," "atomicity," or "quantivalence", the resulting stoichiometric "valence" values, as they eventually came to be called, essentially gave chemists the ability to predict the most probable relative compositional formulas of a given atom's compounds with other atoms and radicals.

10.9 The Periodic Law and Table

For the first half of the 19th-century the most common textbook classifications of the chemical elements were based on elaborations of Lavoisier's original table of 1789 made by the French chemist, Louis-Jacques Thenard, in his *Traité de chimie* of 1813 and by the Scottish chemist, Thomas Thomson, in his *System of Chemistry* of 1817. The elements were first divided into the categories of "imponderables" (caloric, light, and later electricity) and "ponderables," and the latter, in turn, into "supporters of combustion" (O and later F, Cl, Br, and I) and "combustibles." Combustibles were further divided into nonmetals and metals, and the metals sorted into groups on the basis of their affinity for oxygen and ease of reduction.

An alternative electrochemical classification of the elements was introduced by Berzelius in 1811 based on his concept of atomic electronegativity (see Section 11.7), in which the elements were arranged in a single progressive "electrochemical" series, with the most electronegative element (oxygen) at the top and the most electropositive element (potassium) at the bottom. Though considered as a useful summary of certain aspects of both chemical and electrochemical behavior, this approach, unlike those of Lavoisier, Thenard, and Thomson, was seldom used to organize textbook discussions of descriptive chemistry.

Independent attempts to classify the elements based on the newly discovered parameter of atomic equivalency or stoichiometric valence were made in 1864 by the British chemists, Alexander Williamson and William Odling, in which the elements were first divided into the categories of even (*artiads*) and odd (*perissads*) valence and then into individual valency groups, and similar valence classifications soon began appearing in the textbook literature (Frankland 1866, Rammelsberg 1867, Miller 1867, Naquet 1868, Cooley 1869, Cooke 1869). These classifications were eventually elaborated via attempts to establish numerical relationships between the atomic weights of the elements within each valence group, either by showing that the atomic weights of the middle members were the averages of the atomic weights of the extremes (Newlands 1863, Odling 1864) or by showing that the



			Ti =50	Zr = 90	? =180
			V =51	Nb = 94	Ta =182
			Cr =52	Mo = 96	W =186
			Mn =55	Rh =104·4	Pt =197·4
			Fe =56	Ru =104·4	Ir =198
			Ni=Co =59	Pd =106·6	Os =199
H =1			Cu =63·4	Ag =108	Hg =200
	Be = 9·4	Mg =24	Zn =65·2	Cd =112	
	B =11	Al =27.4	? =68	Ur =116	Au =197?
	C =12	Si =28	? =70	Sn =118	
	N =14	P =31	As =75	Sb =122	Bi =210
	O =16	S =32	Se =79·4	Te =128?	
	F =19	Cl =35.5	Br =80	I =127	
Li =7	Na =23	K =39	Rb =85·4	Cs =133	Tl =204
		Ca =40	Sr =87·6	Ba =137	Pb =207
		? =45	Ce =92		
		?Er =56	La =94		
		?Yt =60	Di =95		
		?In =75·6	Th =118?		

Reihen	Gruppe I. — R^2O	Gruppe II. — RO	Gruppe III. — R^2O^3	Gruppe IV. RH^4 RO^2	Gruppe V. RH^3 R^2O^5	Gruppe VI. RH^2 RO^3	Gruppe VII. RH R^2O^7	Gruppe VIII. — RO^4
1	H=1							
2	Li=7	Be=9,4	B=11	C=12	N=14	O=16	F=19	
3	Na=23	Mg=24	Al=27,3	Si=28	P=31	S=32	Cl=35,5	
4	K=39	Ca=40	—=44	Ti=48	V=51	Cr=52	Mn=55	Fe=56, Co=59, Ni=59, Cu=63.
5	(Cu=63)	Zn=65	—=68	—=72	As=75	Se=78	Br=80	
6	Rb=85	Sr=87	?Yt=88	Zr=90	Nb=94	Mo=96	—=100	Ru=104, Rh=104, Pd=106, Ag=108.
7	(Ag=108)	Cd=112	In=113	Sn=118	Sb=122	Te=125	J=127	
8	Cs=133	Ba=137	?Di=138	?Ce=140	—	—	—	— — — —
9	(—)	—	—	—	—	—	—	
10	—	—	?Er=178	?La=180	Ta=182	W=184	—	Os=195, Ir=197, Pt=198, Au=199.
11	(Au=199)	Hg=200	Tl=204	Pb=207	Bi=208	—	—	
12	—	—	—	Th=231	—	U=240	—	— — — —

Plate III

Top: Mendeleev’s vertical periodic table of 1869.

Bottom: His horizontal table of 1871 which became the standard for the 19th century.

differences between the atomic weights of successive members were multiples of one another (Meyer 1864, Hinrichs 1867).

The first of these attempts, known as the "triad" approach, can be traced back to the work of the German chemist, Johann Döbereiner (1817, 1829), and was developed by several chemists throughout the first half of the century (Dumas 1851; Kremers 1852, 1856; Gladstone 1853; Lenssen 1857; Odling 1857; Lea 1860), whereas the second, known as the "homolog" approach, dated back to the speculations of the British chemist, WilliamProut (1815, 1816) on the possible composite nature of the chemical elements, and also had a long history (Pettenkofer 1850; Cooke 1854; Dumas 1857, 1858; Mercer 1858).

The final stage came when attention was refocused on intergroup, rather than intragroup, trends in atomic weights, leading to the discovery that, when the elements were placed in order of increasing atomic weight, the members of each valence group appeared at regular intervals in the sequence – in short, the discovery that stoichiometric valence was a periodic function of atomic weight. Imperfectly anticipated in 1864 by the British chemist, John Newlands, with his "Law of Octaves," the full implications of this discovery for the development of improved valence classifications, as well as its generalization to include the periodicity of other chemical and physical properties, was first realized by the Russian chemist, Dmitri Mendeleev, in 1869 and by the German chemist, Lothar Meyer, in 1870 (who, however, acknowledged Mendeleev's priority of publication). Known in its fully developed form as the "periodic law," the resulting classification tables, based on its application, eventually became known as "periodic tables," and still form the basis of modern chemical classification.

10.10 Molecular Structure

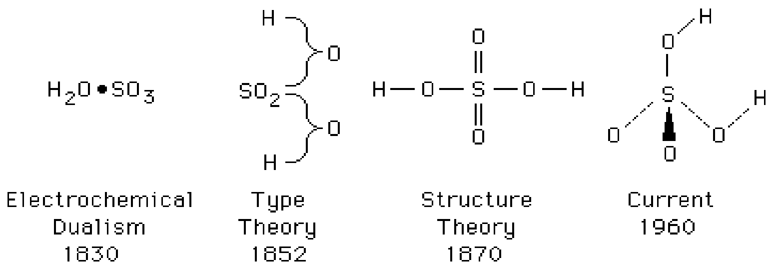
Though early speculations on the arrangement of atoms within molecules appear in the writings of Higgins (1789), Dalton (1803-1830), Thomson (1807), and Wollaston (1808), these were not amendable to experimental verification and were largely moot until reliable absolute compositional formulas became available in the last half of the century.

An important aspect of Lavoisier's oxygen theory was his "dualistic" formulation of inorganic salts as the product of an acidic nonmetallic oxide and a basic metallic oxide, and his suggestion that this model could be extended to organic compounds as well, in which case the nonmetallic element was replaced by a compound "radical" composed of carbon and hydrogen, and possibly nitrogen and phosphorus as well. The concept of electronegativity was introduced in the early 19th century by Avogadro (1809) and Berzelius (1811) on the basis of the contact electrification series and qualitative electrolysis experiments made possible by the newly discovered voltaic pile (see Section 9.3 and 11.7). Using this concept, Berzelius transformed Lavoisier's original acid-base dualistic theory into a generalized "electrochemical dualism" in which binary inorganic compounds, like the elements themselves, were arranged in a continuous electrochemical series, with strongly electronegative acids at one extreme and strongly electropositive bases at the other. Within this system, the greater the electronegativity difference between the component acid and the component base, the greater their affinity and the more stable the resulting salt.

Though attempts (known as the "old radical theory") to apply electrochemical dualism to organic compounds appeared to have some initial success in the period 1820-1839, things began to seriously unravel in the 1840s as more and more organic compounds and reactions were discovered, including the phenomena of isomerism and polymerism (terms coined by Berzelius in 1831and 1832 respectively). The result was a series of transient theories attempting to correlate the known facts of organic chemistry in which the basic premises of electrochemical dualism were progressively abandoned. Most of these were formulated by French chemists (Dumas, Laurent, Gerhardt) and include the nucleus theory, the substitution or unitary theory, and the old type theory. Since the fundamental questions of atomic weights and compositional formulas were still undecided, many of these speculations (based largely on the systematization of organic substitution reactions) were of only limited value.

The eventual victor in this struggle was the "new type theory" (Hofmann 1850, Williamson 1852, Gerhardt 1856, Kekulé 1857), which rose to prominence in the 1850s. Just as neutralization or addition reactions had formed the centerpiece of the dualistic system, so substitution reactions formed the centerpiece of the new type theory, which derived organic compounds from a series of simple inorganic hydrogen compounds or "types" (dihydrogen, water, ammonia, and methane) via the substitution of one or more of their hydrogen atoms either by organic radicals (e.g., CH_3-, C_2H_5-, C_2H_3O-, etc) or by other univalent inorganic atoms and radicals (e.g., the halogens, -OH, -NO_2, etc.).

The final stage came with the recognition of the stoichiometric valence concept, mentioned in the previous two sections, and its structural reinterpretation in terms of bond formation (Frankland, Williamson). This equating of valence with bond formation led, in turn, to a resolution of the various organic radicals into their individual atom-atom linkages via the concept of the tetravalent carbon atom and the hypothesis of carbon-carbon chain and ring formation (Couper 1858; Kekulé 1858, 1865). An overview of these progressive changes can be had by examining the various alternative "structural" formulas for sulfuric acid summarized below:



By the 1860s and early 1870s these changes had given rise to classical structure theory and to the formulation of several important principles for the determination of a molecule's bonding topology, including the principle of constant valence (Kekulé), the principle of least structural change (van't Hoff), and the principle of isomer counting (Körner).

Application of these principles led, in turn, to the discovery by the German chemist, Johannes Wislicenus, of a discrepancy between the number of known and predicted isomers for lactic acid and to his suggestion in 1869 that one had to expand the concept of molecular structure to include three-dimensional geometry as well as two-dimensional bonding connectivity. This suggestion was finally taken to heart by van't Hoff in 1874 with his hypothesis of the tetrahedral carbon atom (often incorrectly attributed to the French chemist, Joseph Le Bel, as well). This was followed by the hypotheses of the trigonal-pyramidal nitrogen atom (Hantzch,1890), and that of both square planar and octahedral metal atoms (Werner, 1893), thereby giving rise to classical stereochemistry (a term coined by Victor Meyer in 1890).

Both van't Hoff's tetrahedral carbon hypothesis and Le Bel's more general studies of chirality and net molecular shape also brought to prominence the earlier work of Pasteur (1848, 1860) on optical activity and molecular dissymmetry or chirality. Other important concepts of classical stereochemistry soon followed, including tension or strain theory (von Baeyer 1885), steric hindrance (Kehrmann 1888, Meyer 1894), conformational analysis (Sachse 1890), restricted bond rotation (Bischoff 1890), and the Walden inversion (Walden 1896).

In 1893 the Swiss chemist, Alfred Werner, combined data from the theory of ionic dissociation with the basic principles of classical stereochemistry and molecular chirality to create his coordination theory of complex inorganic compounds, as summarized in his 1905 monograph, *Neure Anschauungen auf dem Gebiete der anorganischen Chemie*, which finally gave inorganic chemistry an independent structural viewpoint. Rather than being organized around the concepts of homocatenated rings, chains, functional groups, and homologous series – ideas which had proven so fruitful in dealing with the structures of typical organic compounds – coordination theory introduced an entirely new set of structural concepts, including central atom, ligand, coordination number, and chelation – concepts which would prove of value in describing not only the structures of the discrete complex ions studied by Werner, but also the crystal structures of the nonmolecular inorganic solids soon to be uncovered by the advent of X-ray crystal analysis in the first few decades of the 20th century (see Section 14.9).

Our current method of writing structural formulas using bond lines to connect the various atomic symbols was proposed by both the Scottish chemist, Alexander Crum Brown, and the German chemist, Lothar Meyer, in 1864, though anticipated by Higgins in 1789. Three-dimensional molecular models were used as early as the first decade of the 19th century by Dalton and became increasingly common after the 1860s and the rise of structure theory. The most common forms corresponded to our current ball and stick models, though coordinated polyhedral models based on the sharing of the vertices, edges and faces of tetrahedra also had limited use after the introduction of van't Hoff's tetrahedral carbon hypothesis.

Just as purely compositional formulas proved inadequate to distinguish one organic compound from another, so the compositional nomenclature introduced by Lavoisier and his collaborators in the *Méthode* of 1787 proved inadequate as a naming system for organic chemistry, which clearly required some method of indicating molecular structure as well. Just how inadequate is illustrated by an amusing quote from Lavoisier's *Traité* of 1789 in which he naively suggested that just 10 combinations of the terms "hydrocarbon" and "oxide" would "suffice for indicating all the varieties [of organic plant materials] in nature." Little did he realize that by the end of the 19th century literally tens of thousands of organic compounds would be known and that by the end of the 20th century they would be numbered in the hundreds of thousands.

In lieu of an adequate structural theory, most organic compounds discovered during the first half of the 19th century were given arbitrary Greek- or Latin-based names suggested by some outstanding property of the compound in question or, more commonly, by the material from which the compound was first prepared or isolated (e.g., vinyl, from the Latin *vinum*, meaning "wine," or butyl, from the Latin *butyrum*, meaning "butter," etc.). However, by mid-century a number of chemists (Gerhardt 1853, Hofmann 1865) began suggesting methods of making these names more systematic based on the twin concepts of homologous series and functional groups, in which the dominant functional group was indicated by a suffix (e.g., propanol, propanal, propanone, etc.) and the compound's position in the corresponding homologous series by a numerical Latin or Greek prefix (e.g., pentane, hexane, heptane, etc.), though it was not until the

Geneva Congress of 1892 that these suggestions received formal international endorsement along with the practice of using numbers to indicate the positions of substitution on the underlying carbon chain or ring.

10.11 Chemical versus Physical Structure

Though we have described the events outlined in the last section as the discovery of "molecular structure" or constitution, this is not necessarily how the majority of 19th-century chemists initially viewed them. Rather they preferred to talk about the discovery of "chemical structure" – a term introduced in 1861 by the Russian chemist, Aleksandr Butlerov, and one which paralleled the distinctions between chemical versus physical elements and between chemical versus physical atoms, mentioned earlier. By this term, the 19th-century chemist meant to imply that his structural formulas were not intended to represent the actual physical structures of molecules, but rather to function as a symbolic summary of a given molecule's observed chemical behavior by rationalizing the various ways in which it could be decomposed – an interpretation of chemical formulas first advocated by the French chemist, Charles Gerhardt, in the 1840s. For this reason, early structural formulas were sometimes referred to as "rational" (i.e., rationalized) or "synoptic" (i.e., summarized) formulas.

A clear enunciation of this viewpoint was given by the American chemist, Ira Remsen, in the 1883 edition of his textbook, *Principles of Theoretical Chemistry*:

> *Constitutional formulas are those which suggest certain reactions and recall analogies. The formula* CH_3*-OH does not mean that hydroxyl (OH) is necessarily present in the compound, or that* CH_3 *is present, but that the different parts of the compound bear such relations to each other that when the compound is decomposed it acts as if the parts were united as the formula indicates. The formula suggests possibilities; it may not represent realities.*

This distinction between chemical and physical structure will strike the modern chemist as overly cautious. If a structural formula is consistent with everything that is known about the chemical behavior of a molecule, then there would seem to be nothing wrong with accepting the formula as a tentative model of the actual physical arrangement of the atoms in the molecule until evidence to the contrary comes to light. Finding examples where 19th-century chemists explicitly articulated their reasons for rejecting this "pragmatic realist" approach to structural formulas are hard to come by, but seem to revolve around two possible issues:

a. A belief that, in keeping with Newtonian mechanics, true physical molecules had to be dynamic in nature and involve the mutual and simultaneous, centro-symmetric, attraction of each atom for all of the other component atoms, as well as their rotation, like miniature solar systems, around some common center of gravity (Mendeleev 1871, Cooke 1880) – a picture totally unlike the static atoms and local, paired, directional bonds represented in structural formulas.

b. A belief that atoms were logical fictions, which, however convenient as an intellectual crutch when dealing with the facts of chemistry, should be eliminated from physical science if possible and replaced with less metaphysical concepts grounded in rigorous mathematics (Brodie 1866) and/or phenomenological thermodynamics (Helm 1894, Wald 1895, Ostwald 1895, Mach 1896, Duhem 1902).

Though a few of the chemists involved in the discovery of valence and molecular structure, such as Pasteur, Williamson, and Couper, accepted the pragmatic realist interpretation of structural formulas from the beginning, the vast majority, such as Kekulé, Frankland, Odling, and Crum Brown, professed to believe in the "structural agnosticism" of Gerhardt. However, with the discovery of the electrical structure of the atom and the rise of a newer generation of chemists exposed to the triumphs of van't Hoff's tetrahedral carbon atom and stereochemistry, serious opposition to both the atomic theory of matter and structural realism largely ceased after the first decade of the 20th century. Nevertheless, it is of interest to note that the most popular introductory college chemistry textbook in the United States in the period 1906-1925, by the British-American chemist, Alexander Smith, was still advocating the structural agnosticism of Gerhardt as late as 1912:

> *This illustration [of the various structural formulas for sulfur compounds] shows the sort of reasoning, based upon chemical properties and modes of formation of a substance, which lead us to the devising of an appropriate graphic or structural formula. The latter is not supposed in any sense to represent the actual physical structure of the molecule, but simply to be a diagrammatic representation of the chemical relations of the constituents and of the chemical behavior as a whole.*

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Lecture XI

The Nineteenth Century

(1801-1900)

Equilibrium, Thermodynamics, and Kinetics

Chemical theories grow more and more kinetic.

Lothar Meyer 1895

11.1 Chemical Affinity

With respect to the theory of chemical affinity, four important changes occurred during the 19th century:

a. The concept of an either/or elective affinity was replaced by that of a chemical equilibrium, and the dependence of the latter on such factors as concentrations, states, and temperature was fully articulated.

b. The static view of equilibrium as a balancing of Newtonian interparticle forces was replaced by a dynamic view of equilibrium as an equalization of the forward and reverse reaction rates.

c. The distinction between the thermodynamic and kinetic aspects of reactions was fully developed and the latter given a molecular interpretation in terms of collision frequencies and activation energies.

d. The relationship between chemical affinity, on the one hand, and such emerging topics as thermochemistry, electrochemistry, and photochemistry, on the other, was clarified and given a thermodynamic foundation.

11.2 Elective Affinity versus Equilibrium

The 18th-century concept of chemical affinity was based on the tacit assumption that it was "elective" so that, in the competition between substances B and C for a common reactant A:

$$C + AB \rightarrow AC + B \qquad [1]$$

the reactant A would "elect" to combine completely with either B or C but not with both, its choice depending on which had the greater affinity for A. In other words, it was assumed that the reaction went to completion in either the forward or reverse direction. Affinity tables were supposedly empirical summaries of how this selectivity varied with the chemical characters of B and C. Beginning about 1799, however, Berthollet began publishing a series of papers which showed that affinity orders were dependent not only on the inherent chemical characters of the reactants, but also on such factors as their concentrations, temperatures, and states – conclusions which he summarized in 1801 in his monograph *Recherches sur les lois de l'affinité*, and again, in greater detail, in his *Essai de statique chimique* of 1803.

Berthollet showed that most acid-base-salt reactions in solution were not only incomplete, but also reversible, and that the ability of a given species to compete for a common substrate depended both on its inherent affinity and its "quantity" (by which he meant the quantity in solution or the concentration). He coined the term "chemical action" or "intensity of action" to describe the product of these two factors:

chemical action of C = (quantity C)(affinity C) [2]

and postulated that the ratio of AC to AB formed in reaction 1 (which he called the degree of saturation of A with respect to C versus B) was directly proportional to the ratio of the chemical actions of C to B:

(AC formed)/(AB formed) =
(chemical action C)/(chemical action B) [3]

which, on substituting relation 2 and using our modern bracket symbolism for concentrations, gives:

$$[AC]/[AB] = [C](\text{affinity } C)/[B](\text{affinity } B) \qquad [4]$$

The modern chemist can better get his bearings if we shift the concentrations of B and C to the left side and represent the affinities of B and C as characteristic constants (k_B and k_C) for the substances in question. The result is, of course, our modern equilibrium expression for reaction 1:

$$[AC][B]/[AB][C] = k_C/k_B = K \qquad [5]$$

Unfortunately, Berthollet not only made use of ambiguous terminology (i.e. quantity and saturation rather than concentration), he also expressed his results verbally, rather than symbolically, as we have done above:

> *It results then from the preceding experiments ... that when a substance acts on a combination, the subject of the combination divides itself between the two others, not only in proportion to the energy of their respective affinities, but also in proportion to their quantities. Two substances which act on the combination ought to be considered as two antagonistic forces, which act in opposition while they act on, and share between them the subject of the combination in proportion to the intensity of their action; which intensity depends on the quantity of the substance, and on the energy of the affinity; so that the effect increases or diminishes according as the quantity increases or diminishes.*

Berthollet argued that when C was initially mixed with AB it had a high concentration and hence a large action which allowed it to effectively decompose AB. However, as the decomposition of AB proceeded, the concentration of free C decreased while that of the displaced B simultaneously increased, thus making C less and less effective in decomposing AB, and B more and more effective in decomposing AC. This competition would continue, he wrote, until the resulting "equilibrium of the contending forces ends the operation and limits the effect" (i.e., causes the reaction to stop before it goes to completion).

On the basis of relation 4, Berthollet recognized that reaction 1 could be driven to the left or right not only by selectively increasing the concentrations of C versus B, but also by any natural circumstance that effectively diminished the solution concentrations of one or more of the reactants or products, such as precipitation or gas formation. This further implied that an increase in temperature should shift the reaction equilibrium towards the side with the most volatile and/or least soluble species, whereas as a decrease in temperature should shift it in the opposite direction.

Berthollet's results not only called into question the data used to construct most 18th-century affinity tables, they also underscored the hopelessness of any future program that sought to reduce the known facts of chemical reactivity to a simple tabular summary, as separate columns were now required not only for each known reaction type, but also for each temperature and concentration variation. Despite this, most textbooks in the period 1810-1865 continued to discuss affinity in terms of both Fourcroy's laws (recall Section 7.3) and affinity tables, though this discussion was now qualified by a brief resume of Berthollet's results presented under the rubric of "factors which tend to modify the exercise of affinity."

One unfortunate by-product of Berthollet's rather ambiguous terminology was that the effects of concentrations on equilibria (and later on reaction rates as well) became known as the law of "mass action," rather than as the law of concentration action. After more than 200 years of use, this misleading descriptor is so firmly entrenched in the chemical literature that it would be virtually impossible to replace it with a more appropriate term. Such are the burdens of history and tradition.

11.3 Static versus Dynamic Equilibrium

The experiments which Berthollet cited in support of his laws were all qualitative and it was not until the 1850s that other chemists undertook the task of quantifying them (Margueritte 1854, Gladstone 1855, Malaguti 1857, Berthelot & Saint-Gilles 1862, etc.), the most ambitious attempt being the experimental program undertaken in 1864 by the Norwegian team of Cato Guldberg and Peter Waage. On the basis of more than 300 quantitative measurements on double displacement reactions of the type:

$$\mathrm{A} + \mathrm{B} \rightarrow \mathrm{A}' + \mathrm{B}' \qquad [6]$$

Guldberg and Waage mathematically reformulated Berthollet’s law of mass action and equilibrium as:

$$\alpha(p - x)^{a}(q - x)^{b} = \alpha'(p' + x)^{a'}(q' + x)^{b'} \qquad [7]$$

in which p and q were the initial concentrations of the reactants, p' and q' were the initial concentrations of the products, α, α', a, a', and b, b' were constants characteristic of the species in question, and x was the quantity of reaction at equilibrium.

Guldberg and Waage gave two possible interpretations to the mathematical products $\alpha(p - x)^{a}(q - x)^{b}$ and $\alpha'(p' + x)^{a'}(q' + x)^{b'}$ which appeared on each side of equation 7. The first, based on Berthollet’s original concept of “chemical action,” equated them with the “forces” of affinity in the forward and reverse directions, respectively:

$$f = \alpha(p - x)^{a}(q - x)^{b} \qquad [8]$$

$$f' = \alpha'(p' + x)^{a'}(q' + x)^{b'} \qquad [9]$$

and interpreted the equilibrium condition as a static balancing of these two opposing forces:

$$f = f' \quad \textit{(at equilibrium)} \qquad [10]$$

The second equated them with the velocities of the forward versus the reverse reactions, these velocities being directly proportional to the corresponding forces:

$$v = dx/dt = kf = k\alpha(p - x)^{a}(a - x)^{b} \qquad [11]$$

$$v' = dx'/dt = kf' = k\alpha'(p' + x)^{a'}(q + x)^{b'} \qquad [12]$$

and interpreted the equilibrium condition as a dynamic balancing of these two opposing velocities:

$$v = v' \quad (at\ equilibrium) \qquad [13]$$

Initially the work of Guldberg and Waage attracted little attention, though they presented their conclusions again in 1867 and yet a third time in 1879. As a consequence, van't Hoff unknowingly duplicated their dynamic interpretation of equilibrium as an equalization of the forward and reverse reaction rates in 1877. Indeed, this interpretation of Berthollet's equilibrium concept had been proposed in passing as early as 1857 by the Italian chemist, Faustino Malaguti, and was based, in turn, on recent developments in the newly emerging field of chemical kinetics.

11.4 The Rise of Chemical Kinetics

The first quantitative measurement of a reaction rate, aside from the misdirected efforts of Wenzel in the late 18th century, was given by the German physicist, Ludwig Wilhelmy, in 1850. Wilhelmy studied the rate of the acid-catalyzed conversion of optically active sucrose into an optically active mixture of glucose and fructose (i.e., the so-called inversion of cane sugar):

$$H_2O + C_{12}H_{22}O_{11} \rightarrow 2C_6H_{12}O_6 \qquad [14]$$

using a polarimeter and expressed his results in the form of a differential equation:

$$-dZ/dT = MZS \qquad [15]$$

where *Z* is the concentration of the sugar (*Zucker*), *S* is the concentration of acid (*Säure*), *T* is the time, and *M* is a rate constant. Wilhelmy's result was largely ignored by chemists, and it was not until the rate studies of the esterfication reaction by Marcellin Berthelot and Péan de Saint-Gilles in 1862, and of various redox reactions by the British team of Augustus Harcourt and William Esson in the period 1864-1867, that chemical kinetics began to truly emerge.

Since all of these studies showed that the rates of reactions were strongly dependent on the concentrations of the various reactants and products, their success depended on finding methods of determining the concentrations of the various species in solution without disturbing the reaction rate. The monitoring of concentration-dependent physical properties, using polarimetry or colorimetry, for example, was ideal for this purpose. If traditional chemical methods were used, it was necessary to "quench" the reaction or employ analytical procedures having reaction rates much greater than that of the reaction being studied.

By the 1880s sufficient kinetic data had been collected for van't Hoff to write the first monograph on the subject – his *Études de dynamic chimique* of 1884. Here, among other things, van't Hoff generalized the mass action law for reaction rates using the equation:

$$-dC/dt = kC^n \qquad [16]$$

and kinetically classified reactions for the first time as unimolecular, bimolecular, etc., based on the value of the exponent *n* in their rate laws.

As noted in Section 7.4, by the end of the 18th century Fourcroy had already distinguished between chemical stability, on the one hand, and ease of formation or speed of reaction, on the other, and had clearly identified chemical affinity with the former rather than the latter. Nevertheless, a number of phenomena were discovered in the late 18th and early 19th centuries which tended to blur these distinctions. Among these was the observation that the reactivity of gases often varied with their mode of preparation – behavior for which the term "nascent state" was coined (Priestley 1790) – and the observation that Pt metal and other solids could accelerate or even initiate chemical reactions by mere contact with the reactants – an observation that was soon extended to the effect of certain soluble substances, such as acids and organic ferments, on the rates of homogeneous solution reactions. Originally dubbed "contact action," these latter observations were eventually grouped together under the rubric of "catalysis" by Berzelius in 1835.

Though a variety of molecular interpretations were proposed for these observations throughout the century, and constitute our first known examples of reaction mechanisms, it was the work of Ostwald on catalysis, in the period 1883-1901, which finally – albeit unconsciously – brought Fourcroy's original distinctions back into focus. Using the laws of thermodynamics, Ostwald showed that catalysis was a kinetic rather than a thermodynamic phenomenon and, as such, could influence only the rate of reaction but not the final position of equilibrium. In other words, reaction kinetics and reaction thermodynamics were separate and distinct phenomena. In 1897 Ostwald formulated his "law of successive reactions" which stated that, in a given reaction system, the least stable of the possible alternative products are formed first and only later are they progressively transformed into thermodynamically more stable alternatives. This law had, in fact, been stated earlier by George Liveing (1885) and Gay-Lussac (1842), and was, of course, implied by Fourcroy's initial statement of 1783. Ostwald used the term "metastable" to describe these kinetically transient species, whereas Duhem preferred to characterize their formation as examples of "false equilibria."

11.5 Equilibrium and Thermochemistry

The caloric theory, which continued to dominate thermochemistry throughout the first half of the century, made two explicit predictions about heats of reaction:

a. Reactions involving a net increase in the number of liquids and/or gases should be endothermic and those involving a net decrease in the number of liquids and/or gases should be exothermic.

b. Dissociation reactions should be endothermic and association reactions should be exothermic.

Neither of these implied a necessary correlation between chemical affinity and heats of reaction. In the first case, the heats of reaction were interpreted as a measure of the change in the amount of combined caloric resulting from the various changes in state, whereas in the second case it reflected the idea that there was less free atomic surface area to bind caloric in the compound AB than in the separated atoms A and B. Indeed, within the context of the caloric theory, interpretation of calorimetric data was more an issue of chemical composition than one of chemical affinity.

Extensive calorimetric data on specific heats, heats of transition, and heats of reaction were collected in the period 1840-1854 by, among others, the Russian thermochemist, Germain Hess; the Irish chemist, Thomas Andrews; and the French team of Pierre Favre and Johann Silbermann. Though their results verified the law of constant heat summation implicitly used by Lavoisier and Laplace in the 1780s (Hess 1840), they also showed that both of the above predictions were incorrect. The most obvious exception to the first prediction was the ignition of gun powder, an example already known to Lavoisier, and Favre and Silbermann uncovered an apparent exception to the second in the exothermic dissociation of nitrogen oxide (NO).

Based on his theory of electrochemical dualism (see Section 11.7), Berzelius attempted to rationalize these exceptions. In keeping with Fourcroy's principle, both heat evolution and the intensity of chemical affinity were postulated to correlate with the difference in the electronegativities of the reacting atoms (which measured the degree of difference in their chemical character), rather than with changes in latent heat and atomic surface area. However, Berzelius failed to develop the calorimetric consequences of his theory in detail.

In 1853 a new era in thermochemistry was initiated when the Danish thermochemist, Hans Peter Jørgen Thomsen, in response to the newly established law of energy conservation, announced his postulate that heats of reaction were a measure of changes in the intramolecular potential energies of the atoms and hence a direct measure of their chemical affinities. In keeping with Berthollet's earlier rules about the modification of inherent affinities by such factors as changes in concentrations and state, Thomsen, who was fully aware of the existence of spontaneous endothermic reactions, was careful to restrict his "law of maximum work" to cases where these additional disturbing factors were kept constant. In other words, as Lothar Meyer pointed out in 1888, it was necessary to dissect the experimentally measured net heat of reaction (ΔH_{rx}) into the sum of the hypothetical changes in the chemical enthalpy (ΔH_{chem}) and the changes in the purely physical enthalpy (ΔH_{phy}):

$$\Delta H_{rx} = \Delta H_{chem} + \Delta H_{phy} \qquad [17]$$

as only the former was presumed to be a measure the resulting change in intramolecular bond strengths or chemical affinity.

Thomsen's extensive thermochemical investigations over the next three decades were summarized in his four-volume magnum opus, *Thermochemische Untersuchung*, published between 1882 and 1886. Essentially the same hypothesis was put forward by Berthelot in 1864, whose extensive thermochemical investigations were summarized in his *Essai de méchanique chimique fondée sur la thermochimie* of 1879 and his *Thermochimie: données et lois numériques* of 1897.

