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# **AN INTRODUCTION TO MATERIALS ENGINEERING AND SCIENCE**

## **FOR CHEMICAL AND MATERIALS ENGINEERS**

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Brian S. Mitchell  
Department of Chemical Engineering,  
Tulane University



A JOHN WILEY & SONS, INC., PUBLICATION



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*To my parents; whose  
Material was loam;  
Engineering was labor;  
Science was lore;  
And greatest product was love.*





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\*Sections marked with an asterisk can be omitted in an introductory course.



## **PREFACE**

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This textbook is intended for use in a one- or two-semester undergraduate course in materials science that is primarily populated by chemical and materials engineering students. This is not to say that biomedical, mechanical, electrical, or civil engineering students will not be able to utilize this text, nor that the material or its presentation is unsuitable for these students. On the contrary, the breadth and depth of the material covered here is equivalent to most “traditional” metallurgy-based approaches to the subject that students in these disciplines may be more accustomed to. In fact, the treatment of biological materials on the same level as metals, ceramics, polymers, and composites may be of particular benefit to those students in the biologically related engineering disciplines. The key difference is simply the organization of the material, which is intended to benefit primarily the chemical and materials engineer.

This textbook is organized on two levels: by engineering subject area and by materials class, as illustrated in the accompanying table. In terms of topic coverage, this organization is transparent: By the end of the course, the student will have covered many of the same things that would be covered utilizing a different materials science textbook. To the student, however, the organization is intended to facilitate a deeper understanding of the subject material, since it is presented in the context of courses they have already had or are currently taking—for example, thermodynamics, kinetics, transport phenomena, and unit operations. To the instructor, this organization means that, in principle, the material can be presented either in the traditional subject-oriented sequence (i.e., in rows) or in a materials-oriented sequence (i.e., in columns). The latter approach is recommended for a two-semester course, with the first two columns covered in the first semester and the final three columns covered in the second semester. The instructor should immediately recognize that the vast majority of “traditional” materials science concepts are covered in the columns on metals and ceramics, and that if the course were limited to concepts on these two materials classes only, the student would receive instruction in many of the important topics covered in a “traditional” course on materials. Similarly, many of the more advanced topics are found in the sections on polymers, composites, and biological materials and are appropriate for a senior-level, or even introductory graduate-level, course in materials with appropriate supplementation and augmentation.

This textbook is further intended to provide a unique educational experience for the student. This is accomplished through the incorporation of instructional objectives, active-learning principles, design-oriented problems, and web-based information and visualization utilization. Instructional objectives are included at the beginning of each chapter to assist both the student and the instructor in determining the extent of topics and the depth of understanding required from each topic. This list should be used as a guide only: Instructors will require additional information they deem important or eliminate topics they deem inappropriate, and students will find additional topic coverage in their supplemental reading, which is encouraged through a list of references at the end

	Metals & Alloys	Ceramics & Glasses	Polymers	Composites	Biologics
<b>Structure</b>	Crystal structures, Point defects, Dislocations	Crystal structures, Defect reactions, The glassy state	Configuration, Conformation, Molecular Weight	Matrices, Reinforcements	Biochemistry, Tissue structure
<b>Thermo-dynamics</b>	Phase equilibria, Gibbs Rule, Lever Rule	Ternary systems, Surface energy, Sintering	Phase separation, Polymer solutions, Polymer blends	Adhesion, Cohesion, Spreading	Cell Adhesion, Cell spreading
<b>Kinetics</b>	Transformations, Corrosion	Devitrification, Nucleation, Growth	Polymerization, Degradation	Deposition, Infiltration	Receptors, Ligand binding
<b>Transport Properties</b>	Inviscid systems, Heat capacity, Diffusion	Newtonian flow, Heat capacity, Diffusion	non-Newtonian flow, Heat capacity, Diffusion	Porous Flow, Heat capacity, Diffusion	Convection, Diffusion
<b>Mechanical Properties</b>	Stress-strain, Elasticity, Ductility	Fatigue, Fracture, Creep	Viscoelasticity, Elastomers	Laminates	Sutures, Bone, Teeth
<b>Electrical, Magnetic &amp; Optical Properties</b>	Resistivity, Magnetism, Reflectance	Dielectrics, Ferrites, Absorbance	Ion conductors, Molecular magnets, LCDs	Dielectrics, Storage media	Biosensors, MRI
<b>Processing</b>	Casting, Rolling, Compaction	Pressing, CVD/CVI, Sol-Gel	Extrusion, Injection molding, Blow molding	Pultrusion, RTM, CVD/CVI	Surface modification
<b>Case Studies</b>	Compressed air tank	Ceramic piping	Polymeric packaging	Composite drive shaft	Tooth coatings

of each chapter. Active-learning principles are exercised through the presentation of example problems in the form of Cooperative Learning Exercises. To the student, this means that they can solve problems in class and can work through specific difficulties in the presence of the instructor. Cooperative learning has been shown to increase the level of subject understanding when properly utilized.\* No class is too large to allow students to take 5–10 minutes to solve these problems. To the instructor, the Cooperative Learning Exercises are to be used only as a starting point, and the instructor is encouraged to supplement his or her lecture with more of these problems. Particularly difficult concepts or derivations are presented in the form of Example Problems that the instructor can solve in class for the students, but the student is encouraged to solve these problems during their own group or individual study time. Design-oriented problems are offered, primarily in the Level III problems at the end of each chapter,

