3

Background You Need to Know

CHAPTER PREVIEW

In this chapter we will summarize three concepts fundamental to all materials science: atomic structure, thermodynamics, and kinetics. You should be familiar with these topics from introductory chemistry, physics, and materials science classes so we give only a brief review here. Books are written on each of these topics. In ceramics, you can often avoid such books, but the details become more critical as you delve deeper into the subject.

The properties of a material are determined, to a large extent, by how the constituent atoms bond together. The nature of this bonding is determined by the electron configuration of the atoms. The electron configuration of an atom also determines the properties of the atom and materials that contain it. For example, the ceramic magnetite (Fe_3O_4) is magnetic due to the presence of unpaired electrons in the 3d level of Fe; you need to know what the 3, the d, and "unpaired" denote. To understand why Mn ions can exist with many different charge states but we invariably find only Al ions with a 3+ charge, you must know the electron configuration of the respective atoms.

Knowledge of both thermodynamics and kinetics is necessary to understand how ceramic materials behave and what happens when they are processed. Thermodynamics tells us what is possible while kinetics tells us how long we have to wait for the inevitable. Thus, thermodynamics tells us if a specific chemical or physical reaction can occur. In ceramics these changes are often brought about because samples are routinely heated and cooled. Ceramics may be processed at temperatures above 1800°C and then cooled to 25°C. Some processes may occur at 1800°C, but may continue or change as we cool the sample. Conversely, some ceramics change their properties at quite low temperatures: $BaTiO_3$ changes from the paraelectric cubic phase to the ferroelectric tetragonal phase at 120°C. Kinetics tells us how rapidly these reactions will proceed. Diamond is thermodynamically unstable at room temperature and atmospheric pressure, but the phase change occurs much too slowly to worry jewelers.

3.1 THE ATOM

The bases for understanding the structure of the atom are quantum theory and wave mechanics, which were developed in the early 1900s. The important conclusions of these studies, particularly as they relate to materials, are as follows:

- Electrons in atoms can move only in certain stable orbits, that is, only certain energy values are possible. We expand on this fact when we describe energy bands, which are used to explain electron conductivity.
- Transition between orbits involves the emission or absorption of energy. These transitions can be the source of color and we use them to analyze chemistry by spectroscopy.
- No two electrons in the same atom can have the same four quantum numbers. This requirement led to the introduction of the spin quantum number. Atoms containing electrons with unpaired spins will have magnetic properties.
- It is impossible to know simultaneously the position and momentum of an electron with certainty. We use this property in tunnel diodes.
- Electrons have wavelike properties. This means that they can be diffracted. Electron diffraction, like X-ray diffraction, gives us the crystal structure.

In the following sections we summarize how these conclusions lead to our present view of the structure of the atom and, in particular, the nature and arrangement of the electrons in the atom. We are not attempting to summarize modern physics, but only the concepts that we use in this text. You need to understand the main aspects of the nature of the chemical bond in ceramic materials: what is an ionic bond, what is a covalent bond, and why do most bonds show a mixture of the two. In spectroscopy and microscopy we will probe the electronic structure to determine the local chemistry of the ceramic.

3.2 ENERGY LEVELS

THE BOHR ATOM

Quantization of angular momentum

$$m_e vr = n\frac{h}{2\pi} \tag{Box 3.1}$$

Radius of possible electron orbits

$$r = \frac{\varepsilon_0 n^2 h^2}{\pi m_e e^2} \tag{Box 3.2}$$

Energy of the electron

$$E = \frac{m_e e^4}{8\varepsilon_0 n^2 h^2} \tag{Box 3.3}$$

The quantization of energy is a key aspect in understanding atomic structure. Bohr's model involves electrons moving only in certain stable orbits. The angular momentum of the orbiting electrons is quantized so that only specific orbits are allowed and only certain energy values are possible.

These orbits are known as stationary states, and the one with the lowest energy is called the ground state.

The quantization of angular momentum is $nh/2\pi$, where n is the principal quantum number. As the principal quantum number increases

1. The radius, r, of the electron orbit increases, that is, the electron is further from the nucleus.
2. The energy, E, of that electron is also increased.

The first five Bohr orbits, that is, $n = 1$ through 5, are also referred to as shells; we define a shell as a group of states that have the same n. A letter is used to denote each shell:

Shell	K	L	M	N	O . . .
n	1	2	3	4	5 . . .

Charles Barkla, an early X-ray spectroscopist, introduced this terminology for electron shells in 1911. We still use it today to designate characteristic X-rays in both X-ray diffraction and in chemical analysis using electron microscopy. Barkla named the two types of characteristic X-ray emissions he observed as the K-series and L-series. He later predicted that an M-series and a J-series might exist. An M-series was subsequently discovered, but no J-series. The K shell is hence the first shell.

The other aspect of Bohr's theory is that while an electron is in a stationary state, the atom does not radiate. Electrons can be excited into higher energy orbits if the atom is stimulated (thermally, electrically, or by the absorption of light). These orbits are the excited states and are more distant from the nucleus. The residence time of an electron in the excited state may be very short (~1 ns) before it spontaneously descends to a lower energy state and eventually the ground state. During each transition the excess energy is emitted in the form of a photon. Any transition between orbits involves either the emission or absorption of energy. Understanding this concept is necessary in, for example, appreciating how a laser works. If the energy emitted is in the visible part of the electromagnetic spectrum (Table 3.1), then we will be able to observe the emission. The emission from the ruby laser (ruby is a ceramic) is at 694 nm (in the red). A frequency doubled Nd-doped yttrium aluminum garnet (YAG) laser (YAG is another ceramic) operates in the green part of the spectrum at 530 nm.

Bohr's model was quite popular at the time because an electron circling the nucleus is conceptually similar to the earth circling the sun. The idea that orbiting electrons did not radiate was less easy to accept, Bohr simply insisted they did not and that was that! Most importantly, the model explained a number of physical phenomena. Bohr's assumption that electrons are particles with well-defined orbits was not consistent with the concept of "simultaneous interdeterminacy" of position and momentum as propounded in the Heisenberg uncertainty principle.

What you should remember from this discussion is the origin of KLMNO and the terminology. We will use this again in Chapter 10.

Electron energy levels and the Bohr model are important for understanding the following:

- Atomic radii—as we fill shells going down a particular period the atoms get bigger (r increases).
- Ionization energy—as we fill shells going down a particular period it becomes progressively easier to remove the outer electron(s) (E increases with respect to the ground state).
- Covalent bond formation—ionization energies must be high (E large).

TABLE 3.1 The Visible Part of the Electromagnetic Spectrum

Energy, E (J)	*Wavelength, λ (nm)*	*Color*
2.84×10^{-19}	700	Red
3.20×10^{-19}	620	Orange
3.42×10^{-19}	580	Yellow
3.75×10^{-19}	530	Green
4.23×10^{-19}	470	Blue
4.73×10^{-19}	420	Violet

- Magnetic ceramics—we need to have an M shell.
- X-ray spectroscopy—we use the Barkla notation, the energy of the characteristic X-rays depends on the electron energy levels involved.

THE DE BROGLIE HYPOTHESIS

All matter possesses wave properties. Every moving particle can be associated with a wavelength, λ, given by

$$\lambda = \frac{h}{mv} = \frac{h}{p}$$

3.3 ELECTRON WAVES

Demonstrating electron diffraction (a property associated with waves) was proof of their wave nature. In 1927 C.J. Davisson and L. Germer in the United States and, independently, G.P. Thomson and A. Reid in the United Kingdom showed that electrons could be diffracted in much the same way as X-rays. We care because we cannot explain the properties of electrons and X-rays without this understanding.

The wavelike nature of electrons enables electron diffraction studies of materials. Most electron diffraction patterns are obtained in a transmission electron microscope, which allows us to obtain structural information from very small regions. This is of particular importance in many new ceramics where we are often dealing with thin interface layers (such as at grain boundaries) and very small grains (nanopowders).

SCHRÖDINGER WAVE EQUATION

The time-independent form is

$$\nabla^2\Psi + 8\pi^2 m/h^2\,(E - V)\Psi = 0 \qquad \text{Box 3.4}$$

∇^2 is the operator

$$\partial^2/\partial x^2 + \partial^2/\partial y^2 + \partial^2/\partial z^2 \qquad \text{Box 3.5}$$

In polar coordinates Ψ has the form

$$\Psi(r,\theta,\phi) = R(r)\Theta(\theta)\Phi(\phi) \qquad \text{Box 3.6}$$

$R(r)$, $\Theta(\theta)$, $\Phi(\phi)$ are each only functions of r, θ, and ϕ.

