# ATOMIC ARCHITECTURE FOR THE GENERAL COLLEGE CHEMISTRY STUDENT

### ROBERT C. BRASTED

Department of Chemistry, University of Minnesota, Minneapolis, Minnesota

The approach used in presenting atomic structure to the first year college chemistry student is predicated upon several factors: 1. a very early presentation of the subject, after introduction of principles of units (fundamental and derived) and stressing of dimensions in the realm of the ultraminute; 2. a reasonably complete picture at this early stage, on the assumption that a usable working model will be developed; 3. an attempt to capture interest in the chemical area rather than devoting time at an early stage in the physics-chemistry borderline area of kinetic molecular theory; and 4. introduction of the subject in a fashion which allows a maximum of reasoning by the student and a minimum of memorization in order to understand chemical and physical behavior of the elements and their compounds. The descriptive chemistry of the elements discussed later in the course, the reactions of qualitative analysis, the principles of acids, bases, amphoterism, solution, conductivity, complex ion formation and many other topics are then developed by considering the electron distribution within atoms. It is obvious that size and charge relationships also play an important part in the discussion of these topics. These relationships are continuously stressed.

The student body to which this presentation has been offered should be defined:
1. Students both with and without high school chemistry background. Approximately some 15 to 20 percent have had no high school chemistry. 2. Students in a state supported institution, with an enrollment in the order of 26,000. The entrance requirements are such that any student in the upper 50 percent of his high school class may be admitted. 3. Students with major interests in virtually any field excepting chemistry, chemical engineering, and other fields of engineering. The majority are in the premedical, predental, prenursing, and agriculture cur-

The Ohio Journal of Science 59(1): 15, January, 1959.

ricula. Actually, a similar approach in presenting chemistry is used with the chemistry majors. 4. Class size of approximately 250 with four or five such sections being taught.

The essential points, then, in the development of atomic architecture that are presented very early in the course are briefly summarized: 1. experimental evidences for fundamental particles; 2. experimental evidences for relationships between the nucleus and the extra nuclear portion of the atom; 3. nuclear particles and atomic number; 4. experimental evidence for the electron arrangement through spectroscopic observation; and 5. the arrangement of electrons and their designations by four quantum numbers in terms of energy levels is finally developed. These lectures on atomic structure are followed by a systematic presentation of the periodic table and the classification of the elements on the basis of atomic number. This is accompanied by a thorough consideration of types of chemical bonds, both as to similarities and fundamental differences.

The types of materials covered in the unit on atomic architecture will be mentioned principally in topical form by referring to a number of figures. This material is presented by a combination of lectures, lecture demonstrations, the use of lantern slides, and with "chalk-talks." The manner of the intensive treatment of these topics will vary somewhat depending upon the composition of the various groups and the needs of the lecturer.

The main areas of the problems involved in studying the atoms of elements systematically are presented in the following steps.

I. The importance, nature, and behavior of the electron is developed through discussions based upon—  $\,$ 

1. The Millikan oil drop experiment (fig. 1).

2. Information derived from the vacuum tube in magnetic fields. The

concept of canal rays comes also from vacuum tube experiments (fig. 2).

3. The x-ray tube and the concept of bombardment of a target by electrons resulting in x-ray emmission. This observation fits nicely into later discussions relating energy of light to electron excitation and return of electrons to normal states (fig. 3).

- II. The general observations of particles and energy from radioactive materials (fig. 4).
- III. Particles derived from atomic nuclei. These particles are more or less dogmatically described as coming from the nucleus at this point, with evidence to be presented later (fig. 5).
- IV. Moseley's Law and the relation between x-ray wave length and mass of the nucleus, in turn related to proton content of the nucleus (fig. 6). The point is stressed that the chemical behavior of an element is a function of the proton number since the number of electrons and their final arrangement will be related to this value.
  - V. The neutron and its derivation by a nuclear reaction:

$${}_{4}^{9}$$
Be  $+{}_{2}^{4}$ He  $={}_{0}^{1}$ n  $+{}_{6}^{12}$ C.

The treatment of this topic includes a brief discussion of the history of the discovery and the unusual properties of this nuclear particle (fig. 7).

VI. The positron and its derivation by a nuclear reaction:

There is a discussion of "antiparticles" at this point. Thus, the positron is the antiparticle of the negative electron (fig. 8).

VII. The Rutherford gold leaf experiment: The great importance of this experiment, surprising in its fundamental simplicity, is discussed as showing for the first time the approximate sizes of atoms and nuclei. There is a qualitative discussion of the experiment to show that gold atoms have nuclei about 4 x  $10^{-12}$  cm in size, and that most of an atom must be empty space (fig. 9).

