

## Report: New England Association of Chemistry Teachers

### Logic, History, and the Chemistry Textbook

#### I. Does Chemistry Have a Logical Structure?

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*The following is the first of three invited keynote lectures given at the 57th annual summer conference of the New England Association of Chemistry Teachers held in August of 1995 at Sacred Heart University in Fairfield, Connecticut. The remaining two lectures will appear in future issues of the Journal.*

##### Introduction to the Lecture Series

My assignment, if I correctly understand the charge given me by the organizers of this conference, is to discuss the relevance of the history of chemistry to the teaching of chemistry. Traditionally there have been two approaches to this topic. The first, largely championed by chemistry teachers, has tended to center on the use of biographical sketches and humorous anecdotes as a means of "humanizing" chemistry for students. The second, largely championed by historians of science, has tended to use the history of chemistry, not so much as a vehicle for teaching the current principles of the science, than as a case study of either the scientific method or of the impact of science and technology on society. Historians of science generally consider the first approach to be historically trivial, whereas chemistry teachers generally consider the second approach to be either too general or too philosophical to meet the specific needs of a modern chemistry course.

What I would like to suggest in the following lectures is that there is a third approach to this topic, in which the study of the history of chemistry provides us with a blueprint for how to logically organize the current concepts and models of chemistry, while simultaneously revealing many of their underlying assumptions and interrelationships. Although this approach gradually evolved out of my own study of the history of chemistry, I am going to invert the order of discovery and begin instead in Lecture I with a summary of the final organizational scheme for the current concepts and models of modern chemistry implied by the study of its history. In Lecture II, we will examine how this organizational scheme can be used to critically analyze the current textbook and educational literature, and finally, in Lecture III, we look at its historical basis. As will become apparent from the historical allusions in Lectures I and II, it is impossible to completely suppress the fact that this organizational scheme was first suggested by a study of the historical evolution of chemistry. Nevertheless, I feel that it is best, for purposes of this conference, to first explain the final scheme and to underscore its pedagogical relevance before discussing in detail its historical foundations.

One final caveat: the following lectures are addressed to you as chemists and teachers and not to your students. Part of my assignment is to deepen and stimulate your own un-

derstanding of chemistry. How you translate that increased understanding into specific classroom and textbook activities for your students will naturally vary from teacher to teacher, depending on the level of the chemistry course being taught and on the degree of control that you are given over both the course content and the mode of presentation. The important point, if I correctly understand the purpose of the NEACT lectures, is that whatever increases your own understanding and enthusiasm for chemistry cannot help but impact favorably on your teaching, however indirectly.

##### Does Chemistry Have a Logical Structure?

Turning now to our first question and to the subject of the first of our three lectures—"Does Chemistry Have a Logical Structure?"—I must immediately apologize for a certain ambiguity in my title. Having made a passing reference to philosophy and the scientific method in the introduction, it is perhaps natural to assume that I intend to talk about the logic of the thought processes and procedures used by chemists, or about the relation between experiment and theory in chemistry and such attendant questions as the roles played by prediction, validation, accommodation, etc. However, in actual fact, I intend on addressing the much simpler, and educationally more pertinent, question of whether chemistry has a logical organization—in short, the question of whether it is possible to logically interrelate the large number of concepts and approximate theoretical models found in the average introductory chemistry text.

What I hope to do in today's lecture is to share with you my vision of what this overall logical structure might look like via the classification scheme shown in Table 1.<sup>1</sup> For most of this lecture we will systematically explore the various categories or boxes in this table by means of examples drawn from the introductory general, organic, and physical chemistry courses. Though I fully realize that some of you, especially those of you who teach high school, do not cover many of these topics, they are all part of the standard undergraduate curriculum at the college level and thus form a part of the professional background of anyone with a BS degree in chemistry. Indeed, I believe that it is just as important to know how the subjects which you actually teach fit into the larger scheme of things as it is to master the details of your particular area of specialization.

##### Dimensions and Levels of Chemical Discourse

As can be seen, Table 1 divides the concepts and models of chemistry into three broad classes or dimensions, based on whether they deal with composition/structure, with en-

Table 1. The Logical Structure of Chemistry

	Composition & Structure Dimension	Energy Dimension	Time Dimension
Molar Level	1. Relative composition of simple & compound pure substances, solutions & mixtures. Empirical designation of allomorphs (state, color, crystal form, $\alpha$ , $\beta$ , etc.).	4. Calorimetric entropies & heats of formation. Free energies & equilibrium constants.	7. Experimental rate laws. Experimental Arrhenius parameters and/or entropies and heats of activation.
Molecular Level	2. Absolute & structural formulas. Rationalization of allomorphs as variations in either absolute composition (polymers) or structure (isomers).	5. Molecular interpretation of entropy. Interpretation of heats of formation in terms of heats of atomization, average bond energies, etc. Molecular mechanics.	8. Molecular reaction mechanisms. Molecular view of activation entropies and activated complexes.
Electrical Level	3. Electronic formulas (Lewis str. & electronic config.). Variations in either electronic or nuclear composition (ions & isotopes) or structure (excited states).	6. Calculation of energies based on electronic structure. Interpretation of spectra. Calculation of heats of atomization, spectroscopic entropies, etc.	9. Ionic & photochemical reaction mechanisms. Isotope effects. Calculation of activation energies. Electronic reactivity indices.