\*Smith, K. *Cooperative Learning and College Teaching*, 3(2), 10–12 (1993).

that incorporate concepts from several chapters, that involve significant information retrieval or outside reading, or that require group activities. These problems may or may not have one “best” answer and are intended to promote a deeper level of understanding of the subject. Finally, there is much information on the properties of materials available on the Internet. This fact is utilized through the inclusion of appropriate web links. There are also many excellent visualization tools available on the Internet for concepts that are too difficult to comprehend in a static, two-dimensional environment, and links are provided to assist the student in their further study on these topics.

Finally, the ultimate test of the success of any textbook is whether or not it stays on your bookshelf. It is hoped that the extent of physical and mechanical property data, along with the depth with which the subjects are presented, will serve the student well as they transition to the world of the practicing engineer or continue with their studies in pursuit of an advanced degree.

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# The Structure of Materials

## 1.0 INTRODUCTION AND OBJECTIVES

A wealth of information can be obtained by looking at the structure of a material. Though there are many levels of structure (e.g., atomic vs. macroscopic), many physical properties of a material can be related directly to the arrangement and types of bonds that make up that material. We will begin by reviewing some general chemical principles that will aid us in our description of material structure. Such topics as periodic structure, types of bonding, and potential energy diagrams will be reviewed. We will then use this information to look at the specific materials categories in more detail: metals, ceramics, polymers, composites, and biological materials (biologics). There will be topics that are specific to each material class, and there will also be some that are common to all types of materials. In subsequent chapters, we will explore not only how the building blocks of a material can significantly impact the properties a material possesses, but also how the material interacts with its environment and other materials surrounding it.

By the end of this chapter you should be able to:

- Identify trends in the periodic table for  $IE$ ,  $EA$ , electronegativity, and atomic/ionic radii.
- Identify the type of bonding in a compound.
- Utilize the concepts of molecular orbital and hybridization theories to explain multiple bonds, bond angle, diamagnetism, and paramagnetism.
- Identify the seven crystal systems and 14 Bravais lattices.
- Calculate the volume of a unit cell from the lattice translation vectors.
- Calculate atomic density along directions, planes, and volumes in a unit cell.
- Calculate the density of a compound from its crystal structure and atomic mass.
- Locate and identify the interstitial sites in a crystal structure.
- Assign coordinates to a location, indices to a direction, and Miller indices to a plane in a unit cell.
- Use Bragg's Law to convert between diffraction angle and interplanar spacing.
- Read and interpret a simple X-ray diffraction pattern.
- Identify types of point and line defects in solids.

- Calculate the concentration of point defects in solids.
- Draw a Burger's circuit and identify the direction of dislocation propagation.
- Use Pauling's rules to determine the stability of a compound.
- Predict the structure of a silicate from the Si/O ratio.
- Apply Zachariasen's rules to determine the glass forming ability of an oxide.
- Write balanced defect reaction equations using Kroger–Vink notation.
- Classify polymers according to structure or formability.
- Calculate the first three moments of a polymer molecular weight distribution.
- Apply principles of glass transition and polymer crystallinity to polymer classification.
- Identify nematic, smectic, and cholesteric structures in liquid crystalline polymers.
- Identify the components in a composite material.
- Approximate physical properties of a composite material based on component properties.
- Be conversant in terms that relate to the structure of biological materials, such as fibronectin and integrins.

### 1.0.1 The Elements

Elements are materials, too. Oftentimes, this fact is overlooked. Think about all the materials from our daily lives that are elements: gold and silver for our jewelry; aluminum for our soda cans; copper for our plumbing; carbon, both as a luminescent diamond and as a mundane pencil lead; mercury for our thermometers; and tungsten for our light bulb filaments. Most of these elements, however, are relatively scarce in the grand scheme of things. A table of the relative abundance of elements (Table 1.1) shows that most of our universe is made up of hydrogen and helium. A little closer to home, things are much different. A similar table of relative abundance (Table 1.2) shows that helium on earth is relatively scarce, while oxygen dominates the crust of our planet. Just think of how much molecular oxygen, water, and aluminosilicate rocks are contained in the earth's crust. But those are molecules—we are concentrating on atoms for the moment. Still, elements are of vital importance on earth, and the ones we use most often are primarily in the solid form.