However, the key to unraveling the true relationship between heat and chemical affinity came, not through the application of the first law of thermodynamics, as advocated by Thomsen and Berthelot, but rather through the application of the second law of thermodynamics, first proposed by Clausius in 1850 and again by Lord Kelvin (William Thomson) in 1852. While the establishment of the law of mass action had been based largely on the experimental study of aqueous displacement reactions, the establishment of the relation between heat and chemical equilibrium was based largely on the experimental study of heterogeneous thermal dissociation reactions:

$$\text{heat} + Ca(CO_3)(s) \leftrightarrow CaO(s) + CO_2(g) \qquad [18]$$

$$\text{heat} + (NH_4)Cl(s) \leftrightarrow HCl(g) + NH_3(g) \qquad [19]$$

$$\text{heat} + PCl_5(s) \leftrightarrow PCl_3(g) + Cl_2(g) \qquad [20]$$

Though important results had been obtained as early as 1837 by the French chemist, Georg Aime, it was only with the systematic investigations of the French chemist, Henri Sainte-Claire Deville, and his associates in the years 1856-1865 that the true importance of these systems for the study of equilibrium became apparent. These studies, which Deville summarized in his *Lecons sur la dissociation* of 1864, and again in greater detail in his *Lecons sur l'affinite* of 1867, revealed that the equilibria for these reactions not only confirmed Berthollet's law of mass action, they also showed striking thermal effects which were analogous to those involved in the endothermic evaporation of liquids and seemed to support an underlying identity between the laws of chemical versus physical equilibria. In 1873 the German chemist, August Horstmann, applied Clausius' entropy formulation of the second law of thermodynamics (first introduced in 1865) to the study of these equilibria and, in so doing, laid the foundations for the field of modern chemical thermodynamics as distinct from those of the older field of thermochemistry.

According to the second law, the change in the entropy (dS) of an isolated system with respect to a spontaneous change (dx) within the system must be positive ($dS/dx > 0$) and reaches a maximum ($dS/dx = 0$) when the change in question comes to equilibrium. Horstmann wrote an equation for the change in the entropy (dS) of a dissociation reaction as a function of the degree of dissociation (dx), which, at equilibrium, became:

$$dS/dx = q/T - ARln(u/u_0) + C = 0 \qquad [21]$$

where q is the heat of reaction, T is the absolute temperature, R is the universal gas constant, A is the mechanical equivalent of heat, u is the concentration of a species at equilibrium, and$C$ is the entropy or "disgregation" of the species in its standard state or concentration u_0. Modern chemists, who are accustomed to discussing equilibrium in terms of the Gibbs free-energy function (ΔG), can better get their bearings if they substitute the following identities:

$$(dS/dx) = -(\Delta G/T), \; q = -\Delta H°, \; C = \Delta S°, \; Aln(u/u_0) = lnK \qquad [22]$$

which reveal the equivalence of Horstmann's result and ourmodern free-energy equation:

$$-\Delta G/T = -\Delta H^\circ/T - R\ln K + \Delta S^\circ = 0 \quad \text{or} \qquad [23]$$

$$\Delta G = \Delta H^\circ - T\Delta S^\circ + RT\ln K = 0 \qquad [24]$$

Horstmann's equation showed that, though the heat of reaction was but one factor involved in determining the magnitude of the equilibrium constant, it did play a key role in determining how that constant changed as a function of temperature – a result made more explicit by van't Hoff's famous "isochore" equation, first given in his *Etudes* of 1884:

$$d\ln K/dT = \Delta H^\circ/RT^2 \qquad [25]$$

In other words, increasing the temperature shifted the equilibrium in the endothermic direction, whereas decreasing the temperature shifted it in the exothermic direction. Shortly after van't Hoff's monograph appeared, the French chemist, Henri Le Chatelier(1884, 1888), and the German physicist, Karl Ferdinand Braun (1888), each independently subsumed this result, along with the earlier rules concerning mass action and pressure shifts, under the general law for equilibrium shifts which still bears their names:

If, to a system in equilibrium, a perturbation be applied, a change will take place in the equilibrium tending to moderate the effect of that perturbation.

Though Max Planck also used the total entropy change as the criterion for chemical equilibrium in his 1897 book, *Vorlesung über Thermodynamik*, and the British chemist, George Liveing, published a small volume on chemical equilibrium in 1885 based on Kelvin's interpretation of the second law in terms of energy dissipation, the entropy concept did not loom large in late 19th-century physical chemistry. The same is also true of the free-energy function or chemical potential introduced by Gibbs in 1875. Despite the fact that German and French translations of Gibbs' papers on heterogeneous equilibrium were published by Ostwald (1892) and Le Chatelier (1899), and that the physicists, Pierre Duhem and Johannes van Laar, each wrote books arguing for its use (1886, 1893, 1906), it would not be widely applied in chemical circles until the 1920s. Rather most late 19th-century chemists preferred to discuss the thermodynamics of chemical equilibrium in terms of the *Arbeit* or affinity (A) functions and osmotic pressure analogs advocated in the writings of van't Hoff and Nernst. Though mathematically equivalent to the functions of Horstmann and Gibbs, these approaches managed to completely disguise the role of entropy in chemical reactions (a situation made worse by varying sign conventions and multiple use of symbols):

van't Hoff: $-RT\ln K = A = \Delta H[(T_{equil} - T)/T_{equil}]$ [26]

Nernst: $-RT\ln K = A = U + T(dA/dT)$ [27]

11.6 Kinetics and Thermochemistry

Early kineticists also studied the temperature dependence of reaction rates and represented their results with empirical equations based on curve fitting. Indeed, Laidler, in reviewing the literature between 1850 and 1895, discovered no less than eight different equations relating rate constants and temperature. The eventual winner was proposed by van't Hoff in his *Études* of 1884. If the temperature dependence of the equilibrium constant, interpreted as the ratio of the forward and reverse rate constants ($K = k_f/k_r$), obeys equation 25, then the simplest possible equation for the temperature dependence of the individual rate constants must be of the form:

$d\ln k/dT = a/T^2 + b$ [28]

where the constant b is identical for both the forward and reverse reactions and the difference between the a constants for the forward and reverse reactions must be related to the net heat of reaction:

$$\Delta H_{net}/R \; = \; a_f - a_r \qquad [29]$$

In 1889 the Swedish chemist, Svante Arrhenius, suggested that the constant *b* in equation 28 could be set at zero by interpreting the *a* constant as the enthalpy (q) required to activate the reacting molecules. Integration of the simplified equation between the temperatures T_0 and T_1 and conversion to exponential form, gave the following relationship between the corresponding rate constants (k_0 and k_1):

$$k_1 \; = \; k_0 e^{q(T_1 - T_0)/(RT_1T_0)} \qquad [30]$$

Separation of this equation into the ratio of two equations of the form preferred by 20th-century kineticists:

$$k \; = \; Ae^{-E^*/RT} \qquad [31]$$

(where $-E^* = q$ and A is an empirical constant not to be confused with the *Arbeit* or affinity functions mentioned earlier) was first done for the differential form by van't Hoff in the second edition (1895) of his *Études*.

11.7 Equilibrium and Electrochemistry

In 1800, shortly after Volta's announcement of his discovery of the voltaic pile (recall Section 5.7), William Nicholson and Anthony Carlisle reported on its ability to decompose water, and William Cruckshank on its ability to decompose aqueous solutions of salts, acids, and alkalis. In addition to the initial question of the origin of the pile's electromotive force, these results raised the further question of the underlying mechanism by which the pile's electric current was able to chemically decompose various liquids and solutions.

It was the observations of the Italian physician, Luigi Galvani, in 1791 on the twitching of severed frog legs when in contact with various strips of metal that led to Volta's invention of the pile nine years later. Galvani had postulated that the electric force was derived from some residual nervous force present in the muscles of the frog legs, whereas Volta, whose invention of the pile had shown that living tissue was not required for the generation of electricity, believed instead it was due to the contact of the dissimilar metals used in the construction of the pile. However, as early as 1796, the German chemist, Johann Wilhelm Ritter, had shown that there was a correlation between the intensity of the electrical effects observed in Galvani's experiments and the chemical affinity of the metals strips for oxygen, thus implying that the electricity was the result, not of nervous force or mere metallic contact, but of a chemical reaction between the pile's various components.

These results initiated a flurry of electrochemical experimentation and speculation among British and European chemists during the first two decades of the century, and at least a half dozen different chemists proposed their own speculative theories of electrolysis and the relationship between electricity and chemical affinity – the most influential of which were those of Berzelius in Sweden and of Sir Humphry Davy in England. Though both men accepted Ritter's premise that the driving force of the pile was the result of a chemical reaction between its various components, and also assumed that there was a correlation between the chemical affinities of the various solution components and their ease of electrolysis, there were significant differences in how they viewed the underlying molecular mechanisms.

Davy, who threw out alternative hypotheses in rapid succession and whose true position is often difficult to determine, can be interpreted in some cases (1807, 1812) as having suggested that chemical affinity was the result of electrical attractions between opposite charges induced on the atoms when they came into physical contact, and that electrolytic decomposition was the result of the charged atoms or particles being more strongly attracted to the charged poles of the electrolysis cell than to each other:

> *In the present state of our knowledge, it would be useless to speculate on the remote cause of the electrical energy, or the reason why different bodies after being brought into contact should be found differently electrified; its relation to chemical affinity is, however, sufficiently evident. May it not be identical with it, and an essential*

property of matter? The coated glass plates of Beccaria strongly adhere to each other when oppositely charged, and retain their charges on being separated. This fact affords a distinct analogy to the subject; different particles on combining must still be supposed to preserve their particular states of energy.

Berzelius, on the other hand, assumed that the atoms and molecules of matter already contained unequal amounts of positive and negative electrical fluid prior to combining and that these were concentrated at opposite poles on their particles. Particles attracted to the negative wire during electrolysis had an excess of positive over negative fluid whereas those attracted to the positive wire had an excess of negative over positive fluid. When atoms combined to form molecules, their oppositely charged electrical fluids reacted with one another to form free caloric and the residual unneutralized electrical fluids then redistributed themselves at opposite poles of the product molecules:

... in all chemical combinations there is a neutralization of opposing electricities, and this neutralization produces fire in the same manner that it produces it in the discharge of the electric jar, the electric pile, and thunder, without being accompanied in these latter phenomena, by chemical combination.

In other words, the electrical charges, which were destroyed on combination, accounted not for the bonding between the particles, as in Davy's theory, but rather for the heat that was evolved when they reacted. Electrolysis reversed compound formation by restoring the electrical fluids to the levels found in the atoms prior to combination.

Berzelius took the excess of negative over positive fluid to be a measure of a given atom's "unipolarity" or "electronegativity" (1811) and, following the earlier work of Avogadro (1809), attempted to arrange all of the then known chemical elements in a continuous "electrochemical" series, with the most electronegative (oxygen) at the top and the most electropositive (potassium) at the bottom. This was in many ways a relic of the affinity tables popular in the 18th century, since the resulting electronegativity scale was, in effect, measuring the relative affinities of the various atoms for the two electrical fluids.

According to Berzelius, the greater the difference in the electronegativities of the reacting atoms, the greater their chemical affinity and the greater the heat evolution produced when their oppositely charged fluids combined. However, as already noted in Section 11.5, though these assumptions implied a direct correlation between affinity and heats of reaction, Berzelius never quantitatively followed up their thermochemical implications. Instead, he applied his theory to the classification and naming of chemical compounds and to establishing restrictions on what atoms and groups could displace one another in chemical reactions.

Our modern electrochemical vocabulary (ion, cation, anion, electrode, cathode, anode, electrolyte, etc.) is largely due to Faraday, whose extensive electrochemical studies in the period 1833-1840 uncovered the first quantitative laws of electrolysis (see next section) and did much to disentangle which chemical effects were dependent on the current and which were dependent on the voltage – issues that were thoroughly confused by Berzelius. The increasing inability of Berzelius' theory to account for the facts of organic chemistry led to a decline in electrochemical speculations among chemists in the period 1840-1880, and much of the work in the field during this period was done instead by physicists – most notably by the Germans, Wilhelm Hittorf and Friedrich Kohlrausch, who developed and refined the measurement of ionic conductivities.

Despite these advances, however, two major questions continued to haunt 19th-century electrochemistry:

a. What did the ions responsible for electrolyte conductivity correspond to at the molecular level and were they created by the applied voltage in the electrolysis cell or did they preexist in the electrolyte before the voltage was applied?

b. What was the mechanism by which the electrodes were provided with a continuous supply of ions during the course of the electrolysis?

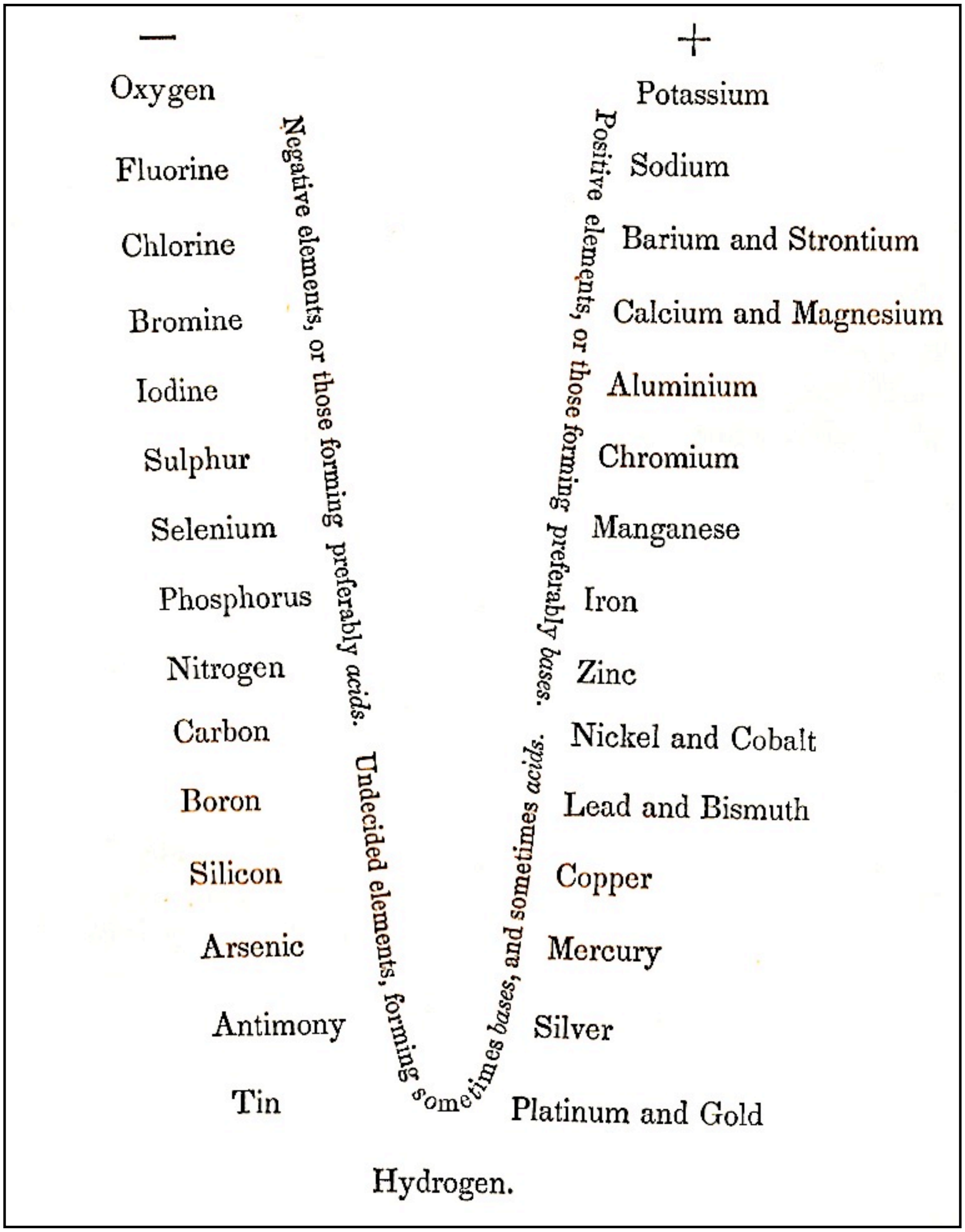

Plate IV

Berzelius's electronegativity scale as presented in the English translation of J. Stöckhardt's 1850 textbook, *Principles of Chemistry*.

The answer to the first question changed with time. During the first half of the century it was generally assumed that the cation and anion corresponded to the electropositive and electronegative oxides of the dualistic system, in which copper sulfate, for example, was represented as CuO^+, SO_3^-. However, in 1844 the English chemists, John Daniell and William Miller, presented electrochemical evidence suggesting that Cu^{2+} and SO_4^{2-} were the true ionic components and, after the rise of type theory and structure theory in the period 1855-1865, this became the common mode of representation. Though assumed to preexist within the electrolyte molecules prior to electrolysis, in neither case were the ions assumed to be free or dissociated prior to the application of the cell voltage.

During the first half of the century, the answer to the second of these questions was based on the so-called "chain theory" of electrolysis, first proposed by the German chemist, Theodore Grotthuss, in 1805 – a theory which illustrates how difficult it was to imagine a viable molecular reaction mechanism within the context of the static Newtonian model of solids, liquids, and gases popular at the time. According to Grotthuss, the molecules of the solute (AB) were polarized into positive and negative parts (A^+B^-) by the applied voltage of the electrolysis cell. This applied voltage also caused the polarized molecules to aligned themselves in a continuous chain between the positive and negative electrodes, with the positive ends of the molecules pointing toward the negative electrode and the negative ends of the molecules pointing towards the positive electrode:

(-) electrode: A^+B^- A^+B^- A^+B^- A^+B^- A^+B^- A^+B^- A^+B^- :(+) electrode

The (+) end of the molecule closest to the negative electrode and the (-) end of the molecule closest to the positive electrode then gave up their electrical fluids to the electrodes in question thereby forming neutral reaction products which escaped from the solution:

(-) electrode: A B^- A^+B^- A^+B^- A^+B^- A^+B^- A^+B^- A^+ B :(+) electrode

The remaining halves of these molecules than reacted with the adjacent molecules in the chain causing an exchange of (+) and (-)

parts which propagated down the chain, thus creating a new chain in which the (+) and (-) parts were reversed with regard to the wires:

(-) electrode: B^-A^+ B^-A^+ B^-A^+ B^-A^+ B^-A^+ B^-A^+ :(+) electrode

These new molecules than rotated in order to realign their (+) and (-) ends with the oppositely charged electrodes and the entire process repeated itself. Presumably the continuous insertion into the chain of fresh molecules from the surrounding solution allowed it to maintain the proper length as the electrolysis proceeded.

In 1857 Clausius applied the new kinetic theory of matter to the phenomenon of electrolysis. He pointed out that the fluctuations in the kinetic energies of the colliding electrolyte molecules would occasionally result in their dissociation into free ions, and that collision of these free ions with other neutral electrolyte molecules would lead to ion displacement and thus to a net random movement of the ions through the solution. Eventually, however, oppositely charged ions would collide with one another and recombine to once again form a neutral electrolyte molecule. In other words, in an electrolyte solution at a given temperature there was a dynamic equilibrium which maintained a small but characteristic population of free ions. Application of a voltage to an electrolysis cell did not create the free ions, rather it caused a net drift of the randomly colliding ions in the direction of the oppositely charged electrodes.

The work of Arrhenius in 1884 revealed that the molar conductivities of most electrolyte solutions increased with dilution, suggesting that the degree of ionic dissociation (defined as the molar conductivity at the concentration in question, divided by the molar conductivity at infinite dilution) also increased – a result in keeping with Clausius' dynamic model of free ion formation, but one that led to the shocking conclusion that, in very dilute solutions, not just a few, but virtually all of the electrolyte molecules were dissociated into free ions. In 1887 Arrhenius showed that the degrees of ionic dissociation calculated from his conductivity studies correlated with both those calculated from van't Hoff's recently proposed theory of osmotic pressure and those calculated from Raoult's law for freezing point depression. Yet additional evidence for free ions was provided by the additive nature of the heats of neutralization, specific volumes, conductivities, and molar refractivities of salt solutions.

The full implications of the resulting "theory of ionic dissociation," as it came to be called, for the law of mass action and for the traditional methods of wet analysis were, as already noted in the last lecture, worked out by Ostwald in his 1894 textbook, *Die wissenschaftlichen Grundlagen der analytischen Chemie*, where he explicitly pointed out the necessity, in the writing of rate laws and equilibrium constants for electrolyte systems, of treating each ion as an independent species.

With the discovery of the law of conservation of energy it became apparent that voltaic cells and electrolysis cells were devices forthe mutual interconversion of chemical energy and electrical energy:

$$\textit{chemical energy} \leftrightarrow \textit{electrical energy} \tag{32}$$

and by the 1850s the flawed molecular models of Davy and Berzelius had been replaced by the proposition that the chemical affinity of the reaction in an electrochemical cell correlated in some manner with the cell's electrical potential. Thermodynamic treatments of cell potentials by Helmholtz (1847) and Lord Kelvin (1851), based on the first law of thermodynamics, further suggested that this potential difference ($\mathscr{E}$) should also correlate with the heat or enthalpy of the cell reaction:

$$\mathscr{E} = f(\Delta H) \tag{33}$$

However, experimental work by, among others, Raoult in 1865 and Favre in the period 1866-1871 showed that this was incorrect, and, in the last quarter of the century, fresh thermodynamic treatments (Gibbs 1878, Helmholtz 1882, van't Hoff 1884) based on the second law, rather than the first law, revealed that cell potentials should instead correlate with the free-energy or *Arbeit* of the chemical reaction:

$$\mathscr{E} = f(A) \qquad [34]$$

The final step was taken by Nernst in the period 1888-1889 when he related the cell potential to the osmotic pressures (π) of the cell reactants and ultimately to the equilibrium constant of the cell reaction itself:

$$\mathscr{E} = A/zF = (RT/zF)ln(\Pi\pi_p{}^{\nu}/\Pi\pi_r{}^{\nu}) = (RT/zF)lnK \qquad [35]$$

The quantification of redox potentials based on half-cell reactions at inert electrodes was first undertaken by the American physical chemist, Wilder D. Bancroft, in 1892, though he failed to find the concentration dependency predicted by Nernst. In 1897 Nernst further suggested the use of the hydrogen electrode as the zero-point standard for reporting cell potentials. This proposal was experimentally implemented by Wilsmore in 1900, who determined the hydrogen-scale half-cell potentials for 31 elements, and was also adopted by the first reference work dealing with the tabulation of cell potentials, the 1911 publication,*Messungen elektromotorischer Kräfte galvanischer Ketter mit wässerigen Elektrolyten*, edited by Abegg, Auerbach and Luther.

11.8 Kinetics and Electrochemistry

One of the few kinetic results of electrochemical interest obtained during the 19th century was Faraday's law of electrolysis, though it is not apparent that its status as a kinetic law was fully appreciated at the time. First stated nonmathematically by Faraday in 1834, and independently by the Italian chemist, Carlo Matteucci, in 1835, it was traditionally broken into two separate laws:

a. The chemical power of a current of electricity is in direct proportion to the absolute quantity of electricity which passes.

b. The masses of different substances liberated by the same quantity of electricity are proportional to their chemical equivalent weights.

but is usually written today in the form of a single equation:

$$it = zFN \quad [36]$$

in which i is the electrical current, t is the time, N is the moles of product formed, z is the moles of electrons required per mole product, and F is the number of coulombs per mole of electrons. This is, in fact, the integrated form of the rate equation:

$$i = zF(dN/dt) \quad [37]$$

relating the absolute rate of the electrolytic reaction to the applied current and which applies equally well to the rate of reaction in a voltaic cell.

11.9 Kinetics and Photochemistry

The ability of certain colors of light to selectively induce certain kinds of chemical reactions was well known by end of the 18th century, and by 1835 Fiedler was able to document more than 45 known photochemical reactions (both inorganic and organic). In 1817 Grotthuss put forward the law that only the fraction of light that was actually absorbed, rather than reflected or transmitted, was active in inducing chemical reactions. This was made more explicit by Malaguti in 1839, when he noted that the total photochemical effect was proportional to the product of the absorbed light intensity (I) and the time of exposure (t):

$$It = \textit{total photochemical effect} \quad [38]$$

a formulation which is essentially the photochemical equivalent of Faraday's first law of electrolysis.

The distinction between the kinetic and thermodynamic aspects of photochemical reactions was first stated by Helmholtz in 1847 when he observed that, from an energetic viewpoint, photochemical reactions could be classified into two groups: those in which the light served merely to initiate a sluggish, but otherwise spontaneous energy-releasing reaction (e.g., the reaction between H_2 and Cl_2), and those in which the light served to drive an otherwise non-spontaneous energy-absorbing reaction (e.g., the decomposition of the silver halides).

In 1855 the German physicist, W. C. Wittwer, published the first explicit photochemical rate law for the photochemical decomposition of chlorine water:

$$-dc/dt = kcI \qquad [39]$$

where c is the concentration of the dissolved chlorine, t is the time, I is the light intensity, and k is a rate constant. When integrated, this equation explicitly incorporated Malaguti's earlier law:

$$ln(c_0/c) = kIt \qquad [40]$$

Extensive experimental work on photochemical reactions was conducted by the British-American chemist, John Draper, in the years 1841-1851, and by the German-English team of Robert Bunsen and Henry Roscoe in the period 1855-1867, which largely verified these earlier generalizations. In 1893 Nernst pointed out that Wittwer's original result was a special case the generalized rate equation:

$$v = kc_1^{n_1}c_2^{n_2} \ldots k'c_1^{n_1'}c_2^{n_2'} \qquad [41]$$

in which it was assumed that:

... the velocity coefficients k and k' depend upon the intensity of light, and ... that, for the same kind of light, the changes of these coefficients follow in proportion to the intensity of the light.

In other words, it was equivalent to the assumption that:

$$k = f(I) \qquad [42]$$

Nernst further noted that, since the intensity of the absorbed light decreased as it penetrated a solution, the values of the rate constants for photochemical reactions would also vary with depth or spatial position.

Despite these advances, 19th-century photochemistry wasnever successful in providing a convincing molecular mechanism for the interaction of light and matter, and it was not until the 20th century and the development of quantum mechanics and the photonconcept that this became possible.

11.10 Molecular Motion and Chemical Reactivity

One of the problems with the original formulation of the law of mass action, in both its equilibrium and kinetic forms, was that it was difficult to imagine an underlying molecular mechanism for concentration shifts, using the prevailing static Newtonian model of matter, that did not also have compositional consequences – a difficulty that was noted earlier in connection with the mechanism for electrolysis. Thus, if A was attracted to B with a force of 3 and to C with a force of 2, then the only way C could take A away from B, via mass action, would be to form the compound AC_2 in which two C particles worked in unison to overcome the attraction of A for a single B particle. However, if, via mass action, C removed A from its combination with another particle D, which was attracted to A with a force of 5, then it would require at least three C particles working in unison and would result instead in the formation of the compound AC_3. Thus the stoichiometry of the compound formed between A and C would vary with the circumstances of its formation.

In other words, the only molecular explanation for mass action within the context of a static Newtonian model was that an increase in concentration changed, not the frequency of collision among the reactants, as in our current kinetic model, but rather the number of particles simultaneously attracting a given reactant and thus the composition of the resulting product. This picture was apparently consistent with Berthollet's interpretation of solutions as compounds of variable composition, but presented problems for those chemists who accepted Proust's interpretation and the law of definite proportions (recall Section 10.6).

The first suggestion of a possible mechanism for mass action not involving such consequences appears in the writings of the British chemist, Alexander Williamson. In several papers published in the years 1850-1851, Williamson suggested that the analogous parts (whether atoms or radicals) of neighboring molecules were continuously exchanging places with one another at a rate that varied inversely with their bond strengths. In a pure substance, AB, all of the neighbors were identical and the system looked exactly the same before and after the exchange of A and B among the neighbors. However, in a binary mixture of two different molecules, AB and CD, the fraction of the exchanges producing AD and CB rather than reproducing AB and CD would obviously increase as more and more of the molecules adjacent to a given AB molecule corresponded to CD rather than AB. In other words, the amount of AD and CB formed would increase as the concentration of CD was increased and visa versa as the amount of AB was increased. Though this model invoked a limited kind of molecular motion (atom or radical exchange between nearest neighbors) and explained mass action without recourse to changes in stoichiometry, Williamson's mechanism had little in common with either the mechanical theory of heat or the kinetic theory of gases then coming into vogue.

The first truly kinetic rationale of a chemically relevant process was given by Clausius in 1857 for the evaporation of liquids. He viewed the vapor pressure characteristic of a liquid at a given temperature as the result of a dynamic equilibrium between the number of molecules escaping from the liquid surface per unit time and area, on the one hand, and the number of molecules captured by the liquid surface from the surrounding vapor per unit time and area, on the other. Since the kinetic theory of gases predicted that an equilibrium collection of molecules always displayed a distribution of kinetic energy values rather than a single fixed value, only a certain fraction of the liquid molecules had sufficiently high energy to escape the liquid surface at a given temperature and only a fraction of the gaseous molecules had sufficiently low energy to be recaptured by the liquid surface. Increasing the temperature shifted these fractions in favor of evaporation and lowering the temperature shifted them in favor of condensation. Likewise, removal of vapor at constant temperature decreased the frequency of collision of the gas molecules with the surface and shifted the equilibrium in favor of evaporation, whereas addition of vapor increased the frequency of collision and shifted the equilibrium in favor of condensation.

In 1867 the Austrian chemist and physicist, Leopold Pfaundler, wrote a long paper in which he applied these principles to the effects of temperature and mass action on chemical equilibria in the cases of both hetero- and homogeneous thermal dissociation reactions (as well as single and double displacement reactions), thus predating Horstmann's purely thermodynamic rationale of these reactions by almost six years. In each case, the reactions were viewed as a dynamic equilibrium involving an equalization of the forward and reverse reaction rates, each of which was characterized by a critical reaction energy determined by the nature of the reactants, and a characteristic collision frequency determined by their concentrations and surface areas. Changing the temperature changed the reaction rates by changing both the collision frequencies and the fraction of molecules having the necessary critical energy to react, whereas changing the concentrations changed the rates by changing the collision frequencies only. Pfaundler also discussed the formation of transient collision complexes whose mode of decomposition determined whether a given collision resulted in the formation of products or in a simple rebound of the initial reactants, as well as how these alternative outcomes depended on the momentary conversion of the translational energies of the colliding molecules into the internal vibrational energies of the complex.

Though Pfaundler's exposition was nonmathematical, it obviously contained all of the basic elements of our modern molecular view of chemical reactions, including Arrhenius' later concept of activation. Unfortunately, though his ideas were briefly mentioned in several advanced textbooks published during the last quarter of the century (e.g. Naumann 1882, van't Hoff 1884, Pattison Muir 1884, Ostwald 1886), very little managed to filter down to the level of the average introductory chemistry textbook and, by the time chemists began quantifying this kinetic molecular model of reaction rates and equilibria in the second decade of the 20th century, Pfaundler's pioneering work was largely forgotten.

11.11 Reaction Stoichiometry

In volume I of his *A New System of Chemistry* (1808) Dalton translated Lavoisier's principle of the conservation of chemical elements in chemical reactions (recall Section 7.5) into the principle of the conservation of chemical atoms in chemical reactions:

> *Chemical analysis and synthesis go no further than to the separation of particles one from another and to their reunion. No new creation or destruction of matter is within the reach of chemical agency. We might as well attempt to introduce a new galaxy into the solar system, or to annihilate one already in existence; as to create or destroy a particle of hydrogen. All changes we can produce consist in separating particles that are in a state of cohesion or combination, and joining those that were previously at a distance.*

Affinity diagrams continued to be used to represent chemical reactions well into the 1860s, though the hypothetical numerical affinity estimates were soon replaced by numerical equivalent weight values instead (Lee 1833). Starting in the 1840s, more and more examples of linear chemical equations using Berzelius' symbolism began to appear (Fownes 1847), and by the 1870s they had largely displaced the older and more cumbersome diagrams. It has been argued that this switch from diagrams to linear equations reflects a change in emphasis from the inequality of Newtonian forces of affinity to the conservation of Daltonian atomic and/or equivalent weights in chemical reactions.

By the late 1820s separate monographs dealing with chemical calculations, based on balanced chemical equations, began to appear (Ehrmann 1829, Buff 1829, Kühn 1837) and the term "stoichiometry" – first coined by Richter in 1792 – began to come into general use to describe this numerical aspect of chemical reactivity. In 1878 the English chemist, James Bottomley, proposed a rigorous algebraic method for balancing chemical equations, essentially identical to the modern method of material balance.