ergy, or with the role of time in chemical processes (7). Each of these dimensions can, in turn, be approached at any one of three conceptual levels—the molar, the molecular, or the electrical—each of which corresponds historically, as we will see in Lecture III, to a major chemical revolution (2). We have used the term “molecular” to describe level 2, rather than the longer term “atomic–molecular”, as we will be treating an isolated atom as nothing more than a monoatomic molecule. Likewise, we have used the term “molar” for level 1, rather than an equivalent term, such as “macroscopic” or “bulk”, because it is the proper linguistic parallel for the word molecular.<sup>2</sup> According to Webster, the term “molar” comes from the Latin word *moles*, meaning a large mass, and the term “molecular” from the Latin word *molecula*, meaning a small mass, in which the suffix *-cula* denotes a diminutive version of the word that it modifies.

The term “molar” was first introduced into chemistry in 1865 by the German chemist August W. Hofmann in order to describe the bulk or mechanical properties of matter, in contrast to its molecular or “physical” properties, on the one hand, and its atomic or “chemical” properties, on the other (3). Though the term eventually came to signify the general concept of any large mass, its original specific meaning in Latin had to do with a massive millstone, whence its second use in modern English in connection with the act of grinding, as in the case of “molar” teeth or the furry little animal known for its propensity to grind up people’s lawns. Our current, more restricted, use of the words “mole” and “molar” in chemistry to denote, not just any bulk sample of a material, but rather one whose mass in grams is directly

proportional to that of its constituent molecules in atomic mass units, appears to be due to the German chemist Wilhelm Ostwald and seems to have become current in the first decade of this century (4). In what follows, any use of the adjective “molar” without a numerical qualifier (as in a 1.5 molar solution) should be taken to imply Hofmann’s usage rather than Ostwald’s more restricted version.

### The First Dimension: Composition/Structure

Since our most detailed and familiar definitions of composition and structure are those corresponding to the molecular level, it is simplest to begin at this level (i.e., at box 2) and then proceed to contrast it with the information available at both the molar and electrical levels (5). We use the rather awkward composite term “composition/structure” for this dimension because we believe that these two aspects of molecular “anatomy” are logically distinct, though inseparably linked. By composition at the molecular level (Fig. 1), we mean all information relating to both the kind and number of atoms present in a molecule. In short, it is an inventory of the parts used to assemble the molecule. Information relating to the kind of atoms is obtained via a qualitative analysis of a material and that relating to the number of atoms via a quantitative analysis of the material. In the case of discrete molecular species, this quantitative compositional characterization generally proceeds in two stages—one of which yields information on the relative numbers of atoms present and results in a relative or so-called empirical formula, and the other of which yields information on the ab-

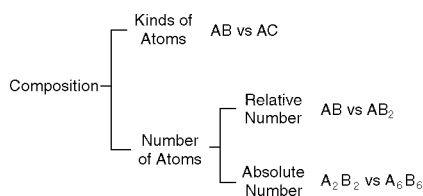


Figure 1. Composition at the molecular level.

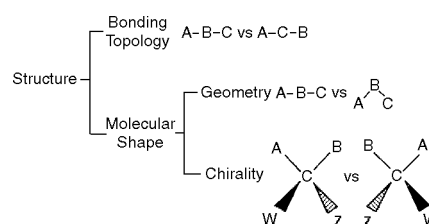


Figure 2. Structure at the molecular level.

solite numbers of atoms present and results in an absolute or so-called molecular formula. Of course, in the case of solids, such as sodium chloride, which contain infinitely extended, rather than discrete, molecular units, only the first of these levels can be specified.

Substances that differ in either the kinds of atoms present or in the relative numbers of atoms present are simply considered to be different species and are given no particular qualifier to indicate the origins of that difference beyond that specified by the differences in their formulas and names. On the other hand, species that differ only in their absolute formulas are further said to be “polymers” of one another (from the Greek for “multiple part”).<sup>3</sup>

By structure at the molecular level (Fig. 2), we mean all information relating to both the connectivity and three-dimensional spatial arrangement of the atoms present in a molecule.<sup>4</sup> Species that are identical in all aspects of their composition, but that differ in some aspect of their structure, are said to be “isomers” of one another (from the Greek for “same part”), and these may, in turn, be further differentiated as being either “topological isomers”, “geometric isomers”, or “chiral isomers”, depending on which aspect of structure—topology, geometry or chirality—accounts for the origins of their difference at the molecular level.<sup>5</sup>

In addition to these six ways of varying the nature of a material at the molecular level, yet a further difference can be created in the case of solids by varying the way in which otherwise identical molecules are packed in the resulting crystal lattice (Fig. 3). This was traditionally referred to as “physical isomerism”, though the term “packing isomerism” would be more appropriate (6). Current textbooks use neither term and simply refer to this as “polymorphism”, though, as will be discussed in Lecture II, this is not a good choice of terminology. Since the intermolecular order required for this type of differentiation disappears on vaporization or on melting to an isotropic liquid, this form of isomerism is found only among crystalline solids and liquid crystals (7).