VIII. The concept of the spectrum of an element obtained with spark and arc-activated elements and a spectrograph. This discussion is accompanied with

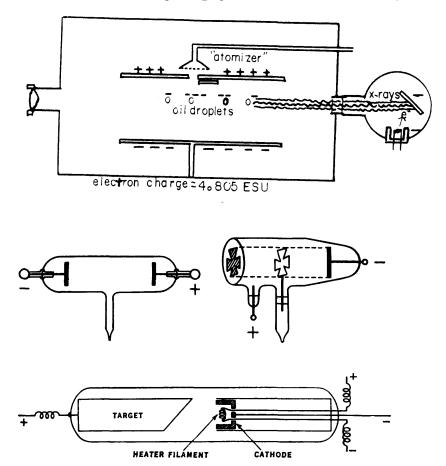


FIGURE 1. Millikan oil drop experiment. FIGURE 2. Studies with cathode ray tubes. FIGURE 3. The x-ray tube (Coolidge type).

demonstrations of flame tests (fig. 10). Chalk-talk techniques are extensively used at this time to bring out the following concepts:

1. General concepts of the wave nature of light and the relation of energy to wave length.

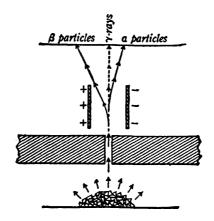
2. The concept of activated electrons within atoms and the release of energy as electrons drop from outer to inner orbits.

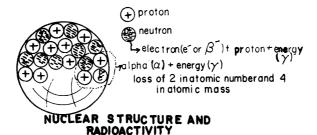
3. The concept of the principal quantum number (fig. 11).

IX. The need for additional energy levels to account for the multiple lines

of the spectrum (fig. 12). At this point there is consideration of the second quantum number and the designations of the subshells.

- X. The third quantum number. The element sodium is used to bring out the meaning of the third quantum number (fig. 13).
- XI. The fourth or spin quantum number. The discussion brings out the fact that all the electrons in any given atom have an "address" no matter how





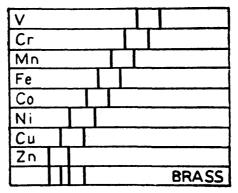


FIGURE 4. Radiations from radioactive subtances.
FIGURE 5. Particles derived from nuclei.
FIGURE 6. The contribution of Moseley.

large the atomic number. It is pointed out that no two electrons can have the same address or state. This is a way of stating to general chemistry students that no two electrons in the same atom can have the same four quantum numbers (fig. 13).

XII. The development of the first transition series follows at this point after having developed the structures of the elements through calcium (fig. 14). The apparent inconsistency of chromium is not stressed; though the 4s<sup>1</sup>, 3d<sup>5</sup> arrange-

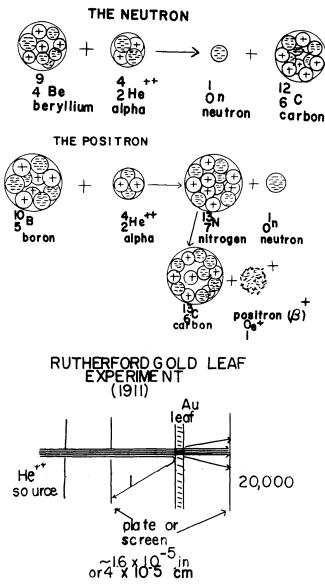


FIGURE 7. The neutron.
FIGURE 8. The positron.
FIGURE 9. The Rutherford gold foil experiment.

ment should not be unexpected considering the effect of the increasing nuclear charge and the increased attraction for the electrons, making for the stable configuration with the differentiating electron in the 3d subshell. The Cr(II) and Cr(III) oxidation states become logical as does the Cr(VI) (fig. 15).

Some knowledge of the spin quantum number has been found of interest even for the first year student. He is likely to wonder how we know that there is a

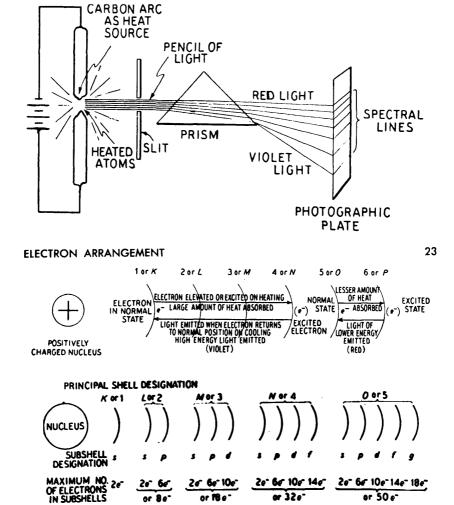


FIGURE 10. Schematic diagram of a spectrograph. FIGURE 11. The principal orbits or shells of the atom showing electrons in normal and excited states. FIGURE 12. The electron subshells of the atom.

ar 350.