The replacement of the equal sign in linear chemical equations with double arrows to indicate a reversible equilibrium was first introduced by van't Hoff in his *Études de dynamic chimique* of 1884, though a related proposal using a flattened "**z**" was made by Ostwald in 1894, and the use of a double barb was first suggested by Marshall in 1902. The use of a single arrow for irreversible reactions soon followed. In 1859 Cooke introduced the practice of indicating the physical states of the reactants and products in a balanced equation by printing the formulas of gases, liquids, and solids in different font styles. The current practice of indicating states by appending an abbreviation in parentheses after the formula gradually evolved out of the 19th-century thermochemical literature (Berthelot 1879, Naumann 1882) and appears to have reached its present form in the writings of G. N. Lewis in connection with his quantification of chemical thermodynamics in the early decades of the 20th century, as indicated by its use in his 1923 text with Randall (see Section 15.3).

11.12 Conclusion

By the last decade of the 19th-century, the triumph of the statistically based kinetic approach to chemical and physical phenomena over the older 18th-century static Newtonian equilibrium approach was complete – so much so that the German chemist, Lothar Meyer, in the 1895 edition of his textbook, *Outlines of Theoretical Chemistry*, not only felt compelled to explicitly comment on this "kinetic" trend, as seen in the quote at the beginning of this lecture, but was also willing to predict the impending demise of the Newtonian interparticle force concept as well:

> *... although, partly from habit and partly from want of a better expedient, the existence of an attractive force between the atoms is frequently used in explaining chemical phenomena, this only happens in the conviction that this hypothetical affinity is merely an expression of the real, though imperfectly known, cause of the internal cohesion of chemical compounds.*

As we will see in Lecture XIV, the discovery of that "imperfectly known cause of the internal cohesion of chemical compounds," will rank as one of the great achievements of 20th-century chemistry.

11.13 Selected References

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Lecture XII

The Twentieth Century

(1901-2000)

Specialization Rampant

> So large a proportion of everything scientific that has ever occurred is happening now, within living memory. To put it another way, using any reasonable definition of a scientist, we can say that 80 to 90 percent of all the scientists that ever lived are alive now.
>
> *Derek J. de Solla Price 1966*

12.1 Chemical Education

Most 20th-century trends in professionalization are continuations of those already established in the 19th century. In what follows, we will focus primarily on the changes in the American chemical community, for which the most data are available. However, similar changes, usually scaled down in accord with population demographics, are also to be found for the chemical communities of Great Britain and most other major European countries.

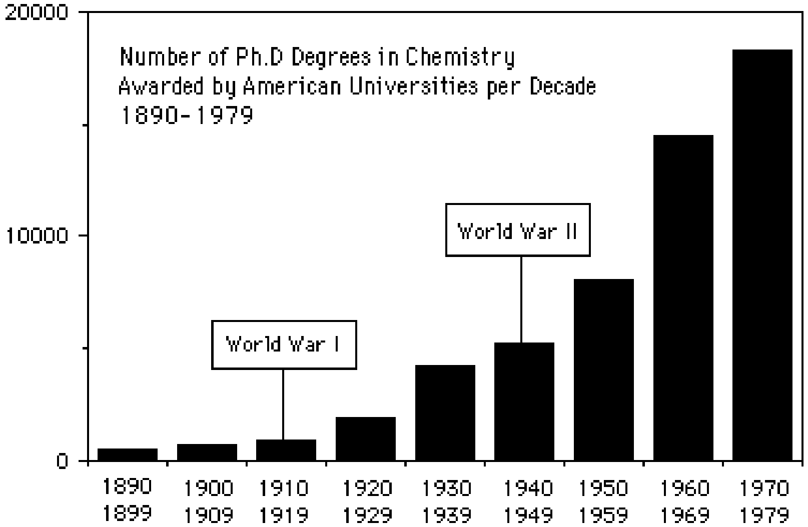
As noted in Lecture VIII, prior to World War I, both undergraduate and graduate degrees in chemistry were available at only a few larger American universities and colleges, and the majority of chemists seeking training at the doctoral level did so in Germany. Most smaller colleges offered only one year of introductory chemistry at the undergraduate level. World War I broke the educational connection with Germany, as well as cutting off supplies of much needed German dyes and pharmaceuticals. Although American industry was already the world leader in heavy chemicals, such as iron, sulfuric acid, alkalis, etc., and made minimal use of analytical chemists, it had no fine chemical industry based on the skills of synthetic organic chemists with advanced research training. The resulting drive to develop its own independent fine chemical industry (based in part on confiscated German patents) also gave the needed impetus for the development of both undergraduate and graduate level chemical education in the United States. The educational link with Germany was not renewed after the war. Instead, the period between 1914 and the outbreak of World War II in 1939 saw the establishment of complete undergraduate curricula in chemistry at essentially all American colleges, however small, and the establishment of graduate programs at essentially all of the larger universities.

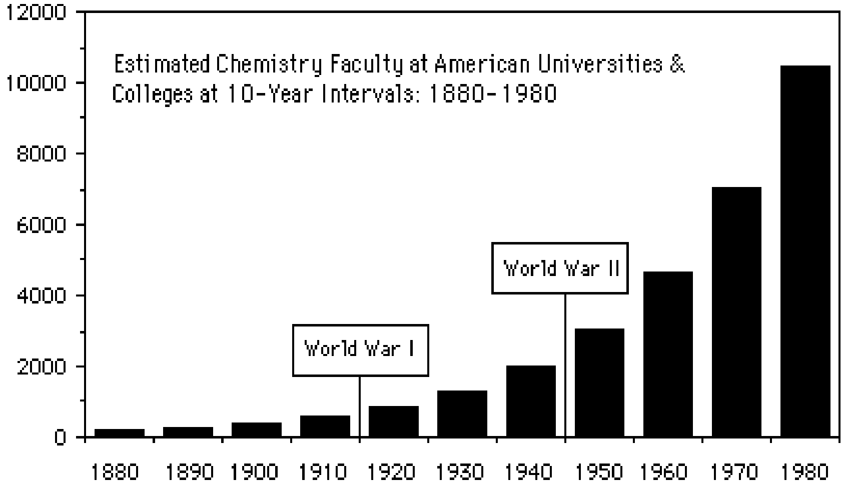
After World War II, the developing cold war and the ensuing arms and space race with the Soviet Union resulted in an unprecedented infusion of government money into university research programs and led to a corresponding growth of graduate programs in chemistry. At most large universities the number of faculty involved in graduate education and research now far outnumbers those engaged in undergraduate education and, in some cases, these institutions have developed an explicit two-tier faculty system. The influx of government research money and overhead now forms a substantial portion of the annual income of many universities and has resulted in increasing administrative pressure on the faculty to "publish or perish." In more recent years, it has also led to an increasing incidence of scientific fraud, especially in the field of medical research.

Some quantitative indications of the growth of 20th-century academic chemistry in United States are provided by the graphs on the following page, which show the number of doctoral degrees in chemistry conferred per decade by American universities from 1890-1979 and the estimated number of chemistry faculty at 10-year intervals from 1880-1980. Both plots are approximately exponential, though the data on degrees shows a slight discontinuity following World War I, as might be expected from the above discussion.

12.2 Professional Organizations

The trend toward ever-greater specialization already noted for the 19th century continued unabated throughout the 20th century. Though only analytical chemistry had evolved its own separate professional organizations by the end of the 19th century, the 20th century saw an ever-increasing number of such organizations, especially in the case of industry related specialities, such as electro-





chemistry and chemical engineering, as shown in Table 12.1 on the following page.

In order to avoid loss of membership to these specialty organizations, national chemical societies also began establishing subdivisions or groups devoted to various specialties as the century progressed. Thus, in 1908 the American Chemical Society adopted its first divisional structure consisting of specialized sections for industrial and engineering chemistry, agricultural and food chemistry, fertilizer and soil chemistry, organic chemistry, and inorganic and physical chemistry. As shown in Table 12.2, the society now has more than 34 divisions, encompassing such diverse areas as chemical education, history of chemistry, and computers in chemistry.

Table 12.1 Specialist Chemical Societies in the United States

Organization	*Year Established*
American Water Works Association	1881
Association of Official Analytical Chemists	1884
Society of Chemical Industry, American Section	1894
American Society for Testing Materials	1898
American Ceramics Society	1899
Electrochemical Society	1902
American Leather Chemists Society	1903
American Society of Biological Chemists	1906
American Institute of Chemical Engineers	1908
American Oil Chemists Society	1909
American Association of Cereal Chemists	1915
Societé de Chimie Industrielle, American Section	1918
American Association of Textile Chemists and Colorists	1921
Association of Consulting Chemists and Chemical Engineers	1928
American Society of Brewing Chemists	1934
American Microchemical Society	1935
Association of Analytical Chemists	1941
Association of Vitamin Chemists	1943
Society of Cosmetic Chemists	1945
American Association for Clinical Chemistry	1948
Histochemical Society	1950
Coblentz Society (Molecular Spectroscopy)	1954
Geochemical Society	1955
Society of Flavor Chemists	1959
Phytochemical Society of North American	1960
Catalysis Society of North American	1966
American Society of Neurochemistry	1969

Table 12.2 Specialty Divisions in the American Chemical Society

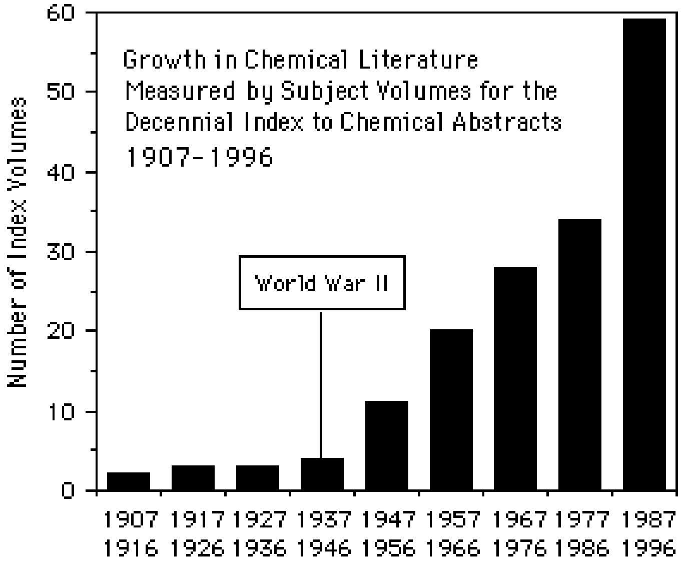
Division	*Year Established*
Industrial and Engineering Chemistry	1908
Agriculture and Food Chemistry	1908
Fertilizer and Soil Chemistry	1908
Organic Chemistry	1908
Physical and Inorganic Chemistry	1908
Medical Chemistry	1909
Rubber	1909
Biological Chemistry	1913
Environmental Chemistry	1913
Carbohydrate Chemistry	1919
Cellulose, Paper, and Textile	1919
Dye Chemistry	1919
Leather and Gelatine Chemistry	1919
Chemical Education	1921
History of Chemistry	1921
Fuel Chemistry	1922
Petroleum Chemistry	1922
Organic Coatings and Plastics Chemistry	1923
Colloid and Surface Chemistry	1926
Analytical Chemistry	1936
Chemical Information	1948
Polymer Chemistry	1950
Chemical Marketing and Economics	1952
Inorganic Chemistry	1956
Microbial and Biochemical Technology	1961
Fluorine Chemistry	1963
Nuclear Chemistry and Technology	1963
Pesticide Chemistry	1969
Professional Relations	1972
Computers in Chemistry	1974
Chemical Health and Safety	1977
Geochemistry	1978
Small Chemical Business	1978
Chemistry and the Law	1982

12.3 Chemical Literature

As we saw in Lecture VIII, the 19th century saw the establishment of separate journals for the fields of analytical, physical, inorganic, physiological, agricultural, and industrial chemistry. In the 20th century both the number of independent journals devoted to each speciality and the degree of specialization increase. Currently we not only have journals devoted to analytical or organic chemistry in general, but to individual instrumental procedures (e.g., *Journal of Chromatography, International Journal of Mass Spectroscopy, Atomic Spectroscopy*, etc.) and individual classes of compounds (e.g., *Journal of Heterocyclic Chemistry, Organometallics*, etc.), as well as to various subsubdisplines, such as colloid and surface chemistry, polymer chemistry, solid-state chemistry, materials science, etc., etc.

As of 2000 the ACS estimates that, world-wide, there are 66 journals devoted to analytical chemistry, 37 to inorganic and nuclear chemistry, 48 to organic chemistry, 90 to physical chemistry, 295 to biochemistry, and 110 to chemical engineering. These numbers do not include the large number of journals devoted to interdisciplinary areas with a heavy chemical component, such as medicinal chemistry, agricultural chemistry, food science, toxicology, materials science, etc. Starting with only the *Journal of the American Chemical Society* in 1879, the American Chemical Society alone now publishes more than 36 separate journals, including *Chemical Abstracts*, and the latter annually abstracts 8000 technical journals containing articles deemed of interest to the chemical community.

As a rough indicator of the growth of the chemical literature during the 20th century, the following graph shows the number of volumes devoted to the subject index of the decennial index of *Chemical Abstracts* from 1907 to 1996. Note the discontinuity following World War II, indicating the sudden increase in government support of academic research, though some of this increase is also accounted for by the publication of wartime research which was initially postponed either because of other priorities or because it was originally classified.



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Lecture XIII

The Twentieth Century

(1901-2000)

The Instrumentation Revolution

> Nothing tends so much to the advancement of knowledge as the application of a new instrument. The native intellectual powers of men in different times are not so much the causes of the different success of their labors, as the peculiar nature of the means and artificial resources in their possession.
>
> *Sir Humphry Davy 1812*

13.1 General Laboratory Handbooks

By the end of the 19th-century chemistry had outgrown the single-volume comprehensive monograph on laboratory apparatus and techniques, and by 1900 this form of literature had been largely displaced by elementary laboratory manuals, on the one hand, and by massive multivolume specialty handbooks dealing with advanced laboratory techniques and apparatus, on the other (see Table 13.1 at the top of next page). The first of these trends was driven by the introduction of undergraduate university laboratory courses during the latter part of the 19th century, and the second by the rise, during this same period, of well-defined subdisciplines within chemistry itself, including analytical, organic, inorganic, physical, and biochemistry (recall Lecture VIII).

13.2 Energy Sources (Thermal)

If the greatest advance in laboratory heat sources in the 19th century was the displacement of the charcoal furnace by the laboratory gas burner, so the greatest 20th-century advance was the perfection of electrical laboratory heat sources, including hot plates, heating mantels, heating tape, and baths and ovens of various types.

Table 13.1 20th-Century Handbooks Dealing with Laboratory Practice

Date	*Editor*	*Title (Volumes)*
1906-1910	Abderhalden	*Handbuch der Biochemischen Arbeitsmethoden* (9 vols)
1913-1925	Stahler	*Arbeitsmethoden in der anorganischen Chemie* (5 vols)
1921-1924	Houben-Weyl	*Die Methoden der organischen Chemie* (4 vols)
1945-1969	Weissberger	*Technique of Organic Chemistry* (14 vols)
1959-1980	Kolthoff-Elving	*Treatise on Analytical Chemistry* (33 vols)

The first British patent for an electric furnace was granted to William Siemans in 1878, and mention has already been made (Section 9.2) of Henri Moissan's carbon arc furnace of 1892. Though a number of electric laboratory heating devices were available by the end of the 19th century, they were of limited value because of the relatively short life spans of their heating elements – a problem that was finally solved with the introduction of inexpensive and durable chromel (a Ni-Cr alloy) heating elements by the American chemical engineer, Albert Marsh, in 1906.

The 20th century also saw the gradual displacement of the mercury thermometer by the thermocouple and the resistance thermometer, again due in part to the replacement of their expensive platinum metal components by such alloys as chromel and alumel (Marsh 1905) and, more recently by the replacement of bulky recording charts and deflection meters with compact liquid-crystal digital displays.

13.3 Energy Sources (Electrical)

The most important 20th-century developments in electronics, all of which ultimately impacted on chemical instrumentation, include the following:

a. Advances in the modulation, rectification and amplification of electrical signals (the diode vacuum tube: Fleming 1904; the triode vacuum tube: De Forest 1907; the transistor: Shockley et al. 1948,**1952**).

b. The miniaturization of electronic circuits (printed circuits; integrated circuits: Kilby & Noyce:1959, **1962**).

c. Advances in the electronic storage and processing of information (micro-processor: **1971**; the personal computer: **1975**, **1977**).

d. Advances in the display of electronically processed information (cathode-ray tube: Dieckmann 1906, light emitting diodes: 1962, liquid crystal displays: Hoffman-La Roche 1971).

13.4 Energy Sources (Electromagnetic)

The 19th-century photochemist and spectroscopist had to rely on sunlight and, to a lesser degree, on luminous flames, as their principle light sources. The first practical electric light bulbs were invented in 1879 by Edison in the United States and by Swan in Great Britain and, by the early 20th century, both electrical UV (Hg arc lamp: Hewitt 1902, UV lamp: 1904) and IR sources were also available. Of far greater importance, however, was the development of the maser (Townes et al 1954) and the laser (Maiman, 1960), which provided the chemist with high intensity sources of coherent, monochromatic, electromagnetic radiation.

As noted in Section 9.4, prior to the 20th century, most devices for measuring light intensities and quantities depended either on the human eye (split-field optical photometers) or on photography. However, in 1904 Elster and Geitel introduced the first practical UV-visible sensitive phototube and by the 1920s IR-sensitive photocells were also available. A further increase in sensitivity occurred with the introduction of the commercial photomultiplier tube around 1940. As a consequence, starting in the late 1920s, electronic detection, in combination with the advances in the processing of electrical signals noted in the previous section, began to gradually replace the older visual and photographic methods, and, by the 1960s even such traditional 19th-century optical instruments as the refractometer and polarimeter had been adapted to automated electronic detection and readout.

13.5 Energy Sources (Radioactivity)

With the discovery of the radioactivity of uranium (Becquerel 1896), thorium (Curie 1898), radium (Curie 1898), polonium (Curie 1898), actinium (Debierne 1899), and radon (Dorn 1900), the chemist and physicist were presented with yet another natural energy source.

Early methods of measuring radioactivity included photography (Becquerel 1896) and the rate of discharge of a charged electroscope (Curie 1898). Building on work begun in 1908 with Rutherford, Geiger and Müller developed the first successful electronic counter in 1928 based on radiation induced electrical discharges inside a low pressure, high-voltage vacuum tube. In their famous gold foil experiments of 1908 Geiger and Rutherford had also used visual counting of the light scintillations on a ZnS screen to estimate relative radiation intensities, and in 1947 Kallman was able automate this technique by using advances in the technology of photomultiplier tubes to develop the first commercial electronic scintillation counter.

Early radiochemists were restricted to the study of naturally occurring radioelements and their decay products. They soon made use of the fact that the resulting radioactivity could be used to trace the path of these elements through a series of conventional chemical reactions and separations even when they were present in extremely minute quantities (Curie 1898). In 1913 Hevesy and Paneth reversed this process by purposely adding the radioactive isotope of an element to a chemical system in order to monitor the chemistry of its corresponding nonradioactive isotopes or carriers, thus giving birth to the technique of radioactive tracer or indicator analysis.

The development of the cyclotron by Lawrence in 1931 gave classical radiochemistry a new lease on life. The ability to make thousands of artificial radioactive isotopes allowed chemists to extend the tracer technique to almost every element of the periodic table and also resulted in a new method of chemical analysis (activation analysis 1946). Beginning with the synthesis of neptunium in 1940, the cyclotron also resulted in the synthesis of more than 25 artificial elements and in a significant extension of the periodic table.

13.6 General Apparatus

As noted in Section 9.5, the problem of reducing the breakage of laboratory glassware due to thermal stress was partially solved in the 19th century via the introduction of flasks, beakers, and retorts made of thin-walled Bohemian glass. A much better solution was found in the 1880s by the German glass chemist, Otto Schott, with his discovery of the low thermal-expansion borosilicate glasses. Initially used to make glass shades and lens for oil and gas lamps, as well as thermometers, borosilicate laboratory glassware began to appear in laboratory supply catalogs in the closing years of the 19th-century under the trade name of Jena glass.

By 1918 at least six brands of borosilicate laboratory glassware were being offered for sale in the United States, including – in addition to Jena glass – Fry, Nonsol, Libbey, Macbeth-Evans and Pyrex glass. In a comparative study published that year by the National Bureau of Standards, the Pyrex brand produced by Corning Glass received the highest rating for its resistance to chemical corrosion, thermal stress, and mechanical breakage, and, as a result, eventually came to dominate the market. Other improvements in glassware included the commercial introduction of fused-silica (quartz) ware (Schott 1900, Vitreosil 1903) for high-temperature work and sintered glass filters and bubblers (Schott 1924).

The use of ground-glass stoppers dates back to the 17th-century distillation literature (French 1651), and in the 18th century Priestley also described the use of ground glass joints in connection with his pneumatic apparatus. However, every stopper or joint was a unique custom fit and if one part was broken the other half was useless. It was not until 1926 that J. Friedrichs introduced the concept of interchangeable standard-taper glass joints, which give this type of apparatus the same modular interchangeability as corks or rubber stoppers. By the 1930s a small selection of standard-taper Pyrex glassware was available in most laboratory supply catalogs, and by the 1960s this type of connector had largely displaced cork and rubber for research purposes, though it was not until the late 1970s that it began to find its way into the undergraduate organic laboratory.

In addition to the traditional laboratory materials (glass, ceramics, metal, rubber, wood, and cork), the 20th century also saw the gradual encroachment, especially since the 1950s, of various plastics and synthetic polymers, including teflon (used primarily for stopcocks and stirring bars), polypropylene (used for flexible tubing), and polyethylene (used primarily for stoppers, bottles, graduated cylinders, and nonheatable flasks and beakers). Besides diminishing losses due to breakage, these materials have proved valuable when working with substances that aggressively corrode glass, including strong alkalies and anhydrous fluorides.

The traditional analytical balance also underwent extensive changes during the 20th century, including the introduction of the chainomatic method of adjusting the fractional milligram weights (Becker 1916), mechanical key or dial weight changers covering the $1\text{-}10^{-4}$ gram range, air dampers, magnetic dampers, and optically extended pointers. Though many of these innovations had been suggested in the late 19th century, they did not become common until the mid-1930s. An even more radical departure from traditional balance design came with the introduction of the single-pan substitution balance by Mettler in 1946. More recently, both mechanical mass compensation (via addition or removal of weights) and visual readout by means of the spatial displacement of a mechanical or optical pointer have been largely replaced by electrical and/or magnetic compensation, on the one hand, and by pzeoelectric detection and electrical readout systems, on the other. Again, though some of these principles were selectively applied to balance design as early as 1916, it is only since the late 1970s that they have become commonplace (Sartorius 1977, Mettler 1978).

13.7 Separation Techniques

As we saw in Section 9.6, continuously acting solid-liquid and liquid-liquid extractors, such as the Soxhlet and Schwarz extractors, were being used by the end of the 19th century. However, they suffered from a number of limitations:

a. They operated at relatively high temperatures (required for the evaporation and recirculation of the extracting solvent) and consequently caused problems when working with temperature-sensitive complex biomolecules.

b. They did not completely resolve complex mixtures into their various components, but rather separated them into only two groups: those that were soluble versus those that were insoluble in the extracting solvent.

c. They were relatively large scale (of the order of 50 mL or more) thus restricting their use when dealing with micro-quantities of the substances of interest.

In an attempt to deal with the first two of these limitations, biochemists and organic chemists began to develop semi-automated, multi-stage counter-current liquid-liquid extraction trains, the most famous of which was the Craig extractor (1949, 1951). These devices, which mechanically mimicked repeated extractions using a conventional separatory funnel, were quite large, often occupying an entire bench top, and had to be rocked back and forth by hand or with a timed electric motor in order to move the extract from one separation stage to the next. Depending on the number of cells in the extraction train (between 25 and 200), it could take up to 20 hours to move a sample through the entire system.

A recognition that the components of a liquid solution could be separated via their selective adsorption on a suitable solid, such as filter paper, dates back to the 19th century (Runge 1850, Schönbein 1861). This simple technique was first systematized around the turn of the 20th century under the rubric of "capillary analysis" by the Swiss chemist, Friedrich Goppelsröder, who made it the subject of at least five monographs published between 1901 and 1910. An independent variation of this technique using powdered adsorbents and continuous eludation of the adsorbed sample by the pure solvent was first applied to the analysis of plant pigments by the

Russian botanist, Mikhail Tswett, starting around 1903. Since his separations produced bright bands of color on the adsorbent, Tswett coined the term "chromatography" (from the Greek*chroma*, meaning "color" and *graphein*, meaning "to write") to describe his separation technique.

Initially ignored, like Goppelsröder's earlier work, chromatography did not begin to seriously impact on biochemical and organic practice until the 1930s, after which its growth became exponential. Since then, countless variations and extensions of the technique have been developed, of which the following is only a partial listing:

1. adsorption chromatography (Tswett 1903, Kuhn & Lederer1931)
2. ion exchange chromatography (Taylor & Urey 1938, **1940s**)
3. thin-layer chromatography (Izmailov & Shraiber 1938)
4. partition chromatography (Martin & Synge 1941)
5. displacement chromatography (Tiselius 1940)
6. gas chromatography (James & Martin 1952, **1955**)
7. gel chromatography (Porath & Flordin 1959)
8. high-pressure liquid chromatography (Hamilton 1940, **1961**)
9. affinity chromatography (Cuatrecasas *et al* 1968)

Like the Craig countercurrent extractor, chromatography can separate the components of a complex mixture without thermal degradation. In contrast, however, it is far easier to use and is readily adapted to micro-separations if necessary.

As noted in Section 9.11, elementary mathematical treatments of the separation process in the cases of solid-liquid, liquid-liquid, and liquid-gas systems had already appeared by end of the 19th century. In particular, the mathematical theory of fractional distillation, known as "plate theory," continued to attract the attention of chemical engineers and was made the subject of detailed studies by Kuenen in Holland (1906) and by W. K. Lewis (1909) in the United States, who also applied it to industrial-level countercurrent liquid-liquid extraction processes (1916). In 1922 the American chemical engineer, W. A. Peters, introduced the concept of the "height of an equivalent theoretical plate" or HETP as a measure of column efficiency in fractional distillation, and in 1935 Thiele applied it to liquid-liquid extraction. Finally, in 1941, Martin and Synge, recognizing that their newly developed technique of liquid-liquid chromatography was, in effect, an example of a continuous counter-current liquid-liquid extraction process, applied HETP theory to the chromatographic processes for the first time.

Both classical macro separation processes and their chromatographic analogs are based on the use of phase transfers driven by concentration gradients. The recognition that other kinds of gradients could also be used to drive separation processes came with the development of the ultra-centrifuge (Svedberg 1923), which made use of a gravitational gradient, and the technique of electrophoresis (Tiselius 1930), which made use of an electrical potential gradient.

A significant advance involving the much more traditional separation technique of evaporation was also made by Craig in 1950 with the introduction of the rotary vacuum film evaporator or rotavap. This device allowed for the rapid and efficient evaporation of solutions containing thermally sensitive organic and biochemical solutes by combining large surface areas for evaporation, produced by the solution film on the inside of the rotating flask, with low ambient vapor pressures, produced by the vacuum pump, and supplemented, when necessary, by moderate heating provided by a hot water bath. Both massive drum evaporators and vacuum evaporators were used by chemical engineers long before Craig proposed his apparatus, but it was his genius to combine both principles into a single, scaled-down, practical laboratory device.

Though textbooks and monographs dealing with all of the above individual separation techniques appeared at regular intervals throughout the century, by the early 1960s there was an increasing tendency to merge all of these methods together under the common label of "separation science" (Table 13.2). Now recognized as an official subdiscipline of analytical chemistry, separation science is currently the subject of at least a half dozen independent journals (with at least another half dozen devoted to chromatography alone) and has also been given its own unified theoretical basis (Giddings 1991).

Table 13.2 Early Textbooks Dealing with Separation Science

Date	*Author*	*Title*
1963	Berg	*Physical and Chemical Methods of Separation*
1964	Morris & Morris	*Separation Methods in Biochemistry*
1971	King	*Separation Processes*
1973	Karger et al.	*An Introduction to Separation Science*

13.8 Characterization Techniques (Molecular Composition)

Major 20th-century developments in characterization techniques reflected a number of underlying trends:

a. The progressive miniaturization of classical chemical methods.

b. A growing concern with the underlying theory of the analytical process.

c. A movement away from destructive chemical techniques towards nondestructive physical or so-called instrumental techniques.

Indicative of the first trend was the development of organic micro-combustion analysis by the Austrian chemist, Fritz Pregl, as summarized in his 1917 monograph, *Die quantitative organische Mikroanalyse*, and the development of qualitative spot analysis by the Austrian chemist, Fritz Feigl, as summarized in his 1931 monograph, *Qualitative Analyse mit Hilfe von Tüpfel-reactionen*, as well as its later extension under the guise of ring-furnace analysis (Weisz 1954).

In keeping with the second trend, and following the lead set by Ostwald's volume of 1894 (recall Section 9.11), numerous specialist monographs exploring the physical chemistry behind the techniques of classical qualitative, quantitative, and volumetric analysis began to appear (Table 13.3). This trend was also reflected in the undergraduate textbooks dealing with these subjects as more and more space was devoted to the theoretical background rather than to the actual laboratory procedures – a trend personified in the title of Louis Hammett's 1929 manual of qualitative analysis, *Solutions of Electrolytes*.

Table 13.3 Early Monographs on the Theory of Classical Chemical Analysis

Date	*Author*	*Title*
1910	Chesneau	*Theoretical Principles of the Methods of Analytical Chemistry*
1915	Bjerrum	*Theorie der Alkalimetrischen und Azidimetrischen Titrierungen*
1917	Prideaux	*The Theory and Use of Indicators*
1920	Kolthoff	*Der Gebrausch von Farbenindicatoren*
1929	Smith	*Analytical Processes: A Physico-Chemical Interpretation*

An explicit understanding of the theory underlying classical analytical procedures also led to practical advances as well, especially in the case of volumetric analysis. The theory of acid-base titration curves and indicator end points was worked out in some detail early in the century as evidenced by the monographs by Bjerrum, Prideaux and Kolthoff listed in the above table. This work, when combined with insights from coordination theory, showed that sharp endpoints were possible for these reactions because the neutralization process occurred in a single step. In other words, the $H^+(aq)$ ion, in contrast to most hexa- or tetracoordinate aqueous metal ions, was monocoordinate and could thus be saturated using a single monodentate ligand or base. By the 1940s these insights had led to the design of various polydentate ligands, such as ethylenediaminetetraacetic acid or EDTA, and to the discovery of a number of metallochromic dyes or indicators which allowed one to extend traditional acid-base titration techniques to the determination of aqueous metal ions in general. The Swiss chemist, Gerold Schwarzenbach, was particularly prominent in the development of this technique, which he first summarized in his 1955 monograph, *Die komplexometrische Titration*.

Indicative of the third trend was the refinement and diversification of various traditional optical, spectroscopic, and electroanalytical procedures in conjunction with significant advances in the electronics of signal detection, amplification, and processing as described in Sections 13.3-13.4.

Generally speaking, photometric or spectroscopic methods involve the determination of chemical character (μ) and/or concentration (c), as a function of absorbed and/or emitted wavelength (λ) and light intensity (I). Important 20th-century compositional spectroscopic techniques include:

1. solution absorption spectrophotometry (Berg 1911, **1925**)
2. flame emission photometry (Lundegardh 1928, **1936**)
3. atomic or flame absorption spectroscopy (Walsh 1955, **1957**)
4. X-ray fluorescence spectroscopy (Moseley 1913, **1948**)
5. electron-probe spectroscopy (Castaing & Guinier 1949)

As we saw in Section 9.7, solution absorption spectrophotometry was essentially a late 19th-century development. As a consequence, it was also the first spectroscopic method to benefit from 20th-century advances in electronics, when, in 1911, Berg first replaced the split-field visual photometer with photocells. By the late 1920s solution spectrophotometers using photocells were being commercially manufactured, though, in the case of simple colorimeters, the traditional split-field visual instrument of Duboscq remained popular until the 1950s.

Likewise, modern flame emission spectroscopy represents the successful quantification of classical qualitative 19th-century flame spectroscopy (recall Section 9.7) – an advance made possible by improved methods of sample atomization and flame control and the use of photographic detection. The technique was first summarized in detail in Henrik Lundegardh's classic two-volume monograph of 1929-1934, *Die Quantitative Spektralanalyse der Elemente*.

X-ray spectroscopy and its various derivatives (electron-probe spectroscopy, etc) are based on the characteristic excitation of core electrons, and are, in many ways, the example *par excellence* of a nondestructive instrumental method for compositional analysis. First used by Moseley in 1913 to establish the atomic number concept, the X-ray technique was applied to the qualitative analysis of minerals by Hadding in 1922 and played a significant role in the discovery of the element hafnium by Coster and von Hevesy the next year. The method was first summarized in monograph form in Manne Siegbahn's 1924 book, *Spekroskopie der Rontgenstrahlen*. The first commercial X-ray secondary emission spectrometer was built in 1948 (Friedman and Birks) and the first electron-probe instrument in 1949 (Castaing and Guinier).