One of the most important consequences of the dual nature of electrons is Heisenberg's uncertainty principle, which states that it is impossible to know simultaneously both the momentum and position of a particle with certainty. If we are describing the motion of an electron of known energy or momentum, we can speak only in terms of the probability of finding that electron at a particular position. This leads to the electron-density or electron-cloud representation of electron orbitals.

The Schrödinger equation, as central to quantum mechanics as Newton's equations are to classical mechanics, relates the energy of an electron to its wave properties. The equation describes the likelihood that a single electron will be found in a specific region of space. The wave function, Ψ, depends on E and V, the total energy and the potential energy of the electron, respectively.

The importance of the wave function has been expressed by Atkins and de Paula (2002): "A wave function contains all there is to know about the outcome of experiments that can be done on a system." Thus, the Schrödinger wave equation includes information about the chemical behavior of all atoms and compounds and the answer to whether any proposed chemical reaction will take place or not.

Mathematically, Ψ describes the motion of an electron in an orbital. The modulus of the wave function squared, $|\Psi(r)|^2$, is a direct measure of the probability of finding the electron at a particular location. The Schrödinger wave equation can be solved exactly for hydrogen. To apply it you must first transform it into polar coordinates (r,θ,ϕ) and then solve using the method of separation of variables (described in, e.g., Kreyszig, 1999).

The solution of these equations leads to three quantum numbers: n, l, and m_l.

The Schrödinger wave equation can be set for atoms with more than one electron, but it cannot be solved exactly in these cases. The second and subsequent electrons introduce the complicating feature of electron–electron repulsion. Nevertheless, the basic characteristics of the orbitals do not change and the results obtained for hydrogen are applied to many-electron atoms.

Methods are now becoming available that allow us to calculate the structure of some "bulk" materials. Generally, this is still done only rarely by starting with the Schrödinger equation. The calculations are just too difficult or too time-consuming. Actually, it is worse than it looks because we also have to deal with charge.

3.4 QUANTUM NUMBERS

Four quantum numbers are necessary to specify the state of any electron:

- n principal quantum number
- l orbital shape, or orbital angular momentum, quantum number
- m_l orbital orientation, or orbital magnetic, quantum number
- m_s spin, or spin magnetic, quantum number

A shell is a group of states that has the same n and corresponds to Bohr's n. A subshell is a smaller group of

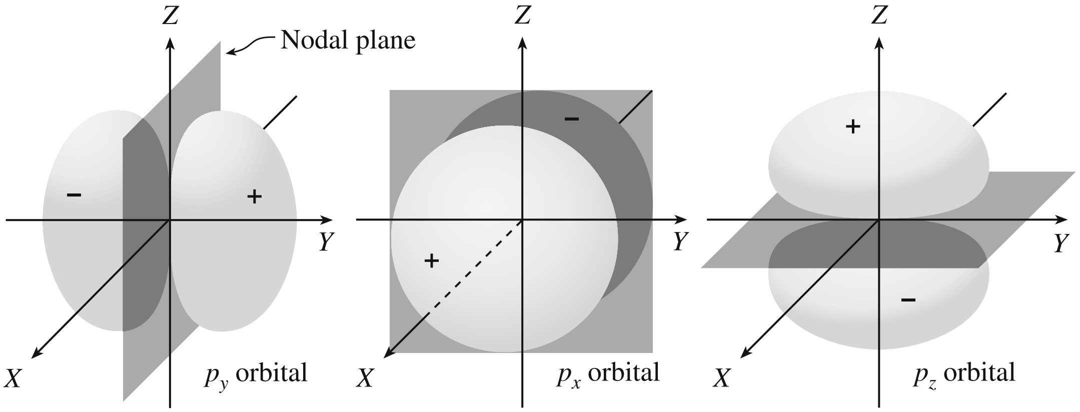


FIGURE 3.1 The $2p_x$, $2p_y$, and $2p_z$ orbitals. The nodal plane represents the area in which the probability of finding the electron is zero.

states having both the same value of n and l. An orbital is specified by n, l, and m_l, and can contain a maximum of two electrons with opposite spins.

QUANTUM NUMBERS

Li, Na, K and Cs have many common features because they all have a single electron in an outer s shell: 2s, 3s, 4s and 5s.

The main difference between MnO, FeO, CoO and NiO is due to the change in the d ($l = 3$) electrons on the transition-metal ion.

- n has integer values, 1, 2, 3, . . . and determines the size
- l has integer values, 0, 1, 2, . . . , $n - 1$ (for any value of n) and determines shape
- m_l has integer values between $-l$ and $+l$ including 0 (for any value of l) and determines orientation
- m_s can have values of ±1/2 and specifies the direction of spin

The introduction of an external magnetic field provides the most convenient reference axis for m_l. The values of m_l are determined by the l quantum number. For each value of l there are $(2l + 1)$ values of m_l. For historical reasons the 0, 1, 2, and 3 values of the l quantum number are designated by the letters s, p, d, and f, respectively. (This choice is a relic of early spectroscopic studies when certain spectral series were designated "sharp," "principal," "diffuse," or "fundamental.")

The s orbitals are spherical and the three 2p orbitals have directional properties as shown in Figure 3.1. For example, the $2p_z$ orbital has regions of greatest concentration or probability along the z-axis and the probability of finding a $2p_z$ electron in the XY plane is zero. The shapes of the five 3d orbitals are more complicated (because there are more of them) (Figure 3.2) and we usually do not talk about f.

Are these numbers important for ceramics? The answer, of course, is yes.

- The color of a ceramic, such as ruby, derives directly from transitions between energy levels. The energy levels are the result of which orbitals are occupied and their relative energies.
- We use transitions for chemical analysis of ceramics—certain transitions are allowed (quantum mechanical selection rules).

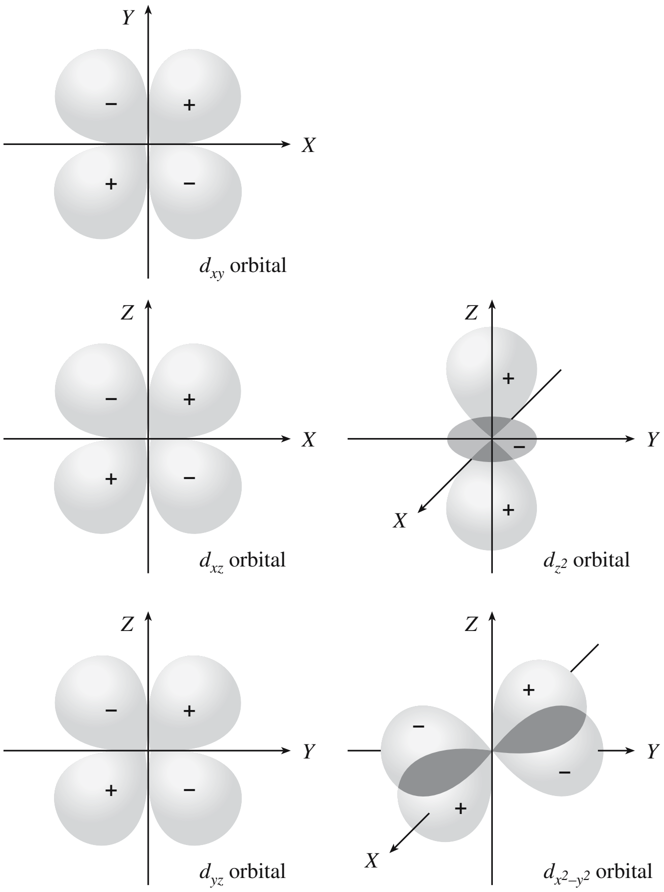


FIGURE 3.2 The 3d atomic orbitals. The 4d, 5d, and 6d orbitals are essentially identical to the 3d orbitals except they are bigger. The sign of the wavefunction changes from one lobe to the next in a given orbital and is important when we consider the formation of molecular orbitals.

- Magnetism relates directly to the spin of the electrons. If we have more spins up than down then we have magnetization.
- Atomic arrangements in covalently bonded ceramics can be understood by considering hybridization of atomic orbitals. It is the sp^3 hybridization of atomic orbitals in carbon that allows the tetrahedral arrangement of atoms in diamond. The s and the p in sp^3 refer to the atomic orbitals.

SUMMARY OF QUANTUM NUMBERS (QN)

Name	Symbol	Value
Principal QN	n	1, 2, 3, . . .
Orbital-shape QN	l	0, 1, 2, . . . $(n - 1)$
Orbital-orientation QN	m_l	Integral values from $-l$ to $+l$ including zero
Spin QN	m_s	± 1/2

IONIZATION

For ceramics, the important feature in all these models is which electrons we can move to make the ion and how easy it is going to be.