Recall from your introductory chemistry course that the elements can be systematically arranged in a periodic table according to their electronic structure (see Table 1.3\*). An overall look at the periodic table (Figure 1.1) shows that many elements are solids (white boxes) at room temperature. The fact that many of these elements remain solid well above ambient temperatures is important. As we heat to 1000°C, note that many of the IIIA–VA elements have melted (light shaded); also note how many of the alkali metals (IA) have vaporized (dark shaded), but how most of the transition elements are still in solid form. At 2000°C, the alkali earths are molten, and many of the transition elements have begun to melt, too. Note that the highest melting point element is carbon (Figure 1.1d). Keep in mind that this is in an inert atmosphere. What should happen to

\*Note that the Lanthanide (atomic numbers 58–71) and Actinide (90–103) series elements, as well as the synthetic elements of atomic number greater than 87, are omitted from all the periodic tables in this text. With the possible exception of nuclear fuels such as uranium and plutonium, these elements are of little general engineering interest.

**Table 1.1 Relative Abundance of Elements in the Universe**

Element	Relative Abundance (Si = 1)
Hydrogen (H)	12,000
Helium (He)	2,800
Oxygen (O)	16
Nitrogen (N)	8
Carbon (C)	3
Iron (Fe)	2.6
Silicon (Si)	1
Magnesium (Mg)	0.89
Sulfur (S)	0.33
Nickel (Ni)	0.21
Aluminum (Al)	0.09
Calcium (Ca)	0.07
Sodium (Na)	0.045
Chlorine (Cl)	0.025

**Table 1.2 Relative Abundance of Selected Elements in the Earth's Crust**

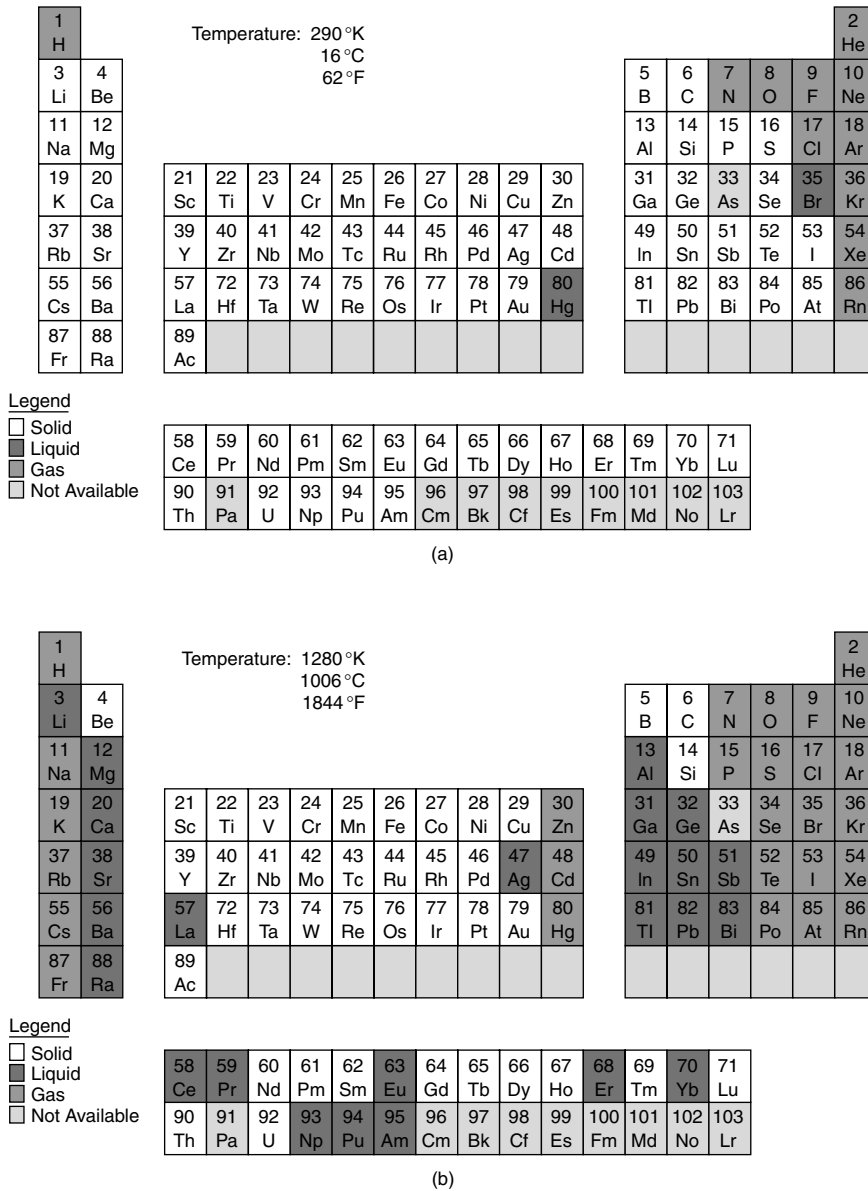
Element	Relative Abundance (ppm)	Element	Relative Abundance (ppm)
Oxygen (O)	466,000	Fluorine (F)	300
Silicon (Si)	277,200	Strontium (Sr)	300
Aluminum (Al)	81,300	Barium (Ba)	250
Iron (Fe)	50,000	Zirconium (Zr)	220
Calcium (Ca)	36,300	Chromium (Cr)	200
Sodium (Na)	28,300	Vanadium (V)	150
Potassium (K)	25,900	Zinc (Zn)	132
Magnesium (Mg)	20,900	Nickel (Ni)	80
Titanium (Ti)	4,400	Molybdenum (Mo)	15
Hydrogen (H)	1,400	Uranium (U)	4
Phosphorus (P)	1,180	Mercury (Hg)	0.5
Manganese (Mn)	1,000	Silver (Ag)	0.1
Sulfur (S)	520	Platinum (Pt)	0.005
Carbon (C)	320	Gold (Au)	0.005
Chlorine (Cl)	314	Helium (He)	0.003