Electrometric methods involve the determination of chemical character (μ) and/or concentration (c) as a function of either electrochemical potential ($\mathscr{E}$), current (i), specific conductivity ($\varkappa$), and/or time (t). The older technique of electrogravimetric analysis (recall Section 9.7) is usually excluded from the class of electrometric methods because the analytically determined parameter (mass of electroplated metal) for this technique does not correspond to one of the above electrochemical variables. The most important 20th-century electrometric methods include:

1. potentiometry ($\mathscr{E}$ versus c)
2. conductometry ($\varkappa$ versus c)
3. voltammetry ($\mathscr{E}$ versus i)
4 amperometry (i versus c)
5 coulometry (i versus t)

The first potentiometric titrations were carried out in the last years of the 19th century (Behrend 1893, Böttger 1897, Crotogino 1900) and the technique was first summarized in Erich Müller's 1921 monograph, *Elektrometrische Massanalyse*. One of the most important applications of potentiometric techniques involves the measurement of hydrogen ion concentrations or pH – a concept introduced by the Danish biochemist, Søren Sørensen, in 1909. Sørensen made use of a standard Pt/H_2 electrode for this purpose. The same year Haber and Klemensiewicz began their study of the glass electrode and, by the 1930s, advances in electronics had made possible the development of the compact commercial electronic pH meter (Beckman 1935).

The first conductometric titrations were carried out by Küster and Grüters in 1903, and the technique was first summarized in book form by Izaak Kolthoff in his 1923 monograph, *Konduktometrische Titrationen*.

The most important voltammetric procedures include polarography and cyclic voltammetry. Polarography measures the potential-current curves due to electrolysis at a dropping mercury electrode. Developed by the Czech chemist, Jaroslav Heyrovsky, in the period 1922-1925, the technique was first summarized in book form in 1932 by Semerano in his monograph, *Polarography: Its Theory and Applications* (in Italian) and soon after by Heyrovsky himself in his 1933 monograph, *Applications of Polarography in Practical Chemistry* (in Czech).

Though the first amperometric titration was carried out in 1897 by Salomen, it was not until 1939 that Kolthoff and Pan began to systematically evaluate the analytical potential of the method and coined its current name. It was first summarized in monograph form as a chapter in the second edition (1941) of the book *pH and Electro Titrations*, by Kolthoff and Laitinen.

For the first four decades of the century much of the electronic circuitry for electrometric measurements was large scale and modular, consisting of individually purchased resistance boxes, Wheatstone bridges, slide resistors, voltmeters, and galvanometers strung together with wire and powered by dry cells. However, as early as 1925 Heyrovsky had boxed the necessary components for polarography into a single instrument and, beginning in the late 1930s and 1940s, advances in electronics made it easier and easier, as in the case of the pH meter, to package and sell the various techniques as self-inclusive instruments.

13.9 Characterization Techniques (Molecular Weights)

The most important 20th-century extensions of methods for the determination of molecular weights include:

1. counter-pressure osmometry (Berkeley & Hartley 1907, Duclaux *et al* 1911)
2. viscosity measurements (Biltz 1913, 1916)
3. sedimentation rates (the ultacentrifuge: Svedberg 1923, 1925)

4. end-group analysis (Staudinger *et al* 1925)
5. light scattering measurements (Debye 1944, Doty *et al* 1944)
6. mass spectrometry (Thomson 1913, Aston 1919, **1954**)

The first five of these methods were developed in conjunction with the study of macromolecules, both natural and synthetic, since the more traditional techniques, discussed in Section 9.9, are largely restricted to the study of small to moderate sized molecules. Thus, for example, most macromolecules cannot be vaporized forpurposes of a gas density determination, and the freezing-point depression and boiling-point elevation methods often result in the denaturation of delicate biomolecules, or are limited by the low molar solubilities of the macromolecules in question.

First developed by the British physicist, Francis Aston, in 1919, based on J. J. Thomson's earlier positive-ray technique (1913),mass spectroscopy was originally limited to monoatomic species and initially played an important role in the development of the isotope concept and in the determination of accurate atomic weights. Prior to the Second World War, most instruments were one of a kind devices built and operated by a few specialists in the United States and Great Britain. The significance of the technique to the wartime atomic bomb program and to the subsequent postwar development of atomic energy resulted in a massive infusion of government funding and by 1954 at least three companies (General Electric, Consolidated Engineering, and Process Industries) were manufacturing commercial mass spectrometers. Since then, improvements in sample vaporization and ionization methods have extended its range to include not only discrete molecules, but macromolecules as well, and the accurate measurement of ionization energies and the systematic study of fragmentation patterns have resulted in an ability to obtain, not just molecular weights, but also significant compositional and structural data.

The origins of the technique were first summarized in J. J. Thomson's 1913 monograph, *Rays of Positive Electricity and their Application to Chemical Analysis*, and its subsequent application to isotope analysis in Aston's 1924 volume, *Isotopes*, and its various revisions (1933, 1942). One of the first monographs to include a discussion of its potential applications to the analysis of molecular composition and structure was the 1952 volume, *Methoden und Anwendungen der Massenspektroskopie*, by Ewald and Hintenberger.

13.10 Characterization Techniques (Molecular Structure)

By the turn of the 20th century hundreds of thousands of organic compounds had been prepared and characterized. When properly classified in terms of their functional groups and relative positions within a given homologous series, this vast array of compounds formed an impressive interlocking system which greatly facilitated the identification and characterization of any newly discovered compounds. By the first decade of the century, these consequences had resulted in the development of a systematic scheme for the rapid characterization of organic compounds whereby the position of a compound within this vast organizational array could be determined by means of a series of quick qualitative tests based on its solubility in various solvents, certain characteristic functional group reactions, the preparation of various derivatives, and the determination of melting points. Largely the work of the American chemist, Samuel Mulliken, whose massive four-volume reference work, *A Method for the Identification of Pure Organic Compounds*, was published between 1905 and 1922, and the German chemist, Hans Meyer, whose monograph, *Analyse und Konstitutions-Ermittlung organischer Verbindungen*, first appeared in 1903, qualitative organic analysis or functional group analysis, as it came to be known, had become a standard university course for organic chemists by the 1920s and continued to be taught through the 1960s, when it was gradually displaced by newer instrumental methods of analysis.

The most important of these newer 20th-century instrumental methods for the determination of molecular and bulk-phase structure include:

1. parachor measurements (Sugden 1924)
2. UV - visible spectroscopy (Hartley 1879, **1941**)
3. IR spectroscopy (Coblentz 1905,**1942**; Fourier transform IR **1963**)
4. Raman spectroscopy (Raman, 1928, **1950**)

5. NMR spectroscopy (Purcell, Bloch 1945, **1949**)
6. ESR spectroscopy (Zavoisky 1945)
7. X-ray photoelectron spectroscopy or ESCA (Siegbahn *et al* 1958, **1969**)
8. X-ray structure analysis (von Laue, Bragg & Bragg 1912; **1920s**)

The parachor, which measures the molecular volume of a liquid at constant surface tension, rather than at the boiling point, as in Kopp's earlier technique, was first introduced in 1924 by the British chemist, Samuel Sugden, as a candidate for a constitutive molecular property which could be partitioned, like refractivity and atomic volume (recall Section 9.10), among the various component atoms and bonds and thus serve as a method for selecting the most probable of several competing isomeric structures consistent with a given absolute compositional formula. Summarized by Sugden in his 1930 monograph, *The Parachor and Valency*, the technique, though important in its time, was largely displaced by the rise of structural absorption spectroscopy and NMR in the late 1940s and early 1950s.

Following Hartley's pioneering work of 1879, progress in the field of structural UV spectroscopy was slow. Most instruments were custom built and data collection tedious. Nevertheless, by 1929 the Swiss spectroscopist, Victor Henri, was able to tabulate the UV-visible spectra of nearly 200 organic compounds for inclusion in the first edition of the *International Critical Tables*, and by 1951 Friedel and Orchin were able to provide a similar tabulation of the UV-visible spectra of 579 aromatic compounds. Rapid acceleration in the use of the technique occurred with the introduction in 1941 of the first commercial electronic UV-visible spectrophotometer – the Beckman DU. With this event, the technique ceased to be largely the province of specialists in spectroscopy and began to be applied as a routine characterization technique by practicing organic chemists, as reflected in a 1965 survey, which showed that it was used in between 20% and 25% of all chemical papers published in American journals between 1952 and 1964 (see Plates).

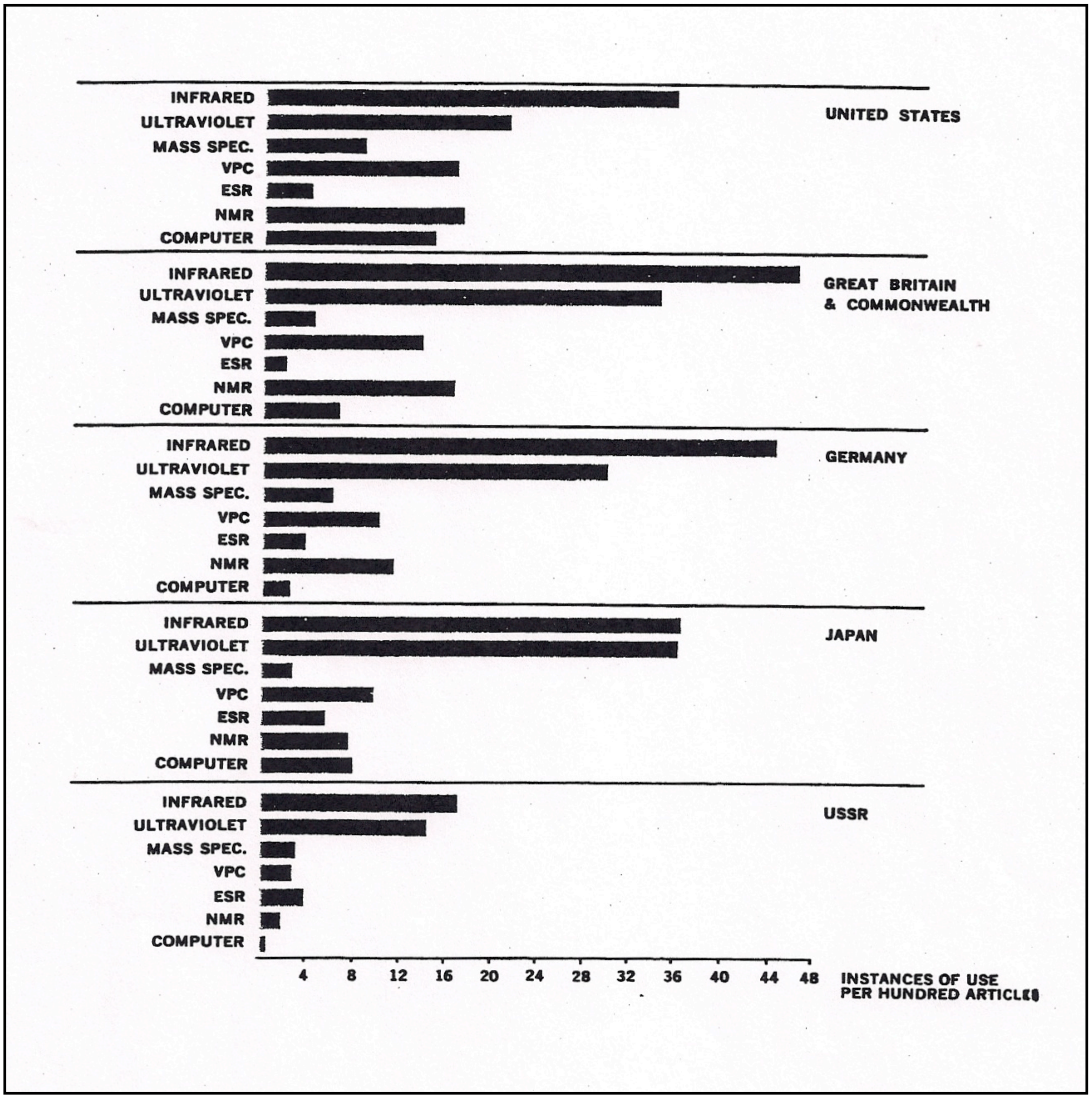

Plate V
Instrumentation usage by country during the 1950s and 1960s

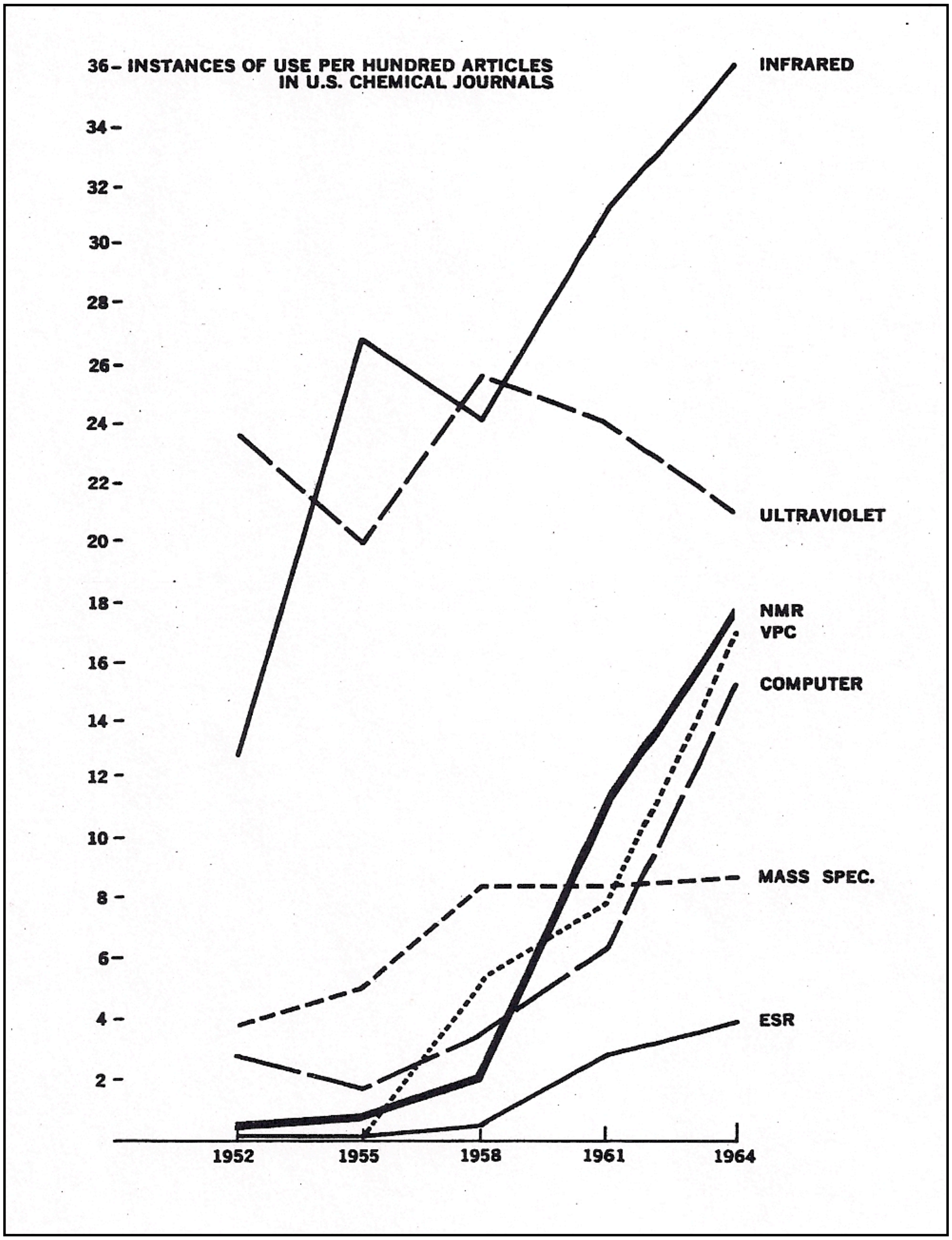

Plate VI
Comparative instrumentation usage in the United States 1952-1964.

Likewise, following the pioneering work of Abney and Festing in 1881, roughly a half dozen spectroscopists investigated correlations between organic functional groups and IR spectra during the remaining years of the 19th century. However, the first truly comprehensive survey came in 1905 with the publication of the first volume of William Coblentz's detailed study, *Investigations of Infra-Red Spectra.* By the early 1940s the first commercial electronic IR instruments had appeared on the market (Beckman 1942, Perkin-Elmer 1944) and the bibliography of publications dealing with chemical applications of IR spectroscopy assembled by Barnes *et al* in 1944 would already list over 2700 items. A related survey of IR usage in the period 1952-1964 found that the percentage of chemical papers published in American journals making use of the technique increased from about 12.5% in 1952 to over 36% in 1964 (see Plates). A final indicator of its importance was, the publication, starting in 1956, of the Sadtler Research index to published IR spectra.

Discovered in 1928 by the Indian physicist, Chandrasekhara Raman, Raman spectroscopy was first summarized in the 1939 monograph, *The Raman Effect and Its Chemical Applications*, by J. H. Hibben. Lagging behind UV and IR instruments, commercial electronic Raman spectrometers did not begin to appear on the market until the early 1950s (Hilger 1950, Carey 1953).

Nuclear magnetic resonance (NMR) was independently discovered in late 1945 by the physicists Felix Block and Edward Purcell and is based on radio-frequency excitation of nuclei in a strong magnetic field, though the phenomena of chemical shift and spin-spin coupling, which form the basis of its chemical applications, were not observed until several years later (Knight 1949, Dickinson 1950, Proctor & Yu 1950). The first commercial NMR instrument was introduced by Varian in 1949, and the first monograph to summarize the potential chemical applications of the technique, *Nuclear Magnetic Resonance*, by the British physicist, E. R. Andrews, was published in 1954. The survey cited above indicates that the percentage of published chemical papers using NMR techniques increased from less than 1% in 1952 to roughly 18% by 1964 and, by the 1970s, it had become the characterization method of choice for most practicing organic chemists.

The closely related technique of electron-spin resonance (ESR) is based on the microwave excitation of unpaired electrons in a strong magnetic field. First observed for the Cu^{2+} ion by Zavoisky in 1945, and for an organic radical species by Kozyrev and Salkov in 1947, the method was first summarized in book form in the 1955 monograph, *Spectroscopy at Radio- and Micro-wave Frequencies*, by D. J. E. Ingram.

The technique of XPS (X-ray photoelectron spectroscopy) or ESCA (electron spectroscopy for chemical analysis) was first applied to the qualitative compositional analysis of solid surfaces by Steinhardt and Serfass in 1951. However, it was the development of a high resolution electron analyzer by Kai Siegbahn and associates and their subsequent discovery of the chemical shift for core electrons in 1958 that made it into a tool for the determination of structure. The technique was first summarized by Siegbahn and associates in their 1967 monograph, *ESCA – Atomic, Molecular, and Solid Surface Structure Studied by Means of Electron Spectroscopy*, and the first commercial ESCA instrument was introduced by Varian in 1969.

The diffraction of X-rays by crystals was first observed in 1912 by von Laue, Friedrich and Knipping and the first full structure determinations (KCl, NaCl, KBr, ZnS, CaF_2, $CaCO_3$, diamond) were made by William Lawrence Bragg and William Henry Bragg in 1913, followed by the publication in 1915 of their monograph, *X-Rays and Crystal Structure*. The related technique of X-ray powder diffraction was introduced in 1916 by Debye, Scherrer and Hull. As with the other techniques discussed above, significant improvements were made in X-ray crystal analysis throughout the 20th century, though perhaps the most important was the impact of the computer in automating both the collection and analysis of diffraction data. Despite its restriction to crystalline solids, the technique is, without a doubt, the single most important method of structure determination available to the chemist and is unique in its ability to determine both intra- and intermolecular bond distances and angles, and to map electron-density distributions within crystals.

In addition to the above techniques for the determination of molecular structure, it should be noted that the 20th century also saw the development of a number of important techniques for characterizing the structures of colloids and solid surfaces, including:

1. the ultramicroscope (Zsigmondy & Siedentopf 1903)
2. the electron microscope (Ruska 1931, **1935**)
3. the field-ion microscope (Mueller 1955)
4. the scanning tunneling microscope (Rohrer & Binnig 1980)
5. electron diffraction and its many variations (LEED etc.)

13.11 The Emergence of Instrumental Analysis

In reviewing the most important 20th-century characterization techniques, it is striking how many of them can be traced back to developments in the late 19th century or in the first third of the 20th century. In each case the technique in question displayed an induction period characterized by custom-built instruments and usage by researchers (often physicists rather than chemists) whose primary focus was the technique or instrument itself.

The so-called instrument revolution of the 1940s and 1950s centered less around the development of new techniques then around the commercial repackaging and refinement of these older techniques made possible by advances in electronics which significantly decreased the time and effort required to collect and analyze the necessary data. It is this repackaging which largely accounts for their widespread adoption and routine use by chemists who were interested less in their construction and refinement then in their application as a means to other ends.

This instrumentation revolution was also reflected in the changing structure of analytical chemistry itself. Though, beginning in the 1920s, textbooks and monographs covering optical and spectrographic techniques (both compositional and structural), on the one hand, and electrometric techniques, on the other, began to appear at regular intervals, there was a growing tendency by the early 1950s, as shown in Table 13.4, to combine these various methods, along with a basic survey of the necessary electronics background, under the common rubric of "instrumental analysis" – a convergence which occurred roughly a decade after the beginning ofthe instrument revolution and roughly a decade before the related coalescence of separation science discussed earlier (Section 13.7).

Table 13.4 Early Textbooks Dealing with Instrumental Analysis

Date	*Author*	*Title*
1951	Willard et al	*Instrumental Methods of Analysis*
1952	Botlz et al	*Selected Topics in Modern Instrumental Analysis*
1954	Ewing	*Instrumental Methods of Chemical Analysis*
1954	Harley & Wiberly	*Instrumental Analysis*
1956	Biffen & Seaman	*Modern Instruments in Chemical Analysis*
1957	Delahay	*Instrumental Analysis*

Writing in 1767, Joseph Priestley foreseen the use of light and electricity as potential keys to uncovering the inner structure of matter:

> *Hitherto philosophy has been chiefly conversant about the more sensible properties of bodies. Electricity, together with chymistry and the doctrine of light and colours, seems to be giving us an inlet into their internal structure, on which all their sensible properties depend. By pursuing this light, therefore, the bounds of natural science may possibly be extended beyond what we can now form an idea of. New worlds may open to our view, and the glory of the great Sir Isaac Newton, and all his contemporaries, be eclipsed.*

Priestley's projected alliance of electricity, chemistry, and light came to fruition in the 20th century. Whereas 19th-century instrumentation was largely restricted to absorption and emission phenomena in the visible region of the electromagnetic spectrum, 20th-century instrumentation not only exploited the entire spectrum, from radio waves to gamma radiation, it has also made use of elementary particles, such as the electron, proton and neutron, and such diverse phenomena as fluorescence, resonance, reflection, scattering, and diffraction in its attempts to probe the inner structure of matter.

The results have truly been beyond even Priestley's most wild imaginings.

13.12 Synthesis and Extreme Environments

Prior to the 20th century, most chemistry centered on systems that were stable at room temperature and pressure and compatible with both an oxygen-rich atmosphere and a water-based solvent system. The successful liquefaction of most of the important gases by the end of the 19th century provided chemists with coolants that have allowed them to work at temperatures approaching absolute zero and to explore the chemistry of such unusual solvents as liquid ammonia (Bronn 1905) and liquid sulfur dioxide (Walden & Centnerszwer 1901). Likewise, improvements in vacuum pumps (Geissler 1857, Sprengel 1865, Gaede 1903-1923, Langmuir 1916) and the commercial availability of the inert gases have led to the development of both vacuum-line (Schleede 1925) and glove-box techniques which have allowed chemists to successfully work with air and moisture sensitive systems. Important classes of chemical compounds discovered in this fashion include the boron hydrides, whose synthesis and characterization were pioneered by the German chemist, Alfred Stock, as summarized in his 1933 Baker lectures, *Hydrides of Boron and Silicon*, and the synthesis of vast numbers of organometallic species involving a new class of π-ligands, stimulated in large part by the preparation of ferrocene by Pauson and Kealy in 1951. As noted in the following lecture, both events would present significant challenges to 20th-century bonding theory.

Though moderately high pressures were employed throughout the 19th century in connection with the liquefaction of gases, the first truly systematic studies of the effects of pressure on phase transitions from the standpoint of thermal analysis and the phase rule did not begin until the 20th century (Tammann 1903, Cohen 1919, Bridgman 1931, etc.). These early workers used conventional hydraulic presses (some as large as several stories), coupled with ever-increasing improvements in seals and gaskets, to attain the necessary high pressures. The true revolution in high-pressure chemistry, however, came with the introduction of the diamond anvil cell in 1959 (Jamieson *et al*, Van Valkenberg *et al*). This not only allowed the attainment of high pressures ($P \geq 300$ kbar) with the simple turn of a screw, it was also small enough to fit under a microscope or in a spectrometer, where its clear diamond cell allowed for easy visual and/or spectroscopic monitoring of the resulting phase changes.

13.13 Synthesis and Natural Products

Though the basic principles of organic synthesis established by the end of the 19th century remain unchanged today, the 20th century saw their elaboration and application to the synthesis of ever more complex molecules, many of which are of considerable biochemical and/or pharmacological interest (Table 13.5).

Table 13.5 Selected Syntheses of Important Natural Products

Date	*Author*	*Substance*
1904	Perkin	Camphor
1917	Robinson	Tropoline
1929	Fischer	Hemin
1944	Woodward, Doering	Quinine
1949	Isler	Vitamin A
1951	Woodward, Robinson	Cortisone
1952	Gates	Morphine
1954	Woodward	Strychnine
1957	Sheehan	Penicillin
1960	Woodward	Chlorophyll

These molecules are usually polyfunctional in nature and have very specific stereochemical requirements. Their chemical synthesis from readily available starting materials may involve up to a dozen or more individual steps and requires an intimate knowledge of various alternative ways of modifying existing functional groups, temporarily suppressing functional group activity through the use of protecting groups, introducing new functionalities, extending or shortening carbon chains, opening or closing carbon rings, retaining or suppressing chirality. etc., not to mention a knowledge of the proper order in which to apply these various techniques.

For the first half of the century this knowledge was largely intuitive – an art or skill learned only through years of intimate contact with and knowledge of organic type reactions – a situation aptly described by G. N Lewis in 1927:

> *... as we pass from the simple to the complex structures, the difference between each substance and its neighbors grows smaller; and the substitution of atoms or groups for one another, although each is a distinct act, makes such slight and apparently gradual changes in the properties that the skilled organic chemist can mold and remold to his desire, as though he were working in a plastic continuum. So, as the organic chemist acquires a proficiency in his art, for indeed it is almost an art, he acquires an intimate acquaintance with his material. This leads him to a few great generalizations, to a large number of work rules of limited or sporadic applicability, and to many vague guesses or little tricks of thought, which he cannot or will not impart to others. In fact, much of his knowledge does not fully emerge into his own scientific consciousness, and has been called chemical instinct (chemisches Gefühl); yet it is extraordinary with what precision he will calculate the properties of a substance he has never seen or the consequences of a reaction he has never tried. It is amazing to find how few of the structures which he has assigned to various molecules are still in doubt.*

Though the published papers of such 20th-century masters of natural product synthesis as Sir Robert Robinson and R. B. Woodward provided detailed after-the-fact examples of how specific syntheses were accomplished, there was a general movement, beginning in the late 1960s, to try to replace both the "chemische Gefühl" component and resulting case by case learning approach with a more generalized logical approach to the *a priori* design of complex multi-step organic syntheses. The major proponent of this movement was, without a doubt, the American chemist, E. J. Corey, who first outlined his vision of "retrosynthetic analysis" in an important article published in the journal *Science* in 1969. By the last quarter of the century this movement would result in the publication of such books as Warren's,*Designing Organic Syntheses: A Programmed Introduction to the Synthon Approach* (1978), and Corey and Cheng's *The Logic of Chemical Synthesis* (1989), as well as in Corey being awarded the 1990 Nobel Prize for his "development of the theory and methodology of organic synthesis."

A feel for the vast quantity of information on organic reactivity which these volumes attempted to systematize may be approximated by citing the magnitude of the current literature dealing with such subjects as functional group reactivities, name reactions, protective groups, etc. Thus the famous encyclopedic*The Chemistry of Functional Groups*, edited by S. Patai, which was begun in 1964, currently occupies more than 50 volumes. Likewise, the first book to systematically tabulate important organic name reactions – Surrey's 1954 volume, *Name Reactions in Organic Chemistry* – was only 192 pages in length, whereas the recent volume (2005) on the same subject by Mundy is 882 pages in length. Similarly, while the first edition of Greene's 1981 book on *Protective Groups in Organic Synthesis* was 349 pages in length, the current edition (2007) now occupies more than 1082 pages.

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THE INSTRUMENTATION REVOLUTION

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Lecture XIV

The Twentieth Century

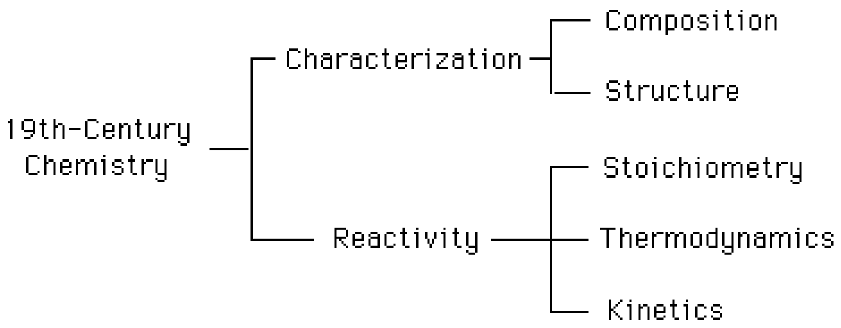
(1901-2000)

The Electrical Theory of Matter

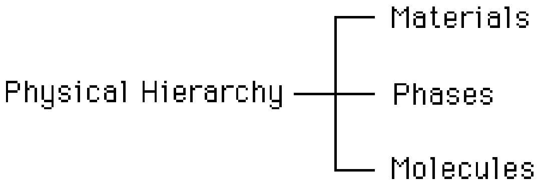
Tell me what electricity is and I will tell you everything else.
Lord Kelvin

14.1 Introduction

As we saw in Lectures X and XI, by the end of the 19th-century chemistry had bifurcated into the two great branches of "characterization" and "reactivity." Characterization, in turn, had resolved itself into the study of composition and structure, and reactivity into the study of the stoichiometric, thermodynamic, and kinetic aspects of physico-chemical change:



Each of these five fundamental themes was applied, in turn, to each of the three levels of the physical hierarchy known to 19th-century chemists: the study of heterogeneous mixtures (i.e., materials), the study of the homogeneous phases (i.e., both solutions and pure substances) which functioned as the components of these materials, and the study the molecules which functioned, in turn, as the components of the phases:

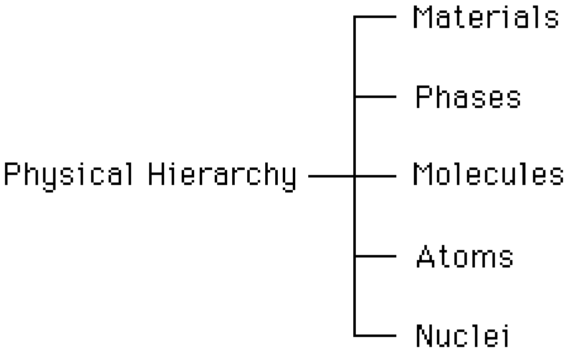


Of the three central themes of 18th-century chemistry – states of matter had been subsumed under the more general study of phase structure and reactivity, chemical composition under the study of molecular composition, and chemical affinity under the study of thermodynamics. As we move into the 20th century this newer organizational structure will continue to evolve and diversify.

14.2 Composition and Structure

With respect to the theory of composition and structure, five important events occurred during the 20th century:

a. The levels of the physical hierarchy studied by chemists were significantly extended through the discovery of the electrical composition and structure of both the atom and the atomic nucleus:



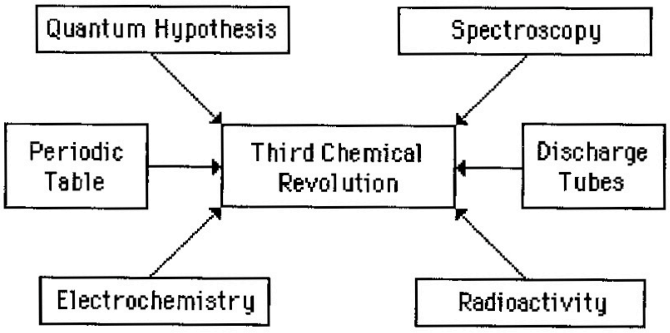
b. The resulting knowledge of the electrical composition and structure of atoms and nuclei was used to reinterpret the periodic law and table in terms of the emerging concepts of electronic configuration, atomic number, and isotopes.

c. The resulting knowledge of the electrical composition and structure of atoms and nuclei was used to develop a corresponding electrical theory of both intra- and intermolecular bonding and structure.

d. The traditional concept of the finite discrete molecule was supplemented by the discovery of both macromolecules and infinitely polymerized solids, and the original Proust-Berthollet controversy finally resolved.

e. Both phase structure and molecular structure were fully quantified via the successful measurement and/or calculation of both inter- and intramolecular bond angles, bond lengths, and bond strengths.