3.5 ASSIGNING QUANTUM NUMBERS

A shorthand notation that expresses the quantum numbers for each electron represents the electron configuration. The importance of this step is that it allows us, for example, to calculate the magnetic moment of magnetite and determine what happens if we replace the Fe^{2+} ions with Ni^{2+}.

The key to the building process for many-electron atoms is the Pauli exclusion principle: No two electrons in an atom can have the same set of four quantum numbers.

For example, the two electrons in the ground state of atomic He ($Z = 2$) must possess the following quantum numbers:

$$n = 1, \quad l = 0, \quad m_l = 0, \quad m_S = +1/2$$

$$n = 1, \quad l = 0, \quad m_l = 0, \quad m_S = -1/2$$

The two electrons in the He atom are placed in the 1s orbital with opposite spins, consistent with the Pauli's principle. The electron configuration of He is abbreviated as $1s^2$. The next row in the periodic table is similar; we are just filling the next shell ($n = 2$ and so on).

Lithium ($Z = 3$) has the electron configuration $1s^2 2s^1$. We fill the 2s orbital before the 2p because of shielding effects that lower the energy of the 2s orbital with respect to the 2p orbital. Both the 2s and 2p orbitals in the Li atom are shielded from the +3 nuclear charge by the 1s electrons. However, the 2s orbital has a larger probability density close to the nucleus and is not shielded as strongly as the 2p orbital.

For a C atom ($Z = 6$) there are a number of possible configurations for the second electron in the set of three 2p orbitals. We use Hund's rule to determine where the electron will go: For any set of orbitals of equal energy the electronic configuration with the maximum number of parallel spins results in the lowest electron–electron repulsion. Thus the ground state for atomic carbon is $1s^2 2s^2 2p_x^1 2p_y^1$.

We can build the ground-state electron configuration of atoms of all elements by filling the orbitals in order of increasing energy, making sure that the Pauli exclusion principle and Hund's rule are obeyed. (Hund's rules are inviolate in predicting the correct ground state of an atom. There are occasional exceptions when the rules are used to discuss excited states that we encounter, e.g., in spectroscopy.) The total number of electrons that the orbitals can hold is given in Table 3.2.

There is no single ordering of orbital energies, but the following order is a useful guide:

$$\begin{aligned} &1s < 2s < 2p < 3s < 3p < 4s < 3d < 4p < 5s \\ &\quad < 4d < 5p < 6s < 4f \approx 5d < 6p < 7s < 5f \approx 6d \end{aligned}$$

Figure 3.3 shows a mnemonic diagram that can be used for determining the filling order. You simply follow the arrows and numbers from one orbital to the next. Orbital energies depend on the atomic number and on the charge on the atom (ion).

In the sequence of orbital energies shown above the 4s orbitals have a lower energy than the 3d orbitals and so they will be filled first in keeping with the minimum energy principle. For example, the electron configuration of the outer 10 electrons of calcium (atomic number $Z = 20$) is $3s^2\ 3p^6\ 3d^0\ 4s^2$. In the filling of the electron orbitals for elements 21 to 29, there are two irregularities, one at 24 (chromium) and one at 29 (copper). Each of these elements contains one 4s electron instead of two. The reason

TABLE 3.2 The s, p, d, and f Orbital Sets

Type of orbital	*Orbital quantum numbers*	*Total orbitals in set*	*Total number of electrons that can be accommodated*
s	$l = 0$, $m_l = 0$	1	2
p	$l = 1$, $m_l = 1, 0, -1$	3	6
d	$l = 2$, $m_l = 2, 1, 0, -1, -2$	5	10
f	$l = 3$, $m_l = 3, 2, 1, 0, -1, -2, -3$	7	14

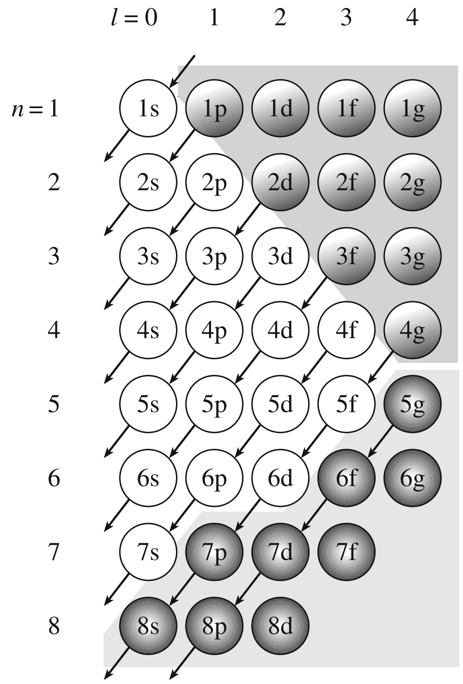


FIGURE 3.3 Mnemonic for predicting the filling order of the atomic orbitals. The upper gray block shows imaginary orbitals; orbitals in the lower gray block are not filled in the known elements.

TABLE 3.3 Arrangement of Electrons for the First Row Transition Elements (Z = 21–29)

Z	Element	Electron configuration
21	Sc	$1s^22s^22p^63s^23p^63d^14s^2$
22	Ti	$1s^22s^22p^63s^23p^63d^24s^2$
23	V	$1s^22s^22p^63s^23p^63d^34s^2$
24	**Cr**	**$1s^22s^22p^63s^23p^63d^54s^1$**
25	Mn	$1s^22s^22p^63s^23p^63d^54s^2$
26	Fe	$1s^22s^22p^63s^23p^63d^64s^2$
27	Co	$1s^22s^22p^63s^23p^63d^74s^2$
28	Ni	$1s^22s^22p^63s^23p^63d^84s^2$
29	**Cu**	**$1s^22s^22p^63s^23p^63d^{10}4s^1$**

for this apparent anomaly is that exactly filled and half-filled 3d orbitals are particularly stable (they have a lower energy) compared to the neighboring occupancies of four and nine, respectively. The electron configurations of the first row transition elements are given in Table 3.3. The electron configurations of the first row transition metals will be of importance when we discuss electrical conduction and magnetic behavior of ceramics that contain these elements.

The electron configurations of all the elements in the periodic table are shown in Table 3.4 where we use the shorthand representation for the electron configurations (start with the nearest filled noble gas).

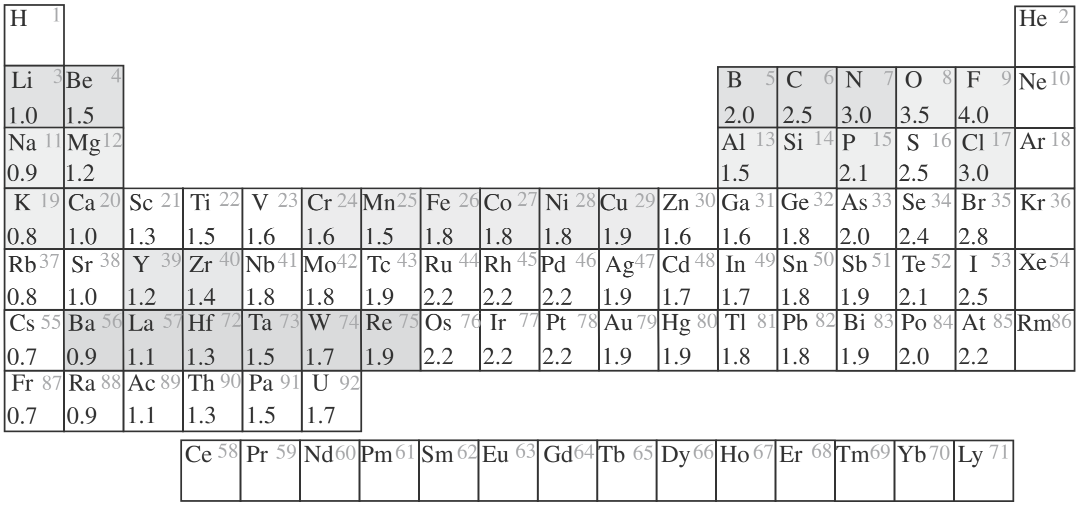
Examination of the electron configuration of the elements clearly shows the basis for their periodic behavior. Elements with atomic numbers 2, 10, and 18 are the noble gases. These elements are stable and chemically inert. Inertness is equated with completely filled shells of electrons. Elements with similar outer shell configurations possess many similar properties. Figure 3.4 shows the Periodic Table of Elements. It is clearly a good idea to know where the atoms lie in the periodic table since this is going to determine whether they lose or gain electrons more easily and, thus, how the ion is charged as we will now discuss.