As we have seen, we can create a difference between two species at the molecular level by varying any of the above aspects of their composition/structure. This flexibility stands in sharp contrast to the degree of characterization available at the molar level, (i.e., box 1) (8). Since structure, by definition, is a molecular concept, this aspect is completely missing at the molar level and even the concept of composition is severely curtailed by the absence of any reference to atoms. On the basis of both their behavior in the laboratory and use of the phase rule, we can distinguish at this level between simple and compound pure substances, and between solutions and mixtures. We can also determine what kinds of elements are present in a material and their relative

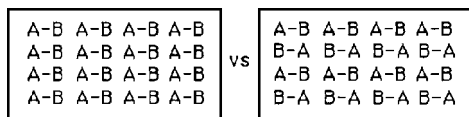


Figure 3. Packing isomerism.

amounts expressed as a percentage by weight, though all reference to relative and absolute atomic formulas disappears.

If two materials are found to contain both the same kinds of elements and to have the same composition by weight and yet are still found to exhibit different properties, all we can do is to give them some additional distinguishing label. Generally, we do this by indicating their states (gas, liquid, solid) or, if the states are the same, by indicating their color (e.g., white, red, and black phosphorus), crystal form (e.g., rhombic and monoclinic sulfur), or their order of appearance on a phase diagram (e.g.,  $\alpha$ - and  $\beta$ -tin). Many species in metallurgy and mineralogy are still characterized in this fashion, especially in compilations of thermodynamic data.

Indeed, as we will see in greater detail in Lecture II, it would be convenient if we had a general term to designate the existence of two or more isocompositional pure substances at the molar level, irrespective of whether the substances in question happen to be simple pure substances or compound pure substances (9). In addition, the term should be independent of the particular underlying molecular rationale (i.e. polymerism, isomerism, etc.) which ultimately accounts for the various forms, and should not depend on whether they happen to correspond to different states (e.g., ice, water, and steam); to different solid phases (e.g., the various polymorphs and glassy states of silicon dioxide), or to different liquid or mesomorphic phases (e.g., the smectic C, smectic A, nematic, and isotropic liquid phases of 4-*n*-pentylbenzenethio-4'-*n*-decyloxybenzoate). For the present, I would like to tentatively suggest the use of the term “allomorph” (from the Greek for “other form”) for this purpose. Though this word, along with its analog, “allomer” (from the Greek for “other part”), seem to have had some currency in the classical crystallographic literature as synonyms for the terms polymorph and isomorph, they do not seem to have caught on in the modern chemical literature (10).

Note that our proposed generalization of the term would make polymorphism a special case of allomorphism. The reason for coining such a term is to underscore the “molecular agnosticism” inherent in a purely molar approach to chemical composition and to contrast this with the compositional and structural diversity available at the molecular level. This is illustrated in Figure 4 for the various allomorphs of phosphorus and tin. As can be seen, virtually all cases of molar allomorphism are the result of either polymerism or isomerism (if one includes intermolecular packing isomerism) at the molecular level.<sup>6</sup>

However, as powerful as the molecular level is, it still leaves many questions unanswered. Why do atoms stick together to form molecules in the first place? Why do they combine in certain ratios but not others? Why is one isomer more

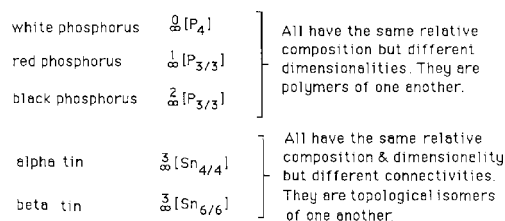


Figure 4. Example molecular interpretations of isocompositional molar varieties or “allomorphs.”

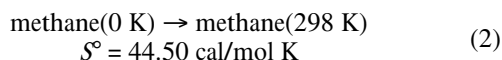
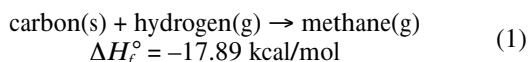
stable than another, etc.? To answer these questions we need to move to the third or electrical level of Table 1 (i.e., to box 3) (11). By electrical, we mean the theory that all matter is made of a small set of electrical particles (for our purposes: electrons, protons, and neutrons); by electronic, we mean only the electron aspect of this electrical composition/structure; and by nuclear, we mean only the proton/neutron aspect of this electrical composition/structure. We can now talk about the arrangement of the electrons and nuclei in a species rather than about the atoms and describe this arrangement using either an electronic configuration or a Lewis diagram.

