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**MODERN  
INORGANIC  
CHEMISTRY**

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# MODERN INORGANIC CHEMISTRY

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**William L. Jolly**

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## MODERN INORGANIC CHEMISTRY

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	Pr	59	140.907	(147)	151.96	157.25	158.924	162.50	164.930	167.26	168.934	173.04	174.97
	Nd	60	144.24	(147)	151.96	157.25	158.924	162.50	164.930	167.26	168.934	173.04	174.97
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	Sm	62	(231)	(242)	(243)	(247)	(249)	(254)	(253)	(256)	(253)	(257)	
	Eu	63	(231)	(242)	(243)	(247)	(249)	(254)	(253)	(256)	(253)	(257)	
	Gd	64	(231)	(242)	(243)	(247)	(249)	(254)	(253)	(256)	(253)	(257)	
	Tb	65	(231)	(242)	(243)	(247)	(249)	(254)	(253)	(256)	(253)	(257)	
	Dy	66	(231)	(242)	(243)	(247)	(249)	(254)	(253)	(256)	(253)	(257)	
	Ho	67	(231)	(242)	(243)	(247)	(249)	(254)	(253)	(256)	(253)	(257)	
Actinide series	Er	68	(231)	(242)	(243)	(247)	(249)	(254)	(253)	(256)	(253)	(257)	
	Tm	69	(231)	(242)	(243)	(247)	(249)	(254)	(253)	(256)	(253)	(257)	
	Yb	70	(231)	(242)	(243)	(247)	(249)	(254)	(253)	(256)	(253)	(257)	
	Lu	71	(231)	(242)	(243)	(247)	(249)	(254)	(253)	(256)	(253)	(257)	
	Th	90	(231)	(242)	(243)	(247)	(249)	(254)	(253)	(256)	(253)	(257)	
	Pa	91	(231)	(242)	(243)	(247)	(249)	(254)	(253)	(256)	(253)	(257)	
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## PREFACE

The purpose of this text is to provide a systematic discussion of the important phenomena of modern inorganic chemistry. Topics have been included because of their presumed importance, not because of the thoroughness with which they are understood or the ease with which they are taught. For example, the book includes sections on metallic compounds, polyhedral cluster compounds, and heterogeneous catalysis even though these topics have not been systematized as well as many other topics in inorganic chemistry.

It is assumed that the reader has completed a one-year course in general chemistry and an introductory course in organic chemistry. Thus familiarity with the rudiments of thermodynamics, kinetics, atomic and molecular orbital theory, orbital hybridization, the electronegativity concept, and simple bonding theory is assumed. The book is a greatly expanded and updated version of *The Principles of Inorganic Chemistry*, published in 1976. The expansion has allowed me to include more "descriptive" material and to go into greater detail in many topics. Instructors will have considerable freedom in choosing the topics which they wish to emphasize in their courses.

Some elementary but very important topics, such as atomic quantum theory and Lewis structures, are included for review and emphasis. Data from advanced experimental techniques such as photoelectron spectroscopy and Mössbauer spectroscopy are occasionally included, after brief introductions of these techniques. In such cases, literature references for further background are provided. A chapter on symmetry and the elements of group theory and separate chapters on homogeneous and heterogeneous catalysis have been added. Many new tables of data (thermodynamic data, ionization potentials, acidity data, structural data, etc.) have been added. A discussion of inorganic nomenclature has been added as an appendix. I believe the text covers all the important aspects of modern inorganic chemistry. Although the large amount of descriptive material is organized topically rather than in a periodic table arrangement, the reader has easy access to this material through the Index.

Too many chemistry students graduate with only a hazy notion of the applied side of chemistry. Therefore I offer no apologies for occasionally describing practical applications (and potential applications) of inorganic systems. It is important for students to recognize that much of the chemistry described in this book closely affects their daily lives and that soon they may be called upon to use inorganic chemistry to solve important problems.

I hope the text gives the impression that inorganic chemistry is an active, fascinating (even frustrating) field. With this in mind, some of the illustrative examples have been chosen because of their unusual or exotic character and the belief that they may represent entries into new areas. Pedestrian data can always be found in handbooks and compendia.

Problems are provided at the end of each chapter, and answers to about half of these problems are given after Appendix G. The problems range from simple to difficult (the latter being indicated by asterisks) and should be attempted by all students who seriously want to master the subject matter.

I am very grateful to George Brubaker, James Espenson, Craig Hill, Andrew Streitwieser, Jr., and Paul M. Treichel, Jr., for their helpful criticisms of an early draft of the manuscript. I also wish to thank Lawrence F. Dahl for permission to use his drawing of the  $\text{Pt}_{38}(\text{CO})_{44} \text{H}_x^{2-}$  cluster in the cover design.