TABLE 3.4 Electron Configurations of the Elements

Z	Element	Electron configuration	Z	Element	Electron configuration
1	H	1s	53	I	$[Kr]4d^{10}5s^25p^5$
2	He	$1s^2$	54	Xe	$[Kr]4d^{10}5s^25p^6$
3	Li	[He]2s	55	Cs	[Xe]6s
4	Be	$[He]2s^2$	56	Ba	$[Xe]6s^2$
5	B	$[He]2s^22p$	57	La	$[Xe]5d6s^2$
6	C	$[He]2s^22p^2$	58	Ce	$[Xe]4f5d6s^2$
7	N	$[He]2s^22p^3$	59	Pr	$[Xe]4f^36s^2$
8	O	$[He]2s^22p^4$	60	Nd	$[Xe]4f^46s^2$
9	F	$[He]2s^22p^5$	61	Pm	$[Xe]4f^56s^2$
10	Ne	$[He]2s^22p^6$	62	Sm	$[Xe]4f^66s^2$
11	Na	[Ne]3s	63	Eu	$[Xe]4f^76s^2$
12	Mg	$[Ne]3s^2$	64	Gd	$[Xe]4f^75d6s^2$
13	Al	$[Ne]3s^23p$	65	Tb	$[Xe]4f^96s^2$
14	Si	$[Ne]3s^23p^2$	66	Dy	$[Xe]4f^{10}6s^2$
15	P	$[Ne]3s^23p^3$	67	Ho	$[Xe]4f^{11}6s^2$
16	S	$[Ne]3s^23p^4$	68	Er	$[Xe]4f^{12}6s^2$
17	Cl	$[Ne]3s^23p^5$	69	Tm	$[Xe]4f^{13}6s^2$
18	Ar	$[Ne]3s^23p^6$	70	Yb	$[Xe]4f^{14}6s^2$
19	K	[Ar]4s	71	Lu	$[Xe]4f^{14}5d6s^2$
20	Ca	$[Ar]4s^2$	72	Hf	$[Xe]4f^{14}5d^26s^2$

TABLE 3.4 *Continued*

Z	*Element*	*Electron configuration*	*Z*	*Element*	*Electron configuration*
21	Sc	[Ar]$3d4s^2$	73	Ta	[Xe]$4f^{14}5d^3 6s^2$
22	Ti	[Ar]$3d^2 4s^2$	74	W	[Xe]$4f^{14}5d^4 6s^2$
23	V	[Ar]$3d^3 4s^2$	75	Re	[Xe]$4f^{14}5d^5 6s^2$
24	Cr	[Ar]$3d^5 4s$	76	Os	[Xe]$4f^{14}5d^6 6s^2$
25	Mn	[Ar]$3d^5 4s^2$	77	Ir	[Xe]$4f^{14}5d^7 6s^2$
26	Fe	[Ar]$3d^6 4s^2$	78	Pt	[Xe]$4f^{14}5d^9 6s$
27	Co	[Ar]$3d^7 4s^2$	79	Au	[Xe]$4f^{14}5d^{10}6s$
28	Ni	[Ar]$3d^8 4s^2$	80	Hg	[Xe]$4f^{14}5d^{10}6s^2$
29	Cu	[Ar]$3d^{10}4s$	81	Tl	[Xe]$4f^{14}5d^{10}6s^2 6p$
30	Zn	[Ar]$3d^{10}4s^2$	82	Pb	[Xe]$4f^{14}5d^{10}6s^2 6p^2$
31	Ga	[Ar]$3d^{10}4s^2 4p$	83	Bi	[Xe]$4f^{14}5d^{10}6s^2 6p^3$
32	Ge	[Ar]$3d^{10}4s^2 4p^2$	84	Po	[Xe]$4f^{14}5d^{10}6s^2 6p^4$
33	As	[Ar]$3d^{10}4s^2 4p^3$	85	At	[Xe]$4f^{14}5d^{10}6s^2 6p^5$
34	Se	[Ar]$3d^{10}4s^2 4p^4$	86	Rn	[Xe]$4f^{14}5d^{10}6s^2 6p^6$
35	Br	[Ar]$3d^{10}4s^2 4p^5$	87	Fr	[Rn]$7s$
36	Kr	[Ar]$3d^{10}4s^2 4p^6$	88	Ra	[Rn]$7s^2$
37	Rb	[Kr]$5s$	89	Ac	[Rn]$6d7s^2$
38	Sr	[Kr]$5s^2$	90	Th	[Rn]$6d^2 7s^2$
39	Y	[Kr]$4d5s^2$	91	Pa	[Rn]$5f^2 6d7s^2$
40	Zr	[Kr]$4d^2 5s^2$	92	U	[Rn]$5f^3 6d7s^2$
41	Nb	[Kr]$4d^4 5s$	93	Np	[Rn]$5f^4 6d7s^2$
42	Mo	[Kr]$4d^5 5s$	94	Pu	[Rn]$5f^6 7s^2$
43	Tc	[Kr]$4d^5 5s^2$	95	Am	[Rn]$5f^7 7s^2$
44	Ru	[Kr]$4d^7 5s$	96	Cm	[Rn]$5f^7 6d7s^2$
45	Rh	[Kr]$4d^8 5s$	97	Bk	[Rn]$5f^9 7s^2$
46	Pd	[Kr]$4d^{10}$	98	Cf	[Rn]$5f^{10}7s^2$
47	Ag	[Kr]$4d^{10}5s$	99	Es	[Rn]$5f^{11}7s^2$
48	Cd	[Kr]$4d^{10}5s^2$	100	Fm	[Rn]$5f^{12}7s^2$
49	In	[Kr]$4d^{10}5s^2 5p$	101	Md	[Rn]$5f^{13}7s^2$
50	Sn	[Kr]$4d^{10}5s^2 5p^2$	102	No	[Rn]$5f^{14}7s^2$
51	Sb	[Kr]$4d^{10}5s^2 5p^3$	103	Lr	[Rn]$5f^{14}6d7s^2$
52	Te	[Kr]$4d^{10}5s^2 5p^4$			



H 1																	He 2
Li 3 1.0	Be 4 1.5											B 5 2.0	C 6 2.5	N 7 3.0	O 8 3.5	F 9 4.0	Ne 10
Na 11 0.9	Mg 12 1.2											Al 13 1.5	Si 14	P 15 2.1	S 16 2.5	Cl 17 3.0	Ar 18
K 19 0.8	Ca 20 1.0	Sc 21 1.3	Ti 22 1.5	V 23 1.6	Cr 24 1.6	Mn 25 1.5	Fe 26 1.8	Co 27 1.8	Ni 28 1.8	Cu 29 1.9	Zn 30 1.6	Ga 31 1.6	Ge 32 1.8	As 33 2.0	Se 34 2.4	Br 35 2.8	Kr 36
Rb 37 0.8	Sr 38 1.0	Y 39 1.2	Zr 40 1.4	Nb 41 1.8	Mo 42 1.8	Tc 43 1.9	Ru 44 2.2	Rh 45 2.2	Pd 46 2.2	Ag 47 1.9	Cd 48 1.7	In 49 1.7	Sn 50 1.8	Sb 51 1.9	Te 52 2.1	I 53 2.5	Xe 54
Cs 55 0.7	Ba 56 0.9	La 57 1.1	Hf 72 1.3	Ta 73 1.5	W 74 1.7	Re 75 1.9	Os 76 2.2	Ir 77 2.2	Pt 78 2.2	Au 79 1.9	Hg 80 1.9	Tl 81 1.8	Pb 82 1.8	Bi 83 1.9	Po 84 2.0	At 85 2.2	Rm 86
Fr 87 0.7	Ra 88 0.9	Ac 89 1.1	Th 90 1.3	Pa 91 1.5	U 92 1.7												
			Ce 58	Pr 59	Nd 60	Pm 61	Sm 62	Eu 63	Gd 64	Tb 65	Dy 66	Ho 67	Er 68	Tm 69	Yb 70	Ly 71	

FIGURE 3.4 The Periodic Table of Elements as viewed by a ceramist showing atomic number and electronegativity. Different shadings show the groupings of some of the most important components of traditional and advanced ceramics. The lighter shading highlights elements used in traditional ceramics. The darker shading shows some of the elements found in advanced ceramics.

3.6 IONS

In ceramics we are usually dealing with materials that have a significant fraction of ionic character in their bonding. The requirements for ionic bonding are simple:

- One element must be able to lose 1, 2, or 3 electrons.
- The other element must be able to accept 1, 2, or 3 electrons.