We also now have an explanation for the observation of variations in properties that cannot be traced to a change in either the kind, number, or arrangement of the atoms in a species. Thus we can alter properties by altering either electronic composition (by creating ions) or electronic structure (by creating excited states). To indicate this in our formulas we now need to use not only the atomic symbols and stoichiometric subscripts of classical chemistry, but superscripts to indicate net charges. We can also produce detectable changes by altering either intranuclear composition (by creating isotopes) or intranuclear structure (by creating so-called nuclear isomers).

### The Second Dimension: Energy

Chemists are generally very comfortable with composition/structure. However, it is only one dimension of chemistry. Atomic and molecular structures must also be animated with energy and characterized by their ability to store and transfer this energy. Energy is the common currency of chemical phenomena and, as such, it plays a key role in determining the feasibility of chemical change. Metaphorically, composition and structure are, so to speak, nothing more than "molecular anatomy", and we now must proceed to a consideration of "molecular physiology".

As with composition/structure, the energy dimension (column 2 of our table) also reflects our three levels of discourse. At the molar level (i.e., box 4) we can measure a heat of formation and an entropy for each material without knowing either its absolute molecular composition or its molecular structure (12):

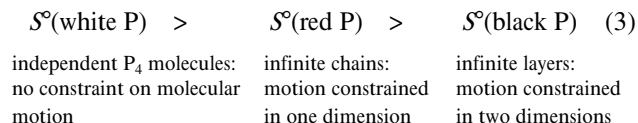


Thus our three allomorphs of phosphorus can be distinguished at this level, not only on the basis of their color, but on the basis of their individual values for these two thermodynamic parameters (Table 2). Using these heats of formation and entropies, we can also calculate heats and entropies of reaction, free energies of reaction, and equilibrium constants.

**Table 2. Thermodynamic Parameters for the Allomorphs of Phosphorus**

Parameter	Allomorph		
	White P	Red P	Black P
$\Delta H_f^\circ$ /kcal mol <sup>-1</sup>	0.00	-4.41	-10.28
$S^\circ$ /cal mol <sup>-1</sup> K <sup>-1</sup>	9.82	5.45	~4.0

At the molecular level (box 5) we can correlate the relative values of the entropy for materials of similar composition with the degree to which their structures constrain the motions of both their molecules and atoms (13). The fewer the constraints or the looser the constraints, the greater the entropy of the structure:



This gives us a satisfying feeling, which was largely missing at the molar level, that we now understand the physical basis of entropy.

At the molecular level we can also shift our reference for heats of formation from the simple substances in their standard states to the isolated gaseous atoms (Fig. 5). These are called heats or enthalpies of atomization ( $\Delta H_a$ ), where:

$$\Delta H_f = \sum \Delta H_a[\text{simple substance}] - \Delta H_a[\text{compound}] \quad (4)$$

They, in turn, can be divided up between the bonds in a molecule to give so-called average bond energies or average bond dissociation energies—tables of which are given in most introductory textbooks:

$$D_{\text{C-H}} = \Delta H_a[\text{CH}_4]/4 = 396/4 = 99 \text{ kcal/bond} \quad (5)$$

Again, this interpretation of enthalpy of formation in terms of competing bond energies, though not altogether rigorous, does give us the feeling of better understanding the origin of this molar thermodynamic parameter (14).

At the electrical level (box 6), we can take the electronic and nuclear composition/structure of a material and use it to calculate the material's electronic energy (15). From this we can obtain both heats of atomization (level 2) and heats of formation (level 1). Changes in electronic energy can also be used to calculate spectral transitions and, ultimately, entropy values. An enormous amount of effort has gone into this level of discourse. Indeed, one can say, with little exaggeration, that 20th-century theoretical chemistry has become fixated on the models in this box of our table, and we will be taking a closer look at some of them in the next lecture.

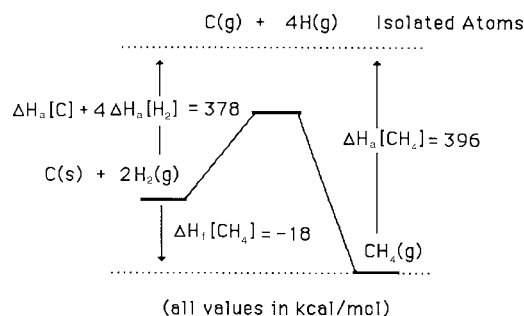


Figure 5. A thermochemical cycle illustrating the relation between enthalpies of atomization and enthalpies of formation.

