3

Background You Need to Know

CHAPTER PREVIEW

We summarize three concepts fundamental to all materials science in this chapter: atomic structure, thermodynamics, and kinetics. You should be familiar with these topics from introductory chemistry, physics, and materials science classes so we only give 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 only find 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, and 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 >1,800°C and then cooled to 25°C. Some processes occur at 1,800°C but may continue or change as we cool the sample. Conversely, some ceramics change their properties at quite low temperatures. For example, $BaTiO_3$ changes from the paraelectric cubic phase to the ferroelectric tetragonal phase at 120°C. Kinetics tells us how rapidly these reactions 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:

- Electrons in atoms can only move in certain stable orbits (i.e., 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 a 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 introduction of the spin quantum number. Atoms containing electrons with unpaired spins 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—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? why do most

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bonds show a mixture of the two? We use spectroscopy and microscopy to probe the electronic structure to determine the local chemistry of the ceramic.

3.2 ENERGY LEVELS

The quantization of energy levels 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.

THE BOHR ATOM

Quantization of angular momentum

$$m_e v r = n \frac{h}{2\pi} \qquad \text{(Box 3.1)}$$

Radius of possible electron orbits

$$r = \frac{\varepsilon_0 n^2 h^2}{\pi m_e e^2} \qquad \text{(Box 3.2)}$$

Energy of the electron

$$E = \frac{m_e e^4}{8\varepsilon_0 n^2 h^2} \qquad \text{(Box 3.3)}$$

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

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 (i.e., the electron is further from the nucleus)
2. The energy, E, of that electron is also increased

The first five Bohr orbits (i.e., $n = 1$–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 for both X-ray diffraction and chemical analysis with 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 although 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 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 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), we can 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 didn't 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 use this again in Chapter 10.

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

- Atomic radii—As we fill shells going down a particular period, the atoms get bigger (r increases).

TABLE 3.1 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

- 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).
- 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.

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 can't 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 with a transmission electron microscope, which allows us to get structural information from very small regions. This is of particular importance in many new ceramics, where we are often dealing with thin interface layers (e.g., at grain boundaries) and very small grains (nanopowders).

THE DE BROGLIE HYPOTHESIS

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

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

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 a probability of finding that electron at a particular position. This leads to the electron-density or electron-cloud representation of electron orbitals.

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.

The Schrödinger equation is as central to quantum mechanics as Newton's equations are to classical mechanics and 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 (2009): "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.

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 it using the method of separation of variables (described in, e.g., Kreyszig 2011).

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 don't change, and the results obtained for hydrogen are applied to many-electron atoms.

Methods are becoming available that allow us to calculate the structure of some "bulk" materials. Generally, this calculation is done only rarely, by starting with the Schrödinger equation. The calculations are just too difficult or too time-consuming. Actually, it's 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 have the same n and corresponds to Bohr's n. A subshell is a smaller group of states having both the same values 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.

- 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 $\pm 1/2$ 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").

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.

The s orbitals are spherical. 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 don't 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).
- Magnetism relates directly to the spin of the electrons. If we have more spins up than down, we have magnetization.

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	$\pm$ 1/2

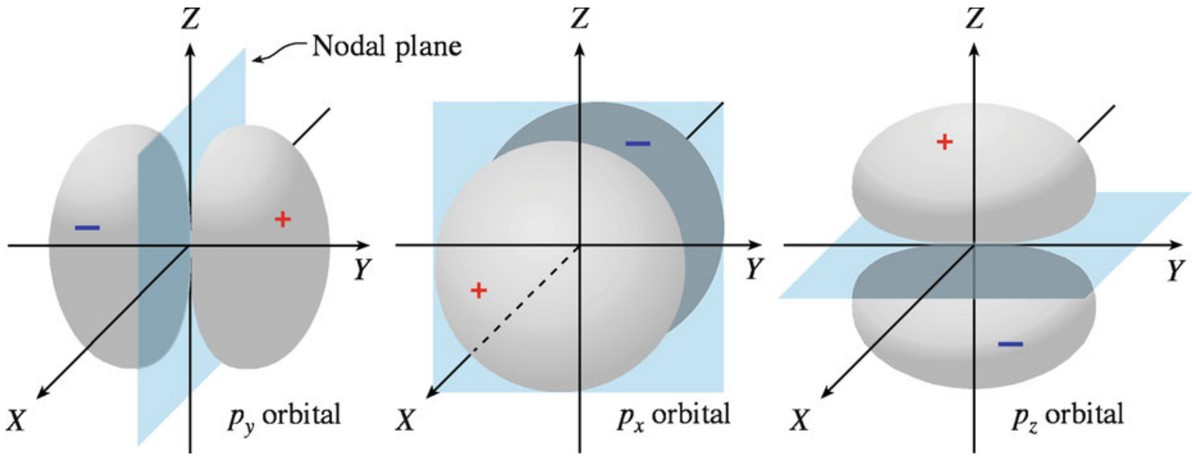


FIGURE 3.1. The $2p_x$, $2p_y$, and $2p_z$ orbitals. The nodal plane represents the area where the probability of finding the electron is zero.