this element in the presence of oxygen? Such elements as tungsten, platinum, molybdenum, and tantalum have exceptional high-temperature properties. Later on we will investigate why this is so.

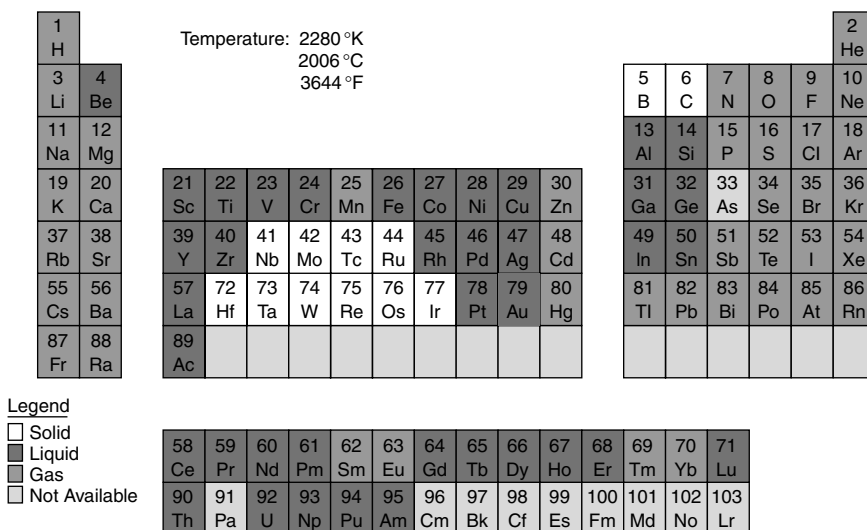
In addition, many elements are, in and of themselves, materials of construction. Aluminum and copper are just a few examples of elements that are used extensively for fabricating mechanical parts. Elements have special electrical characteristics, too. Silver and gold are used not just for jewelry, but also for a wide variety of electrical components. We will visit all of these topics in the course of this textbook.

## 1.0.2 Trends in the Periodic Table

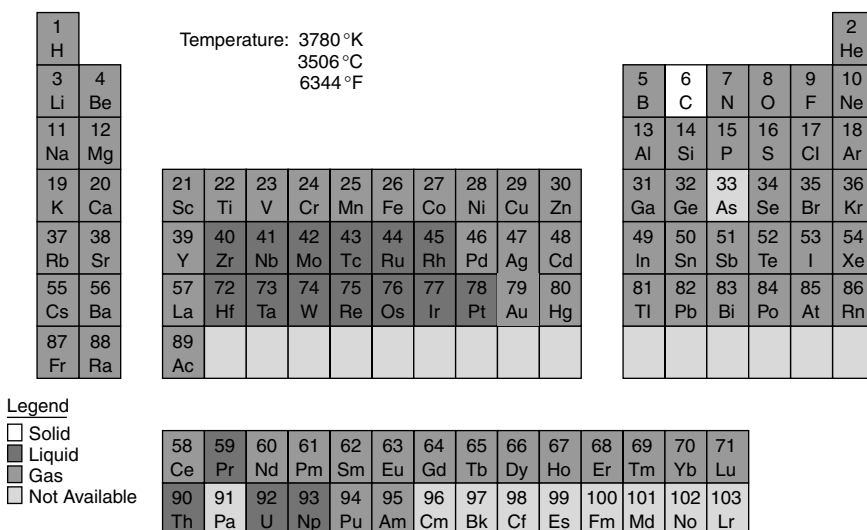
A closer look at the periodic table points out some interesting trends. These trends not only help us predict how one element might perform relative to another, but also give us some insight into the important properties of atoms and ions that determine their performance. For example, examination of the melting points of the elements in Table 1.3 shows that there is a general trend to decrease melting point as we go down



**Figure 1.1** The periodic table of the elements at (a) room temperature, (b) 1000°C, (c) 2000°C, and (d) 3500°C.



(c)



(d)

Figure 1.1 (continued).

a column for the alkali metals and alkali earth elements (columns IA and IIA), but that the column trend for the transition metals appears to be different. There are some trends that are more uniform, however, and are related to the electronic structure of the element.