In both cases the "3" is rare and it must not involve too much energy exchange. The ionization energy is the energy required to remove an electron from the gaseous atom. The first ionization energy (IE_1) is the energy required to remove one electron from the neutral gaseous atom to produce a gaseous ion with charge +1.

IONIZATION ENERGY

$$\text{Atom (g)} + IE_1 \rightarrow \text{Ion}^+ \text{(g)} + e^-$$

This reaction is always endothermic ($IE_1 > 0$). The sign is a convention of thermodynamics; some fields use the opposite convention.

The noble gases have a complete shell of outer electrons and have very high ionization energies, whereas the elements in Group I, for example, Na and K, have an outer ns^1 orbital and have much lower ionization energies. Second ionization energies, the energy required to remove an electron from a gaseous ion with charge +1, are significantly higher than first ionization energies because when an electron is lost the effective nuclear charge, Z_{eff}, increases. As a result, the effective radius of an atom or ion de-creases and the net attraction between the electrons and the nucleus increases (Table 3.5).

The electron affinity (EA) of an atom is the energy change

TABLE 3.5 Ionization Energies of the Elements (MJ/mol)

Z	*Element*	*I*	*II*	*III*	*IV*	*V*
1	H	1.3120				
2	He	2.3723	5.2504			
3	Li	0.5203	7.2981	11.8149		
4	Be	0.8995	1.7571	14.8487	21.0065	
5	B	0.8006	2.4270	3.6598	25.0257	32.8266
6	C	1.0864	2.3526	4.6205	6.2226	37.8304
7	N	1.4023	2.8561	4.5781	7.4751	9.4449
8	O	1.3140	3.3882	5.3004	7.4693	10.9895
9	F	1.6810	3.3742	6.0504	8.4077	11.0227
10	Ne	2.0807	3.9523	6.122	9.370	12.178
11	Na	0.4958	4.5624	6.912	9.544	13.353
12	Mg	0.7377	1.4507	7.7328	10.540	13.628
13	Al	0.5776	1.8167	2.7448	11.578	14.831
14	Si	0.7865	1.5771	3.2316	4.3555	16.091
15	P	1.0118	1.9032	2.912	4.957	6.2739
16	S	0.9996	2.251	3.361	4.564	7.013
17	Cl	1.2511	2.297	3.822	5.158	6.54
18	Ar	1.5205	2.6658	3.931	5.771	7.238
19	K	0.4189	3.0514	4.411	5.877	7.976
20	Ca	0.5898	1.1454	4.9120	6.474	8.144
21	Sc	0.631	1.235	2.389	7.089	8.844
22	Ti	0.658	1.310	2.6525	4.1746	9.573
23	V	0.650	1.414	2.8280	4.5066	6.294
24	Cr	0.6528	1.496	2.987	4.74	6.69
25	Mn	0.7174	1.5091	2.2484	4.94	6.99
26	Fe	0.7594	1.561	2.9574	5.29	7.24
27	Co	0.758	1.646	3.232	4.95	7.67
28	Ni	0.7367	1.7530	3.393	5.30	7.28
29	Cu	0.7455	1.9579	3.554	5.33	7.71
30	Zn	0.9064	1.7333	3.8327	5.73	7.97
31	Ga	0.5788	1.979	2.963	6.2	
32	Ge	0.7622	1.5374	3.302	4.410	9.02
33	As	0.947	1.7978	2.7355	4.837	6.043
34	Se	0.9409	2.045	2.9737	4.1435	6.59
35	Br	1.1399	2.10	3.5	4.56	5.76
36	Kr	1.3507	2.3503	3.565	5.07	6.24
37	Rb	0.4030	2.632	3.9	5.08	6.85
38	Sr	0.5495	1.0643	4.21	5.5	6.91

TABLE 3.5 *Continued*

Z	*Element*	*I*	*II*	*III*	*IV*	*V*
39	Y	0.616	1.181	1.980	5.96	7.43
40	Zn	0.660	1.267	2.218	3.313	7.86
41	Nb	0.664	1.382	2.416	3.69	4.877
42	Mo	0.6850	1.558	2.621	4.477	5.91
43	Tc	0.702	1.472	2.850		
44	Ru	0.711	1.617	2.747		
45	Rh	0.720	1.744	2.997		
46	Pd	0.805	1.875	3.177		
47	Ag	0.7310	2.074	3.361		
48	Cd	0.8677	1.6314	3.616		
49	In	0.5583	1.8206	2.705	5.2	
50	Sn	0.7086	1.4118	2.9431	3.9303	6.974
51	Sb	0.8337	1.595	2.44	4.26	5.4
52	Te	0.8693	1.79	2.698	3.610	5.669
53	I	1.0084	1.8459	3.2		
54	Xe	1.1704	2.046	3.10		
55	Cs	0.3757	2.23			
56	Ba	0.5029	0.96526			
57	La	0.5381	1.067	1.8501		
58	Ce	0.528	1.047	1.949	3.543	
59	Pr	0.523	1.018	2.086	3.758	5.543
60	Nd	0.530	1.034			
61	Pm	0.536	1.052			
62	Sm	0.543	1.068			
63	Eu	0.547	1.085			
64	Gd	0.591	1.17			
65	Tb	0.564	1.112			
66	Dy	0.572	1.126			
67	Ho	0.581	1.139			
68	Er	0.589	1.151			
69	Tm	0.596	1.163	2.288		
70	Yb	0.6034	1.174	2.43		
71	Lu	0.5235	1.34			
72	Hf	0.68	1.44	2.25	3.21	
73	Ta	0.761				
74	W	0.770				
75	Re	0.760				
76	Os	0.84				
77	Ir	0.88				
78	Pt	0.87	1.7911			
79	Au	0.8901	1.98			
80	Hg	1.0070	1.8097	3.30		
81	Tl	0.5893	1.9710	2.878		
82	Pb	0.7155	1.4504	2.0815	4.083	6.64
83	Bi	0.7033	1.610	2.466	4.37	5.40
84	Po	0.812				
85	At					
86	Rn	1.0370				
87	Fr					
88	Ra	0.5094	0.97906			
89	Ac	0.67	1.17			
90	Th		1.11	1.93	2.78	
91	Pa					
92	U					
93	Np					
94	Pu	0.56				
95	Am	0.58				

TABLE 3.6 Electron Affinities of the Elements (kJ/mol)

Element	*Theory*	*Experimental*	*Element*	*Theory*	*Experimental*
1. H	72.766	72.9	27. Co	90.3	
2. He		<0	28. Ni	123.1	
3. Li	59.8	58	29. Cu	173.8	
4. Be	−18[a]	<0	30. Zn	−87[c]	
5. B	29		31. Ga	17[c]–48[d]	
6. C	113	121	32. Ge	116[c]–132[d]	
7. $\mathrm{N} \rightarrow \mathrm{N}^-$	−58[b]	121	33. As	58[c]–71[d]	
$\mathrm{N}^- \rightarrow \mathrm{N}^{2-}$	−800[b]		34. $\mathrm{Se} \rightarrow \mathrm{Se}^-$	204[d]–212[c]	−420
$\mathrm{N}^{2-} \rightarrow \mathrm{N}^{3-}$	−1290[b]		$\mathrm{Se}^- \rightarrow \mathrm{Se}^{2-}$		
8. $\mathrm{O} \rightarrow \mathrm{O}^-$	120	142	35. Br		324.5
$\mathrm{O}^- \rightarrow \mathrm{O}^{2-}$		−780[b]	36. Kr		<0
9. F	312–325	328–333	37. Rb		19–39
10. Ne	<0	<0	42. Mo		96
11. Na	52		48. Cd	−58[c]	
12. Mg	−54[c]	<0	49. In	19[c]–69[d]	
13. Al	48		50. Sn	142[d]	
14. Si	134		51. Sb	59[d]	
15. P	75		52. Te	220[c]	
16. $\mathrm{S} \rightarrow \mathrm{S}^-$	205	200	53. I		296
$\mathrm{S}^- \rightarrow \mathrm{S}^{2-}$		−590	54. Xe		<0
17. Cl	343	348	55. Cs		19–39
18. Ar		<0	74. W		48
19. K	45	34–72	75. Re		14
20. Ca		<0	81. Tl	117[d]	
22. Ti	37.7		82. Pb	173[d]	
23. V	90.4		83. Bi	−33[d]	
24. Cr	94.6		84. Po	190[d]	
26. Fe	56.2				

Source: Berry, R.S. (1969) *Chem. Rev.* **69**, 533, except [a] Edlen, B. (1960) *J. Chem. Phys.* **33**, 98; [b] Baughan, E.C. (1961) *Trans. Faraday Soc.* **57**, 1863; [c] Ginsberg, A.P. and Miller, J.M. (1958) *J. Inorg. Nucl. Chem.* **7**, 351; [d] Politzer, P. (1968) *Trans. Faraday Soc.* **64**, 2241.

accompanying the addition of one electron to a neutral gaseous atom to produce a negative ion. Values of EA are shown in Table 3.6. A positive value indicates that the reaction

$$\text{Atom (g)} + e^- \rightarrow \text{Ion}^- \text{ (g)} + \text{EA}$$

is exothermic.