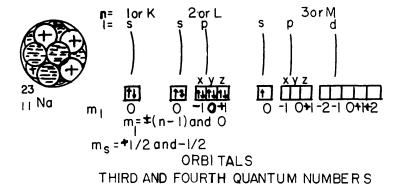
or 50e-

maximum unpairing in a given atom. The magnetic susceptibility measurement follows with no additional theory. Dia- para- and ferromagnetism of elements and their compounds are easily explained in terms of unpaired electrons.

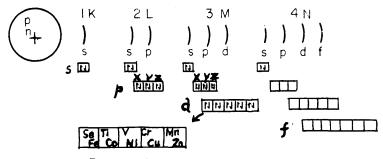
XIII. The importance of filled and half-filled energy levels is then stressed

to account for the chemical properties of certain elements. Thus, the chemical properties of zinc and copper atoms can be contrasted with those of chromium and manganese. This is brought out in the following observations:

- 1. The zinc atom has a constant oxidation state of 2 because all its subshells are filled (fig. 16).
- 2. The oxidation state of Cu(I) is to be expected. The evidence for the Cu(II) state must be accounted for by the loss of a single 3d electron (fig. 16). The blue color of the Cu(II) ions as due to an unpaired electron can be mentioned. However it is reasonable to assume that a Cu(III) state is hardly to be expected.



## THE FIRST TRANSITION SERIES



3d crbitals

FIGURE 13. The third and fourth quantum numbers.
FIGURE 14. The first transition series.

- 3. The manganese atom serves as a good example for a number of points of chemical interest. It's relative inertness as a metal follows from filled and half filled subshells as well as the small size, in contrast to calcium with its strong electron donating potential (fig. 15). As the magnitude of positive oxidation state increases it is logical to believe that there will be less ionic nature to the bonds formed. The half filled orbitals make reasonable a certain amount of difficulty in attaining state higher than (II); however, all states up to and including (VII) are possible. Compounds in states above (II) are likely oxidizing agents, and auto-oxidation and reduction reactions can occur.
- XIV. The use of ion-electron or half cell equations is initiated at this point for simple cases in the discussion of the loss or gain of electrons by atoms in the

formation of the ionic bond. A good example of the application of these ideas is the ionization of sodium with the resultant diminution in size from 1.86 to 0.95 Å (fig. 17). The student is then ready to understand the relative inertness of the sodium ion as due to the stability of filled orbital systems or paired electrons in the s and p subshells. This is much more meaningful to the student than an explanation based upon the octet rule. Thus a considerable body of information is derived through individual reasoning by the student, which is a distinct aid to

### The Chromium Atom

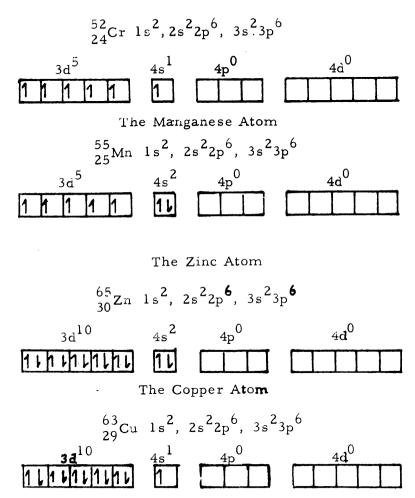


FIGURE 15. Chromium and manganese as transition elements. FIGURE 16. Comparison of the structures of atoms of zinc and copper.

the morale of the students. The subject of gaseous ionization potential is introduced at this point as a fairly quantitative and useful method for comparing the tendencies of metals to lose electrons and the reluctance of nonmetals to do so.

XV. The importance of the sizes of atoms in explaining chemical and physical properties of the elements is now pointed out by calling attention to the decreasing

size of atoms with increase in atomic number, say in the third series of the periodic table (fig. 18). The student has no difficulty in understanding the effect of the increasing nuclear charge on the attraction for the electrons which are all distributed within three main levels. From this time on the student is urged to resort continually to the use of the Campbell chart of the periodic table which shows the relative sizes of atoms and ions.

XVI. The stabilization of higher oxidation states is briefly touched upon at this point using the concept of available d orbitals. This topic as well as bonding in coordination compounds is not presented in any great detail at this time. However, the way has been paved for a fuller treatment in the third quarter in connection with qualitative analysis. In the third quarter, the student is also presented the concept of hybridization of orbitals. This is nicely introduced in discussing the structure of the carbon atom in methane, wherein a 2s electron is promoted to the 2p state permitting sp³ bonding. The dependence of the structure or molecular aggregates are also discussed at this time. Examples are given of square coplanar (dsp² bonding), tetrahedral (sp³ bonding) and octahedral (d²sp³ bonding) configurations.