William L. Jolly

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## ELECTRON CONFIGURATIONS OF ATOMS AND THE PERIODIC TABLE

Most of the chemical properties of compounds are predictable from the electron configurations of the constituent atoms. Thus it is very important for chemists to be familiar with the electronic structures and related properties of atoms. In this chapter we briefly discuss these topics and show how the periodic table may be used to correlate various properties of atoms with electronic structure.

Although some of the material covered in the chapter is discussed in elementary chemistry texts, you should not assume that this material is easily understood. It is included here because of its fundamental importance in the study of inorganic chemistry and to give you the opportunity to review. Throughout the remainder of the text, it will be assumed that you are familiar with the principles discussed in this chapter. You may find it helpful occasionally to refer back to parts of this chapter.

### QUANTUM NUMBERS

In 1926 Schrödinger<sup>1</sup> proposed a differential equation (which now bears his name) for relating the energy of a system to the space coordinates of its constituent particles. For a particle in three dimensions, the equation may be written

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} + \frac{8\pi^2 m}{h^2} (E - V) \psi = 0$$

<sup>1</sup> E. Schrödinger, *Ann. Phys.*, **79**, 361, 489; **81**, 109 (1926).

where  $\psi$  is the "wave function,"  $x$ ,  $y$ , and  $z$  are the cartesian coordinates of the particle,  $m$  is its mass,  $E$  is the total energy, and  $V$  is the potential energy. This equation incorporates both the wave character of the particle and the probability character of the measurements. The wave function  $\psi$  has properties analogous to the amplitude of a wave; its square,  $\psi^2$ , is proportional to the probability of finding a particle at the coordinates  $x$ ,  $y$ ,  $z$ .

When the Schrödinger equation is applied to the hydrogen atom or to any system with one electron and one nucleus, the solution includes three "integration constants." These are the familiar quantum numbers  $n$ ,  $l$ , and  $m_l$ . The "principal" quantum number  $n$  may have any integral value from 1 to infinity:

$$n = 1, 2, 3, \dots$$

The "azimuthal" or "orbital angular momentum" quantum numbers  $l$  may have any integral value from zero to  $n - 1$ :

$$l = 0, 1, 2, \dots, (n - 1)$$

However, for historical reasons,  $l$  is usually not specified by these integers, but rather by the letters  $s, p, d, f, g, \dots$  (continuing alphabetically), which correspond to  $l = 0, 1, 2, 3, 4, \dots$ , respectively. The  $n$  and  $l$  values of an electron are often designated by the notation  $nl$ , in which the value of  $l$  is indicated by the appropriate letter. Thus a  $2p$  electron has  $n = 2$  and  $l = 1$ . The "magnetic" quantum number  $m_l$  may have an integral value from  $-l$  to  $+l$ :

$$m_l = -l, -(l - 1), \dots, -1, 0, +1, +2, \dots, l - 1, +l$$

Because an electron has spin, and consequently a magnetic moment which can be oriented either up or down, yet a fourth quantum number must be specified, the "spin" quantum number  $m_s$ . The permissible values of  $m_s$  are  $\pm \frac{1}{2}$ .

As a consequence of the restrictions on the quantum numbers, the electron of a hydrogen atom may be assigned only certain combinations of quantum numbers. These permissible combinations for  $n = 1, 2, 3$ , and 4 are indicated in

**Table 1.1 Some allowed values of the hydrogen atom quantum numbers**

$n$	$l$	$m_l$	$m_s$	No. of combinations
1	0	0	$\pm \frac{1}{2}$	2
2	0	0	$\pm \frac{1}{2}$	2
2	1	-1, 0, +1	$\pm \frac{1}{2}$	6
3	0	0	$\pm \frac{1}{2}$	2
3	1	-1, 0, +1	$\pm \frac{1}{2}$	6
3	2	-2, -1, 0, +1, +2	$\pm \frac{1}{2}$	10
4	0	0	$\pm \frac{1}{2}$	2
4	1	-1, 0, +1	$\pm \frac{1}{2}$	6
4	2	-2, -1, 0, +1, +2	$\pm \frac{1}{2}$	10
4	3	-3, -2, -1, 0, +1, +2, +3	$\pm \frac{1}{2}$	14

Table 1.1. Each allowed combination of  $n$ ,  $l$ , and  $m_l$  corresponds to an atomic "orbital." We say that the electron may be "put into" or "assigned to" a particular orbital. Of course, in any orbital, the  $m_s$  quantum number may be either  $+\frac{1}{2}$  or  $-\frac{1}{2}$ .