ELECTRON AFFINITY

$$\text{Atom (g)} + e^- \rightarrow \text{Ion}^- \text{ (g)} + \text{EA}$$

Note: The sign convention used for EA is in contradiction to that usually found in thermodynamics, an unfortunate historical artifact.

The values of EA also show a periodic behavior that can be explained by examining the electron configurations of the elements. The electron affinity is high for elements in Group VII, for example, F and Cl. The addition of one electron to these atoms forms negative ions with a noble gas electron configuration—a stable arrangement. Atoms that already have full (e.g., He, Ne) or half-full orbitals (e.g., Be, N) often have negative electron affinities. Full and half-full orbitals are more stable.

As we will see in Chapter 4, ionic compounds generally form only between very reactive metallic elements and very reactive nonmetals. Two requisites are that the ionization energy to form the cation and the electron affinity to form the anion must be energetically favorable. The overall reaction will cost some, but not too much, energy.

Recap:

- Ionization energy, IE: the energy required to remove an electron from the neutral gaseous atom
- Electron affinity, AE: the change in energy when one electron is added to a neutral gaseous atom

3.7 ELECTRONEGATIVITY

Electronegativity is a measure of the strength with which an atom in a molecule attracts electrons. Like IE and EA, the dependence of electronegativity on Z can be explained by examining electron configurations. Atoms with almost completely filled outer energy levels, like F and Cl, are strongly electronegative and readily accept electrons. However, atoms with nearly empty outer shells, such as Li and Na, readily give up electrons and are strongly electropositive. Higher Z elements also have a low electronegativity; because the outer electrons are at a greater distance from the positive nucleus, electrons are not as strongly attracted to the atom.

The electronegativity scale of the elements is included in Figure 3.4 using Pauling's classification: F is assigned the largest electronegativity, 4, and the other elements are then based on this value. The differences in the electronegativities of two atoms in a molecule can be used to estimate bond strengths and bond ionicities (i.e., the percentage of ionic character in the bond—the extent of "mixed" bonding; see Section 4.6 for numerical examples).

GIBBS FREE ENERGY

The change in free energy is defined by

$$\Delta G = \Delta H - T\Delta S \qquad \text{Box 3.7}$$

The change in enthalpy is given by

$$\Delta H = \Delta E + P\Delta V \qquad \text{Box 3.8}$$

When the process involves no volume change, i.e., $P\Delta V = 0$, so $\Delta H = \Delta E$ we can write

$$\Delta G = \Delta E - T\Delta S \qquad \text{Box 3.9}$$

CONVENIENT FORMS OF ΔG

Mixing A and B to form a solution (important in constructing phase diagrams)

$$\Delta G = RT(X_A \ln a_A + X_B \ln a_B)$$

Oxidation of a metal to form a ceramic

$$\Delta G = RT \ln pO_2$$

Electrochemical process (such as in a fuel cell)

$$\Delta G = -zFE \, \Delta G = RT \ln pO_2$$

3.8 THERMODYNAMICS: THE DRIVING FORCE FOR CHANGE

Thermodynamic principles are important in all aspects of materials science. In this section we introduce some of the fundamentals, but thermodynamics will be used in several other chapters (e.g., point defects, Chapter 11, and surfaces, Chapter 13). The primary role of thermodynamics in ceramics is to indicate whether a system is stable and what conditions (usually changes in temperature or pressure) will cause it to change. Our system may be a crystal structure, a phase, a grain boundary, an aggregate of powder particles, or a concentration of defects. Table 3.7 lists some of the important thermodynamic parameters we meet in ceramics together with their units.

Thermodynamic Stability

The Gibbs free energy (G) is a property that provides a convenient measure of the driving force of a reaction and may be used to define thermodynamic stability. When we want to know whether a process is energetically favorable, we have to determine the change in free energy (ΔG) associated with that process. For the change

$$A \rightarrow B$$

which may be an oxidation reaction or a phase transformation, the change in free energy is

$$\Delta G = G_B - G_A$$

where G_B is the free energy of the final state and G_A is the free energy of the initial state.

- $\Delta G < 0$ for a favorable process. There is a natural tendency to move spontaneously from A to B.
- $\Delta G > 0$ for an unfavorable process. The reaction as written will not proceed spontaneously; the reverse reaction will be the spontaneous one.
- $\Delta G = 0$ for a process at equilibrium.

In many processes, particularly those that occur in ceramics, there is little if any volume change and so $P\Delta V = 0$. Because the sign of ΔG is dependent upon temperature and pressure, a particular system, such as a crystal structure, can be stable only within a certain range of P and T. By varying P and/or T, ΔG will eventually become negative relative to some other structure

TABLE 3.7 Important Thermodynamic Parameters

Parameter	*Definition*	*Units*
C_P	Heat capacity at constant pressure	J/K
c_P	Molar heat capacity at constant pressure	$J K^{-1} mol^{-1}$
C_V	Heat capacity at constant volume	J/K
c_V	Molar heat capacity at constant volume	$J K^{-1} mol^{-1}$
E	Energy	J
G	Gibbs free energy	J
H	Enthalpy	J
μ_i	Chemical potential	J
P	Pressure	Pa
S	Entropy	J/K
T	Temperature	K

and a phase transition will occur. This may be a transition from one crystal structure to another (e.g., the phase transformation in quartz), or it may be a transition from one aggregate state to another state (e.g., during sintering when we get grain growth and reduction in total grain boundary area), or it could be when we melt a solid to form a liquid.

The Gibbs free energy is a function of temperature, pressure, and the numbers of moles of all the species present in the system.

Effect of Temperature

Many of the processes of interest in ceramics occur at high temperature. At absolute zero, $T = 0$ K, the term containing the entropy change, $T\Delta S$, is zero and ΔG depends only on ΔE. However, as T increases the $T\Delta S$ term becomes increasingly important and at some temperature a process can occur spontaneously even though ΔE is positive. The values of ΔE and ΔS depend on temperature and we can rewrite Box 3.9:

$$\Delta G_T = \Delta E_T - T\Delta S_T \tag{3.1}$$

The subscript indicates that the values are given at a temperature, T. To obtain values of ΔE_T and ΔS_T we need to use the heat capacities of the material.

The molar heat capacities are

$$c_{\mathrm{P}} = \mathrm{d}H/\mathrm{d}T \tag{3.2}$$

$$c_{\mathrm{V}} = \mathrm{d}E/\mathrm{d}T \tag{3.3}$$

In many solids, particularly ceramics, with low coefficients of expansion $c_{\mathrm{p}} \sim c_{\mathrm{v}}$. It is easier to obtain values of c_{p} and the variation with temperature is normally fitted to an analytical expression of the form

$$c_{\mathrm{P}} = a + bT + cT^{-2} \tag{3.4}$$

We use Eq. 3.4 in Chapter 34 (Eq. 34.3) to determine c_{P} for various ceramics.

Using c_{P} we can obtain expressions for ΔE_T and ΔS_T

$$\Delta H_T = \Delta H_{298} + \int_{298}^{T} \Delta c_{\mathrm{P}} dT \tag{3.5}$$

$$S_T = S_0 + \int_{0}^{T} \frac{c_{\mathrm{P}}}{T} dT \tag{3.6}$$

If the external work of expansion due to heating is zero, as it is when a material is heated at constant volume, or if it is negligible, as it is when solids are heated at atmospheric pressure, all the heat supplied goes into internal energy and we can approximate ΔH_T by ΔE_T. It is values of ΔH_{298} that you will find tabulated. The variation of ΔG with temperature is illustrated in Figure 3.5.

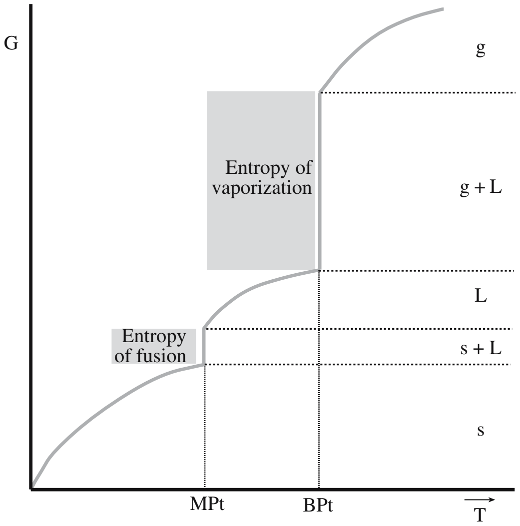


FIGURE 3.5 Variation in the Gibbs free energy as a function of temperature. The vertical segments are associated with phase transformations.