### The Third Dimension: Time

The final and least developed dimension of chemistry is time (column 3). This is the aspect with which most teachers and students are least comfortable. As can be seen, at the molar level (box 7), we can measure empirical rate laws, as well as heats and entropies of activation (16). At the molecular level (box 8), we are able to give a molecular interpretation to both the rate laws and the activation entropies—the first in terms of plausible reaction mechanisms, and the second in terms of a plausible activated complex (17). At the electrical level (box 9), we are able to add on mechanisms involving ions and excited-state species, as well as isotope effects. We can also attempt to calculate heats and entropies of activation from the postulated electrical structures of the transition states. All of the simple reactivity indices that you learned about in organic chemistry (for example, using resonance to calculate the favored point of electrophilic attack in monosubstituted benzenes) are really trying to assess which of a series of postulated transition states (here a simple sigma complex of the aromatic and electrophile) has the most favorable heat of activation (Fig. 6) (18).

It should also be noted that time plays a fundamental role not only in conventional chemical kinetics, but also in the very definition of what we consider to be an individual chemical species. All species are characterized by their specific properties at the molar level. If the time required to measure one of these properties is greater than the time required for the species to undergo some reversible change in either its composition or structure:

$$t_{\text{change}} < t_{\text{measurement}} \quad (6)$$

then we do not detect this variation. Instead we see an average of the properties of the various forms and they appear to act as a single species relative to the measurement in question (19). Thus the rates of vibration and rotation of a typical molecule are generally more rapid than the time required to measure such properties as its boiling point, density, etc. and we do not consider the individual vibrational and rotational conformations to be independent chemical species. If, however, we slow down the rate of interconversion (for example, by cooling) or decrease the time required for measurement (for example, via the use of new kinds of instrumentation), then we often see a resolution into distinct species. The classic example of this is the study of fluxional molecules as a function of temperature using NMR. Likewise, though liquid water is really a mixture of rapidly interconverting H-bonded polymers, thermodynamically it behaves like a single substance, since the rate at which the H-bonded polymers interconvert is much greater than the rate of either vaporization or solidification (20).

In addition to this “laboratory time” dimension, chemistry also has an “historical time” dimension which deals with such questions as the origins and relative stabilities of the chemical elements, the geochemical abundance and distribution of the elements on Earth, their astrochemical abundance and distribution in both the solar system and the universe as a whole, their biochemical abundance and distribution in living organisms, etc.—in short, with the general question of how our “chemical environment” has come to assume its present form. Unlike “laboratory time”, in which the operator has full control of the environmental constraints and

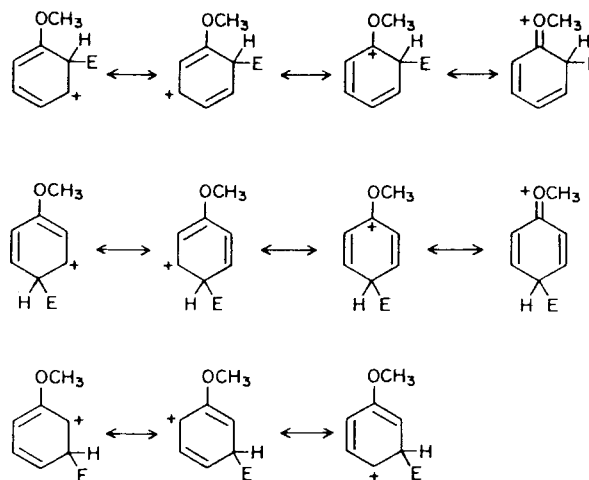


Figure 6. The use of resonance to assess the relative stabilities of alternative transition states for electrophilic attack at a monosubstituted benzene.

so can successfully predict the time evolution of the system being studied, historical time represents a unique course of past events for which these constraints are either largely unknown or of such a magnitude that they cannot be effectively reproduced in a conventional laboratory setting. As a result, work in this area is usually characterized by a high ratio of speculation to concrete fact, not unlike that employed in other areas of science dealing with historical time, such as a biologist attempting to trace an evolutionary tree, a geologist trying to unravel a geological time sequence, or a cosmologist speculating on the origins of the universe.

Interestingly, in keeping with chemistry's image as an “abstract” rather than a “concrete” science, that is, as a science concerned only with the general laws of chemistry as they apply to pure substances, rather than with the specific origins of individual complex objects (Figs. 7 and 8), chemists are seldom interested in this “historical” aspect, and as a result, it has largely become the province of departments of geology and astronomy rather than chemistry.

### A Fourth Dimension?

One final bit of speculation. Is there yet a fourth dimension to chemistry which is missing from Table 1—a dimension that deals with the spatial aspects of chemical reactions? By this I do not mean the study of the spatial arrangement of atoms in molecules, which, as we have seen, is already subsumed under the rubric of composition/structure, but rather the study of the spontaneous evolution of spatial patterns at the molar level as a result of on-going chemical reactions, such as the famous “Belousov–Zhabotinsky” oscillating reaction or the equally famous Brusselator reaction. These are currently of enormous interest relative to trying to understand the origins of growth regulator gradients in living organisms and their role in directing embryonic development, as well as in understanding the biochemical origins of various biological cycles (21). One might also include in this category the theory of generating molar spatial distributions of molecules for the purpose of separating them from one an-