All of these changes were the product of yet a third chemical revolution, which came to fruition in the years 1904-1924, and which parallels both the first chemical revolution of the late 18th century (1770-1790), and the second chemical revolution of the mid-19th century (1855-1875).



However, unlike the first chemical revolution, which was largely the product of a single chemist (Lavoisier), and the second revolution, which involved the efforts of several chemists (Cannizzaro, Williamson, Frankland, Odling, Wurtz, Kekulé, Couper, etc.), this third revolution was shared by both the sciences of chemistry and physics and was the joint product of the efforts of many chemists and physicists.

14.3 The Composition and Structure of Atoms

Eighteenth-century chemistry was largely restricted to the interpretation and classification of chemical phenomena at the macroscopic or molar level of discourse. The 19th century saw the successful development of the molecular-atomic level of discourse, and the 20th century the addition of the subatomic or electrical level of discourse.

The traditional distinction between chemical and physical elements, on the one hand, and between chemical and physical atoms, on the other (recall Sections 6.6 and 10.8), shows that chemists had long suspected the provisional status of both Lavoisier's list of simple substances and Dalton's chemical atoms – a suspicion which was also revealed in the persistent attempts made throughout the 19th century to sustain various modifications of Prout's hypothesis. In addition to these metaphysical predispositions, other important 19th-century prerequisites for the development of the 20th-century electrical atom include the concept of the particulate nature of electricity (Faraday 1833), the discovery of X-rays (Roentgen 1895), the discovery of radioactivity (Becquerel 1896), and the discovery of the electron (Thomson 1897).

Though the period 1880-1910 saw the formulation of several crude electrical models of the atom (Helmholtz 1881, Kelvin 1902, Abegg 1904, Thomson 1904, Stark 1908, Kaufmann 1908), our current model dates from the inception of the Rutherford nuclear model of 1911, which viewed the atom as composed of a small, positively charged, central nucleus containing most of the atom's mass, and a surrounding cloud of negative electrons sufficient in number to neutralize the positive charge of the nucleus.

From 1911 to 1931 the chemical and physics communities were split with regard to their models of the electron cloud of this atom, with the physicists preferring a quantized dynamic model suitable for the interpretation of the facts of spectroscopy (Bohr 1913, Sommerfeld 1916), and the chemists preferring a static model suitable for the interpretation of the facts of stereochemistry and the periodic law (Lewis 1916, Langmuir 1919). In this regard it is interesting to observe that, while an earlier generation of chemists had rejected a literal physical interpretation of the static formulas of classical structure theory and stereochemistry because of their belief in the ultimate dynamic nature of molecular structure (recall Section 10.11), many chemists of this generation now reversed this commitment and rejected the dynamic atomic models of the physicist because of their faith in the ultimate reality of the static formulas of classical structure theory and stereochemistry. This conflict was finally resolved within the context of the newer matrix mechanics (1925) and wave mechanics (1926) of Heisenberg and Schrödinger via the introduction of the concept of orbital hybridization by Pauling and Slater in 1931, which appeared to provide a mechanism for the formation of directional, localized chemical bonds consistent with both wave mechanics and the facts of stereochemistry.

Questions of dynamic versus static models aside, considerable effort also went into unraveling the details of the structural arrangement of the electrons within the electron cloud (Abegg 1908, Bohr 1913, Lewis 1916, Kossel 1916, Langmuir 1919, Ladenburg 1920, Bury 1921, Bohr, 1921), leading finally to the establishment of our current spectroscopic configurations by Hund in 1925, as summarized in his 1927 monograph *Linienspektren und periodisches System der Elemente*. As a result, groups within the periodic table were no longer defined in terms of maximum stoichiometric valence, but rather in terms of isoelectronic valence configurations. A final correction to the electronic configurations of the transactinide elements was made with the introduction of the actinide hypothesis by Seaborg in 1945, which established the existence of a fourth major electronic block within the periodic table (the f-block).

14.4 The Composition and Structure of Nuclei

The first significant advance in unraveling nuclear composition and structure was van den Broek's suggestion (1911) that the nuclear charge of an atom corresponded to its ordinal number or position in the periodic table and its subsequent experimental confirmation by Moseley and Soddy in 1913 using X-ray spectroscopy and the radioactive displacement laws, respectively. As a result, the periodic law was amended to reflect the fact that the properties of the elements were a periodic function of their nuclear charges or atomic numbers, rather than their atomic weights – a change which finally resolved a number of persistent exceptions (e.g. Te versus I, K versus Ar, and Co versus Ni) to the original version of the law.

Early attempts to rationalize the masses and charges of nuclei were initially based on the hypothesis that they were composed of alpha and beta particles (i.e., He nuclei and nuclear electrons), both of which had been observed as products of radioactive decay. After Rutherford's experimental observation of the proton in 1919, these were displaced by proton-beta particle models, and after Chadwick's discovery of the neutron in 1932, by our current proton-neutron models. The further development of models of nuclear structure and the discovery of additional subnuclear particles, such as quarks, belong more to the history of modern particle physics than to the history of chemistry proper.

The recognition that a given element type could correspond to several different varieties of nuclei differing in both their masses and radioactive half-lives was first formulated by Soddy in 1911 for the radioelements, and was verified and extended to the nonradioactive elements by Aston, starting in 1919, using the newly developed technique of mass spectroscopy. In 1913 Soddy further suggested that these nuclear variants be called "isotopes" (from the Greek *iso-*, meaning "same" and *topos*, meaning "place.") in order to indicate that they occupied the same place in the periodic table. The isotope concept soon led to a reinterpretation of the atomic weight of an element as the average mass of its naturally occurring isotopes and to the eventual establishment of a new standard for the atomic weight scale ($^{12}C = 12$, 1960).

It also briefly led, along with the transmutation theory of radioactivity proposed by Rutherford and Soddy in 1902, to a vigorous discussion between Soddy and the Polish and German radiochemists, Kasimir Fajans and Fritz Paneth, over the question of whether, in light of these discoveries, the use of the traditional terms "atom" and "element" should be abandoned or at least modified. In the end, Soddy's terminology triumphed, and the older operational definition of an element "as the last stage of chemical analysis" was abandoned and replaced by the definition of an element as a class of nuclei having identical atomic numbers, but variable masses and radioactive properties (or, in more modern terms, identical proton counts but variable neutron counts).

However, no such similar resolution was arrived at for the term atom and currently this term – in contradiction to its literal meaning – denotes little more than a neutral mononuclear molecule. Though elements are conserved in chemical reactions (but not in nuclear reactions), the modern electrical atom, unlike Dalton's chemical atom, is not, since both its electronic composition and/or structure are altered as a result of the electron redistribution that forms the essence of all chemical change.

14.5 The Composition and Structure of Molecules (Bonding)

The earliest qualitative electronic interpretations of the chemical bond were based on the electron-transfer or ionic model (Helmholtz 1881, Abegg 1904, Thomson 1904, Ramsay 1908), and were finally reformatted in terms of our current Rutherford-Bohr nuclear atom by Kossel in 1916. Though crude quantitative calculations based on this model also date from the late 19th century (Richarz 1894, Ebert 1895), it was only with the development of quantitative lattice calculations for ionic crystals by Born and Landé in the period 1918-1919, and their graphical representation in terms of thermochemical cycles (Haber 1919), that they truly became predictive. Less rigorous quantitative results were also obtained in the field of coordination chemistry in the 1920s (Kossel, Magnus, Garrick), culminating in the formulation of the ionic radius-ratio rules (Hüttig 1920, Magnus 1922, Goldschmidt 1926), and the Kapustinski equation (1933). The ionic model was first summarized in book form by van Arkel and de Boer in the 1929 Dutch monograph, *Chemische Bindung als elektrostatisch Verschnijnsel.*

Suggestions that the bonds in nonpolar molecules were better represented in terms of electron sharing rather than electron transfer also appeared early in the century (Stark 1908, 1915; Kaufmann 1908; Thomson 1914, Arsem 1914, Parsons 1915) and culminated in the Lewis shared electron-pair or covalent bond of 1916.

Within the context of Lewis' theory, the bonds of classical structure theory corresponded to shared electron-pairs, thus giving rise to localized 2c-2e or single bonds, localized 2c-4e or double bonds, and localized 2c-6e or triple bonds. In addition, Lewis postulated the existence of unshared lone pairs or 1c-2e components which roughly corresponded to the latent valencies of classical structure theory. The Lewis model was extensively developed by Langmuir in the period 1919-1921 and was also applied to transition metal coordination chemistry by Huggins (1922) and Sidgwick (1923). It was elegantly summarized by Lewis himself in his 1923 monograph, *Valence and the Structure of Atoms and Molecules*, and again, in greater detail, by Sidgwick in his 1927 monograph, *The Electronic Theory of Valency*.

Reconciliation of the shared electron-pair bond with the newer quantum mechanics of Schrödinger and Heisenberg and with the Pauli exclusion principle (1925) was first undertaken by the German physicists Heitler and London in 1927 and more extensively by Pauling, beginning in 1931, on the basis of the so-called resonance and orbital hybridization concepts. This localized quantum-mechancial approach to covalent bonding eventually became known as the valence-bond (VB) method and was first summarized in book form by Pauling in his 1939 monograph, *The Nature of the Chemical Bond*.

A more revolutionary approach to covalent bonding, which evolved out of the study of molecular spectroscopy, was also developed about the same time (Hund 1926, Mulliken 1928, Lennard-Jones 1929). Known as molecular-orbital (MO) theory, because of its attempt to extend the orbital model of atomic spectra to polyatomic molecules, the method was first successfully applied in a simplified quantitative form to unsaturated and aromatic organic species by Hückel starting in 1930, as summarized in his 1938 monograph, *Grundzüge der Theorie ungesättigter und aromatischer Verbindungen*. In sharp contrast to the localized picture of chemical bonding given by Lewis and VB theory, the MO model made use of radically delocalized orbitals which extended over the entire molecule.

Initially most chemists tended to favor VB theory, largely because its qualitative consequences could be represented in terms of familiar Lewis dot diagrams. However, not only was MO theory computationally more tractable and better suited to the rationalization of spectra, it was also able, unlike VB theory, to offer simple rationales of such phenomena as the paramagnetism of dioxygen gas and the aromaticity or antiaromaticity of various monocyclic hydrocarbon rings. Consequently, with the widespread adoption of commercial spectroscopy, the rise of organic photochemistry, and the increasing availability of computing facilities in the 1950s, both experimental and theoretical chemists began to increasingly favor the use of MO theory, which has essentially dominated the advanced chemical literature since the 1960s.

However, despite this apparent dominance, it was long known that the simple VB and MO wavefunctions become equivalent if sufficiently elaborated and, by the early 1950s, it was also known that both the total electronic energy and the total electron density of a molecule could be carved into sets of contributing orbitals in several alternative ways, one of which corresponded to the delocalized symmetry-adapted orbitals of conventional MO theory and the other to the localized orbitals of VB and Lewis theory (Lennard-Jones 1949, Pople 1957). Indeed, Mulliken, in his Nobel acceptance lecture of 1966, emphasized the complementary nature of these alternatives, suggesting that delocalized orbitals (or "spectroscopic orbitals," as he called them) were best suited for discussing the spectroscopy and excited states of molecules, whereas localized orbitals (or "chemical orbitals," as he called them) were best suited for discussing their ground-state structures and stereochemistry.

With regard to the question of localized versus delocalized covalent bonding models, mention should also be made of two extreme approximations designed to deal with each of these alternatives, which, though no longer of research interest, are still of great pedagogical value. The first of these was the "free-electron" or "Kasten" (box) approximation of the delocalized bonding extreme. Developed by Otto Schmidt in the period 1937-1943, this model treated the bonding electrons as free particles in a box whose dimensions varied from those of a single bond to those of the entire length of a conjugated chain or ring. This model attracted the attention of several investigators after the Second World War and, in particular, that of Kuhn in Switzerland and that of Platt and associates at the University of Chicago. Platt *et al* summarized their work in the 1962 monograph, *Free-Electron Theory of Conjugated Molecules: A Source Book*, and Kuhn in a series of lectures published in 1963 as *Die Methode des Elektronengases*.

The second of these was the "charge-cloud" approximation of the localized bonding extreme introduced by Kimball *et al* in the period 1951-1959, in which localized orbitals were represented as nonoverlapping spherical electron clouds of net charge 2- and covalent structures were reduced to the electrostatic packing of these spherical electron-pair domains and the positively charged atomic cores in a manner analogous to the packing of spherical anions and cations in the older ionic model. Kimball published very little on this model himself. However, in the period 1963-1968, Bent extensively publicized its qualitative consequences under the rubric of the "tangent-sphere" model, and it was also made the basis of the *Chemical Bond Approach (CBA*) to high school chemistry (Strong *et al*. 1964). The model is still used today, largely in connection with the VSEPR approach to molecular geometry (see next section), where it is represented using a new class of mechanical models in which the mutually repulsive localized electron domains are represented either with balloons (Jones *et al* 1961) or with plastic spheres interconnected by means of rubber bands (King 1964).

Quantitative localization studies in the early 1960s (Boys 1960, Edmiston & Ruedenberg 1963) also confirmed the necessity of expanding the set of localized bonding components beyond the 2c-2e bonds and 1c-2e lone pairs of the conventional Lewis picture. Several of these additional components had actually been recognized on an *ad hoc* basis over a decade earlier, including the localized 3c-2e bond (Lonquet-Higgins 1943, 1949: Pitzer 1945) widely used by Lipscomb in his work on the electron-deficient boron hydrides and in his development of his famous *styx* rules (1954), and also applied to the description of the transition states for electrophilic addition (Dewar 1946) and displacement (Lewis *et al* 1958, Olah 1972) reactions; and the so-called 3c-4e bond (Rundle 1947, Pimentel 1951) used to describe the bonding inhypervalent species, such as the interhalogens, the noble-gas compounds, and the transition states for nucleophilic displacement reactions.

These localization studies clearly demonstrated the arbitrary nature of the resonance concept, which Pauling had formulated as one of the cornerstones of qualitative VB theory. With the introduction of explicit symbols to represent various kinds of multicentered bonds, the need for the use of qualitative 2c-2e resonance structures for these species evaporated, thus revealing that, far from being a fundamental chemical concept, resonance was in fact merely an artifact of an impoverished chemical symbolism (Linnett 1964, Harcourt 1982).

The use of these multicentered components was also intimately connected with 20th-century debates concerning the validity of what is arguably the single most important bonding principle for the main-block elements – the octet rule. First formulated by Mendeleev in 1871, the rule initially stated that the sum of a given element's maximum valence toward oxygen (v_O) and its maximum valence toward hydrogen (v_H) was equal to eight:

$$v_O + v_H = 8 \qquad [1]$$

The rule was electrochemically reformulated by Lothar Meyer in the 1880s in terms of the sum of a given element's maximum electropositive valence (v_+) and its maximum electronegative valence (v_-):

$$v_+ + v_- = 8 \qquad [2]$$

and again by Abegg in 1908 in terms of the sum of a given element's valence-electron count (e) and its valence-vacancy count(v):

$$e + v = 8 \qquad [3]$$

The association of the rule with the concepts of both shell completion and chemical stability received further reinforcement in the writings of Kossel and Langmuir in the period 1916-1921 and eventually resulted in a fundamental change in the arrangement of the groups within the periodic table, whereby the noble gases were moved from group 0, in front of the alkali metals, to group VIII, following the halogens, in order to emphasize the parallelism between valence-shell completion, on the one hand,

and period completion, on the other (Gray 1923).

In the 1920s Lewis and Langmuir carried on a debate over the validity of the rule. Lewis, wishing to assert the supremacy of the 2c-2e bond, maintained that the rule was violated for both electron-deficient molecules (e.g., $B(CH_3)_3$) and for electron-rich or hypervalent molecules (e.g., SF_6), whereas Langmuir maintained its universal validity by assigning ionic rather than covalent structures to the compounds in question. To this day, many inorganic textbooks and essentially all introductory textbooks continue to maintain Lewis' viewpoint, though the introduction of both the 3c-2e bond and the 3c-4e bond in the late 1940s and early 1950s essentially brought all of Lewis' exceptions into compliance with the rule and, since the 1970s, its validity for the main-block elements has been repeatedly confirmed by quantitative *ab initio* calculations.

In 1921 Langmuir first proposed that the transition elements conformed to a corresponding eighteen-electron rule, which he applied to several transition-metal carbonyls. This rule was further developed by Sidgwick under the guise of the so-called effective atomic number or EAN rule (1927, 1934). Though not as universal as the octet rule, the eighteen-electron rule has, nevertheless, proved quite valuable in rationalizing and predicting the structures of many transition-metal species, and especially those of their organometallic compounds.

In the case of the atoms of the main-block elements, the valence electrons are confined to the outer-most shell and the spherically symmetric inner core of the atom suffers only minor perturbation during molecule formation. The same is not true of the atoms of the transition elements in which the valence electrons are derived not only from the outer-most or *n* shell but also from the partially filled inner *n-1* shell as well. The energies and arrangement of the electrons in this inner shell are highly sensitive to the nature, number, and arrangement of the ligands in the outer shell and play an important role in determining the spectroscopic, magnetic, and chemical properties of transition-metal compounds.

The first attempt to deal with this difference was made in 1929 by the German physicist, Hans Bethe. Known as "crystal-field theory," Bethe's approach was based on the assumption of an ionic bonding model and was elaborated in the 1930s primarily by physicists interested in the theory of magnetism (Penney *et al* 1932, 1934; Van Vleck 1932). In the 1950s the theory attracted the attention of coordination chemists as a means of rationalizing the visible spectra of coordination complexes and was further elaborated to take into account the effects of covalent bonding. This extended treatment became known as "ligand-field theory" and was the subject of at least four major monographs published between 1960 and 1962 (Orgel 1960, Griffith 1961, Ballhausen 1962, Jørgensen 1962). At present, the ligand-field model is considered to be a special case of the MO model, as was already anticipated by Van Vleck as early as 1935.

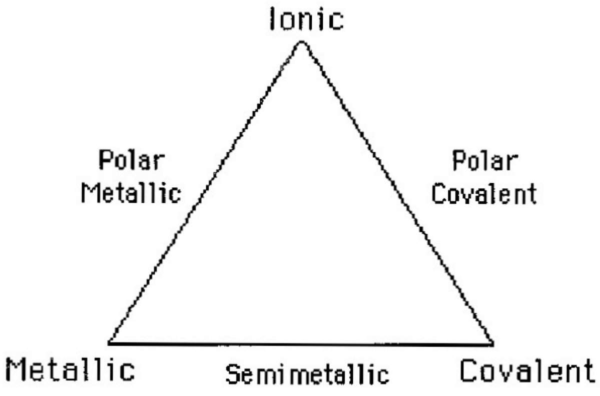
A final important result of the application of the electronic theory of bonding to the transition metals was the introduction of yet another localized covalent bonding component – the 2c-8e bond or "quadruple bond" - first proposed by Cotton *et al* in 1965 for the Re-Re bond in $[Re_2Cl_8]^{2-}$. More recently, there have been reports of 2c-10e and even higher order bonds between transition metal atoms (Powers *et al* 2005).

Though Lewis explicitly recognized the existence of yet a third type of bond for metal-metal bonding in 1913, the development of the theory of the metallic bond was left largely to physicists and materials scientists. First formulated in terms of a classical free-electron gas at the turn of the century by Drude (1900) and Lorentz (1904), the model was quantized by Sommerfeld in 1928 and reformulated in terms of the newer wave mechanics by Bloch the same year, thus laying the foundations of modern band theory.

Lewis not only recognized the existence of the three limiting cases of ionic, covalent, and metallic bonding, he also envisioned the possibility of intermediate bond types or semi-polar bonds due to an unequal sharing of the bonding electrons. By 1913 chemists had explicitly reinterpreted the electronegativity concept of Avogadro and Berzelius in terms of an atom's ability to attract and retain its valence electrons (Stark 1903, Fajans 1913) and in 1916 Lewis further suggested that the polarity of a covalent bond should be a direct reflection of the difference in the electronegativities of the bonded atoms. In 1932 Pauling combined this concept with average thermochemical bond energy data to generate the first empirical quantitative electronegativity scale. This was followed in

1934 by the Mulliken scale, based on the average of an atom's electron affinity and first ionization energy. Since then, at least another 25 quantitative measures of electronegativity have been proposed, the most popular of which has been the Allred-Rochow force definition (1958). It is of interest to note that Pauling's approach to electronegativity, which postulates a direct correlation between the electronegativity differences of two atoms and the strength of their mutual bond, is in many ways a quantification of the original postulates of Fourcroy and Berzelius relating the differences in the chemical character of two atoms to the intensity of their mutual chemical affinity.

Based on the earlier writings of Grimm (1928), the concept of intermediate bond types was extended by Fernelius and Robey in 1935 to include not only polar covalent bonds, but semimetallic and polar metallic bonds as well, and was also first expressed in the form of a triangular bond-type diagram (see also van Arkel 1941 and Ketelaar 1949):



14.6 The Composition and Structure of Molecules (Geometry)

The introduction of X-ray crystal analysis in the period 1912-1913 revolutionized the determination of molecular structure and, by1928, all of the major postulates of classical stereochemistry had been experimentally confirmed:

Table 14.1 X-Ray Confirmations of Classical Stereochemistry

Date	*Geometry*	*Crystal*	*Investigator*
1913	tetrahedral C	diamond	Bragg & Bragg
1917	trigonal-planar C	graphite	Debye & Scherrer
1921	octahedral Pt	$(NH_4)_2(PtCl_6)$	Wyckoff & Posnjak
1922	square-planar Pt	$K_2(PtCl_4)$	Dickinson
1923	trigonal-pyramidal N	$(CH_2)_6N_4$	Dickinson & Raymond
1923	trigonal-prismatic Mo	MoS_2	Pauling
1928	aromatic C	$C_6(CH_3)_6$	Lonsdale

In the case of VB theory, theoretical rationalization of these geometries was based on the postulate of maximum orbital overlap (Slater, 1931, Pauling 1931), which, in turn, determined the optimal orbital hybridization (and hence the geometry) around each atom within the molecule. In the case of MO theory, one had to determine how the energies of the various molecular orbitals changed as the geometry of the molecule was varied in order to locate the shape corresponding to the minimum in the total electronic energy. When applied to either a planar molecule or to a two-dimensional cross-section of a nonplanar species, this procedure could be represented graphically in terms of a plot of the various MO energies versus the change in a given bond angle. Often called Walsh diagrams, in honor of the British theoretician who first explored their application in detail (1953), these orbital-angular correlation diagrams were actually first introduced by Mulliken in 1942.

Though both the VB and MO methods have since been successfully adapted to quantitative computer calculations of molecular structures, and the MO approach has the additional advantage of being applicable to both excited and ground-state structures, it soon became apparent, despite some rather heroic attempts to the contrary (Gimarc 1979), that neither was particularly well suited to making simple qualitative predictions. In the case of the older ionic model, the predictions of geometry were based on the application of the radius-ratio rules, mentioned in the previous section. However, these were limited to situations in which no stereoactive lone pairs were present on the cation, and though some attempts were made to correct for this limitation using the concept of ion polarization (Hund 1925, Fajans 1925), this modification did not find wide acceptance within the chemical community.

Instead, recourse was had to the older qualitative Lewis electron-pair model and the postulate that geometry was determined by minimizing the mutual electrostatic repulsions between the various valence-shell electron pairs, both bonding and nonbonding. Now known as "valence-shell electron-pair repulsion theory" or VSEPR, this simple model had actually been independently proposed by nearly a half dozen different chemists during the first half of the century (Martin 1903, Wittig 1930, Ormont 1937, Sidgwick & Powell 1940, Helferich 1946, Linnett & Mellish 1954), but without apparent effect. Only with the publication in 1957 of a major review of inorganic stereochemistry by Nyholm and Gillespie, in which the approach was extended and applied to a wide range of both main-block and transition-block structures, did it begin to attract serious attention. Gillespie further developed and popularized the model throughout the 1960s and summarized his results in his 1972 monograph, *Molecular Geometry*. Initially greeted with skepticism by theoreticians, who viewed it as hopelessly naive, the VSEPR model is now discussed in virtually all inorganic and introductory chemical texts.

However, by far the single most important qualitative structural principle to evolve out of the 20th-century electronic theory of bonding and structure was the so-called "isosteric principle," first proposed by Langmuir in 1919. Rediscovered by molecular spectroscopists in the 1930s and renamed the "isoelectronic principle," it had, like the VSEPR model, a somewhat spotty history throughout the first half of the century, during which it was repeatedly rediscovered within the context of special applications or applied without explicit acknowledgment. In 1966 Bent wrote a major review in which many of these uses were discussed from a unified viewpoint and the principle given its current form:

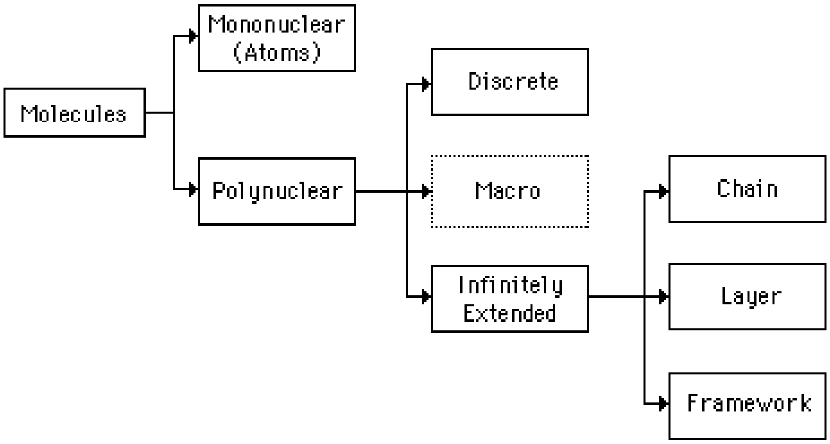
Isoelectronic species (defined as species having identical valence-electron counts and identical nonprotonic or heavy atom counts) *often have similar electronic structures, similar heavy-atom geometries, and similar reactivity patterns.*

The isoelectronic principle is applicable whether one is using the ionic, the Lewis, the VB, or the MO bonding models. It is used to classify the elements in the periodic table and to assign spectra to atoms and molecules. It is implicit in countless electron-counting rules for determining the structures of special classes of compounds (e.g., the Walsh rules for simple hydride structures, the Wade-Williams rules for cluster structures, the Klemm-Busmann rules for Zintl phases, the pseudoatom concept, etc.), as well as in countless derivative bonding principles (e.g., Grimm's hydride displacement law, Dahl's electronic-equivalency principle, the isolobal principle, etc.).

The reason for the use of the qualifier "often" in the above definition is because a given valence-electron and atom count is often compatible with several alternative electronic and/or molecular structures and additional rules are required in order to select the most favorable of these as a function of changing atomic composition. Though both of these questions can now be answered by means of computer calculations, the selection of the most favorable electronic structure for a given heavy-atom geometry is qualitatively governed by the so-called "electroneutrality principle" (Langmuir 1921, Pauling 1948), whereas selection of the most favorable heavy-atom bonding connectivity for a given electronic structure is qualitatively governed by the principle of minimal core-core repulsions (Pauling & Hendricks 1926).

14.7 Supplementing the Molecular Paradigm

The technique of X-ray crystal analysis not only confirmed the basic molecular geometries postulated by 19th-century stereochemistry, it also supplemented the molecular paradigm via its discovery that many crystals were not composed of small discrete atoms or molecules, as had been assumed by virtually all 18th- and 19th-century chemists, but rather contained either large macromolecules or were lacking discrete molecules of any sort – be they macro or otherwise – a situation summarized in the following diagram.



Since the historical development of concepts related to the composition and structure of phases varied, depending on whether the phases in question contained discrete molecules, macromolecules, or infinitely polymerized solids, it is useful to treat the history of each type separately. We will begin with the classic case of discrete molecular phases, then move to the opposite extreme of nonmolecular phases, and conclude with the intermediate case of macromolecular phases.

14.8 The Composition and Structure of Molecular Phases

The term "molecule" was first introduced in the 17th century by Gassendi (1658) to describe small, submicroscopic, polyatomic particles and, within the context of the 18th-century Newtonian theory of interparticle forces, most chemists were careful to distinguish between intramolecular attractions, on the one hand, and intermolecular attractions, on the other. As we saw earlier, both Bergman and Fourcroy, writing in the last quarter of the century, referred to the former as "attractions of composition" and to the latter as "attractions of aggregation."

The few theoretical investigations of intermolecular forces in the 18th and early 19th centuries centered on liquids and the phenomenon of capillary attraction, and were largely undertaken by mathematical physicists. However, with the development of the ideal gas law and the rise of the kinetic theory of gases, beginning in the 1850s (recall Section 10.5), the study of intermolecular forces entered a new phase (both literally and figuratively). Ideal gas behavior, based on the assumption of negligible intermolecular attractions, provided a perfect reference state against which the behavior of real systems could be measured using the correction terms introduced by van der Waals in his famous gas equation of 1873:

$$(P + a/V^2)(V - b) = RT \qquad [4]$$

In honor of this achievement, the various intermolecular forces giving rise to the a/V^2 correction term are still collectively referred to as van der Waals forces.

In actual practice, it turned out that a more effective way of expressing nonideal gas behavior was in terms of the so-called virial expansion (Kmerlingh Onnes 1901):

$$PV/RT = 1 + B(T)/V + C(T)/V^2 + D(T)/V^3 \ ... \qquad [5]$$

in which the second virial coefficient ($B(T)/V$) was assumed to be directly related to the sum of the intermolecular potentials (u) between each pair of interacting molecules. In 1903 Mie suggested that this pair potential could be modeled by a general equation of the form:

$$u = ar^{-n} - br^{-m} \qquad [6]$$

in which the attraction was represented by the $- br^{-m}$ term and varied as the $-mth$ power of the separation distance (r), and the repulsion was represented by the ar^{-n} term and varied as the $-nth$ power of the separation distance.

With the advent of the new electrical theory of matter, physicists began exploring the idea that intermolecular forces, like the intramolecular forces responsible for chemical bonding, might be electrical in origin. The first assumption to be developed in detail was that the attractions between neutral molecules were due to permanent electrical dipoles (van der Waals Jr. 1908, Keesom1912). However, deviations from ideal behavior were also apparent for many molecules (e.g., the noble gases, H_2, O_2, N_2) for which such permanent dipoles were unlikely in the extreme.

The solution to this dilemma came in 1930 when London, building on the earlier work of Debye (1920) on dipole-induced dipole interactions, introduced the concept of dispersion forces due to transient induced dipole-induced dipole interactions. These forces, which gave rise to an br^{-6} attractive term in the pair potential were operative in all molecules, whether polar or otherwise. In 1937 Lennard-Jones showed that the assumption of an ar^{-12} repulsion term in the Mie equation, in conjunction with the br^{-6} attractive term, both simplified the mathematics and gave an adequate fit to much of the experimental data. Known as the Lennard-Jones 6-12 potential, it would dominate much of the work on intermolecular forces through the 1960s, after which it became increasingly apparent that the assumption that pair potentials were additive was defective and that a more sophisticated approach was required. Much of the work on intermolecular forces during the first half of the century was summarized in the classic 1954 monograph, *Molecular Theory of Gases and Liquids*, by Hirshfelder, Curtiss and Bird.

In the case of polyatomic molecules with permanent dipoles, the further question of the relationship between molecular structure, bond dipoles, and net molecular dipoles, on the one hand, and such bulk properties as the dielectric constant and the refractive index, on the other, was explored by Debye, starting in 1912, and was summarized in his 1929 monograph, *Polar Molecules*. This work was continued, with a more explicit chemical emphasis and as a possible tool for structure determination, by Smyth and became the subject of his 1931 monograph, *Dielectric Constant and Molecular Structure*.

For practicing chemists, a far more pertinent question than the problem of deviations from ideal gas behavior was the question of the mutual solubility of molecular mixtures and especially those involving liquid solvents. In 1916 Hildebrand suggested that the ideal reference state for a binary solution was given by Raoult's law (1887) relating the solution vapor pressure (p_i) of solution component i to the vapor pressure of the corresponding pure substance ($p_i°$) and its mole fraction (x_i) in the solution:

$$p_{\mathrm{i}} = p_i^{\circ} x_i \qquad [7]$$

The ideality assumption behind this equation was not the absence of intermolecular forces, but rather their nonspecificity and equality for all components, so that the resulting solution had both a zero enthalpy of formation and an ideal entropy of mixing.