**1.0.2.1 First Ionization Energy (IE).** The first *ionization energy*, abbreviated *IE*, is sometimes referred to as the “ionization potential.” It is the energy required to remove

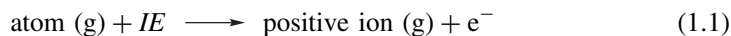
**Table 1.3 Electronic Structure and Melting Points of the Elements**

es	1	<b>H</b>																		2
aw		$1s^1$																		
mp		-259																		
es	3	<b>Li</b>																		10
aw		$He2s^2$																		
mp		180.5																		
es	11	<b>Na</b>																		18
aw		$Ne3s^2$																		
mp		97.8																		
es	19	<b>K</b>																		36
aw		$Ar4s^2$																		
mp		63.2																		
es	37	<b>Rb</b>																		54
aw		$Kr5s^2$																		
mp		39.5																		
es	55	<b>Cs</b>																		86
aw		$Xe6s^2$																		
mp		28.4																		
es	4	<b>Be</b>																		10
aw		9.012																		
mp		1289																		
es	12	<b>Mg</b>																		18
aw		$Ne3s^2$																		
mp		649																		
es	20	<b>Ca</b>																		36
aw		$Ar4s^2$																		
mp		840																		
es	38	<b>Sr</b>																		54
aw		$Kr5s^2$																		
mp		769																		
es	56	<b>Ba</b>																		86
aw		$Xe6s^2$																		
mp		729																		
es	5	<b>B</b>																		10
aw		$Be2p^1$																		
mp		~2103																		
es	13	<b>Al</b>																		18
aw		$Mg3p^1$																		
mp		660.4																		
es	31	<b>Ga</b>																		36
aw		$Ca4p^1$																		
mp		29.8																		
es	33	<b>As</b>																		54
aw		$Ca4p^3$																		
mp		(603)																		
es	35	<b>Br</b>																		54
aw		$Ca4p^5$																		
mp		-7.2																		
es	51	<b>Sb</b>																		86
aw		$Sr5p^3$																		
mp		121.8																		
es	53	<b>I</b>																		86
aw		$Sr5p^5$																		
mp		126.9																		
es	85	<b>At</b>																		86
aw		$Ba6p^5$																		
mp		—																		

Source: Ralls, Courtney, Wulff, Introduction to Materials Science and Engineering, Wiley, 1976.



the most weakly bound (usually outermost) electron from an isolated gaseous atom

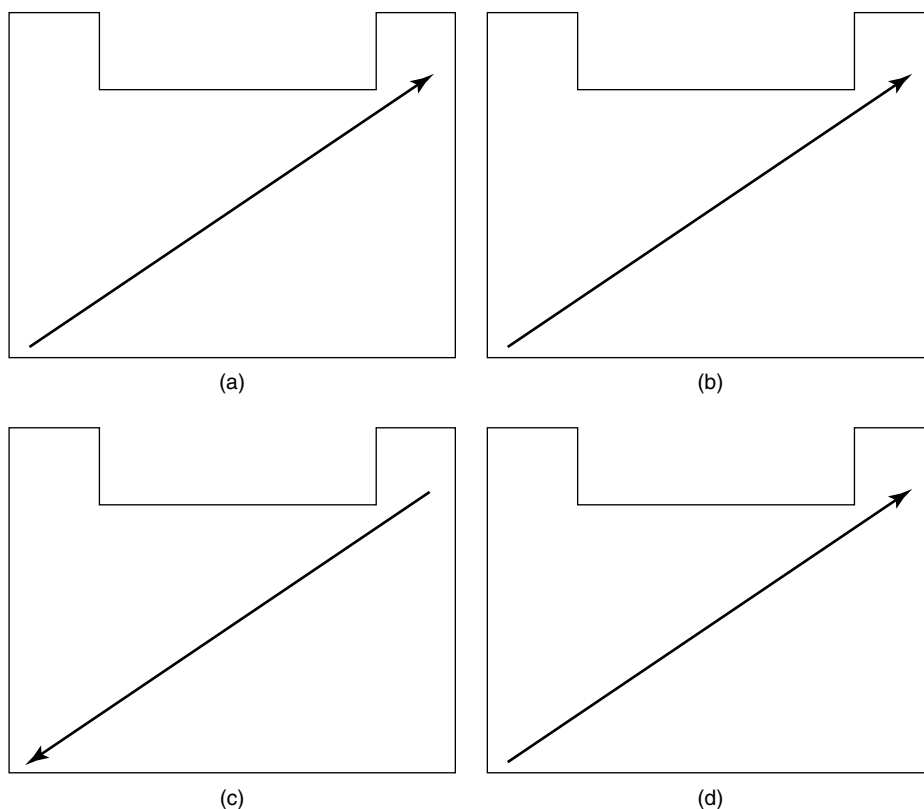


and can be calculated using the energy of the outermost electron as given by the Bohr model and Schrödinger's equation (in eV):

$$IE = \frac{13.6Z^2}{n^2} \quad (1.2)$$

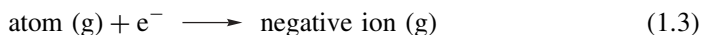
where  $Z$  is the effective nuclear charge and  $n$  is the principal quantum number.

