MODERN INORGANIC CHEMISTRY

J. J. LAGOWSKI

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PREFACE

In the recent past the study of inorganic chemistry has reachieved a level of interest comparable to that exhibited in the earlier phases of the development of the subject of chemistry as a whole. This renewed interest has come to pass largely because of the parallel development of numerous—practically useful—theoretical principles and experimental techniques for synthesis, separation, and structure determination. As a result, an enormous amount of information has accrued in the past twenty years in those general areas classically associated with inorganic chemistry. In addition, compounds containing metal-carbon bonds have received considerable attention from inorganic chemists during this time. Thus, inorganic chemistry as it is presently constituted is more properly described as the chemistry of the elements, with little distinction being drawn to the first member of Group IV in the periodic classification. This text is intended to give senior college or first-year graduate students, as defined in American universities, a working knowledge of the essence of modern inorganic chemistry.

The evolution of this volume has been dictated by two factors: the broad scope of inorganic chemistry and the time normally available in the chemistry curriculum for the study of inorganic chemistry. Under these constraints, the inevitable points of decision concerning the relative emphasis to be placed on certain areas are quickly reached. In some instances the decisions to exclude and/or minimize subjects were rather arbitrary; undoubtedly choices other than those presented could be successfully debated. In an attempt to offset partially some of the restrictions imposed by these constraints, a limited set of selected references to the research literature is included. Supplementary references to more extensive expositions—usually in the review literature—are also included. I hope that these devices will alleviate the shortcomings that some users may see in this volume because of the initial constraints placed upon it.

Since experiment and theory are intimately intertwined, several logically defensible strategies are available for a text of this nature. It is my personal preference to separate these two aspects of chemistry because it is possible to know the unity of the experimental results without using extensive theoretical arguments. Put in another way, a great many experimental results can be correlated, and predictions made on such correlations, without confusing the issue with theory. The point is that these facts still will be valid if current theories are unsuitable or, indeed, even do not exist. Hopefully the student will obtain an appreciation of the experimental results which form the basis for the theoretical discussions organized separately. In this respect several older—and presently outmoded—concepts have been introduced to give the student a sense of the evolutionary nature of theoretical arguments and to put the present theories in proper perspective. In a broad sense, it is often more important to understand the basis on which changes in theoretical outlook are made, whether they be drastic or subtle, than it is to know all of the details of the most modern theory.

I should like to acknowledge my indebtedness to Dr. Maurits Dekker for his suggestions at the inception of this volume and his encouragement during its development. Professor Gilbert Gordon read the manuscript in its entirety and offered numerous suggestions for its improvement, for which I express my appreciation. However, errors which may be present are mine alone. The publisher and his staff have provided invaluable assistance in the production of this volume. Finally but most importantly, I must acknowledge my gratitude to my wife, Jeanne, who not only suffered the usual indirect consequences of living with an author, but also contributed materially by serving as resident professional reader, grammarian, editor, and typist. Without her continual encouragement and assistance, the preparation of this volume would never have been possible.

Austin, Texas   J. J. LAGOWSKI

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ATOMS
AND THEIR
CHARACTERISTICS

Atoms and their varied characteristics are the basic focus of interest of chemists. Since a vast array of chemical compounds with different properties and characteristics can be prepared from a relatively few atomic types, there is the hope that an understanding of the nature of atoms can lead directly to an elucidation of the chemical unity of the elements, the compounds they form, the structures of such compounds, and the properties, both physical and chemical, of these compounds. Thus it is fitting to begin this discussion with a consideration of the nature and properties of atoms as we presently perceive them.

1 / THE ARCHITECTURE OF ATOMS

Our knowledge of the microstructure of atoms stems from studies on (1) the conduction of electricity through gaseous matter, (2) radioactivity, (3) the

production of x rays, and (4) spectroscopy. It is not our purpose here to give a detailed description of all of the pertinent experiments, results, and reasoning in each of these areas which led to establishment of the present model of atomic structure. Rather, we present a synopsis of a few of the key experiments and their contribution to our understanding of atomic structure (*I*).*

1.1 / Electrical Discharge through Gases

Cathode Rays   Studies on the conduction of electricity through matter have provided considerable insight for understanding its constitution. In particular, gases at low pressure ($< 10^{-4}$ torr) conduct an electric current when subjected to a high potential difference; a schematic diagram of the apparatus used in experiments under these conditions is shown in Fig. 1.1. It
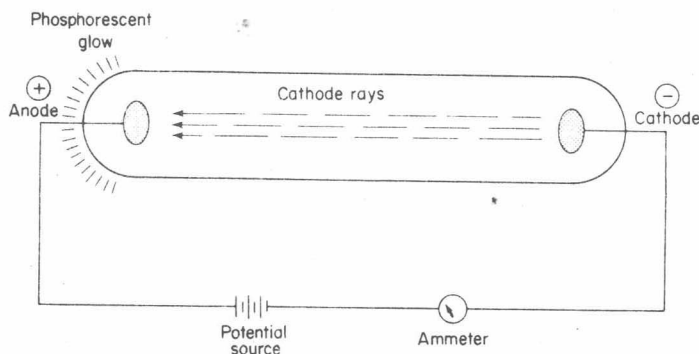
FIG. 1.1   A schematic diagram for an apparatus to create an electrical discharge through a gaseous sample. A phosphorescent glow appears about the anode when current flows through the circuit.

might appear that with a good vacuum in the tube no current would flow through the circuit. However, electricity does flow through the external circuit, as indicated by the ammeter in the diagram, implying that an equivalent charge must pass through the tube. In 1859 Plücker observed that the glass at the anode end of a discharge tube emits a phosphorescent glow which persists as long as the circuit is closed. He suggested that the glow arose from radiation, which he named cathode rays, emanating from the cathode. In addition to glass, substances such as zinc sulfide glow brightly when exposed to cathode rays. Crookes proposed that cathode rays were really particles, and Perrin showed that these particles carry a negative charge.