Noting that the a/V^2 correction term in the van der Waals equation has the units of pressure or force per unit area (F/A) and hence can also be expressed as a cohesive energy density (E/V), Hildebrand showed that the more similar the value of this parameter for the two solution components, the greater their mutual solubility and their conformity to Raoult's law. He would later (1924) adopt the enthalpy of vaporization of a liquid, divided by its molal volume, as an approximate measure of this term:

$$a/V^2 = P_{int} = (E/V)_T \approx (\Delta H_{vap} - RT)/V \qquad [8]$$

These results were initially summarized in Hildebrand's 1924 monograph, *Solubility*. In subsequent refinements and monographs the model became known as the theory of "regular solutions" (defined as solutions having a finite enthalpy of mixing due to nonspecific intermolecular interactions, but an ideal entropy of mixing). In 1931 Scatchard proposed an equation for predicting the solubility of binary regular solutions in which the square roots of the cohesive energy densities of the solvent and solute played a key role, and by 1950 these square root terms had become known as "solubility parameters." Though based on a blend of both theory and empiricism, the solubility parameter concept offers one of the few practical approaches to the question of estimating liquid solubilities and has consequently found widespread application among industrial chemists.

Most deviations from regular solution theory were easily identified with molecules displaying specific directional interactions with their neighbors, including not only permanent dipole-dipole interactions, but more explicit chemical effects as well, such as hydrogen bonding (Huggins 1919, Latimer & Rodebush 1920), Lewis acid-base interactions (Lewis 1923, 1938), and the formation of weak electron donor-acceptor or so-called charge-transfer complexes (Mulliken 1950, 1952). Interest in these various specific chemical interactions increased as the century progressed, in large part because they form a transition between weak, nonspecific, intermolecular interactions, on the one hand, and strong, specific, intramolecular interactions, on the other. Though it soon became apparent that both hydrogen bonding and traditional Lewis acid-base interactions were special cases of generalized donor-acceptor interactions, they are still treated as distinct phenomena in most of the chemical literature. The first monograph devoted exclusively to Lewis acid-base interactions, *The Electronic Theory of Acids and Bases*, by Luder and Zuffanti, was published in 1946; the first monograph dealing exclusively with hydrogen bonding, *The Hydrogen Bond*, by Pimentel and MacClellen, was published in 1960; and the first monograph dealing exclusively with Mulliken's generalization, Briegleb's *Elektronen-Donator-Acceptor-Komplexe*, was published in 1961.

14.9 The Composition and Structure of Nonmolecular Phases

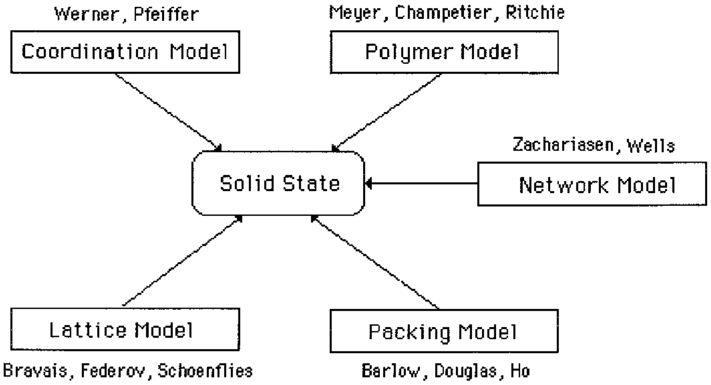
Though some 19th-century chemists with crystallographic interests had suggested that common inorganic crystals might not contain discrete molecules (Meyer 1872, Barlow 1884, von Groth 1906), it still came as something of a surprise when, in 1913, the first X-ray crystal-structure determinations (NaCl, KCl, ZnS, $CaCO_3$, diamond) failed to find any evidence of them. The resulting dismay was well-expressed in a letter which the British organic chemist, Henry Armstrong, wrote to the journal *Nature* in 1927:

> *Professor W. L. Bragg asserts that "In sodium chloride there appear to be no molecules represented by NaCl. The equality in the number of sodium and chlorine atoms is arrived at by a chess-board pattern of these atoms: it is a result of geometry and not of a pairing off of the atoms." This statement is more than "repugnant to common sense." It is absurd to the nth degree, not chemical cricket. Chemistry is neither chess nor geometry, whatever X-ray physics may be. Such unjustified aspersion of the molecular character of our most necessary condiment must not be allowed any longer to pass unchallenged ... It were time that chemists took*

charge of chemistry once more and protected neophytes against the worship of false gods; or at least taught them to ask for something more than chess-board evidence.

As more and more X-ray structure determinations were done, true molecular solids were in fact found (primarily among organic compounds), but, in the case of inorganic compounds and intermetallics, the nonmolecularity of the first structure determinations proved to be the rule rather than the exception. Indeed, recent surveys of the thousands of X-ray structure determinations done since 1913 reveal that the majority (about 98%) of inorganic solids do not contain discrete molecules but are rather composed of infinitely extended chain, layer, and framework structures.

Besides formal lattice theory, whose origins were already described in Section 10.4, the 20th century also saw the development of at least four additional approaches to the description of these infinitely extended structures:



The earliest of these – the "close-packed spheres" model – was developed by the British scientist, William Barlow, in the closing decades of the 19th century (1884, 1894, 1897, 1898). Indeed, Barlow's close-packed models actually played a key role in the initial X-ray crystal structure determinations as the structures in question were not determined *de novo* from the reflection data alone, but rather the data were shown to be consistent with Barlow's already extant models. In the case of inorganic salts, Barlow's approach was later reinterpreted in terms of the ionic bonding model as a close-packed array of anions with the various cations distributed among the resulting octahedral and tetrahedral holes in a manner consistent with the net stoichiometry and overall symmetry of the crystal. Though an impressive number of basic crystal structures can be described in this manner, there are important exceptions (e.g. diamond, the silicates, etc.), and it was not until the 1960s that an extended packing model was developed which could take these into account as well (Ho & Douglas 1968, 1969, 1972).

The alternative "coordinated polyhedra" model was introduced by Paul Pfeiffer (1915, 1916) shortly after the first X-ray crystal structures were reported and was based on an extension of Werner's coordination theory. Infinitely extended structures were viewed as infinitely bridged coordination complexes due to the sharing of the vertices, edges and/or faces of the primary coordination polyhedra about each central atom. It was on the basis of this model and a study of silicate structures that Machatschki (1928) first suggested that infinitely extended structures could be further divided into infinitely extended framework, layer and chain structures, and in 1929 Pauling used an ionic interpretation of the model to formulate a set of important rules governing the relative stability of such structures.

The "polymer model" evolved out of the study of organic and biochemical chain polymers in the 1920s and 1930s (see Section 14.10) and was first generalized by Kurt Meyer in 1942 to include not only infinitely extended chain polymers, but also "cross linked" layer and framework polymers as well, as found among typical solid-state inorganic species. Though several polymer texts of the period (Champetier 1948, Ritchie 1949) included chapters mentioning Meyer's generalization, it really did not gain momentum until the 1960s when it became the subject of several specialty monographs dealing specifically with inorganic polymers (Stone *et al* 1962, Hunter 1963, Ray 1978).

The final approach – the "network" model – was first introduced by Zachariasen in 1932 in connection with his theory of glass formation (see Section 14.11). This approach views solids as one-, two- or three-dimensional bonding networks in which the various atoms or ligands function as nodes of varying connectivity. Starting in the 1950s this approach was extended to crystalline solids by A. F. Wells, who was largely interested in determining whether such an approach could be used to formally set limits to the number of geometrically conceivable structures, and who summarized his conclusions in his 1977 monograph *Three-Dimensional Nets and Polyhedra*.

Interestingly, different disciplines have tended to preferentially favor one or another of these various models. Thus, while the 20th-century mineralogical literature made extensive use of the coordinated polyhedra model, the main-stream chemical literature has remained largely fixated on the close-packed spheres model, whereas the materials science literature has tended to favor the polymer model. More recently, however, the synthesis of large numbers of "open" solid-state structures using gigantic multidentate organic ligands has awakened a growing interest among chemists in the alternative network model (Öhrström & Larsson 2005).

Unlike the case with finite discrete molecules, the concept of an absolute compositional formula has no meaning for these solids and only relative compositional formulas are possible. Nevertheless, one can write approximate linear structural formulas (Machatschki 1938, Niggli 1945) for these solids in which such basic information as dimensionality (i.e., framework, layer, chain) and coordination numbers are explicitly indicated. Again, though these formulas have been used in the mineralogical literature since the 1940s, they only began to appear in the chemical literature in the 1980s. Likewise, unlike finite discrete molecules, which can in principle exist in the solid, liquid, and gaseous states, infinitely extended structures can exist only in the solid state. Melting, vaporization, or dissolution in a solvent can only be accomplished by breaking these structures into smaller molecular-sized fragments. This is, of course, the primary reason why these materials were not amendable to the classical methods of molecular weight determination available to 19th-century chemists (recall Section 9.9).

Essentially the distinction between intermolecular and intramolecular structure has all but disappeared for these solids, as has the distinction between phase changes and chemical reactions. In keeping with 19th-century conclusions regarding the parallels between chemical and physical equilibria, melting and vaporization for these solids correspond to molecular depolymerization and/or dissociation reactions, and polymorphic transitions to isomerization reactions. Though these conclusions have been apparent for more than 80 years, the mainstream chemical literature has been remarkably resistant to them and it is only recently that they have been reemphasized (Dunitz 1996, Jensen 1998).

In the case of melting or vaporization, the energy required to depolymerize and/or dissociate infinitely extended solids comes from the enthalpy of transition, whereas in the case of dissolution in a solvent it must come from a solute-solvent interaction of some sort. Though this conclusion applies irrespective of the type of bonding present, the most detailed 20th-century treatment of solvation effects for these solids was developed in connection with the ionic bonding model and aqueous electrolyte solutions.

Clausius' earlier suggestion (recall Section 11.7) that the energy for ionic dissociation was derived from the kinetic energy of molecular collisions seemed inadequate to account for the extensive degrees of ionic dissociation postulated by Arrhenius for dilute electrolyte solutions and early proponents of his theory were quite remiss when it came to providing an alternative energy source for the dissociation process. However, in the 1890s several investigators (Ciamician 1890, van der Waals 1891) suggested that the necessary energy might come from compensating intermolecular attractions between the water molecules and the resulting free ions, and in 1893 Werner used his newly developed coordination theory of complex ions to suggest that it was the specific result of the formation of complex hydrates between the cation and the solvent water:

$$MgCl_2 + 6H_2O \rightarrow [Mg(H_2O)_6]Cl_2 \rightarrow Mg(H_2O)_6^{2+} + 2Cl^- \qquad [9]$$

This concept was later extended to anions as well and quantified in terms of simplified cycle calculations and the ionic theory of bonding by Fajans (1919) and Born (1920), thus giving rise to our current concept of ionic solvation energies.

Despite their dissociation, the ions in a solution still have, on the average, more ions of the opposite, rather than like, charge as nearest neighbors. Consequently their solutions (save at extremely low concentrations) tend to deviate from ideal behavior predicated on a statistically random distribution of the solution components. To empirically deal with this departure from ideal behavior, Lewis introduced the concept of mean ionic strength in 1921, and in 1923 Debye and Hückel proposed their well-known theory of moderately concentrated ionic solutions, which was, in turn, further extended by Onsager in 1926.

14.10 The Composition & Structure of Macromolecular Phases

As might be expected, the dividing lines between macromolecules and traditional discrete molecules, on the one hand, and between macromolecules and nonmolecular solids, on the other, are not sharp. Adopting the criteria suggested by Staudinger in 1940, the term macromolecule is generally applied to species containing anywhere from between 10^3 and 10^9 atoms. Species containing less than 10^3 atoms generally exhibit the behavior of typical discrete molecules, whereas those containing more than 10^9 atoms generally correspond to microcrystalline fragments of typical nonmolecular phases.

Like typical discrete molecules, macromolecules can exist in both the solid and liquid state. However, unlike discrete molecules, they seldom survive vaporization to the gaseous state. Like discrete molecules, they also can survive dissolution in a solvent, though, unlike discrete molecules, the resulting "solutions" generally show colloid-like behavior. Ironically, it was this resulting colloidal solution behavior which played a key role in delaying the development of the macromolecular concept.

As we saw in Section 10.6, Graham had originally suggested (albeit rather tangentially) that colloidal particles were composed of loosely associated aggregates of smaller discrete molecules, and by the end of the 19th century it was also assumed that suspensions of colloidal particles were stabilized by the presence of net electrical charges due to the adsorption of ions on their outer surfaces (thus accounting for their coagulation when electrolytes of opposite charge were added to the suspensions). This increasing awareness of the role of adsorption and other surface effects soon forged a link between colloid chemistry and the newly developing field of surface chemistry (originally called capillary chemistry), as indicated by the title of Herbert Freundlich's influential 1909 monograph, *Kapillarchemie: Eine Darstellung der Chemie der Kolloide and verwandter Gebiete*. Important early advances in this area included the development of both the Freundlich (1903) and Langmuir (1916) adsorption isotherms.

Just as the phase rule's concept of a solution as "any homogeneous phase of variable composition" had generalized the traditional concept of liquid solutions to include gaseous, solid, and liquid-crystal solutions as well, so colloid chemists had, by the first decade of the 20th century (von Weimarn 1906, Ostwald 1907), also generalized the concept of a colloidal dispersion to include not only the tradition solid-liquid suspensions studied during the 19th century, but also liquid-liquid dispersions or emulsions, solid-gas dispersions or smokes, liquid-gas dispersions or fogs, etc., and had come to argue that colloidal behavior was in fact yet another state of matter, which any substance could be made to assume given the proper conditions and preparation. The founding of several journals devoted exclusively to colloid chemistry soon followed (*Kolloid Zeitschrift* 1906, *Kolloidchemische Beihefte* 1909, etc.) and, under the aggressive leadership of Wolfgang Ostwald, the colloid paradigm soon came to dominate much of the thinking in the fields of biochemistry, plant chemistry, and physiology.

Since solutions of such naturally occurring substances as starch, cellulose, rubber, etc. clearly displayed colloidal behavior, it was assumed that they too were composed, not of large macromolecules, but of small loosely associated molecules with assorted ionic contaminants adsorbed on their surfaces – a picture that was reinforced by the fact that many of these solutes could not be crystallized and were often difficult to compositionally characterize. While it is true that the increasing number of molecular weight determinations done on these solutions using osmometry (Duclaux 1911, Sørensen 1917) and, when possible, other solution colligative properties (Sabanjeff 1891), consistently gave enormous values for the solute "molecular" weights, it was argued that these simply represented the weights of the colloidal particles themselves and could provide no proof as to whether these particles were, in turn, composed of macromolecular or of molecular aggregates.

However, as recently emphasized by Tanford and Reynolds, there were some exceptions to this consensus in the field of protein chemistry. As we now know, proteins, unlike polysaccharides and rubber, are formed from up to 20 different monomers. Consequently, unlike the latter, their elemental analysis often yields an empirical formula corresponding to a relatively large formula weight, especially if the protein contains a low percentage of sulfur or is associated with a metal atom, such as the iron in hemoglobin (e.g., $C_{758}H_{1203}N_{195}O_{218}FeS_3$ for dog hemoglobin). Hence, based on both its crystallizability (known since 1840) and its elemental analysis, several 19th-century physiological chemists (Thudicum 1872, Zinoffsky 1886) were willing to accept the idea that hemoglobin was in fact a macromolecule. In addition, Loeb, in his 1922 monograph, *Proteins and the Theory of Colloidal Behavior*, presented compelling evidence that the ionic charges responsible for the stabilization of colloidal protein solutions were not due to stray ions adsorbed on their surfaces but were inherent to the proteins themselves, as demonstrated by the stoichiometries of their acid-base reactions. However, despite these exceptions, there is little doubt that the molecular aggregate or micelle theory of colloidal behavior remained the ruling paradigm for the first three decades of the century.

It is the German chemist, Herman Staudinger, who first put forward the opposing hypothesis in a lecture published in 1919 that many of these colloids were actually large chain macromolecules (he originally used the term “high molecular compounds”) rather than loosely associated molecular clusters or micelles. The next year he began a research program which, over the next 30 years, would provide a sound experimental basis for the macromolecular concept. Rather than focusing on poorly characterized natural macromolecules, Staudinger made extensive use of synthetic macromolecules produced in the laboratory by means of polyaddition and polycondensation reactions. In this manner he was able to engineer the chain length and so establish important correlations between the sizes of macromolecules and their various properties. As already mentioned in Section 13.9, many of the 20th-century advances in molecular weight determination were introduced in connection with this work.

By the late 1930s Staudinger and all but the most conservative colloid chemists had reached the consensus that both of them had been correct after their fashion and that examples of organic colloids existed corresponding both to Graham's original molecular association concept and to Staudinger's macromolecular chain concept – a resolution that Staudinger elegantly summarized in his 1940 monograph, *Organische Kolloidchemie*. Missing from Staudinger's summary of this resolution, however, were inorganic colloids, though Scherrer had shown as early as 1918 that metallic gold colloids were crystalline and hence presumably corresponded to microcrystalline fragments of their infinitely polymerized bulk phase structures.

Staudinger originally thought of organic chain macromolecules as rigid rods. However, by the early 1930s, several researchers (Mark 1930, Haller 1931, Kuhn 1934, Meyer 1934) had noted that the well-established concept of free rotation about single bonds pointed instead to the concept of a flexible macromolecular chain capable of folding and unfolding itself in response to its environment. In 1942 Huggins and Flory each independently made this model the basis of a detailed statistical mechanical treatment of macromolecular chains and solutions. These results, as well as subsequent work by Flory, were eventually summarized in Fory's 1953 monograph, *Principles of Polymer Chemistry*. Similar work was done in Russia by Volkenstein, but remained largely unknown to western chemists until the publication of an English translation of his monograph, *Configurational Statistics of Polymeric Chains*, in 1963.

Beginning in the 1950s the field of macromolecular chemistry began to split into two distinct subdisciplines: molecular biology, which took the naturally occurring macromolecules, such as the proteins, nucleic acids, and polysaccharides, as its province, and industrial polymer chemistry, which took synthetic organic rubbers, fibers, and plastics as its province. Despite its many valuable contributions to chemistry, one of the unfortunate by-products of the development of the field of synthetic organic polymer chemistry was its gradual trivialization the the term "polymer" to the point that it currently functions as little more than a synonym for an organic macromolecule composed of covalently bonded chains. The term "polymer" (from the Greek, *poly*, meaning "many" and *meros*, meaning "part") was first introduced by Berzelius in 1832 to distinguish between distinct substances having identical relative compositional formulas (e.g, CH), but different absolute compositional formulas (e.g. C_2H_2 versus C_6H_6), whereas the term "macromolecule" was introduced by Staudinger in 1922 to denote large molecules containing more than 10^3 atoms and displaying colloidal solution behavior, irrespective of their composition.

Strictly speaking, these two terms stand for logically distinct concepts. As originally defined, the polymer concept was purely compositional in nature and carried no restrictions concerning the sizes, structures, or bonding in the species being compared. There are many polymers which do not qualify as macromolecules (e.g., SO_3 versus S_3O_9) and many macromolecules that do not compositionally qualify as true polymers (e.g,. so-called copolymers and condensation polymers). In addition, there are many inorganic polymers and macromolecules that are neither chains nor covalently bonded. To argue that one must accept this degraded definition as part of the natural evolution of language, or to try and correct for it by introducing additional qualifying terms, such as "oligomer" (Larsen 1984), simply exacerbates an already unfortunate situation by ignoring the fact that the term polymer is still used in its original sense in many other areas of chemistry (e.g., inorganic solid-state chemistry, glass chemistry, cement chemistry, etc.).

14.11 Other States of Matter

The above discussions have focused largely on the phase structures of solids, liquids, and gases. However, the 20th century also saw substantial advances in the preparation (Vorländer 1908, 1924), classification (Friedel 1922), and theory (Oseen 1929) of thermotropic liquid-crystal phases and in the study of lyotropic liquid-crystal micelles or colloids (Sandqvist 1915, Maclennan 1923). Indeed, more than a half dozen monographs on liquid crystals were published before 1930, ranging from Lehmann's 1904 volume, *Flüssige Kristalle*, to Oseen's 1929 volume, *Flüssige Kristalle: Tatsachen und Theorie*.

Von Fuchs' original theory of the amorphous state (1833) was challenged during the early 19th century by the German physicist, Morris Frankenheim, who claimed that these materials were actually "crypto" crystalline – that is, that they were really composed of submicroscopic crystallites, whereas von Fuchs had compared them to frozen or rigid liquids. As is so often the case, both parties were right after their fashion. After the introduction of the X-ray powder pattern technique by Debye and Scherrer in 1916, it was found that many so-called amorphous materials were in fact microcrystalline, just as Frankenheim had believed, whereas others were truly amorphous. Furthermore, thermal analysis and phase rule studies of this latter class concluded, in keeping with von Fuchs' original views, that these materials were best described as supercooled liquids.

The first attempts to apply the new electrical theory of matter to the amorphous or glassy state were made within the context of the ionic bonding model. Building on the early work of Goldschmidt (1926), Zachariasen (1932) introduced the theory that silicate and related inorganic glasses were based on the formationof random three-dimensional ionic network (i.e., framework) structures in the liquid state and formulated a series of simple rules for predicting which compounds were most likely to form glasses. Beginning in 1933, substantial support for Zachariasen's model was provided by Warren, based on his X-ray diffraction studies of silicate glasses.

Known as the Zarchariasen-Warren theory, the random network model continued to dominate textbook accounts of glass chemistry throughout most of the 20th century, due in large part to the overwhelming commercial importance of silicate and related inorganic glasses. However, it was known, almost from its inception, that this model could not serve as a general theory of glass formation, as Tammann had shown as early as 1898 that many molecular organic compounds could also be forced into the glassy state if they were cooled rapidly enough. In fact, a more general model, capable of dealing with both nonmolecular inorganic glasses and molecular organic glasses, had been proposed by Hägg as early as 1935. According to this model, the tendency to form supercooled liquids or glasses was related to the presence of large, bulky, asymmetric structural units in the liquid state (whether discrete neutral molecules or polymerized complex anions) which inhibited the rapid formation of an organized crystal lattice.

The fact that glass formation depends not only on the chemical nature of the material in question, but also on its rate of cooling, meant that purely structural models, like those of Zachariasen and Hägg, could only tell half the story, and in the 1950s, they were gradually replaced by newer kinetic theories of glass formation (Thomas & Staveley 1952, Staveley 1955), which viewed the process as a competition between the rate of cooling, on the one hand, and the rate of crystallization, on the other. Within the context of these models, it became apparent that the structural factors emphasized by the older theories were indicative of the existence of potentially large activation energies for crystallization and hence conducive to glass formation at even moderate cooling rates.

14.12 Ambiguities Revisited

The concepts of macromolecular and nonmolecular phases not only had important consequences for the traditional distinctions between such concepts as heterogeneous versus homogeneous mixtures, phases versus molecules, and physical versus chemical changes, they also led to a resolution of the original debate between Proust and Berthollet concerning the distinction between solutions and compounds (recall Section 10.6).

Shortly after the discovery of isomorphism (Mitcherlich 1821), it was found that certain isomorphous crystals could form so-called "mixed crystals" with one another (the most famous case being that of chrome and aluminum alum), and with the rise of thermal analysis and phase studies in the 1890s, it became apparent that these crystals were in fact examples of "solid solutions" (a term popularized by van't Hoff in 1890) – that is, they were homogeneous phases of variable composition analogous in their thermodynamic behavior to both liquid and gaseous solutions. Indeed, the phase studies of such chemists as Bakhuis Roozeboom in Holland, Tammann in Germany, and Kurnakov in Russia soon uncovered the fact that crystal isomorphism was neither a necessary nor a sufficient condition for the formation of solid solutions, that the phenomena was quite common, especially at higher temperatures, and that it could be observed for all classes of simple substances and compounds, including metals and nonmetals, inorganic salts, organic molecules, and even liquid crystals.

The initial results of these phase studies were summarized in 1908 by Bruni in his monograph *Feste Lösungen und Isomorphismus*. Though admitting that the discovery of solid solutions did not definitely resolve the question of whether the phases in question were physical mixtures of otherwise stoichiometric components, or true chemical compounds of variable composition, Bruni did argue that the increasing departure of solution properties from the averaged properties of the components on passing from gaseous solutions, through liquid solutions, to solid solutions strongly suggested an increasing role for specific chemical interactions between the components and that, while gaseous solutions were primarily mechanical mixtures, it was not unreasonable to view many solid solutions as compounds of variable composition.

However, an important experimental distinction between gaseous and liquid solutions, on the one hand, and solid solutions, on the other, unavailable to Bruni in 1908, was the fact that after 1913 the structures of the latter, unlike the former, could be determined using X-ray diffraction analysis. When this was finally done, it was discovered, as was the case with the debates over the nature of colloids and the amorphous state discussed earlier, that both Proust and Berthollet had been right. In certain solid solutions (primarily involving organic compounds) the stoichiometric molecules of the pure components were clearly distinguishable and the solutions were in fact merely physical dispersions of one molecule in another. In other cases (mostly inorganic salts and metals) the phases were nonmolecular compounds and the variable composition was due to a continuous substitution of one ion or atom for another within the compound's infinitely extended structure – in short, they were truly compounds of variable composition.

In the case of inorganic salts and minerals, it was soon discovered that this variability could be produced not only by the simple 1:1 substitution of ions having identical charges and similar radii for one another (Grimm 1923) but also by complex coupled substitutions involving three or more ions (e.g., Na^+ and Al^{3+} in place of Si^{4+} in the aluminosilicates: Machatschki 1928, 1929) or by coupling multiple oxidation states of one component with the creation of various lattice defects (Schöttky & Wagner 1930).

Alas, the great revolution in the theory of chemical composition and structure envisioned by these early workers, based on the conclusions of the phase rule and the discovery of nonmolecular compounds of variable composition, never came to fruition. Instead, the increasing specialization of science in the 20th century allowed the impact of these discoveries to be blunted by shunting them into other specialities. Nonmolecular and nonstoichiometric ionic phases became the special province of the mineralogist and the glass technologist; nonmolecular and nonstoichiometric metallic phases became the special province of the metallurgist and solid-state physicist; whereas macromolecular phases and colloids became the special province of the materials scientist and the industrial polymer chemist. Instead, mainstream chemistry remained largely fixated on the paradigm of the discrete stoichiometric molecule, primarily as a result of its continued domination by classical organic chemistry and the subsequent rise of organometallic chemistry.

14.13 The Quantification of Molecular Structure

Though the 19th-century chemist had succeeded in fully quantifying molecular composition, the 19th-century concept of molecular structure remained largely qualitative. One could specify the connectivity of the atoms within a molecule and the idealized geometric disposition of the resulting bonds around a given atom (i.e., as tetrahedral, octahedral, etc.) but quantitative measurements of actual bond distances and angles were out of the question. Again, all of this was changed by the advent of X-ray structure determinations. The quantitative data on bond distances and angles provided by these determinations, as summarized in such compilations as the annual *Structure Reports* (1913-1990), soon allowed the development of the first quantitative scales of ionic radii (Landé 1920, Wasastjerna 1923, Goldschmidt, 1926, Pauling 1927), covalent radii (Bragg 1920, Huggins 1926, Goldschmidt 1926, Pauling 1932) and metallic radii (Goldschmidt 1929, Pauling 1939). By the 1950s this data, as well as that obtained by spectroscopy and electron diffraction for gas- and liquid-phase molecules, had also resulted in the publication of massive compilations of measured bond distances and angles (Sutton *et al* 1958). Many of these compilations have now been absorbed into computerized data banks, which give the modern chemist almost instantaneous access to a wealth of quantitative molecular structural data undreamt of by his 19th-century counterpart.

With the increasing availability of computers, enormous effort was also expended by theoretical chemists in the period 1955-1985 in attempting to develop computational algorithms that would allow the reliable quantum mechanical calculation of molecular properties. This is now the case for smaller molecules and it is possible to purchase programs for a personal computer which, if given the composition and bonding connectivity, will automatically calculate optimal bond angles, distances, atomization energies, electron densities, and ionization energies for most small organic species. In short, from both an experimental and computational viewpoint, molecular structure has been fully quantified.

Yet another important consequence of this quantification was the introduction of several new types of molecular model kits, including space-filling models (Stuart 1934, Briegleb 1950) and framework models (Dreiding 1959), whose parts were accurately scaled to reproduce relative atom sizes and/or bond lengths and angles. The purpose of these models was to deal not only with the bonding topology and local geometries about each atom center, but also with the molecule's ternary structure or overall conformation, due to selective rotation about various bonds.

Though the concept of conformational analysis was first introduced by Sachse in 1890, study of these newer mechanical models helped to provide valuable insights into the stable conformations and selective reactivities of ever more complex molecules. Beginning in the 1960s (Hendrikson 1961, Wiberg 1965), much of this modeling activity was computerized, where it was combined with empirical and semi-classical force field calculations in order to facilitate the computation of optimal molecular conformations. Though this type of calculation had been done by hand earlier (Andrews 1930, Westheimer 1946, Allinger 1959) in conjunction with the use of mechanical models, its computerization greatly extended its range of application. Now known as "molecular mechanics," modern computerized molecular modeling is currently able to cope with even the highly complex conformations of such macromolecules as the proteins and nucleic acids. With 3D computer drawings of molecules it is also possible to assess the degree of similarity between two molecules using superposition, something which was impossible using traditional 3D solid, mechanical models – an ability which has revolutionized the design of drugs and the modeling of drug-receptor interactions.

A final consequence of this 20th-century quantification of structure was the rise of explicit symmetry considerations in chemistry. Though the chemical application of formal symmetry operations had been pioneered by the Dutch chemist, Frans Jaeger, in the early decades of the century, as illustrated by both his 1917 monograph, *Lectures on the Principle of Symmetry and Its Application in All Natural Sciences,* and his 1930 Baker Lectures, *Spatial Arrangements of Atomic Systems and Optical Activity*, this work had little impact on the chemical curriculum, and it was not until the 1960s that graduate courses in symmetry and group theory suddenly became fashionable.

Whereas Jaeger had emphasized the relevance of molecular symmetry to such topics as crystal morphology and optical activity, and was thus using the formal symmetry considerations developed by 19th-century crystallographers to update and clarify the less rigorous work of Pasteur, van't Hoff, and Le Bel on asymmetry, dissymmetry, and optical activity, the resurgence of the 1960s focused instead on its relevance to spectroscopy and MO theory (including both crystal-field and ligand-field theory) – applications which had been developed primarily by physicists starting in the late 1920s. Literally dozens of textbooks and monographs appeared over the next two decades of which one of the earliest and most influential was F. A. Cotton's text, *Chemical Applications of Group Theory*, first published in 1963, and followed two years later by the equally popular text by Jaffe and Orchin, *Symmetry in Chemistry*. Yet further applications came with the discovery of the importance of symmetry considerations in chemical reactivity during this same period (see Section15.5).

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Lecture XV

The Twentieth Century

(1901-2000)

The Electronic Theory of Reactivity

Chemistry is ontologically rich but epistemologically poor.

John Servos 1990

15.1 Chemical Reactivity

With respect to the theory of chemical reactivity, six important events occurred during the 20th century:

a. The traditional stoichiometric classification of chemical reactions was supplemented by an alternative electronic classification.

b. Chemical thermodynamics was both codified and quantified and the basic theory extended beyond equilibrium conditions to include both steady-state and irreversible systems in general.

c. The quantitative theory of chemical kinetics was fullydeveloped and tied to the electrical theory of molecular composition and structure via the concepts of potential energy surfaces and transition states.

d. A detailed electronic theory of organic reactivity was developed in conjunction with the rise of a new subdiscipline known as physical organic chemistry

e. An unified theory of electrochemical kinetics and equilibrium was developed.

f. Both photochemistry and statistical mechanics were revolutionized via the incorporation of the quantum mechanical concept of discrete energy levels.

15.2 Stoichiometry

The term "molar" was first introduced into chemistry by Hofmann in 1865 as a synonym for the term "macroscopic." Its current use, as well as that of the corresponding noun "mole," to denote, not just any macroscopic sample of matter, but rather one whose mass in grams is equal to that of its corresponding formula mass in atomic mass units, is usually attributed to Ostwald sometime around the turn of the 20th century (Ostwald 1900). However, explicit incorporation of the mole concept into routine stoichiometric calculations does not appear to have been common before the1950s (Benson 1952, Anderson 1955).