When the signs of ΔE_T and ΔS_T are the same, some reactions that are not favorable at one temperature become favorable at another, and vice versa. It is often useful to know the temperature at which a reaction becomes favorable. This is the temperature at which a positive ΔG_T switches to a negative ΔG_T due to the $-T\Delta S_T$ term. We find this crossover temperature by setting ΔG_T in Eq. 3.1 equal to 0 and solving for T

$$T = \frac{\Delta E_T}{\Delta S_T} \tag{3.7}$$

Figure 3.6 shows the effect of temperature on reaction favorability. The slopes of the two lines and the crossover temperature will depend on the specific system.

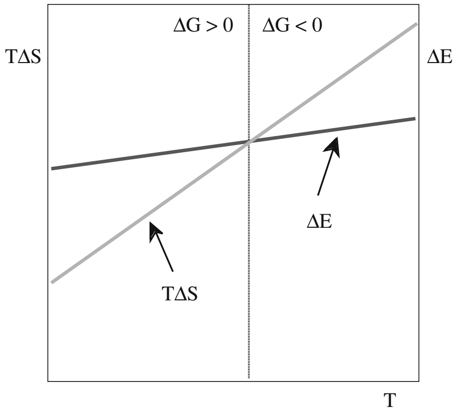


FIGURE 3.6 Effect of temperature on reaction spontaneity. The two lines cross when the energy contribution becomes less than the entropy contribution.

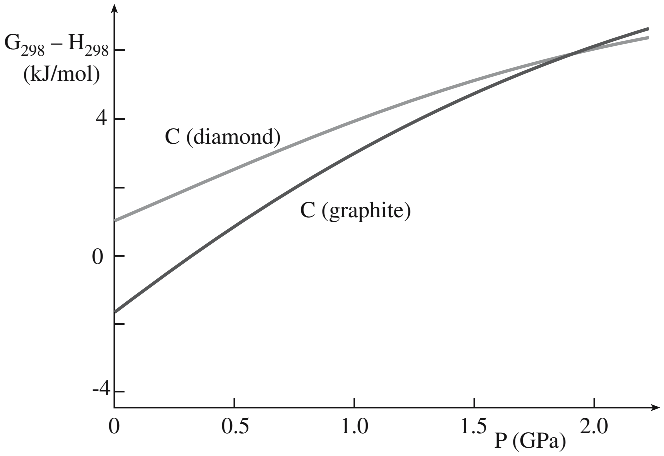


FIGURE 3.7 Pressure dependence of the Gibbs free energies of carbon in graphite and diamond. Diamond becomes more stable at high pressures.

Effect of Pressure

Higher pressures favor structures that have a higher density. Their formation involves a decrease in volume (negative ΔV). For instance, diamond ($\rho = 3.51\,\mathrm{g\,cm^{-3}}$) is more stable than graphite ($\rho = 2.26\,\mathrm{g\,cm^{-3}}$) at very high pressures. At room temperature graphite will transform to diamond at pressures greater than about 1.5 GPa (14,400 atm) as shown in Figure 3.7. Graphite is the stable phase at room temperature and pressure. The influence of pressure, at constant T, on the Gibbs free energies of two phases, α and β, is given by

$$(\partial G_{(\alpha\to\beta)}/\partial P)_T = \Delta V_{(\alpha\to\beta)} \tag{3.8}$$

Effect of Composition

In ceramics we are often dealing with multicomponent systems such as the ternary quartz, clay, and feldspar used in the formation of porcelains or the binary NiO, Al_2O_3 that react to form a spinel. Equilibrium, at constant T and P, is reached in these systems when the chemical potential, $\mu_{i,}$ of a component is the same in all of the phases in which it is present. The chemical potential, or the partial molar free energy of a component in a given phase, is defined as

$$\mu_i = (\partial G/\partial n_i)_{T,P,nj} \tag{3.9}$$

where n_i is the number of moles of component i and n_j is the number of moles of component j.

Deduction of the phase rule (Chapter 8), which defines the conditions of equilibrium in terms of the number of phases and the components of a system, follows directly from the requirement that μ_i of each constituent i be the same in every phase at equilibrium. If μ_i is different then we will get a reaction, the rate of which will be determined by kinetics.

We can combine Eq. 3.9 with our definition of Gibbs free energy and produce a differential form of the Gibbs equation:

$$\partial G = V\partial P - S\partial T + \sum \mu_i \partial n_i \tag{3.10}$$

The importance of Eq. 3.10 is that it links the free energy of the system to our usual experimental variables (T and P) and the observable properties (V and concentration).

3.9 KINETICS: THE SPEED OF CHANGE

Thermodynamics tells us whether a process can happen. Kinetics tells us whether that process will happen at a reasonable, or measurable, rate. The rates of chemical reactions have been found to depend very strongly on the temperature. A useful rule of thumb is that the rate doubles for every 10 K increase in temperature. The rate, k, of many reactions follows the Arrhenius rate law

$$k = A \exp -(E_a/RT) \tag{3.11}$$

where R is the gas constant ($8.314\,\mathrm{J\,K^{-1}\,mol^{-1}}$), A is a temperature-independent preexponential constant, and E_a is the activation energy. A plot of k versus T gives a curve that increases exponentially. The activation energy represents the minimum energy required for a reaction to happen. The value of E_a may be determined from the logarithmic form of the Arrhenius equation:

$$\ln K = \frac{E_a}{RT} + \ln A \tag{3.12}$$

A plot of ln k against $1/T$ yields a straight line with slope $-E_a/R$, as shown in Figure 3.8. This type of plot is called an Arrhenius plot and a reaction giving such a straight line is said to show Arrhenius behavior.

Most reactions that proceed at a moderate rate, that is, occur appreciably in minutes or hours, have values of E_a between 50 and 100 kJ. For such reactions you can use Eq. 3.11 to verify the photographer's guide that reactions go two or three times as fast when the temperature increases by 10°C.

An important example of a process that exhibits Arrhenius behavior is diffusion. The diffusion coefficient D (units of $\mathrm{cm^2/s}$) is a strong function of temperature.

$$D = D_0 \exp(-E_a/RT) \tag{3.13}$$

For ceramics the value of E_a varies over quite a wide range from about 50 kJ/mol to 800 kJ/mol (~0.5 eV per atom to 8 eV per atom). The activation energy represents the energy necessary for an atom to jump from one atomic position to another.

The diffusion coefficient also depends on chemical potential and time. These changes are represented in Fick's laws, which we will describe in Chapter 11.

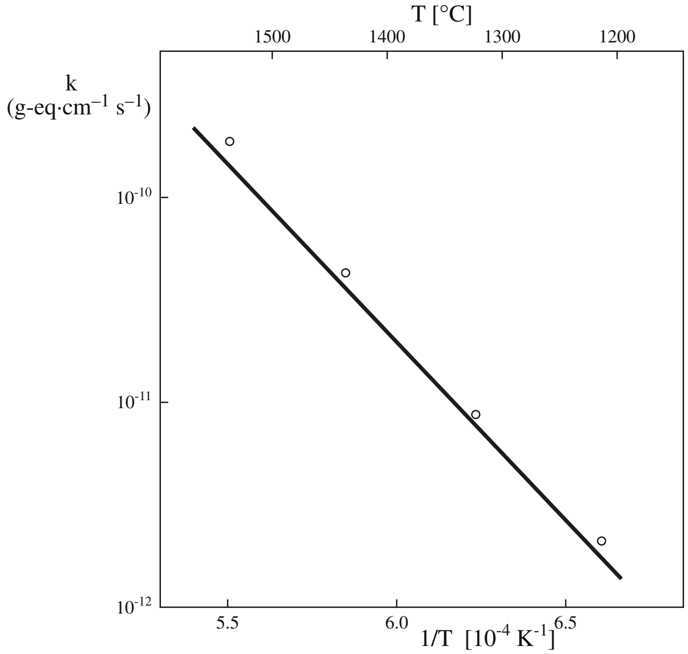


FIGURE 3.8 An Arrhenius plot. The slope of the line gives the activation energy for the process.