   In a series of brilliantly conceived experiments J. J. Thomson elucidated the fundamental nature of cathode rays; a description of one of these experi-

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* Collateral readings are indicated by Roman numerals and collected at the end of each chapter.
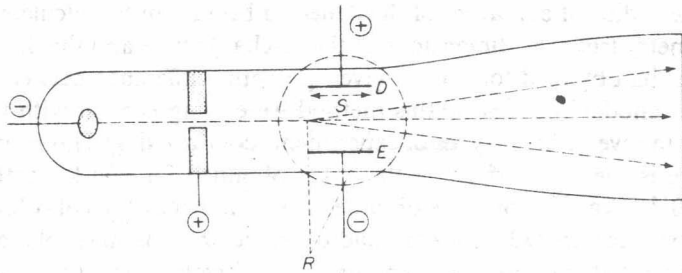
FIG. 1.2 A schematic diagram of the discharge tube used by Thomson to establish the q/m ratio for cathode rays. An electric field could be established perpendicular to the cathode ray beam by charging plates D and E. The dotted circle represents the position of the pole faces of a magnet which is perpendicular to the plane of the paper.

ments is sufficient to show the thrust of his logic (1).* Figure 1.2 is a schematic diagram of the discharge tube Thomson used to determine the ratio of charge to mass (q/m) of cathode rays. Cathode rays are generated in the left side of the tube, and they are accelerated toward the anode, which contains a hole that is collinear with the cathode. Cathode rays pass into the right side of the tube, where they strike the far wall which is coated with zinc sulfide. The tube also contains two parallel plates (D and E in Fig. 1.2) which can be charged by an external potential source. The dotted circle in Fig. 1.2 represents the pole faces of a magnet located above and below the tube. Thus, the cathode rays can be subjected to an electric field acting perpendicular to their path through the discharge tube and a magnetic field perpendicular to both of these directions. The experiment involves balancing the deflection of a magnetic field of known intensity by an electric field. The magnetic field causes the beam to deflect from point A along the line BC, the direction of the deflection depending upon the orientation of the magnetic poles. The beam can be brought back to its original position by applying an electrostatic field generated by charging the plates (D and E) in the appropriate direction. Applying the quantitative relationships which describe the interaction of an electric and a magnetic field with moving charge (a current), Thomson showed that under the conditions of balance the velocity v of the moving charge is related to the magnetic field H, the length S of the condenser plates, and the potential difference V between the plates:

$$v = V/HS. \tag{1}$$

Removal of the electric field while maintaining the magnetic field causes the cathode beam to deviate to point C. Under these conditions q/m is given by

$$\frac{q}{m} = \frac{V}{SH^2R}. \tag{2}$$

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* References to the research literature are designated by arabic numerals and are collected at the end of each chapter.

where R, the radius of curvature of the deflected beam, can be calculated by simple geometry from the dimensions of the discharge tube and the distance CA. The results obtained for v (at a given potential difference between the cathode and anode) and q/m by this method were in agreement with those obtained from several other types of experiments conducted by Thomson. Of interest here is the comparison of the value obtained for q/m for cathode rays $(2 \times 10^{11} \text{ C kg}^{-1})$ with those obtained from the electrolysis of solutions of ionic substances. In 1833 Faraday had observed that the mass of a given substance liberated in electrolysis experiments is directly proportional to the quantity of electricity passed through the circuit. Thus, q/m ratios were known for many chemical species; a selection of values is given in Table 1.1.

TABLE 1.1   The charge-to-mass ratio (q/m) obtained for some ions from electrolysis experiments

Ion	q/m, C kg^{-1}
H^+	9.6×10^7
Cu^{2+}	3.0×10^6
Ag^+	8.9×10^5
Cd^{2+}	1.7×10^6
Fe^{3+}	5.2×10^6

A comparison of the q/m ratios of cathode rays with those for known ionic species strongly indicates that the former are not charged atoms. The ratio of q/m for cathode rays is about 2000 times larger than that of the lightest known ion (H^+), indicating that the particle has either a very small mass or an unusually high charge. Since charges on the majority of ionic species are small multiples of the charge of the hydrogen ion, Thomson reasonably assumed that the difference between the q/m ratios for chemical species and cathode rays primarily arises from a difference in mass. Cathode rays are free negatively charged particles, the discrete unit of negative electricity which Stoney had called an electron many years earlier.

Canal Rays   In 1886, Goldstein detected radiation emitted from a cathode but moving in the direction opposite to that of the cathode rays. A schematic diagram of the Goldstein discharge tube is shown in Fig. 1.3. The discharge tube contains a gas at low pressure, a perforated cathode A, and an anode. When a high potential is impressed across the electrodes, the usual effect of the cathode rays is observed on the glass around the anode. In addition, bundles of light appear in the other compartment, D, of the discharge tube. Goldstein observed that the color of these beams, or canal rays, varied with the gas, and Wein showed that they are deflected by magnetic and