The classification of chemical reactions began in the 18th century with the introduction of affinity tables and diagrams and the resulting division of chemical reactions into the classes of simple attractions, single elective attractions, and double elective attractions (Bergman 1775). With the rise of the concepts of molecular composition and structure in the 19th century, it became possible to further classify reactions in terms of their net molecular stoichiometries as isomerization or rearrangement reactions, addition reactions, decomposition reactions, single and double displacement reactions, etc. or, alternatively, in organic chemistry, as addition, elimination and substitution reactions. Finally, with the advent of the electrical theory of matter in the 20th century, we see the introduction of various electronic schemes for the classification of chemical reactions – a process which mirrored the development of the electronic theory of bonding outlined in Section 14.5.

Within the context of the ionic bonding model, which was dominant from 1904-1925, chemical reactions could be sorted into two electronic classes: those involving conservation of ionic type and those involving the creation of new ionic types via electron transfer (Falk & Nelson 1909, 1911; Fry 1915, 1921) and which roughly corresponded to the older concept of oxidation-reduction reactions.

The dominance of the qualitative Lewis electron-pair model of the covalent bond in the period 1925-1950 further elaborated the first of these classes, thus giving rise to our current tripartite electronic classification (Luder and Zuffanti 1946):

a. Electron coupling reactions or so-called free-radical reactions involving either homogenic covalent bond formation or homolytic covalent bond cleavage:

$$A^{\bullet} + {}^{\bullet}B \leftrightarrow A{:}B$$

b. Electron-pair donor-acceptor reactions or so-called Lewis acid-base reactions involving either heterogenic covalent bond formation or heterolytic covalent bond cleavage:

$$A + {:}B \leftrightarrow A{:}B$$

c. Electron-transfer reactions or so-called oxidation-reduction reactions involving complete electron transfers:

$$A^{\bullet} + {}^{\bullet}B \leftrightarrow A^{+} + {:}B^{-}$$

Of these three, the class corresponding to heterogenic bond formation and/or heterolytic cleavage received the most attention. It was in fact independently proposed at least four times: by Lewis (1923, 1938) in the field of main-block chemistry, under the guise of generalized acid-base reactions; by Sidgwick (1925, 1927) in the field of coordination chemistry, under the guise of donor-acceptor reactions; by Lapworth (1925) and Robinson (1932) in the field of organic chemistry, under the guise of cationoid-anionoid reactions; and by Ingold (1933, 1934), also in the field of organic chemistry, under the guise of electrophilic-nucleophilic reactions.

The 20th-century study of free-radical reactions began with the preparation of the triphenylmethyl radical by Moses Gomberg in 1900. By 1914 a sufficient number of additional examples were known to justify the publication of Schmidlin's 233-page monograph *Das Triphenylmethyl.* This was followed in 1924 by Paul Walden's book, *Chemie der freien Radikale,* and by the 1935 volume, *The Aliphatic Free Radicals,* by F. O. and K. K. Rice. Though Lewis had pointed out as early as 1923 that, from an electronic point of view, free radicals must correspond to paramagnetic species with at least one unpaired electron – an observation that would eventually result in the widespread use of magnetic susceptibility and ESR measurements in their study, the first monograph to explicitly treat free-radical reactions from an electronic, rather than an empirical point of view – *The Chemistry of Free Radicals* by Waters – did not appear until 1946, the same year as the first monograph on Lewis acid-base reactions by Luder and Zuffanti, mentioned in Section 14.8. A similar monographic treatment of the mechanisms of solution-phase electron-transfer reactions had to await the publication of Henry Taube's 1970 volume, *Electron-Transfer Reactions of Complex Ions in Solution*.

The final stage in the development of the electronic classification of chemical reactions reflected the increasing dominance, beginning in the 1950s, of molecular orbital theory and the explicit introduction of orbital notation. Based on Mulliken's elaboration (1950, 1952) of electron-pair donor-acceptor complexes using the bonding and nodal properties of the donor and acceptor orbitals, it expanded the traditional concept of a Lewis base as a nonbonding electron-pair or n-donor to also include both π-bonding donors and σ-bonding donors, and the traditional concept of a Lewis acid as a nonbonding electron-pair or n-acceptor to also include both π*-antibonding and σ*-antibonding acceptors as well.

Though Mulliken's generalization was initially applied only to intermolecular donor-acceptor addition reactions, it has since been shown to be equally applicable to intramolecular donor-acceptor interactions, as manifested in the so-called "anchimeric" or neighboring group effect of the organic chemist (Leffler 1956), and to intermolecular donor-acceptor displacement reactions as well (Jensen 1980, Lewis 1999). A similar orbital classification of photochemically excited diradicals was introduced by Kasha in 1950, and in 1974 Hay attempted to develop a related approach to free-radical reactions in general. Though possible in principle, a parallel orbital elaboration of electron-transfer reactions does not seem to have been widely applied.

15.3 Thermodynamics

As we saw in Lecture 11, both the basic laws of chemical thermodynamics and extensive collections of enthalpy data were available by the last quarter of the 19th century. What was lacking, however, was an agreement as to the best mathematical formalism for presenting these laws and for collecting and formatting the missing thermodynamic data relating to both free-energy and entropy changes. Though Gibbs had introduced the chemical potential in 1875, most 19th- and early 20th-century textbooks dealing with chemical thermodynamics continued to make use of the "Arbeit" or "affinity" functions favored by van't Hoff and Nernst, which, though mathematically equivalent to Gibbs' function, tended to disguise the role of entropy in chemical processes.

It is the 1923 text, *Thermodynamics and the Free Energy of Chemical Substances*, by Lewis and Randall, which summarized the work of Lewis and his associates over the previous two decades, that is generally credited with having finally established the current dominance of the Gibbs function (originally symbolized as ΔF by Lewis and his associates):

$$\Delta G = \Delta G^\circ + RTlnQ = \Delta H^\circ - T\Delta S^\circ + RTlnQ \qquad [1]$$

and with focusing data collection on the question of supplementing the existing enthalpy data with the missing free-energy and entropy values. Lewis was also the first to emphasize the importance of properly defining standard states and was responsible for the decision to adjust equation 1 for departures from ideality via the introduction of both fugacity (1901) and activity (1907) terms in the concentration quotient (lnQ).

Though there are many ways of determining bothΔG° and ΔS°, one of the simplest and most accurate involves the measurement of the potential of an electrochemical cell and its variation with temperature:

$$\Delta G^\circ = -zF\mathscr{E}^\circ \qquad [2]$$

$$\Delta S^\circ = -zF(d\mathscr{E}^\circ/dT) \qquad [3]$$

an approach favored by Lewis and his associates and which ultimately culminated in the publication in 1938 of the monograph, *The Oxidation States of the Elements and their Potentials in Aqueous*

Solutions, by Lewis' colleague, Wendall Latimer.

A second fundamental approach to determining entropy values is based on the Nernst heat theorem or so-called third law ofthermodynamics, first proposed by Nernst in 1906 and summarized by him the next year in his Silliman Lectures, *Experimental and Theoretical Applications of Thermodynamics to Chemistry*, and in much greater detail in his 1918 monograph, *Die theoretischen und experimentellen Grundlagen des neuen Wärmesatzes*. As originally formulated, the theorem stated that the affinity of a reaction became equal to the heat of reaction as the temperature approached absolute zero. Prior to the publication of the Lewis and Randall text, most early 20th-century treatments of chemical thermodynamics (Haber 1905, Pollitzer 1912, Sackur 1912, Nernst 1917), presented the theorem as a method for evaluating the integration constant (I) in the integrated form of the van't Hoff reaction isochore:

$$lnK = -Q_0/RT + (\Sigma\nu\alpha/R)lnT + (\Sigma\nu\beta/R)T + ... + I \qquad [4]$$

and made no attempt to partition the various heat capacity terms in the equation between an explicit enthalpy term and an explicit entropy term. However, within the context of the Gibbs function and the data collection program established by Lewis, which required the separate tabulation of $\Delta G°$, $\Delta H°$ and $S°$ values, it became equivalent to the proposition (first formulated by Planck) that the entropy of a substance (as a perfect crystal) was equal to zero at absolute zero (i.e., $S_0 = 0$), thus allowing one to evaluate the absolute entropies of substances from their heating curves:

$$S_T = {}_0\!\int^{T_m} C_p(s)dT/T + \Delta H_m/T + {}_{T_m}\!\int^{T_v} C_p(l)dT/T + \Delta H_v/T + {}_{T_v}\!\int^{T} C_p(g)dT/T \qquad [5]$$

In their text of 1923 Lewis and Randall included a table of free-energy and entropy values at 298°K for 140 chemical species. By 1930 Randall was able to assemble 81 pages of enthalpy, entropy, and free-energy data for inclusion in the seventh volume of the *International Critical Tables*, and by 1938 Latimer was able to list free-energy values for 531 species in his monograph on oxidation potentials. Most of the data collected by the Berkeley school related to simple inorganic species. However in 1932 Sutton and

Huffman published a small monograph entitled *The Free Energies of Some Organic Compounds* which reported free energies of formation for some 155 organic species.

Building on the 1936 monograph, *The Thermochemistry of the Chemical Substances*, by Bischowsky and Rossini, the National Bureau of Standards undertook a program in 1940 to collect and collate thermodynamic data, the results of which were distributed after the Second World War in the form of loose-leaf tables. These were revised and published as a single volume in 1952 by Rossini and associates under the title, *Selected Values of Chemical Thermodynamic Properties*, and contained more than 1170 pages of enthalpy, free-energy, entropy, and heat capacity data. Beginning in 1959 these efforts were further amplified via the publication of the loose-leaf *JANAF (Joint Army-Navy-Air Force) Thermochemical Table*s, developed by Dow Chemical under government contract with the initial goal of critically evaluating the thermodynamics of various inorganic species with respect to their potential use as rocket propellants.

As more and more data accumulated, patterns became apparent which also allowed one to approximate values for substances that had not been studied experimentally. Thus as early as 1921 Latimer was able to formulate a set of simple rules for approximating the entropies of ionic solids, and in 1951 he and Powell extended the method to the estimation of the entropies of aqueous ions. Similar estimation procedures were developed for organic species, as first summarized by Janz in his 1958 monograph, *Estimation of Thermodynamic Properties of Organic Compounds*. As with the 20th-century quantification of chemical structure, discussed in Section 14.13, the 20th-century quantification of chemical thermodynamics has now given rise to vast computer banks of thermodynamic data available to the chemist at the touch of a computer key board.

A valuable contribution to the graphical representation of thermodynamic data was made in 1944 by the British physical chemist, Thomas Ellingham, when he demonstrated the utility of linear $\Delta G°$ versus T plots (slope = $-\Delta S°$, intercept = $\Delta H°$) when discussing the temperature-dependent feasibility of reactions which could be formally dissected into the difference between two competing half-reactions sharing a common reactant (B):

$$\begin{array}{l} \ \ A + B \rightarrow AB \\ -(C + B \rightarrow CB) \\ \hline \ \ A + CB \rightarrow AB + C \end{array}$$

Now known as Ellingham diagrams, in honor of their originator, these plots have found widespread use in both metallurgy and geochemistry (Reed 1971).

Though the Gibbs-Lewis formulation of chemical thermodynamics continues to dominate the chemical literature, an alternative approach introduced by the Belgian physicist, Théophile De Donder, and summarized in his monograph, *l'Affinité*, published in installments between 1927 and 1934, has also gradually gained acceptance. Among the innovations introduced by De Donder are his well-known "extent of reaction" or "degree of advancement" parameter (1920):

$$d\xi = dn_i/\nu_i \qquad [6]$$

his affinity function (1922):

$$A = -(dG/d\xi) \qquad [7]$$

and his generalization of both reaction velocity (1927):

$$v = d\xi/dt \qquad [8]$$

and the Le Chatelier-Braun principle (1934):

$$-(dG/d\xi)(d\xi/dt) = Av \geq 0 \qquad [9]$$

Classical chemical thermodynamics deals with equilibrium in closed systems. However, there are many open systems that are not at equilibrium which are also of interest, such as the energy and matter exchanges found in a typical ecological system, in an individual organism, or in the continuous flow reaction systems used in chemical engineering. These systems, with their coupled energy and matter flows, can be modeled using a purely kinetic approach.

However, the 20th century saw an increasing interest in exploring their thermodynamic aspects as well, thus giving rise to a new branch of chemical thermodynamics variously known as steady-state, nonequilibrium, or irreversible thermodynamics.

Though the earliest example of such a treatment actually dates back to Lord Kelvin's thermodynamic analysis of the thermoelectric effect (1854), the first serious attempts at generalization occurred with the work of Onsager (1931), Meixner (1941) and Casimir (1945) on the coupling constants or so-called reciprocal relations connecting the various energy and matter flows. As it turned out, De Donder's coupling of the reaction velocity and affinity in equation 9 made his thermodynamic notation particularly adaptable to the needs of the new field and much of its later elaboration has been the work of his academic descendants (collectively known as the Brussels school), the most notable of whom was Prigogine, who authored the first monograph on the subject –*Étude thermodynamique des phénomènes irrèversibles* – in 1947.

Prigogine was also responsible for the discovery of one of the few extremum conditions governing the stability of nonequilibrium systems. Whereas the change in the generated entropy with respect to extent of reaction is at a maximum at equilibrium for a chemical reaction:

$$(d^2S/d\xi^2) < 0 \qquad [10]$$

the change in the generated entropy with respect to time is at minimum for steady states close to equilibrium:

$$(d^2S/dt^2) > 0 \qquad [11]$$

15.4 Kinetics

The 20th century saw the development of two major quantitative theories of reaction rates based on the empirical Arrhenius equation (1889) for the temperature dependency of the rate constant:

$$k = Ae^{-E^*/RT} \qquad [12]$$

The first of these, known as the collision theory, modeled therate constant as the product of a collision frequency (Z) per unit volume and concentration, calculated using the kinetic theory of gases; an empirical steric or orientation factor (P); and a Boltzmann distribution ($e^{-E^*/RT}$) term representing the fraction of the collisions having the necessary activation energy (E^*) for the reaction in question:

$$k = PZe^{-E^*/RT} \qquad [13]$$

First proposed by the German chemist, Max Trautz, in 1916 and again by the British chemist, W. C. McCullagh Lewis, in 1918, collision theory was essentially a quantification of the qualitative model of chemical reactions originally outlined by Pfaundler in 1867 (recall Section 11.10), and was first summarized in book form by Hinshelwood in his classic 1926 monograph, *The Kinetics of Chemical Change in Gaseous Systems*.

The second theory, known as absolute rate theory, built on Pfaundler's earlier concept of a collision complex and interpreted the rate constant as the product of an equilibrium constant (K^*) for the formation of this complex (now called the activated complex or transition state) and a universal frequency factor ($\mathbf{k}T/h$) governing the rate of its unimolecular decomposition into the desired reaction products:

$$k = (\mathbf{k}T/h)K^* \qquad [14]$$

Substitution of the usual thermodynamic interpretation of K in terms of ΔG and of ΔG in terms of ΔS and ΔH gives:

$$k = (\mathbf{k}T/h)e^{-\Delta G^*/RT} = (\mathbf{k}T/h)e^{\Delta S^*/R}e^{-\Delta H^*/RT} \qquad [15]$$

and reveals that the E^* term in the Arrhenius equation represents the enthalpy of formation (ΔH^*) of the collision or activated complex whereas the A factor is a product of the universal frequency factor and the $e^{\Delta S^*/R}$ contributions to the equilibrium constant for the formation of the complex. This may be compared with the alternative interpretation of the *A* factor given by simple collision theory in equation 13:

$$A = PZ = (\mathbf{k}T/h)e^{\Delta S^*/R} \qquad [16]$$

The idea that rates depended in some manner on the free-energy of formation of an activated or "critical" complex was first suggested by the French physicist, René Marcelin, in 1910 and again by the Dutch chemists, Kohnstamm and Scheffer, in 1911, who were also the first to employ explicit entropy and enthalpy of activation terms. The final form of the theory was developed independently in 1935 by Henry Eyring in the United States and by the team of M. G. Evans and Michael Polanyi in Great Britain, and was first summarized in book form in the classic 1941 monograph, *The Theory of Rate Processes,* by Glasstone, Laidler and Eyring.

The third important development in 20th-century kinetics was the concept of a potential energy surface on which the various reactants, products, and reaction intermediates are represented as potential wells of varying depth and the transition states or activated complexes as saddle points connecting these wells. Liveing had actually made qualitative use of a two-dimensional potential surface as early as 1883 when discussing his thermodynamic theory of chemical equilibrium. However, the use of such surfaces in discussing the kinetics of chemical reactions was first suggested by Marcelin in 1914, and their theory was worked out by, among others, Rice (1915), Tolman (1920), Rodebush (1923), Eyring and Polanyi (1931), and Pelzer and Wigner (1932).

One of the more successful applications of absolute rate theory and the potential-energy surface concept was their use by Marcus (1956-1965), in conjunction with the classical theory of aqueous polyelectrolytes, in developing a model of outer-sphere electron-transfer reactions known as RRKM theory – work for which he was awarded a Nobel Prize in 1992.

15.5 The Electronic Theory of Organic Reactivity

By the end of the 19th century the organic chemist was aware of literally thousands of reactions and was increasingly preoccupied with a search for explicit rules which would allow the prediction and control of organic reactivity. In keeping with the earlier 18th-century concept of affinity, this search was largely based on a speculative consideration of competing interatomic forces as a function of molecular composition and structure, and only gradually did the resulting speculations make contact with the formal theories of thermodynamics and kinetics discussed in the previous sections.

In Section 9.12 we dealt with only the simplest type of organic molecule consisting of only a hydrocarbon moiety ($\varkappa$) and a single functional group (ϕ). In actual fact, most organic molecules are considerably more complicated and may contain more than one potential functional group. In a given type reaction in which only one of these potential functional groups is chemically active, the nonreactive groups are referred to as substituents (σ) and our generalized type reaction may be rewritten as an elaboration of equation 9.5:

$$\sigma\text{-}\varkappa\text{-}\phi + \varrho \rightarrow \textit{products} \qquad [17]$$

in which the entire σ-$\varkappa$-ϕ complex now functions as the reaction substrate.

However, even though the substituent is not being formally attacked in the reaction under consideration, it is found to exercise a profound influence on the reactivity of the chemically active functional group – an influence which varies not only with the chemical character of the substituent but also with its position in the molecule relative to the reactive functional group. The power of organic chemistry lies in the fact that the organic chemist is able to study reactivity by systematically and selectively varying σ, $\varkappa$, ϕ or ϱ and so in principle tease out the dependence of organic reactivity on each of these four variables (assuming, of course, that such additional environmental variables as temperature, concentrations, and solvent are also kept constant).

As we saw earlier, it was the variation of ϕ at constant σ, $\varkappa$, ϱ and/or the variation of ϱ at constant σ, $\varkappa$, ϕ that gave rise to the concept of the generalized type reactions characteristic of each distinct functional group, whereas the variation of $\varkappa$ at constant σ,

ϕ, ϱ gave rise to the concept of homologous series. These two concepts form the core of modern systematic organic nomenclature and still serve as the organizational basis of most introductory organic textbooks. It is, however, the systematic variation of σ at constant $\varkappa$, ϕ, ϱ and a concern by various chemists (Markovnikov 1875, Meyer 1887, Ostwald 1889, van't Hoff 1899) in the last quarter of the 19th century as to how the resulting variations in reactivity correlated with the electronegativities and positions of these substituents relative to the active functional group which mark the beginnings of modern electrochemical and stereochemical speculation on the nature of organic reactivity and the origins of the discipline of physical organic chemistry.

Unfortunately, the electrochemical aspects of these early speculations – many of which were summarized in Henrich's 1908 monograph, *Neure theoretische Anschauungen auf dem Gebeite der organischen Chemie* – were hampered by the lack of an underlying electrical model of matter, a situation which was finally remedied by J. J. Thomson's discovery of the electron in 1897 and his subsequent development (1904) of the plum-pudding model of the atom and the electron-transfer or polar model of chemical bonding. From this point on, the 20th-century development of the resulting electronic theory of organic reactivity, like the electronic classification of chemical reactions discussed in Section 15.2 – which was one of its important by-products – reflects the three stages in the development of the electronic theory of bonding outlined in Section 14.5.

Attempts to rationalize organic reactivity in terms of the polar or ionic model of chemical bonding were made by numerous chemists (Falk & Nelson, Fry, Lapworth, Jones, Stieglitz, Noyes) in the period 1909-1925. Since most of the chemists in question were American, their combined efforts are often characterized as the "American school" of organic reactivity. The underlying premise of the approach was that reagents with negative reactive sites would selectively attack positive sites in the organic substrate and vice versa for positive reagents. Assignment of positive and negative ionic character to the atoms in a given bond was relatively unambiguous when the bond was heteroatomic and was based on the relative electronegativities of the atoms in question and on the ionic fragments generated when the bond was heterolytically ruptured. Assignment of ionic charges to the carbon atoms in a homocatenated carbon chain or ring was, however, more difficult and was based on the postulate that the charges on the carbon atoms alternated, the precise sequence of charges having been determined by a polar substituent or "key" atom located at some point on the chain or ring in question. These early polar theories made little or no contact with the formal theory of kinetics. The reactivity data being rationalized was generally the relative yields of the various alternative products formed in the reaction rather than actual rate constants and there seems to have been little explicit understanding that the rationale in question was also heavily dependent on the assumption of a specific mechanism.

Perhaps the most elaborate of these theories was that of H. S. Fry, who developed a detailed polar theory of aromatic substitution (1909-1915) in order to rationalize the earlier (1892) empirical results of Crum Brown and Gibson on the relative yields of disubstituted ortho, para, and meta products formed via the further substitution of various monosubstituted benzenes. Fry was also the only proponent of the polar model to write a full monograph on the subject – *The Electronic Conception of Valence and the Constitution of Benzene* – which was published in 1921.

The 1920s saw an increasing interest among various chemists (Lapworth, Lowry, Robinson, Ingold) in translating the results of the ionic theory of organic reactivity into the idiom of the Lewis shared electron-pair model of the covalent bond. Because the majority of chemists involved in this movement were British, they are often collectively referred to as the "English school" of organic reactivity in order to contrast them with the earlier American school. Within the context of the covalent model, the charges on the atoms of the substrate and reagent were no longer net ionic charges due to complete electron transfer between the atoms, but rather partial charges due to the unequal sharing of the electron pair between atoms of differing electronegativities. This unequal sharing could also induce polarity in adjacent bonds via the so-called "polar" or "inductive" effect (Lewis 1916, 1923).

Likewise, the postulate of alternating ionic charges in a homocatenated carbon chain or ring was replaced by a mechanism of shifting electron pairs involving alternating (i.e., conjugated) single and double bonds and various electron lone pairs. Originally dubbed the "electromeric" or "tautomeric" effect by Ingold (1926), it was later referred to as the "mesomeric" or "resonance" effect. Though both the inductive and resonance effects were operative in isolated molecules, they were greatly enhanced, via polarization, in the presence of an attacking reagent. Consequently Ingold later attempted to further elaborate the resulting classification of electronic effects by distinguishing between static inductive and mesomeric effects, on the one hand, and dynamic inductomeric and electromeric effects, on the other.

The Lapworth-Robinson approach to the electronic theory of organic reactivity was summarized in 1932 by Robinson in a small booklet entitled *An Outline of an Electrochemical (Electronic) Theory of the Course of Organic Reactions*, and Ingold summarized his alternative version in an influential review article published in 1934. The first full monograph dealing with the Ingold approach was probably Watson's 1937 text, *Modern Theories of Organic Chemistry*, and it was not until 1953 that Ingold himself finally wrote his own book, *Structure and Mechanism in Organic Chemistry*, by which time, however, the theory of organic reactivity had already begun to move into its third phase.

As already noted in Section 15.2, the original forms of the competing Robinson and Ingold formulations of the covalent-bond model of organic reactivity were virtually isomorphous. Robinson, however, had developed his model largely as an adjunct to his primary interest, which was the synthesis of natural products, whereas Ingold made the model the central theme of his research school and actively sought to connect it with both the theory of chemical kinetics and the newer quantum mechanical theories of chemical bonding. The result was the emergence of a new subdiscipline known as "physical organic chemistry" (Taylor 1930, Hammett 1940) and the almost complete dominance of Ingold's nomenclature by the late 1930s.

By the 1930s this fusion had also shifted the reactivity data, which the organic theory of reactivity sought to rationalize, from relative product distributions to the magnitudes of measured rate and equilibrium constants (usually in the form of their corresponding logarithms) and to a more rigorous kinetic constraint on postulated reaction mechanisms, leading to the introduction by Ingold and Hughes (1935) of the well-known S_N1 and S_N2 mechanisms for nucleophilic substitution, and the *E1* and *E2* mechanisms for elimination reactions (Hughes 1935). This fusion also led to the gradual development of two distinct approaches to the further elaboration of the electronic theory of organic reactivity, which may, for lack of better terms, be called the "empirical correlation" and the "theoretical computational" approaches, respectively.

The empirical correlation approach was based on the observation that the logarithms of the rate and/or equilibrium constants of related reaction series often showed linear correlations with one another. Hence if one measured the rates for a reaction series in which the nature and/or position of σ was systematically varied at constant $\varkappa, \phi, \varrho$ and then repeated the measurements for a second series having a different set of constant $\varkappa, \phi, \varrho$ values but the same variations in σ, it was found that the rates of the two series were linearly correlated, thus suggesting that the effect of σ on the reactivity of a substrate was transferable from one reaction series to another and could be assigned a definite numerical value.

The first linear correlations between the $logK$ values of related reaction series were reported by Hixon and Johns in 1927, and the first attempt to use such relations to assign numerical values to substituent effects was made by Hammett in 1937, who applied them to the inductive effects of meta- and para- substituents on the degree of ionic dissociation of substituted benzoic acids, which he attempted to model using the equation:

$$log(K_\sigma/K_H) = \sigma\varrho \qquad [18]$$

where K_σ is the rate or equilibrium constant for the substrate containing substituent σ, K_H is the corresponding value for the reference substrate in which the substituent is H, σ is an empirical measure of the substituent inductive effect, and ϱ is a constant characteristic of the reaction in question and subsumes not only possible changes in the attacking reagent, but also any changes in the substrate other than those prescribed for the substituent.

As noted by Branch and Calvin in 1941, generalization of the

Hammett equation to include all of the potential influences postulated by the qualitative electronic theory of organic reactivity is fairly complex and may involve as many as five separate effects:

$$log(K_\sigma/K_H) = I + R + P + H + S \qquad [19]$$

where I is the inductive effect, R is the resonance effect, P is the polarization effect, H is the steric effect, and S is the solvent effect – each of these terms being, in turn, divisible into the product of a σ term, representing the substituent contribution, and a ϱ term, representing the sensitivity of the reaction to effect in question:

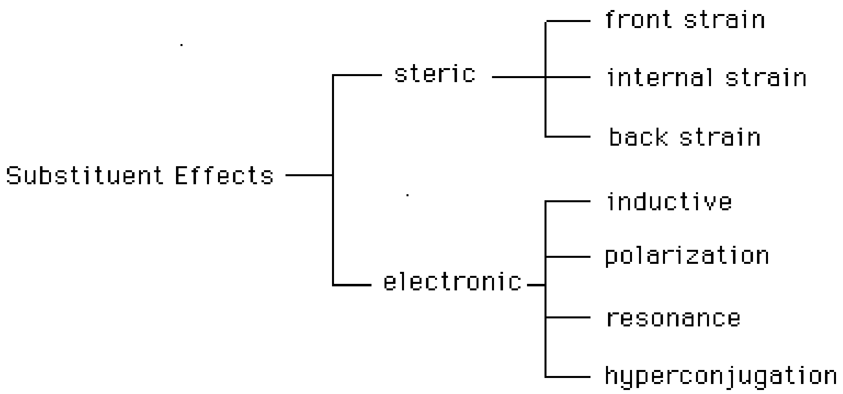
$$log(K_\sigma/K_H) = \sigma_I\varrho_I + \sigma_R\varrho_R + \sigma_P\varrho_P + \sigma_H\varrho_H + \sigma_S\varrho_S \qquad [20]$$

These various σ and ϱ constants are defined such that positive σ values denote substituent effects which are electron withdrawing, whereas negative σ values denote substituent effects which are electron donating. Likewise positive ϱ values denote reactions which are enhanced by electron withdrawing substituents but diminished by electron donating substituents, and vice versa for the case of negative ϱ values.

The game now became one of constructing reaction series in which the substituents exerted their influence using only one of these various mechanisms in order to tease out its numerical contribution to the net substituent effect, a project which consumed the time and efforts of countless physical organic chemists and in which, in particular, the American chemist, Robert Taft Jr. (1956), played a prominent role. Similar correlation equations have proven of practical value in other fields of chemistry, such as drug design, where the analog of equation 19 is known as the Hansch equation.

This enterprise also resulted in several rather acrimonious debates fueled by arguments over the relative importance of the various terms in equation 20, as well as the question of whether terms for yet additional effects were also required. Thus, between 1944 and 1950, the American chemist, Herbert Brown, further resolved the steric effect into three possible components, which he called “front” or F-strain (corresponding to the older concept of steric hindrance), “internal” or I-strain (corresponding to the older concept of ring strain), and the previously unrecognized "back" or B-strain. On the basis of this work, he further (1946) raised the question of whether the relative stabilities of trivalent carbocation reaction intermediates were due primarily to steric effects rather than to the inductive electronic effects and the intramolecular donor-acceptor (anchimeric) mechanisms favored by most physical organic chemists – a conflict which eventually gave rise to the infamous nonclassical ion debate of the 1960s (Brown 1962, 1967).

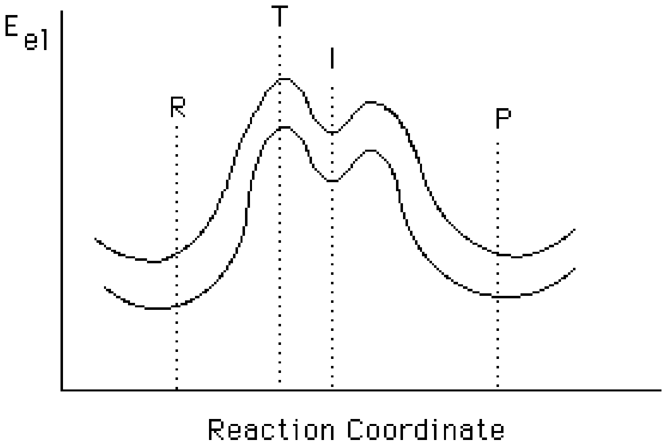
Likewise, on the basis of an apparent anomaly in the accepted order for the inductive effect of alkyl groups (Baker & Nathan 1935), a new electronic mechanism known as "hyperconjugation" was postulated by Mulliken in 1941 which soon spawned a vast literature, much of which was later called into question by Dewar in his classic 1962 monograph, *Hyperconjugation*. Thus, excluding the environmental solvent effect, the number of potential internal effects had increased from five to seven by the end of the 1950s:



According to classical thermodynamics and absolute rate theory, linear correlations between the logarithms of equilibrium and/or rate constants are equivalent to linear correlations between the corresponding $\Delta G°$ and ΔG^* values, and for this reason these relationships are often referred to as linear free-energy relations (Evans & Polanyi 1936), though the terms "extra-thermodynamic relationships" (Leffler & Grundwald 1963), "correlation analysis" (Zhdanov & Minkin 1966), and "structure-reactivity correlations"

(Hine 1972) are also used. The existence of these linear free-energy relations implies that each of the substituent effects in equation 20 represents an incremental and transferable free-energy perturbation, $\delta \Delta G$, on the net free energy of the type-reaction corresponding to the reaction series being studied – an approach which forms the basis of the first monograph to systematically deal with the theory of these correlations – the 1963 volume, *Rates and Equilibria of Organic Reactions*, by Leffler and Grunwald.

The second approach to the elaboration of the electronic theory of organic reactivity – the computational approach – was based on attempts to quantify the original qualitative model by using either VB theory or MO theory to calculate relative reactivities and reflects the third stage in the development of modern bonding theory outlined in Section 14.5. Within the context of absolute rate theory, this quantification should, in principle, be based on the quantum-mechanical computation of the complete potential energy surfaces for the various competing reactions – an approach that is both inefficient and impractical from the standpoint of the average organic chemist. What was done instead was to selectively compare the relative energies of the competing potential energy surfaces at selected points corresponding either to the initial reactants (R), the rate-determining transition states (T), various alternative reaction intermediates (I), or the final products (P):



Methods which compare the relative energies of the initial reactants and/or products are known as static reactivity indices as they attempt to correlate relative reactivity with variations in some electronic parameter characteristic of the isolated reactants and/or the relative stabilities of the alternative products. The ionic charges and partial charges postulated by the older qualitative versions of the electronic theory of organic reactivity are of this nature, and the first quantum mechanical attempt to rationalize these charge distributions was made by Hückel in 1931 for the case of aromatic substitution using simplified MO theory.