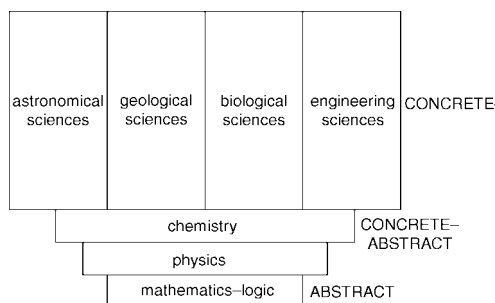


Figure 7. A hierarchical classification of science based on the scheme of Herbert Spencer. Sciences higher in the hierarchy make use of principles established by those lower in the hierarchy, though at each level new forms of organization appear. The concrete sciences deal with specific classes of objects or bodies found in the universe, whereas the abstract sciences attempt to establish universal principles applicable to all of these bodies. Such areas as medicine, psychology, and sociology are subsumed under the biological sciences. Man-made objects and economics are subsumed under the engineering sciences.

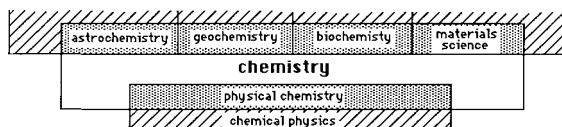


Figure 8. A closeup of the chemical level in Fig. 7 showing the existence of interdisciplinary areas of specialization at the boundaries.

other, whether by means of such time-honored processes as distillation and filtration or via the latest developments in chromatography (22).

### The Fundamental Postulates of Chemistry

Having briefly outlined the composition/structure, energy, and time dimensions of chemistry at the molar, molecular, and electrical levels of discourse, it remains for us to briefly say something about how these various levels are interrelated. The molar and molecular levels are connected by the fundamental postulate that the specific molar properties of substances are a function of their molecular character, concentration, and temperature:

$$\text{specific molar properties} = f(\text{molecular character, concentration, temperature}) \quad (7)$$

where we have used the term "molecular character" as a summary label for both molecular composition and molecular structure. The term "specific property", which appears on the left side of this relation, refers to those properties, such as color, refractive index, molecular optical rotation, boiling point, melting point, density, etc., that are characteristic of a material but independent of the size, shape, or function of the sample being analyzed. They are what we measure in the laboratory at the molar level (23). *What this postulate says, in essence, is that every measurable difference in specific properties at the molar level, after adjustments for differences in tempera-*

*ture and concentration, must be mirrored by a corresponding difference at the molecular level in one or more of the seven aspects of molecular composition/structure outlined earlier. The resolution of apparent violations of this postulate has been the driving force for the progressive elaboration of the molecular level of discourse throughout most of the history of modern chemistry, from the development of structure theory and classical stereochemistry in the 19th century to the development of conformational analysis in this century.*

Similarly, the molecular and electrical levels are connected by the fundamental postulate that the molecular character of a material is a function of its electronic and nuclear composition and structure:

$$\text{molecular character} = f(\text{electronic \& nuclear composition/structure}) \quad (8)$$

and we are applying this postulate every time we write a Lewis diagram, predict the geometry of a molecule using VSEPR theory, or do a full-scale quantum mechanical calculation.

Some of you will have noticed the absence of any mention of statistical mechanics in our discussion of the various categories in Table 1. Ideally, statistical mechanics would be the rigorous way to implement the postulates in equations 7 and 8 and so connect our three levels of discourse—the molar and molecular levels using Boltzmann statistics and the molecular and electrical levels using Fermi–Dirac statistics. However, this is seldom done at the elementary level and chemists often employ these postulates in a more empirical way. In the case of equation 7, for example, chemists have developed a number of algorithms for reducing the bonding topologies of molecules to characteristic numerical indices which can then be used, in combination with linear regression analysis, to correlate and predict molar properties (24). Likewise, because of the approximations used in most bonding theory and the fact that under normal conditions most molecules reside in their electronic ground states, few students realize that they are implicitly applying Fermi–Dirac statistics whenever they distribute electrons among the quantum levels in atoms and molecules or when they pair them in a Lewis diagram.

### Levels of Perturbation

It is also of some interest to further elaborate on our two basic postulates in terms of a fundamental classification of chemical and physical properties proposed by Wilhelm Ostwald in 1895 (25). According to Ostwald, all molar properties may be categorized as being either colligative, additive, or constitutional in nature.

Colligative properties depend only on molecular concentration and temperature, but are independent of the chemical character of the molecules in question. In other words, they correspond to a special limiting case of our first postulate in which the dependency of the property in question on molecular character is either minimal or nonexistent:

$$\text{colligative molar properties} = f(\text{concentration, temperature}) \quad (9)$$

Specific examples include gas pressure, boiling point elevation, freezing point depression, and osmotic pressure. The key role played by these properties in the determination of molecular and atomic weights, as well as the restriction of

this limiting-case idealization to dilute systems, are well known.