At sufficiently low temperatures any structure can be stabilized kinetically. Kinetic stability is not a well-defined term because the limit below which a conversion rate is considered to be negligible is arbitrary. There are many examples of kinetically stabilized materials. Two examples in ceramics are

- Glasses. At room temperature a glass is a kinetically stabilized material. Given enough time all glasses will transform to their crystalline counterpart.
- Tridymite (a high-temperature polymorph of SiO_2). Transformation of quartz at 867°C should lead to the formation of tridymite. However, the transformation is very slow (it involves a complete alteration of the crystal structure) and direct conversion by heating alone has not been proved. All natural tridymite contains other oxides, which it is believed stabilize the structure; pure tridymite cannot be obtained at room temperature.

Notice that we have not considered the environment of the combining atoms/ions, so we have not actually used the crystal/amorphous nature of the ceramic.

CHAPTER SUMMARY

We reviewed some of the fundamentals that underlie all aspects of materials science. Knowing the electron configuration of an atom allows us to understand some of the properties of materials that contain that atom. It also helps us to determine the type of bonding that occurs between different atoms. In ceramics the bonding is important because it is not straightforward. It often involves ionic and covalent contributions and sometimes also a metallic component.

Thermodynamics and kinetics enable us to explain why and how chemical reactions take place. This type of information is important in many areas of ceramics, but particularly in ceramic processing. Traditional processing of ceramic components is carried out at high temperatures because the kinetics would be too slow otherwise. Kinetics is often closely linked to economics. Processes that are slow are usually expensive.

PEOPLE IN HISTORY

Arrhenius, Svante August won the 1903 Nobel Prize in Chemistry for his work on the electrical conductivity of salt solutions (he was also nominated for the Physics Prize). He is often hailed as a pioneer of modern environmentalism for his work on the greenhouse effect. One of his predictions was that the United States might pump its last barrel of oil in 1935. Fortunately he was proved wrong, but his concern about the world's natural mineral resources and the need for alternative sources of energy was prescient. He died in 1927 at age 68.

Barkla, Charles Glover (1877–1944) was born in Widnes, Lancashire, England. After obtaining his master's degree in physics he went to work in the Cavendish Laboratory with J.J. Thomson. In 1913 he accepted the position of Chair in Natural Philosophy in the University of Edinburgh in Scotland and he remained there until he died. He was awarded the 1917 Nobel Prize in Physics for his discovery of the characteristic Röntgen radiation of the elements.

Bohr, Neils (Denmark) in 1913 proposed an atomic model where electrons could move only in certain stable orbits. He won the Nobel Prize in Physics in 1922 and died in 1962 at age 77.

Boltzmann, Ludwig Eduard was born in Vienna in 1844 and died at age 62. His constant is inscribed on his tomb in Vienna. Many argued strongly against his ideas and he committed suicide shortly before experiments justified them.

Davisson, Clinton Davis and Germer, Lester Halbert were working at Bell Labs at the time of their discovery of electron diffraction. Davisson died in 1958 at age 76 (born 1881) and Germer died in 1971 at age 75 (born 1896).

de Broglie, Louis in 1924 hypothesized that all matter possesses wave properties. A French Duke, he won the Nobel Prize in Physics in 1929. He died in 1987 at age 94.

Heisenberg, Werner (1901–1976) was born in Würzburg in Germany. He obtained his PhD in 1923 at the University of Munich. He published his theory of quantum mechanics when he was 23 and for this theory he was awarded the 1932 Nobel Prize in Physics. At the end of World War II he was taken prisoner by American troops and sent to England. He returned to Germany in 1946. He was Director of the famous Max Planck Institute for Physics and in 1953 became President of the Alexander von Humboldt Foundation. He died in 1976 at age 74.

Pauli, Wolfgang (1900–1958) was born in Vienna, Austria. He obtained his doctoral degree in 1921 from the University of Munich. After that he worked with Max Born and then with Neils Bohr. He held various appointments in the United States during World War II, including the Institute of Advanced Study in Princeton. After the war he returned to the Federal Institute of Technology in Zurich as Professor of Theoretical Physics. He won the 1945 Nobel Prize in Physics for developing the eponymous exclusion principle.

Pauling, Linus Carl won the Noble Prize for Chemistry in 1954 and in 1962 for Peace. He died in 1994 at age 93.

Schrödinger, Erwin was born in Vienna, Austria in 1887. His great discovery, Schrödinger's wave equation, was made in 1926, and for that he won the Nobel Prize in Physics in 1933. When Hitler came to power in Germany (1933) Schrödinger moved to England. He then moved back to Austria but had to escape when his native country became annexed in 1938. He eventually moved to the Institute for Advanced Studies in Dublin where he remained until he retired. He died in 1961 at age 73.

Thomson, Joseph John and Thomson, George Paget were father and son. Rutherford was J.J. Thomson's student at Cambridge. J.J. Thomson discovered the electron in 1897 and won the Nobel Prize in Physics in 1906. G.P. Thomson won the Nobel Prize in 1937 together with Davisson; he died in 1976 (born 1892). So, the father "proved" that electrons were particles and the son "proved" they were waves.

GENERAL REFERENCES

Atkins, P.W. and de Paula, J. (2002) *Atkins' Physical Chemistry*, 7th edition, Oxford University Press, Oxford. A physical chemistry text often used at the sophomore/junior level.

DeHoff, R. (2006) *Thermodynamics in Materials Science*, 2nd edition, CRC, Boca Raton, FL. A standard thermodyanamic text for materials science.

Gaskell, D.R. (2003) *Introduction to the Thermodynamics of Materials*, 4th edition, Taylor & Francis, New York. Thermodynamic text for undergraduate courses in materials science.

Huheey, J.E., Keiter, E.A., and Keiter, R.L. (1993) *Inorganic Chemistry: Principles of Structure and Reactivity*, 4th edition, Cummings, San Francisco. A standard inorganic chemistry textbook. Much of this should be background material.

Kreyszig, E. (1999) *Advanced Engineering Mathematics*, 8th edition, Wiley, New York. Senior level undergraduate/graduate-level engineering mathematics text that describes the method for transforming Cartesian coordinates into polar coordinates and the method of separation of variables.

Pauling, L. (1960) *The Nature of the Chemical Bond*, 3rd edition, Cornell University Press, Ithaca, NY. A classic, and one of the most frequently cited of all scientific texts. Gives a detailed description of his scale of electronegativity.

Planck, Max (1922) *Treatise on Thermodynamics*, Dover Publications. Winner of the 1918 Nobel Prize for Physics

SPECIFIC REFERENCES

Arrhenius, S. (1889) "Ober die Reacktionsgeschwindigkeit bei der Inversionvon Rohrzucker durch Säuren," *Z. Phys. Chem.* **4**, 226–248.

Bohr, N. (1913) "The constitution of atoms and molecules," *Phil. Mag.* **26**, 1, 476.

Bohr, N. (1913) "Constitution of atoms and molecules III," *Phil. Mag.* **26**, 1, 857.

Davisson, C. and Germer, L.H. (1927) "Diffraction of electrons by a nickel Crystal," *Phys. Rev.* **30**, 705.

DeBroglie. L. (1925) "Recherches sur la théorie des quanta," *Ann. Phys., Paris* **3**, 22.

Heisenberg, W. (1927) "The problem of several bodies and resonance in quantum mechanics. II," *Z. Phys.* **41**, 239.

Hund, F (1925) "Interpretation of spectra," *Z. Phys.* **33**, 345.

Thomson, G.P. and Reid, A. (1927) "Diffraction of cathode rays by a thin film," *Nature* **119**, 890.

EXERCISES

3.1 Explain the trend in the first ionization energies of elements in the second row (Na to Cl) of the periodic table.

3.2 Explain the trend in ionization energies of singly charged ions of the halogens.

3.3 Explain the trend in electron affinities of elements in the second row (Na to Cl) of the periodic table.

3.4 What is the ionization energy of F^-? Would you expect the process of ionization to be endothermic or exothermic?

3.5 Calculate the energy of the Na $3s^1$ electron. The value of the first ionization energy for Na is 0.50 MJ/mol. Explain the difference, if any, between these two numbers.

3.6 Explain the trend in Pauling electronegativities of elements in the second row (Na to Cl) of the periodic table.

3.7 An electron has the principal quantum number four. What are the possible values of l, m_l, and m_s for this electron?

3.8 Determine the activation energy for the reaction shown in Figure 3.8.

3.9 Even though glasses are not thermodynamically stable, we know they exist at room temperature. Explain this phenomenon and describe briefly how you could increase the rate at which a glass would crystallize.

3.10 Show that the volume change for the transformation graphite → diamond is negative.