Additional important examples of quantum-mechanically based static reactivity indices include the VB-based "free-valence" index introduced by Daudel and Pullman (1945, 1946) and summarized in the 1952 monograph, *Les théories electroniques de la chimie organique* by Pullman and Pullman, and the MO-based "frontier orbital" index introduced by Fukui in 1952 and summarized in his 1975 monograph, *Theory of Orientation and Stereoselection*. This latter approach is based on the further simplification that reactivity is largely determined, not by the total valence shell, but by the nodal and overlap properties of only the highest occupied MO or HOMO of the nucleophile and the lowest unoccupied MO or LUMO of the electrophile. One of the more important static approaches based, not just on the initial reactants, but on a comparison of the net ΔE of reaction, is the so-called perturbational MO or PMO approach to organic reactivity first outlined by Dewar in 1952 and summarized in his 1969 monograph, *The Molecular Orbital Theory of Organic Chemistry*.

Methods which compare the relative energies of postulated transition states and/or reaction intermediates involving a substrate-reagent complex of some sort are known as dynamic reactivity indices. This approach was championed by Pauling and Wheland, who attempted to use VB theory to qualitatively assess the relative resonance energies of various alternative substrate-reagent complexes – an approach summarized by Wheland in his 1944 monograph, *The Theory of Resonance and Its Application to Organic Chemistry,* and one which is still taught in introductory organic courses. Wheland (1942) also introduced a quantified MO approach known as the "localization" index which was based on the difference between the resonance energy of the isolated substrate versus that of the postulated substrate-reagent complex. An alternative MO approach, based on the aromatic stabilization or destabilization of cyclic transition states was developed by Evans in 1938 but had little impact until Dewar called attention to it in the 1970s in connection with the debates surrounding the rationalization of the Woodward-Hoffmann rules.

These rules (Woodward & Hoffmann 1965), which summarized the observed thermal and photochemical reactivity of various pericyclic reactions having cyclic transition states (electrocyclic, sigmatropic, cycloaddition, etc.) as a function of their valence-electron counts, sparked considerable interest in the late 1960s and early 1970s. Alternative theoretical rationales were proposed using frontier-orbital theory (Fukui 1965), PMO theory (Dewar 1966), and the concept of Hückel-Möbius transition states (Zimmerman 1966), to name but a few. Woodward and Hoffmann favored the state correlation diagram approach of Longuet-Higgins and Abrahamson (1965), which they generalized under the rubric of the principle of "the conservation of orbital symmetry," and which they summarized in their 1970 monograph of the same title.

Yet a second qualitative reactivity generalization evolved about the same time out of the correlation approach to organic reactivity. Known as the hard-soft acid-base or "HSAB" principle (Pearson 1963), it was initially based on linear-free energy treatments of nucleophilic reagent reactivity (Edwards 1954, 1956) but was soon generalized to deal with both organic and inorganic systems and given a PMO rationale by Klopman (1968) using the concepts of charge-controlled versus orbital-controlled reactivity.

It is important to recognize that all of the computational approaches mentioned above involve a large number of explicit and implicit assumptions. Not only are the calculated indices based on drastic simplifications of rigorous quantum mechanics – simplifications which restrict their application to only certain classes of compounds – the dynamic indices are based on further assumptions concerning the mechanisms of the reactions being compared and the static indices on the assumption that the energy surfaces of these reactions do not intersect. This latter assumption is variously known as the "noncrossing rule" (Brown 1952) or the "Bell-Polanyi principle" (Polanyi *et al* 1935, Bell 1936). Along with other qualitative generalizations concerning the supposed behavior of energy surfaces, such as the Hammond principle (1955), these so-called rules are perhaps more accurately characterized as optimistic assumptions rather than as rigorously proven principles.

Finally, since all of these approaches deal with changes in electronic potential energy, but seek to correlate these changes with the changes in free energy which ultimately determine the actual magnitudes of the experimental equilibrium and rate constants, there are also additional assumptions concerning the supposed compensation of the enthalpy and entropy terms in these reactions, the validity and range of applicability of which are also still largely unknown (Evans & Polanyi 1936, Hammett 1940, Leffler 1955, Laidler 1959, Ritchie & Sager 1964, Larson & Hepler 1968).

Though this list of explicit and implicit assumptions might suggest that we are dealing with a potential house of cards, it is in fact telling us something very important about the day to day practice of chemistry. First and foremost, it clearly demonstrates that a vast gulf exists between the rigorous principles of quantum mechanics, thermodynamics, and rate theory, and their application to the experimental needs of the typical working chemist – a gulf which is bridged by a vast array of highly simplified, semiempirical, application models whose range of validity is often quite narrow. Virtually all of the daily give and take between theory and experiment, much beloved of the philosopher of science, occurs at the level of these application models and involves testing their limits and refining their accuracy rather than directly testing the fundamental principles of quantum mechanics, thermodynamics, or kinetics themselves.

Secondly, this overview clearly shows how wrong Lothar Meyer's prediction (recall Section 11.12) was concerning the demise of the concept of interparticle affinity forces and the probable course of 20th-century chemistry. Not only did this concept not vanish, it became, via the electronic theory of both inter- and intramolecular forces, the central theme of 20th-century chemistry. The macroscopic concepts of thermodynamic equilibrium and phenomenological rate laws, which were the crowning achievements of 19th-century reactivity theory, ultimately did not succeed in displacing earlier 18th-century speculations about chemical affinity and Newtonian interparticle forces of attraction and repulsion, rather they eventually came to supplement these speculations by providing constraints on possible reaction mechanisms. These mechanisms now had to conform not only to the dictates of net reaction stoichiometry, they also had to be consistent with both the experimental rate laws and the limiting-case equilibrium constant. Indeed, by the late 1950s one sees the emergence of a new approach to the teaching of introductory organic chemistry (Cram & Hammond 1959, Morrison & Boyd 1959) in which the traditional concepts of functional groups and homologous series are supplemented by an explicit consideration of organic reaction mechanisms.

Finally, it is worth noting that most of the computational approaches to organic reactivity developed in the period 1931-1980 were constrained by the necessity of being simple enough to act as “back of the envelope” methods, so that the average working chemist could easily incorporate them into his intuitive thinking about reactivity. However, with the advent of the personal computer, chemists now have daily access on an individual basis to much more powerful computational methods. One of the challenges of 21st-century chemistry will be the question of whether this enhanced access will revolutionize the way in which the average chemist deals with these problems or will result in a vast problematic literature based on a naive acceptance of calculations whose underlying assumptions and limitations are totally unknown to the user.

15.6 Electrochemistry

19th-century electrochemists had established a fundamental link between reaction rate and cell current, via Faraday’s laws of electrolysis, and between cell potential, concentrations, and free-energy via the Nernst equation. What was lacking, however, were rate laws that correlated the cell current with such factors as concentrations, temperature, applied voltage, etc., and a corresponding kinetic derivation of the Nernst equation in terms of an equalization of the resulting forward and reverse reaction rates for an electrochemical process.

The rate of an electrochemical process in an unstirred system operating at a high applied potential is usually limited by the rate of mass transfer to the electrode, whereas that in a stirred system operating at a low applied potential is usually limited by the rate of the chemical reactions occurring at the electrode surface. The fundamental laws of diffusion governing the first of these limits had been enunciated by Fick in 1855 and were first applied to specific electrode configurations and operating conditions by Sand (1901) and Cottrell (1902) and to the more complicated case of the dropping mercury electrode by Ilkovic (1934). The resulting equations relating cell current, electrolyte concentration, diffusion coefficients, and time have all found application relative to the various modern electrometric methods of analysis discussed in Section 13.8.

Treatment of the second of these limits began with the introduction of an empirical equation relating cell current (i) and applied potential or overpotential (η) first discovered by Tafel in 1905 with regard to his studies of the cathodic discharge of hydrogen gas:

$$\eta = a + b \log i \qquad [21]$$

where a and b are temperature-dependent constants. However, another quarter of a century would pass before this equation was given a firm theoretical underpinning.

The first steps in this direction were taken by Butler in 1924 when he used Langmuir's earlier kinetic derivation of the adsorption isotherm to deduce the first tentative kinetic rationale of the Nernst equation in terms of an equalization of the forward and reverse rates for electron transfer at the electrode surface. A more refined kinetic derivation was given by Erdey-Gruz and Volmer in 1930, which not only showed that the resulting rate equation gave the Nernst equation in the limiting case of equilibrium, but also the Tafel equation in the case where the net rate was dominated by the rate of either the forward or reverse reaction. Further refinements were added by Gurney (1931) and Fowler (1932) and the result finally recast in the idiom of absolute rate theory by Eyring *et al* in 1939, thus making explicit the connection between overpotential, on the one hand, and free energy of activation, on the other. The resulting rate equation, now known as the Butler-Volmer equation, forms the cornerstone of modern electrochemical kinetics and is currently written in the form:

$$i_{net} = zFAk_0[C_O e^{\alpha zF\eta/RT} - C_R e^{-(1-\alpha)zF\eta/RT}] \qquad [22]$$

where A is the electrode surface area and C_O and C_R are the time-dependent concentrations at the electrode surface of the oxidized- and reduced-state species, respectively.

Attempts to rationalize the origins of overpotential also led 20th-century electrochemists to a greater understanding of the underlying mechanisms of electrochemical reactions. Any step in the overall electrochemical process, including ion diffusion, ion desolvation, ion adsorption, electron transfer, phase formation, atom recombination, etc. may form the rate determining step and require the application of an overpotential in order to overcome the resulting activation barrier. Indeed, important insights into the exact nature of the mechanism can be deduced from the values of the a and b constants in the Tafel equation. In addition, the introduction of optically transparent electrodes by Kuwana *et al* in 1964 has also allowed electrochemists to bring the full force of modern spectroscopic characterization techniques to bear on the question of elucidating the nature of electrode mechanisms. Thus, while the major thrust of 19th-century electrochemistry was focused on the thermodynamics of electrochemical systems, that of 20th-century electrochemistry has been increasingly kinetic or, more accurately, mechanistic in its emphasis – a trend which parallels that already observed in the previous section for the study of thermal reactions.

This is not to say that significant refinements of electrochemical thermodynamics did not also occur. The impact of both the activity concept (Section 15.3) and the Debye-Hückel theory of ionic solutions (Section 14.9) on the interpretation and use of the Nernst equation were of great importance. Likewise, by the 1930s the origins and numerical values of equilibrium half-cell potentials were well understood at the atomic-molecular level in terms of their decomposition, via thermochemical cycles, into the corresponding contributions of the relevant sublimation and dissociation energies, ionization and electron affinity energies, work functions, and ionic solvation energies – an approach which was applied in great detail to the atomic-molecular rationalization of both cell potentials and the traditional electrochemical displacement series by Gurney in his 1936 monograph, *Ions in Solution*. In addition, a significant advance in the graphical representation of electrochemical thermodynamic data, known as potential-*pH* or *Eh-pH* diagrams, was introduced by the Belgian electrochemist, Marcel Pourbaix, in his doctoral thesis of 1945, which dealt with the study of metallic corrosion, and which culminated in 1963 in his editorship of the important multiauthored reference work, *Atlas d'équilibres électrochimiques*.

15.7 Photochemistry

Ironically, the rise of photochemistry as a well-defined scientific speciality was more closely associated with the rise of physical chemistry as an explicit subdiscipline in the late 1880s (recall Section 8.10), than with the discovery of photography in the 1830s. Though the 19th century saw the publication of dozens of journals and monographs devoted to photography, these publications tended to emphasize the practical, commercial, and artistic, rather than the purely scientific, aspects of the subject. In contrast, physical chemistry's leading propagandist,Wilhelm Ostwald, envisioned the new discipline as the study of the chemical aspects of various energy forms, with well-defined branches dealing, for example, withthermochemistry, electrochemistry, mechanico-chemistry, surface chemistry and, of course, with photochemistry.

By the first two decades of the 20th century this vision had fused the isolated 19th-century advances made by Grotthuss, Malaguti, Draper, Bunsen and Roscoe into a self-conscious specialty and had given rise to the first generation of monographs, handbooks, and textbooks devoted exclusively to photochemistry rather than to photography (see Table 5.1 at top of next page), as well as to at least one specialty journal – the *Zeitschrift für wissenschaftliche Photographie, Photochemie, und Photophysik* – which began publication in 1903. In keeping with these origins, much of the work in the field during this period dealt with the experimental determination of the empirical rate laws and equilibrium conditions for photochemical reactions (Warburg 1907, Weigert 1911).

Table 15.1 Late 19th- & Early 20th-Century Monographs on Photochemistry

Date	*Author*	*Title*
1898	Friedländer	*Einleitung in die Photochemie*
1906	Eder	*Photochemie*
1908	Schaum	*Handbuch die Photochemie*
1908	Kümmell	*Photochemie*
1910	Plotnikow	*Photochemie*
1911	Weigert	*Chemische Lichtwirkungen*
1913	Ciamician	*La fotochimica dell' avenire*
1913	Benrath	*Lehrbuch der Photochemie*
1914	Sheppard	*Photo-chemistry*
1919	Henri	*Etudes de photochimie*

As we saw in Section 11.9, in 1893 Nernst had put forward the claim that photochemical reactions, like thermal reactions, obeyed the law of mass action and differed from the latter solely in the circumstance that their rate constants depended not only on temperature but also on the wavelength and intensity of the irradiating light source. However, this view was challenged by van't Hoff in 1904, who argued instead that the Grotthuss-Draper law required that the quantity of product formed in a photochemical reaction should depend, in analogy with Faraday's laws of electrolysis, only on the quantity of light absorbed and not on the concentrations of the various reactants. This apparent conflict was also reflected in Bunsen's earlier criticism of the rate law deduced by Wittwer for the photochemical decomposition of chlorine water (recall Section 11.9).

Beginning about 1915 Plotnikow attempted to resolve this debate by using Beer's law of light absorption (1852) to derive more sophisticated versions of the Grotthuss-Draper law for various cell configurations and illumination conditions. Thus, in the case of a simple rectangular cell with parallel illumination, Plotnikov obtained the rate law:

$$dc/dt \;=\; dN/Vdt \;=\; k(I_0 - I_l)/l \;=\; k(I_0 - e^{-\varepsilon cl})/l \qquad [23]$$

where c = concentration of the product, t = time, l = path length, I_0 and I_l = initial and final light intensities, and k = the rate constant. In the limiting case of strong absorptions ($\varepsilon \rightarrow \infty$), I_a approximates I_0, and this equation gives, on rearrangement and integration, the earlier equation of Malaguti, Draper, and Bunsen, in keeping with van't Hoff's claim:

$$N_p \;=\; kAI_0t \qquad [24]$$

where N_p = moles of product formed and A = area of exposure.

In retrospect, however, it is apparent that this supposed conflict was more imaginary than real, and was based on a failure to distinguish between Faraday's laws, which, in their differential form, establish a stoichiometric proportionality between two alternative measures of reaction rate (rate of electron consumption and rate of product formation), and an empirical rate law, which establishes the phenomenological relationship between the rate, as measured by either of these two alternative parameters, and such factors as concentrations, temperature, surface areas, overpotential, etc. In the end, this apparent conflict was finally resolved through a realization that many photochemical reactions were in fact the net result of both a primary photochemical process, which obeyed Plotinkow's equation or one of its various limiting cases, and one or more secondary processes involving subsequent reactions of the primary photochemical products, which were subject to the law of mass action – a resolution that was intimately related to the development of the law of photochemical equivalence.

In 1900 Planck put forward the hypothesis that energy was quantized, and in 1905 Einstein, as a result of applying Planck's hypothesis to the study of the photoelectric effect, further suggested that light itself was composed of discrete particles or quanta of energy $E = h\nu$. In 1926 G. N. Lewis proposed that these light quanta be called "photons." In 1908 Stark first put forward the hypothesis that the excitation of the molecules in a photochemical process was due to the absorption of a single light quanta per molecule. This same hypothesis was proposed by Einstein in more quantitative terms in 1912, and was dubbed by him the "law of photochemical equivalence":

> *[By the term photochemical equivalence law] I understand the "Satz" that the decomposition of a gram equivalent by a photochemical process requires an absorbed radiation energy of $Nh\nu$.*

In 1928 Taylor proposed that the Grotthuss-Draper law (actually, as we have seen, the Grotthuss-Malaguti-Draper-Bunsen-Plotnikow law) should be designated as the first law of photochemistry and the Stark-Einstein photochemical equivalence law as the second law of photochemistry in analogy with Faraday's first and second laws of electrochemistry, and the next year Bodenstein and Wagner suggested that a mole of photons be called an "einstein," just as a mole of electrons is known as a "faraday." Since in actual fact the faraday is really the charge per mole of electrons (Ne), the einstein was later redefined as the energy per mole of photons ($Nh\nu$).

Recall that Faraday's first law states that the amount of product formed is proportional to the total charge ($q = it$) passing through an electrochemical cell. The analogy of this statement to the first law of photochemistry (equation 24) becomes more apparent if one writes the integrated form of Faraday's first law using current density ($j = i/A$) rather than current:

$$N_p = kAjt \qquad [25]$$

Faraday's second law then becomes equivalent to the statement that the proportionality constant (k) in this equation is equal to $1/zF$, where F is Faraday's constant and z is the number of moles of electrons consumed per mole of product formed:

$$N_p = (1/zF)Ajt \qquad [26]$$

whereas the Stark-Einstein law or second law of photochemistry becomes equivalent to the statement that the proportionality constant in equation 24 is equal to Φ/E:

$$N_p = (\Phi/E)AI_at \qquad [27]$$

where $E = Nh\nu$ is the energy per mole of photons measured in units of (einsteins)/(mole photons), I_a is measured in units of (einsteins)/(sec cm^2), and Φ – known as the "quantum efficiency" or "quantum yield" of the reaction (Warburg 1918) – in units of (moles product)/(moles photons).

In 1913 Bodenstein attempted to test the Stark-Einstein postulate by calculating the number of quanta absorbed per reacting molecule (i.e., essentially the inverse of Φ and the true analog of z in Faraday's laws) for a number of photochemical reactions. Though several gave values of between 0.8 and 9, many others, and most notably the well-known reaction between H_2 and Cl_2, gave values of the order 10^{-6}. To rationalize these results Bodenstein emphasized the difference between the primary photochemical process, which presumably obeyed the law of photochemical equivalence, and the secondary photochemical process, which involved subsequent thermal reactions of the primary photochemical products.

This distinction had in fact been made earlier by Stark, who had instead referred to "direct" versus "indirect" photochemical reactions. In keeping with this distinction, Noyes and Leighton suggested in 1941 that the net quantum yield (Φ) should be resolved into the product of the quantum yield for the primary process (ϕ_p) and that for the secondary processes (ϕ_s):

$$\Phi = \phi_p \phi_s \qquad [28]$$

where ϕ_p = (moles reactant activated)/(moles quanta absorbed) and ϕ_s = (moles product produced)/(moles of reactant activated). Since the quantum yield for the primary process was assumed to rigorously obey the Stark-Einstein law, any deviations of Φ from the theoretical value of 1 were attributable to the value for the secondary quantum yield. As early as 1918 Warburg had suggested various nonreactive secondary deactivation mechanisms (e.g., fluorescence and thermal decay) to account for those cases in which $\Phi < 1$, and the same year (1918) Nernst refined Bodenstein's earlier concept of secondary chain reactions to account for those cases in which $\Phi >> 1$.

Thus we see that, though there is a formal mathematical analogy between Faraday's laws of electrolysis and the first and second laws of photochemistry, the experimental behavior of electrolytic versus photochemical reactions is often quite different. Electrolysis reactions are normally endoenergetic and a continuous supply of applied electrical energy is required in order to maintain them and to make them thermodynamically feasible. As a consequence there is normally a rigorous, small-number, stoichiometric relationship (z) between the net moles of electrons consumed and the net moles of final product produced. In contrast, the majority of photochemical reactions are exoenergetic or thermodynamically feasible. Light energy is required only to kinetically initiate the reaction, via the endoenergetic primary process, but not necessarily to maintain it once it begins, as the secondary reactions are usually exoenergetic. Consequently the stoichiometric relationship (Φ) between the net moles of products produced and the net moles of photons consumed may vary over many orders of magnitude and often the net moles of products produced highly sensitive to small changes in the reaction conditions.

The complex manner in which the excited products of the primary photochemical process may be disposed of in the subsequent secondary reactions also accounts for the often bewildering complexity of the net empirical rate laws found for many photochemical reactions, of which, perhaps, the most notorious is that for the classic photochemical reaction between dihydrogen gas and dibromine gas (Bodenstein and Lütkemeyer 1925):

$$d[HBr]/dt = (k_1 I_0^{0.5}[H_2])/(1 + k_2[HBr]/[Br_2]) \qquad [29]$$

The impact of these clarifications is well illustrated by the 1933 monograph, *Grundlagen der Photochemie*, by Bonhoeffer and Harteck, which may be taken as representative of the second generation of photochemical texts. Explicitly organized around the law of photochemical equivalence and the distinction between primary, secondary, and net photochemical processes, over half the text was devoted to the new quantum mechanical theory of atomic and molecular spectra, and the remainder to the details of the kinetics and mechanisms of the gas-phase photochemistry of relativelysimple diatomic and triatomic inorganic molecules.

This increasing adoption of the vocabulary of spectroscopy and MO theory by photochemists in the period 1930-1950 tended to temporarily isolate them from the concerns and interests of the practicing organic chemist, who was still using Lewis diagrams and VB theory – neither of which was particularly suited to the description of excited states – to rationalize the mechanisms of the solution-phase thermal reactions which formed the basis of most organic syntheses. Only in the 1950s did this trend begin to reverse itself as both the impact of the instrumentation revolution and the needs of the theoretical chemist began to make the average organic chemist more and more aware of the merits of MO theory. This trend was also reinforced by significant advances in experimental and characterization techniques, such as flash photolysis (Porter & Norrish 1949) and the introduction of ESR and NMR spectroscopy (Section 13.10), which gradually allowed the photochemist to successfully probe the photochemistry of increasingly complex organic compounds and liquid-phase reactions.

With this extension came a simplification of vocabulary exemplified by Kasha's (1950) replacement of the traditional state symbols of spectroscopy by a simplified MO description that characterized the excited-state diradical of a species in terms of the bonding and nodal properties of the orbitals corresponding to the photo-induced electron transition. Thus, for example, $^1(n, \pi^*)$ corresponded to the singlet state produced by exciting an electron from a nonbonding n-orbital to an antibonding π^*-orbital, $^3(\pi, \pi^*)$ corresponded to the triplet state produced by exciting an electron from a bonding π-orbital to an antibonding π^*-orbital, etc. This notation meshed nicely with the increasing emphasis on orbital notation in mainstream organic chemistry, and by the 1960s these various trends had resulted in a veritable explosion of interest in both preparative and mechanistic organic photochemistry that continues to the present day. Thus, as was the case with the study of both thermal and electrochemical reactions, photochemistry had, by the last half of the 20th-century, also become overwhelmingly mechanistic in its emphasis.

The impact of these changes is well illustrated by the 1965 monograph, *Molecular Photochemistry*, by Nicholas Turro, which may be taken as representative of the third-generation of photochemical texts. Gone are the references to thermodynamics and equilibrium found in first-generation texts, as well as the references to empirical rate laws for net processes and the discussions of the photochemistry of simple gas-phase inorganic species characteristic of second-generation texts. Despite the general nature of the book's title, the term photochemistry has in effect become synonymous with mechanistic organic photochemistry, and Kasha's MO notation is used extensively throughout the text. Indeed, even those organic chemists who did not specialize in these emerging fields were made aware of their importance in the late 1960s and early 1970s as a result of the widespread impact of the Woodward-Hoffmann rules for pericyclic reactions and the striking way in which they illustrated the often complementary nature of thermal versus photochemically allowed reaction pathways.

15.8 Statistical Mechanics

As mentioned in Section 10.4, the development of the kinetic theory of gases, beginning in the 1850s, had culminated by the end of the 19th-century in the formation of the more generalized subject of statistical mechanics, as exemplified by the publication of Boltzmann's multivolume, *Vorlesungen über Gastheorie*, between 1896 and 1898, and Gibbs' monograph, *Elementary Principles in Statistical Mechanics*, in 1902.

Application of the principles of classical statistical mechanics to the problem of radiation equilibria by Planck in 1900 had given birth to the quantum hypothesis and to a revolution in our understanding of spectra and of subatomic physics in general. Quantum theory, in turn, impacted on the classical Boltzmann statistics of atoms and molecules by revolutionizing our understanding of the way in which energy was distributed among the component particles of a system (see below), and by the formulation of two alternative versions of statistical mechanics for various classes of subatomic particles, known as Bose-Einstein (1924) and Fermi-Dirac statistics (1926), respectively.

But perhaps the most significant impact of statistical mechanics on chemistry lay in the insights which it provided concerning the physical interpretation of the entropy function in both chemical thermodynamics and in the theory of absolute rate processes. As early as 1862 Clausius had established a qualitative correlation between what he later called the entropy of a system and its degree of molecular dispersion or “disgregation” – a concept that was also mentioned in passing in several advanced chemical texts of the period (Meyer 1872, Pattison-Muir 1884). However, a far more fundamental molecular interpretation of the entropy function was provided by Boltzmann in 1877 when he established a connection between the entropy (S) of a given macro-state and its probability (W) as determined by the number of its component micro-states – a connection which eventually took the form of the famous equation:

$$S = \mathbf{k} ln W \qquad [30]$$

first written in this fashion by Planck in 1908. Planck also extensively developed Boltzmann’s probability interpretation of entropy and his own work was, in turn, popularized by Klein in his 1910 monograph, *Physical Significance of Entropy or of the SecondLaw*.

One of the central postulates of classical statistical mechanics was the equipartition theorem of Maxwell which stated that the changes in the kinetic energy of a system were equally distributed among its various modes of mechanical motion (i.e., translational, rotational, and vibrational), with each degree of freedom changing by an average amount equal to $\mathbf{k}T/2$. In other words, each degree of freedom contributed equally to the system’s *Zustandsumme* or partition function. Already in the 19th century it was known that this assumption led to incorrect predictions concerning the magnitudes of heat capacities and other thermodynamic properties – a discrepancy which was resolved by the introduction of the quantum hypothesis, which showed that the extent to which a given motion shared in the energy change depended on the magnitude of its quantum spacings. Whenever the energy spacings for a particular degree of freedom were much larger than the ambient thermal energy, the motion in question was effectively “frozen out” of the system’s partition function. This newer approach was first successfully applied to the heat capacities of solids by Einstein (1907) and extended to gases by Nernst and Bjerrum in 1911, culminating in the famous equation of Sackur (1911, 1913) and Tetrode (1912) for the calculation of the translational entropies of gases, and in Debye's further refinement (1912) of Einstein's earlier results for solids.

During the next 20 years significant advances were made, based largely on the results of molecular spectroscopy, in refining the partition functions for the various quantized internal motions of gaseous polyatomic molecules, and by the 1930s a consensus had been reached on the relationship between the total partition function of a gaseous system and such traditional thermodynamic parameters as heat capacities, entropies, enthalpies, and free energies. Perhaps the earliest attempt to bring these results to the attention of chemists was Richard Tolman's 1927 monograph, *Statistical Mechanics with Applications to Physics and Chemistry*, followed by James Rice's 1930 text, *Introduction to Statistical Mechanics for Students of Physics and Physical Chemistry*. In 1935 Eyring used statistical mechanics to analyze the free energy of activation parameter in absolute rate theory, thus leading to the establishment of the universal $\boldsymbol{k}T/h$ pre-exponential frequency factor in the absolute rate equation (recall equation 15 in Section 15.4) and to an enhanced understanding of the relationship between absolute rate theory and collision theory.

Likewise, Hammett made use of the insights of statistical mechanics in his classic 1940 monograph, *Physical Organic Chemistry*, in clarifying the relationship between the changes in electronic energy postulated by the electronic theory of organic reactivity and such experimental parameters as the enthalpies, entropies and free energies of reaction and activation. Whereas the conventional thermodynamic analysis of lnK in terms of ΔH° and ΔS° (or the corresponding terms for the rate constant):

$$lnK = -\Delta H^\circ/RT + \Delta S^\circ/R \qquad \text{[31]}$$

fails to separate the roles of potential versus kinetic energy in determining the net result, the corresponding statistical mechanical analysis does:

$$lnK = -\Delta E_{el}/RT + (-\Delta E_{vib}/RT + \Sigma \nu_s lnZ_s) \qquad \text{[32]}$$

where ΔE_{el} is the change in the electronic potential energy so central to the electronic theory of organic reactivity and the terms in the parentheses represent the various kinetic energy terms, where ΔE_{vib} is the change in the zero-point vibrational energy, and the last term represents the sum over the partition functions for the various reactants and products. A significant role was also played by statistical mechanics in the development of the Debye-Hückel theory of ionic solutions (Section 14.9) and in the theory of polymer solutions (Section 14.10).

Though most chemistry majors are now exposed to some of the elementary principles of statistical mechanics in their undergraduate physical chemistry course, few of them ever take a graduate-level course in the subject if they are not majoring in either theoretical or physical chemistry. Consequently, though it isagreed that Fermi-Dirac statistics forms the rigorous bridge between the electronic and atomic-molecular levels of discourse, on the one hand, and that Boltzmann statistics forms the rigorous bridge between the atomic-molecular and molar levels of discourse, on the other, most chemists continue to take a far more empirical approach when connecting the various levels. Indeed, some, like Pauling, in his well-known quantification of the electronegativity concept, see no difficulty in leaping at a single bound from the components of a molar thermochemical cycle to the weighting coefficients in a wave equation.

15.9 Summary and Conclusions

Just as the 19th century was the century of the molecule, so the 20th century was the century of the electron. Just as the last half of the 19th century saw the birth of the concepts of molecular bonding and structure, chemical thermodynamics, and a kinetic-molecular interpretation of chemical reaction rates and equilibria, so the 20th century saw their quantification and interpretation in terms of the electrical theory of matter, statistical mechanics, and quantum theory, and the emergence of mechanism as the central theme of chemical reactivity.

In a popular lecture on the new electrical theory of matter given in 1921, the American chemist, Irving Langmuir, predicted that:

> *These things mark the beginning ... of a new chemistry, a deductive chemistry, one in which we can reason out chemical relationships without falling back on chemical intuition ... I think that within a few years we will be able to deduce 90 percent of everything that is in every textbook on chemistry, deduce it as you need it, from simple ordinary principles, knowing definite facts in regard to the structure of atoms.*

Looking back on 20th-century chemistry, one must give Langmuir's vision mixed reviews. There is no doubt that 20th-century chemistry has yielded a rich conceptual harvest or that the traditional 19th-century natural history approach to descriptive chemistry, with its endless textbook summaries of the preparation, properties, and applications of one substance after another, has largely disappeared. But it must be also admitted that, in its place, one finds not the deductive unity envisioned by Langmuir, but rather an almost random natural history of useful rules of thumb, partial theories, approximate models, and half truths.

Indeed the present-day situation bears a much closer resemblance to the characterization of chemical theory given by the Scottish chemist, Alexander Crum Brown, in 1869 than it does to Langmuir's deductive dream of 1921:

> *What we are pleased to call the theory of chemistry is merely a group of unconnected hypotheses. It would be foolish and mischievous to undervalue these hypotheses; many of them are the fruits of the highest scientific genius, and without them it would have been impossible for mere experimenters to collect the large, and to a great extent, systematic and connected, series of facts which constitutes the science of chemistry. But we must be careful, while honoring them for their use, and maintaining them while they are useful, not to mistake them for a theory, or forget their purely tentative character. Chemistry can obtain a theory only when it ceases to exist as an independent science, when it is absorbed in Dynamics, the one science of matter and energy.*

While there is no doubt that 20th-century chemical theory is much closer to that ultimate absorption into the general theory of "dynamics" projected by Crum Brown than was the case with the chemical theory of his day, what he failed to foresee was that the resulting picture would become so complex that it would necessitate the continued practice of falling back on simplified rules and half-truths in order to remain both manageable and teachable.

In many ways it is the very conceptual richness of chemistry, coupled with its increasing fragmentation into ever more narrowly focused specialties and subdisciplines, that has been its undoing. Important generalizations have been shunted into narrow specialties rather than being allowed to impact on chemistry as a whole, as illustrated by the concepts of nonmolecular and nonstoichiometric phases. Redundant models and vocabularies have been unnecessarily created to serve different subdisciplines, as illustrated by the example of Lewis acid-base theory and the concepts of electrophilic and nucleophilic reactions. Initially generalized concepts have been trivialized to serve the needs of limited fields of application, as illustrated by the polymer concept. And, sad to say, if required, these examples could be multiplied several fold.

Though one cannot help but be impressed by the enormous advances in 20th-century chemical theory, one nevertheless comes away with a lingering impression that one is looking at a science badly in need of a conceptual housecleaning, whereby redundancies are eliminated, generalizations restored to their true status, and approximations assigned their proper places in the overall conceptual hierarchy. But then, perhaps such an ideal structuring of knowledge is much too static, not to mention scholastic and Aristotelian, to survive the realities of the competitive Darwinian rat race for both attention and funding that characterizes so much of the practice of present-day science.

15.10 Selected References

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