Additive properties depend not only on concentration and temperature, but on the composition of the molecules in question. In other words, they correspond to a special limiting case of our first postulate in which the dependency of the property in question on molecular structure is either minimal or nonexistent, but does reflect both the nature and number of the component atoms:

$$\text{additive molar properties} = f(\text{molecular composition, concentration, temperature}) \quad (10)$$

At the time that he was writing, Ostwald was only able to list mass as a strictly additive property, with heat capacity and molecular volume as rough approximations for certain classes of compounds. However, in 1898 Madame Curie showed that radioactivity also fell into this category, and in 1913 Moseley demonstrated that the same was also true of certain characteristic X-ray emission lines (26, 27). Indeed, it is the approximate additivity of this latter property which makes X-ray spectroscopy an invaluable tool for rapidly determining the empirical composition of a substance.

Lastly, constitutional properties, as the name implies, depend on molecular structure, as well as on molecular composition, concentration, and temperature—in short, they correspond to the full use of our first postulate:

$$\text{constitutional molar properties} = f(\text{molecular character, concentration, temperature}) \quad (11)$$

The vast majority of known properties, such as chemical reactivity, thermodynamic stability, UV, visible, IR, and NMR spectra, etc. fall into this category. Their structural dependency makes their theoretical prediction complex but also allows us to exploit their experimental measurement as means of inferring the molecular structures of substances.

Madame Curie used the terminology “atomic property” versus “molecular property” in place of Ostwald’s additive and constitutional categories. In light of our first postulate, we might instead venture to recommend the more descriptive terms: colligative property, compositional property, and structural property.

Analysis of the electrical origins of the two property classes that depend molecular structure and/or molecular composition, using our second fundamental postulate, is based on the classic distinction between the outer-most valence electrons of an isolated atom, which undergo extensive structural rearrangement upon molecule formation, and its atomic core, composed of the inner electrons and nucleus, which remains relatively unperturbed. Such additive properties as mass and radioactive decay constants depend largely on the nuclear portion of the core, whereas characteristic X-ray frequencies depend on the excitation of the inner electron portion of the core. Thus, to a first approximation, we find that:

$$\text{additive or compositional character} = f(\text{atomic core character}) \quad (12)$$

Constitutional properties, on the other hand, depend not only on atomic core character, but also on the number and structural arrangement of the outer valence electrons, and this, in turn, varies from one kind of molecule to another. Thus, to

a first approximation, we find that:

$$\text{constitutional or structural character} = f(\text{valence electron \& core character}) \quad (13)$$

The observation that, strictly speaking, there are no truly additive molar properties, but only approximately additive properties, which display varying levels of constitutional or structural disturbance, is, of course, a reflection of the fact that atomic cores and nuclei are not truly unperturbed in molecule formation. What we are really looking at are levels of perturbation:

$$\text{valence electrons} > \text{core electrons} > \text{atomic nuclei} \quad (14)$$

As our instrumentation becomes more sensitive, effects which at one level were additive, become constitutional at another level. Thus molecular mass shows minute deviations from additivity due to relativistic effects that are usually undetectable at normal levels of chemical sensitivity; certain radioactive processes, such as electron capture, display a sensitivity to molecular composition; and at the levels of detection used in NMR, perturbations of the nuclear environment become the basis of an invaluable method for the determination of molecular structure.

## Summary

In summary, it is proposed that the concepts and models of chemistry may be sorted into nine categories, each of which is characterized as being either molar, molecular, or electrical in nature and as dealing primarily with either the composition/structure, the energy, or the time aspects of chemical phenomena. Lewis dot diagrams and electronic configurations deal with composition and structure at the electrical level, phase diagrams and gravimetric analytical data deal with composition and structure at the molar level, enthalpies and entropies of formation deal with energy at the molar level, bond energies deal with energy at the molecular level, molecular orbital diagrams deal with energy at the electrical level, etc. We have further suggested that attempts to interrelate the molar, molecular, and electrical levels of discourse form the basis of chemistry’s most fundamental postulates and serve to define much of what chemists do and why they do it.

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## Notes

1. The classification scheme in Table 1 was first presented in July of 1991 as part of a Summer Workshop in the History of Chemistry sponsored by the Beckman Center for the History of Chemistry in Philadelphia.

2. For example, the proper linguistic parallel for “macroscopic” would be “microscopic” which, despite the current use of such derivatives as “macrophysics” and “microphysics”, is really misleading since both molecules and subatomic particles are, in contrast to bacteria and viruses, literally submicroscopic, or—to use the term suggested by von Buzágh—amicroscopic.

3. Needless to say, Berzelius' original use of the word "polymer" to denote compounds having the same relative formula but different absolute formulas has been almost forgotten in modern chemistry. The term is now used as a synonym for "macromolecule" regardless of whether its formula is a true multiple of the monomers from which it was made (e.g., condensation polymers and copolymers).