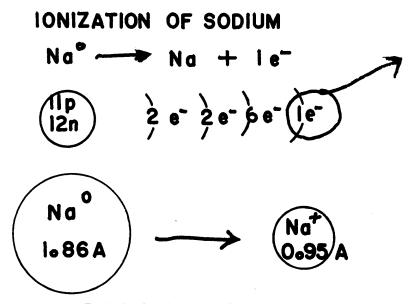
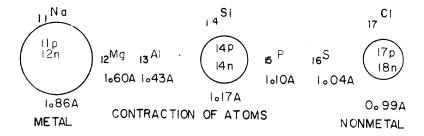


FIGURE 17. The ionization of sodium and a comparison of the sizes of the sodium atom and ion.

XVII. Acid-base relationships are explained right from the beginning in terms of the structural concepts of the central atom utilizing both Lewis and Bronsted theories (fig. 19). Thus, small metal ions with large positive charges may be shown to act as strong electron pair acceptors and therefore acidic or amphoteric in their behavior. The strong attraction of the metal ion for the oxide and resulting repulsion of the proton (as part of the hydroxide ion) gives a partial explanation of the capacity of such metal hydroxides to be amphoteric (or amphiprotic in this case). The same principles are carried through to the nonmetal central group (as S(VI), N(V), P(V)) when these atoms (in varying oxidation states) are associated with the OH group. The large positive charge and the very small size will further enhance the acidic behavior. The converse situation

with the large metal ions with small positive charge and resulting poor electron pair accepting property leads to the strong basic behavior or very weak acidic behavior.

As has been indicated before, essentially all the material outlined in Paragraphs I to XVI inclusive is presented as a total unit early in the course in general chemistry. This leads to a working model for studying the elements and their compounds which is applied throughout the rest of the course. Thus, the presence of a polar bond in water molecules is easily explained and the student is ready to accept and apply the concept of angular molecules polar in character (fig. 20).



# ACID-BASE STRENGTH SIZE &CHARGE RELATION

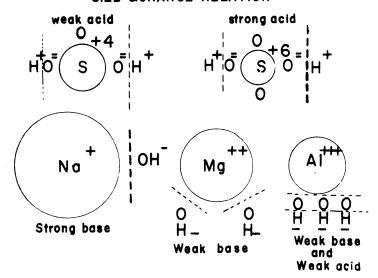


FIGURE 18. The effect of nuclear charge upon atomic size within same series in periodic table.

FIGURE 19. Acid-base strength relations to size and charge on central atom.

Students find this much more meaningful than to refer to water merely as HOH or H<sub>2</sub>O. As a specific example of the many consequences of the polar character of the water molecule, consider the great differences in the behavior of methane (a typical nonpolar covalent molecule) and sodium chloride (a typical ionic compound) in water (fig. 21). Methane is a gas and but slightly soluble in water. Sodium chloride is a crystalline substance of high melting point but quite soluble

in water due to solvation effects dependent upon the polar character of the water molecule. The resulting solution, of course, is very different from the solution of methane in water. It is the feeling of our teaching staff that students, for example, can approach the study of the colligative properties of solutions with greater understanding using our working model than using the traditional physicochemical approach employing Racult's law.

In conclusion, it is the prime purpose of this type of introduction to atomic architecture to give the student a working model, which it must be admitted is derived with many over simplifications, but which appears to have real teaching

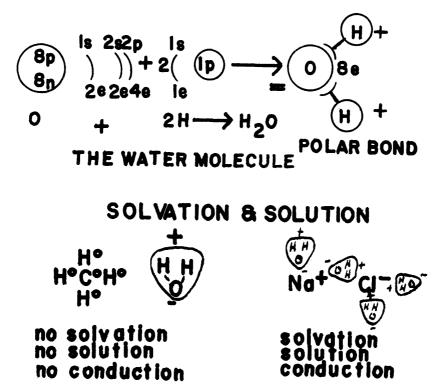


FIGURE 20. The shape and polar character of the water molecule. FIGURE 21. Solution effects dependent upon the polar character of water molecules.

potential. An essentially identical model has been given to high school juniors, with sufficient success so that the feeling exists that we do not need to wait till a senior college course to develop a reasonably precise working model from the chemical point of view. Students going on in chemistry are in a good position to accept the more advanced postulates and theories of quantum mechanics, field theory, and other related topics. These not continuing for a major but taking more chemistry courses and even terminal students, do not find such a presentation too difficult. The few extra periods devoted to structure at this early point pay large dividends in later portions of the course.