As shown in Figure 1.2a, the general trend in the periodic table is for the ionization energy to increase from bottom to top and from left to right (why?). A quantity related to the  $IE$  is the *work function*. The work function is the energy necessary to remove an electron from the metal surface in thermoelectric or photoelectric emission. We will describe this in more detail in conjunction with electronic properties of materials in Chapter 6.



**Figure 1.2** Some important trends in the periodic table for (a) ionization energy, (b) electron affinity, (c) atomic and ionic radii, and (d) electronegativity. Increasing values are in the direction of the arrow.

**1.0.2.2 Electron Affinity (EA).** *Electron affinity* is the reverse process to the ionization energy; it is the energy change (often expressed in eV) associated with an isolated gaseous atom accepting one electron:



Unlike the ionization energy, however, *EA* can have either a negative or positive value, so it is not included in Eq. (1.3). The *EA* is positive if energy is released upon formation of the negative ion. If energy is required, *EA* is negative. The general trend in the periodic table is again toward an increase in *EA* as we go from the bottom to top, and left to right (Figure 1.2b), though this trend is much less uniform than for the *IE*.

**1.0.2.3 Atomic and Ionic Radii.** In general, positive ions are smaller than neutral atoms, while negative ions are larger (why?). The trend in ionic and atomic radii is opposite to that of *IE* and *EA* (Figure 1.2c). In general, there is an increase in radius from top to bottom, right to left. In this case, the effective nuclear charge increases from left to right, the inner electrons cannot shield as effectively, and the outer electrons are drawn close to the nucleus, reducing the atomic radius. Note that the radii are only approximations because the orbitals, in theory, extend to infinity.

**1.0.2.4 Electronegativity.** The ionization energy and electron affinity are characteristics of isolated atoms; they say very little about how two atoms will interact with each other. It would be nice to have an independent measure of the attraction an atom has for electrons in a bond formed with another atom. *Electronegativity* is such a quantity. It is represented by the lowercase Greek letter “chi,”  $\chi$ . Values can be calculated using one of several methods discussed below. Values of  $\chi$  are always relative to one another for a given method of calculation, and values from one method should not be used with values from another method.

Based upon a scale developed by Mulliken, electronegativity is the average of the ionization energy and the electron affinity:

$$\chi = \frac{IE + EA}{2} \quad (1.4)$$

There are other types of electronegativity scales as well, the most widely utilized of which is the one from the developer of the electronegativity concept, Linus Pauling:

$$\chi = \frac{0.31(n + 1 \pm c)}{r} + 0.5 \quad (1.5)$$

where  $n$  is the number of valence electrons,  $c$  is any formal valence charge on the atom and the sign corresponding to it, and  $r$  is the covalent radius. Typical electronegativity values, along with values of *IE* and *EA*, are listed in Table 1.4. We will use the concept of electronegativity to discuss chemical bonding.

### 1.0.3 Types of Bonds

Electronegativity is a very useful quantity to help categorize bonds, because it provides a measure of the *excess binding energy* between atoms A and B,  $\Delta_{A-B}$  (in kJ/mol):