## ORBITAL SHAPES AND ENERGIES FOR THE HYDROGEN ATOM

It is convenient to express the wave function of the hydrogen atom in terms of the polar coordinates  $r$ ,  $\theta$ , and  $\phi$  and to factor the function into three separate parts, each of which is a function of only one coordinate:

$$\psi(r, \theta, \phi) = R(r) \cdot \Theta(\theta) \cdot \Phi(\phi)$$

In Tables 1.2 to 1.4, the functions  $R(r)$ ,  $\Theta(\theta)$ , and  $\Phi(\phi)$  are given for various values of the quantum numbers  $n$ ,  $l$ , and  $m_l$ . Obviously the values of the three functions, and hence also the spatial distribution of the electron of a hydrogen atom, are markedly affected by the values of  $n$  and  $l$ . The spatial distributions can be indicated graphically in several ways. Let us first consider the case of  $l = 0$ , that is,  $s$  electrons. In Fig. 1.1, the radial wave function  $R$  is plotted as a function of  $r$ , the distance from the nucleus, for  $n = 1, 2$ , and  $3$ . Three facts should be noted. First, in each case, the magnitude of the wave function has its maximum value at the nucleus. Second, for  $n > 1$ , the wave function is zero in certain regions called "nodes." (As a general rule, there are  $n - 1$  nodes in an atomic wave function.) Third, the sign of  $R$  changes as it passes through a node.

Table 1.2 Radial wave function  $R(r)$  for hydrogen atom

$n$	$l$	$R(r)^\dagger$
1	0	$2 \left( \frac{Z}{a_0} \right)^{3/2} e^{-Zr/a_0}$
2	0	$\left( \frac{1}{2\sqrt{2}} \right) \left( \frac{Z}{a_0} \right)^{3/2} \left( 2 - \frac{Zr}{a_0} \right) e^{-Zr/2a_0}$
	1	$\left( \frac{1}{2\sqrt{6}} \right) \left( \frac{Z}{a_0} \right)^{3/2} \left( \frac{Zr}{a_0} \right) e^{-Zr/2a_0}$
3	0	$\left( \frac{2}{81\sqrt{3}} \right) \left( \frac{Z}{a_0} \right)^{3/2} \left( 27 - \frac{18Zr}{a_0} + \frac{2Z^2r^2}{a_0^2} \right) e^{-Zr/3a_0}$
	1	$\left( \frac{4}{81\sqrt{6}} \right) \left( \frac{Z}{a_0} \right)^{3/2} \left( \frac{6Zr}{a_0} - \frac{Z^2r^2}{a_0^2} \right) e^{-Zr/3a_0}$
	2	$\left( \frac{4}{81\sqrt{30}} \right) \left( \frac{Z}{a_0} \right)^{3/2} \left( \frac{Zr}{a_0} \right)^2 e^{-Zr/3a_0}$

$^\dagger a_0$  is the "first Bohr radius,"  $0.529 \text{ \AA}$ .



**Table 1.3 Angular wave function  $\Theta(\theta)$  for hydrogen atom**

$l$	$m_l$	$\Theta(\theta)$
0	0	$\frac{\sqrt{2}}{2}$
1	0	$\frac{\sqrt{6}}{2} \cos \theta$
	$\pm 1$	$\frac{\sqrt{3}}{2} \sin \theta$
2	0	$\frac{\sqrt{10}}{4} (3 \cos^2 \theta - 1)$
	$\pm 1$	$\frac{\sqrt{15}}{2} (\sin \theta \cos \theta)$
	$\pm 2$	$\frac{\sqrt{15}}{4} \sin^2 \theta$

Although  $R$  is a function which is not directly related to any experimentally measurable quantity, the function  $R^2$  is proportional to electron density and therefore has considerable physical significance. In Fig. 1.2,  $R^2$  is plotted versus  $r$  for 1s, 2s, and 3s electrons. Note that  $R^2$ , like  $R$ , has its maximum value at the nucleus and that nodes appear for  $n > 1$ . Of course,  $R$  is never negative; a negative electron density is physically meaningless. One important feature of any s-electron distribution that Figs. 1.1 and 1.2 do not make obvious is that the distribution is independent of  $\theta$  and  $\phi$ ; that is, it is spherically symmetric. To

**Table 1.4 Angular wave function  $\Phi(\phi)$  for hydrogen atom**

$m_l$	$\Phi(\phi)$
0	$\frac{1}{\sqrt{2\pi}}$
1	$\frac{1}{\sqrt{\pi}} \cos \phi$
-1	$\frac{1}{\sqrt{\pi}} \sin \phi$
2	$\frac{1}{\sqrt{\pi}} \cos 2\phi$
-2	$\frac{1}{\sqrt{\pi}} \sin 2\phi$