4. Unhappily, the term "structure" is not used in a consistent manner by chemists. In speaking of structural isomers and stereoisomers, organic chemists are using the term structure as a synonym for topology and the term stereochemistry as a blanket term for both geometry and chirality. In speaking of "bonding and structure", inorganic chemists are using the term bonding as a synonym for topology and the term structure as a blanket term for geometry and chirality. Likewise in structure-property correlations, pharmaceutical chemists are using the term structure to subsume variations in both composition and topology. Only solid-state chemists or, more accurately, crystallographers use the terms composition and structure in the way we have defined them. In talking about CaO as having a NaCl structure, they are clearly distinguishing between composition and structure. Likewise, in talking about the NaCl versus the CsCl structure (which have 6/6 and 8/8 topologies respectively) or about the zinc blende versus the wurtzite structure (both of which have the same local 4/4 topology but different overall geometries) or the structures of the left- and right-handed varieties of  $\alpha$ -quartz (which have distinct space groups), they are clearly using the term structure to subsume topology, geometry, and chirality.

5. Both the organic and coordination chemistry literature list dozens of different kinds of so-called isomers, including cis, trans, functional group, positional, skeletal, constitutional, optical, coordination, hydrate, ligand, linkage, summation, and ionization isomers. All of these are examples of the four fundamental types listed here.

6. The formulas used in figure 4 are known as crystal coordination formulas. The numerical ratio following the chemical symbols inside the brackets is a coordination number ratio. In the case of phosphorus, each P center has a coordination number of three, and each of the three P centers to which it is bound also has coordination numbers of three. This pattern repeats according to the dimensionality index which appears as a prefix in front of the brackets. The symbols for the dimensionality index stand for discrete molecular structure (0) infinitely-extended chain structure ( $\frac{1}{2}$ ) infinitely-extended layer structure ( $\frac{2}{3}$ ) and infinitely-extended framework structure ( $\frac{3}{4}$ ), respectively. Polymers, in the original and strict sense of the word, have identical relative compositions but differ either in their absolute composition (if they are discrete molecules) or in their dimensionality index (if they are infinitely-extended). Isomers have identical absolute compositions (if they are discrete molecules) or identical dimensionality indices (if they are infinitely-extended) but differ in either their bonding topology (and hence in their coordination ratios), geometry or chirality (and hence in their Bravais lattice types and cell occupancies). For further details, see Jensen, W. B. "Crystal Coordination Formulas: A Flexible Notation for the Interpretation of Solid-State Structures". *The Structures of Binary Compounds*; de Boer, F. R. and Pettifor, D. G., Eds.; Elsevier: New York, 1989; Chapter 2.

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3. Hofmann, A. W. *Introduction to Modern Chemistry, Experimental and Theoretic*; Walton & Maberley: London, 1865; pp 140–141, 151. According to Hoffmann's terminology, physical changes are intermolecular, whereas chemical changes are interatomic (i.e., intramolecular). Hofmann's text had only one English edition but many German editions. Consequently, though his terminology had little influence on British and American texts, it was adopted by some German authors. See, for example, Lorscheid, J. *Lehrbuch der anorganischen Chemie*; Herder'sche Verlagshandlung: Freiburg, 1874; p 4. A further example can be found in the table of contents for Kelvin, L. *Baltimore Lectures on Molecular Dynamics and the Wave Theory of Light*; Clay & Sons: Cambridge, 1904. Here, the various lecture topics are classified as either molar or molecular.
4. Ostwald is credited with this innovation in Trautz, M. *Lehrbuch der Chemie*; Vereinigung Wissenschaftlicher Verleger: Berlin, 1922; Vol. 1, p 56 and in Nelson, P. G. *The Elusive Mole. Educ. Chem.* 1991, 28, 103–104. According to Nelson, the term first appears in Ostwald, W. *Grundlinien der Anorganischen Chemie*; Engelmann: Leipzig, 1900. Ostwald's use of the word was connected with his growing opposition to the atomic-molecular theory. Unfortunately he did not give a formal linguistic derivation of the term and in several places incorrectly implied that it was merely an abbreviation for the term molecular weight. This incorrect association is often repeated in dictionaries, especially in connection with the abbreviation "Mol.", though some chemical sources do give the correct derivation. See, for example, Kieffer, W. F. *The Mole Concept in Chemistry*; Reinhold: New York, 1963; p 1.
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23. Wilhelm Ostwald even went so far as to suggest that the observation that specific properties can be used to group material objects into classes of substances should be accorded the status of a fundamental law of chemistry. Thus in the 1914 edition of his text, *Principles of Inorganic Chemistry* (Ostwald, W. *Principles of Inorganic Chemistry*; Macmillan: London, 1914; pp 1–2), he wrote, "This fact can also be expressed by saying that in bodies there do not occur all imaginable collocations of [specific] properties, but only certain definite ones. Every such collocation of properties which does really occur, characterizes a definite substance, and the fact that the bodies which occur in nature can be arranged in such groups or 'substance-species', is the statement of an important law of nature, the fundamental law of chemistry."
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