$$\Delta_{A-B} = 96.5(\chi_A - \chi_B)^2 \quad (1.6)$$

**Table 1.4 Ionization Energies, Electron Affinities, and Electronegativities of the Elements<sup>a</sup>**

IE EA χ	1 H 1310 67.4 2.20																		2 He 2372 -60.2 —
IE EA χ	3 Li 519 77.0 0.98	4 Be 900 -18.4 1.57									5 B 799 31.8 2.04	6 C 1088 119.7 2.55	7 N 1406 4.6 3.04	8 O 1314 141.8 3.44	9 F 1682 349.4 3.98	10 Ne 2080 -54.8 —			
IE EA χ	11 Na 498 117.2 0.93	12 Mg 736 0 1.31									13 Al 577 50.2 1.61	14 Si 787 138.1 1.90	15 P 1063 75.3 2.19	16 S 1000 199.6 2.58	17 Cl 1255 356.1 3.16	18 Ar 2372 -60.2 —			
IE EA χ	19 K 1310 67.4 2.20	20 Ca 590 — 1.00	21 Sc 632 — 1.36	22 Ti 661 — 1.54	23 V 653 — 1.63	24 Cr 653 — 1.66	25 Mn 715 — 1.55	26 Fe 761 — 1.8	27 Co 757 — 1.88	28 Ni 736 — 1.91	29 Cu 745 — 1.90	30 Zn 904 — 1.65	31 Ga 577 — 1.81	32 Ge 782 — 2.01	33 As 966 — 2.18	34 Se 941 — 2.55	35 Br 1142 333.0 2.96	36 Kr 1351 — —	
IE EA χ	37 Rb 402 — 0.82	38 Sr 548 — 0.95	39 Y 636 — 1.22	40 Zr 669 — 1.33	41 Nb 653 — 1.6	42 Mo 695 — 2.16	43 Tc 699 — 1.9	44 Ru 724 — 2.28	45 Rh 745 — 2.2	46 Pd 803 — 2.20	47 Ag 732 — 1.93	48 Cd 866 — 1.69	49 In 556 — 1.78	50 Sn 707 — 1.96	51 Sb 833 — 2.05	52 Te 870 — 2.1	53 I 1008 304.2 2.66	54 Xe 1172 — —	
IE EA χ	55 Cs 377 — 0.79	56 Ba 502 — 0.89	57 La 540 — 1.10	72 Hf 531 — 1.3	73 Ta 577 — 1.5	74 W 770 — 2.36	75 Re 761 — 1.9	76 Os 841 — 2.2	77 Ir 887 — 2.2	78 Pt 866 — 2.28	79 Au 891 — 2.54	80 Hg 1008 — 2.00	81 Tl 590 — 2.04	82 Pb 715 — 2.33	83 Bi 774 — 2.02	84 Po — — 2.0	85 At — — 2.2	86 Rn 1038 — —	

<sup>a</sup>Ionization energy (IE) and Electron affinities (EA) are expressed as kilojoules per mole. 1 eV = 96,490 J/mol.  
Source: R. E. Dickerson, H. B. Gray, and G. P. Haight, *Chemical Principles*, 3rd ed., Pearson Education, Inc., 1979.

The excess binding energy, in turn, is related to a measurable quantity, namely the *bond dissociation energy* between two atoms,  $DE_{ij}$ :

$$\Delta_{A-B} = DE_{AB} - [(DE_{AA})(DE_{BB})]^{1/2} \quad (1.7)$$

The bond dissociation energy is the energy required to separate two bonded atoms (see Appendix 1 for typical values). The greater the electronegativity difference, the greater the excess binding energy. These quantities give us a method of characterizing bond types. More importantly, they relate to important physical properties, such as melting point (see Table 1.5). First, let us review the bond types and characteristics, then describe each in more detail.

**1.0.3.1 Primary Bonds.** *Primary bonds*, also known as “strong bonds,” are created when there is direct interaction of electrons between two or more atoms, either through transfer or as a result of sharing. The more electrons per atom that take place in this process, the higher the bond “order” (e.g., single, double, or triple bond) and the stronger the connection between atoms. There are four general categories of primary bonds: *ionic*, *covalent*, *polar covalent*, and *metallic*. An ionic bond, also called a *heteropolar*

**Table 1.5 Examples of Substances with Different Types of Interatomic Bonding**

Type of Bond	Substance	Bond Energy, kJ/mol	Melting Point, (°C)	Characteristics
Ionic	CaCl	651	646	Low electrical conductivity, transparent, brittle, high melting point
	NaCl	768	801	
	LiF	1008	870	
	CuF <sub>2</sub>	2591	1360	
	Al <sub>2</sub> O <sub>3</sub>	15,192	3500	
Covalent	Ge	315	958	Low electrical conductivity, very hard, very high melting point
	GaAs	~315	1238	
	Si	353	1420	
	SiC	1188	2600	
	Diamond	714	3550	
Metallic	Na	109	97.5	High electrical and thermal conductivity, easily deformable, opaque
	Al	311	660	
	Cu	340	1083	
	Fe	407	1535	
	W	844	3370	
van der Waals	Ne	2.5	-248.7	Weak binding, low melting and boiling points, very compressible
	Ar	7.6	-189.4	
	CH <sub>4</sub>	10	-184	
	Kr	12	-157	
	Cl <sub>2</sub>	31	-103	
Hydrogen bonding	HF	29	-92	Higher melting point than van der Waals bonding, tendency to form groups of many molecules
	H <sub>2</sub> O	50	0	

*bond*, results when electrons are transferred from the more electropositive atom to the more electronegative atom, as in sodium chloride, NaCl. Ionic bonds usually result when the electronegativity difference between two atoms in a diatomic molecule is greater than about 2.0. Because of the large discrepancy in electronegativities, one atom will generally gain an electron, while the other atom in a diatomic molecule will lose an electron. Both atoms tend to be “satisfied” with this arrangement because they oftentimes end up with noble gas electron configurations—that is, full electronic orbitals. The classic example of an ionic bond is NaCl, but CaF<sub>2</sub> and MgO are also examples of molecules in which ionic bonding dominates.

A covalent bond, or *homopolar bond*, arises when electrons are shared between two atoms (e.g., H–H). This means that a binding electron in a covalent diatomic molecule such as H<sub>2</sub> has equal likelihood of being found around either hydrogen atom. Covalent bonds are typically found in homonuclear diatomics such as O<sub>2</sub> and N<sub>2</sub>, though the atoms need not be the same to have similar electronegativities. Electronegativity differences of less than about 0.4 characterize covalent bonds. For two atoms with an electronegativity difference of between 0.4 and 2.0, a polar covalent bond is formed—one that is neither truly ionic nor totally covalent. An example of a polar covalent bond can be found in the molecule hydrogen fluoride, HF. Though there is significant sharing of the electrons, some charge distribution exists that results in a polar or *partial ionic character* to the bond. The percent ionic character of the bond can again be related to the electronegativities of the individual atoms:

$$\% \text{ ionic character} = 100\{1 - \exp[-0.25(\chi_A - \chi_B)^2]\} \quad (1.8)$$

### Example Problem 1.1

What is the percent ionic character of H–F?

*Answer:* According to Table 1.3, the electronegativity of hydrogen is 2.20 and that of fluorine 3.98. Putting these values into Eq. (1.8) gives

$$\% \text{ ionic character of H–F} = 100[1 - \exp\{-0.25(2.20 - 3.98)^2\}] = 55\%$$

The larger the electronegativity difference, the more ionic character the bond has. Of course, if the electronegativity difference is greater than about 2.0, we know that an ionic bond should result.

Finally, a special type of primary bond known as a metallic bond is found in an assembly of homonuclear atoms, such as copper or sodium. Here the bonding electrons become “decentralized” and are shared by the core of positive nuclei. Metallic bonds occur when elements of low electronegativity (usually found in the lower left region of the periodic table) bond with each other to form a class of materials we call *metals*. Metals tend to have common characteristics such as ductility, luster, and high thermal and electrical conductivity. All of these characteristics can to some degree be accounted for by the nature of the metallic bond. The model of a metallic bond, first proposed by Lorentz, consists of an assembly of positively charged ion cores surrounded by free electrons or an “electron gas.” We will see later on, when we

describe intermolecular forces and bonding, that the electron cloud does indeed have “structure” in the quantum mechanical sense, which accounts nicely for the observed electrical properties of these materials.

**1.0.3.2 Secondary Bonds.** *Secondary bonds*, or *weak bonds*, occur due to indirect interaction of electrons in adjacent atoms or molecules. There are three main types of secondary bonding: *hydrogen bonding*, *dipole–dipole interactions*, and *van der Waals forces*. The latter, named after the famous Dutch physicist who first described them, arise due to momentary electric *dipoles* (regions of positive and negative charge) that can occur in all atoms and molecules due to statistical variations in the charge density. These intermolecular forces are common, but very weak, and are found in inert gases where other types of bonding do not exist.

Hydrogen bonding is the attraction between hydrogen in a highly polar molecule and the electronegative atom in another polar molecule. In the water molecule, oxygen draws much of the electron density around it, creating positively charged centers at the two hydrogen atoms. These positively charged hydrogen atoms can interact with the negative center around the oxygen in adjacent water molecules. Although this type of

#### HISTORICAL HIGHLIGHT

Dutch physicist **Johannes Diderik van der Waals** was born on November 23, 1837 in Leiden, the Netherlands. He was the eldest son of eight children. Initially, van der Waals was an elementary school teacher during the years 1856–1861. He continued studying to become headmaster and attended lectures on mathematics, physics, and astronomy at Leiden University. From 1866 onwards he taught physics and mathematics at a secondary school in The Hague. After a revision of the law, knowledge of Latin and Greek was no longer a prerequisite for an academic graduation, and in 1873 J. D. van der Waals graduated on the thesis: “Over de continuïteit van de gas—envloeistofoestand” (“About the continuity of gaseous and liquid states”). In this thesis he published the well-known law:

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT$$

This revision to the ideal gas law accounted for the specific volume of gas molecules and assumed a force between these molecules which are now known as “van der Waals forces.” With this law, the existence of

condensation and the critical temperature of gases could be predicted. In 1877 J. D. van der Waals became the first professor of physics at the University “Illustre” in Amsterdam. In 1880 he formulated his “law of corresponding states,” in 1893 he devised a theory for capillary phenomena, and in 1891 he introduced his theory for the behavior of two mixtures of two materials. It was not possible to experimentally show the de-mixing of two gases into two separate gases under certain circumstances as predicted by this theory until 1941.

From 1875 to 1895 J.D. van der Waals was a member of the Dutch Royal Academy of Science. In 1908, at the age of 71, J. D. van der Waals resigned as a professor. During his life J. D. van der Waals was honored many times. He was one of only 12 foreign members of the “Academie des Sciences” in Paris. In 1910 he received the Nobel prize for Physics for the incredible work he had done on the equations of state for gases and fluids—only the fifth Dutch physicist to receive this honor. J. D. van der Waals died on March 8, 1923 at the age of 85.

Source: [www.vdwaals.nl](http://www.vdwaals.nl)