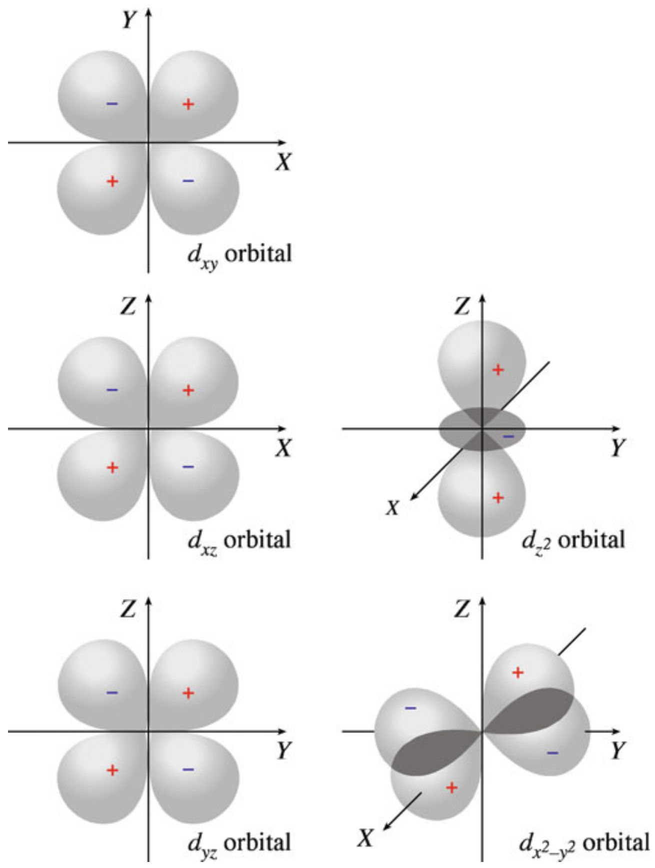


FIGURE 3.2. The 3d atomic orbitals. The 4d, 5d, and 6d orbitals are essentially identical to the 3d orbitals except they are bigger. The sign of wavefunction changes from one lobe to the next in a given orbital, which is important when we consider the formation of molecular orbitals.

- 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.

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, for example, 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:

$$1s < 2s < 2p < 3s < 3p < 4s < 3d < 4p < 5s < 4d < 5p < 6s < 4f \approx 5d < 6p < 7s < 5f \approx 6d.$$

Figure 3.3 is 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 are 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 $3s^2\ 3p^6\ 3d^0\ 4s^2$.

IONIZATION

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

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

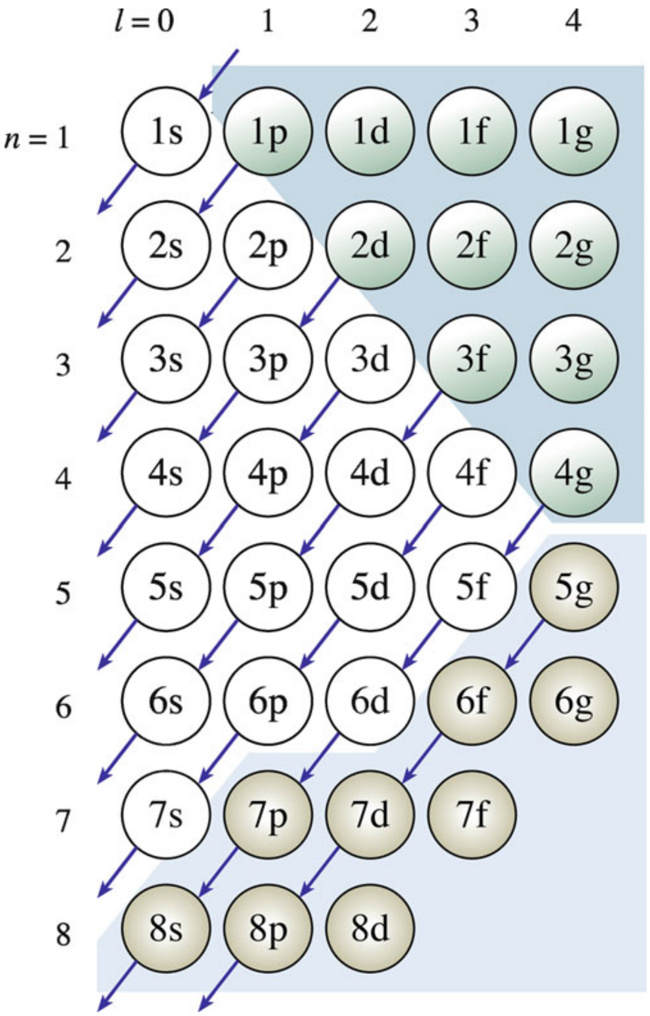


FIGURE 3.3. Mnemonic for predicting the filling order of the atomic orbitals. The *upper colored block* shows imaginary orbitals. Orbitals in the *lower blue block* are not filled in the known elements.

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**	$\mathbf{1s^22s^22p^63s^23p^63d^54s^1}$
25	Mn	$1\ s^22s^22p^63s^23p^63d^54s^2$
26	Fe	$1\ s^22s^22p^63s^23p^63d^64s^2$
27	Co	$1\ s^22s^22p^63s^23p^63d^74s^2$
28	Ni	$1\ s^22s^22p^63s^23p^63d^84s^2$
29	**Cu**	$\mathbf{1s^22s^22p^63s^23p^63d^{10}4s^1}$

In the filling of the electron orbitals for elements 21–29, 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 for this apparent anomaly is that exactly filled and half-filled 3d orbitals are particularly stable (they have 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 are 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 used the shorthand representation for the electron configurations (start with the nearest filled noble gas).

Examination of the electron configuration of the elements shows clearly 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 as it is determines whether they lose or gain electrons more easily and thus how the ion is charged, as we'll now discuss.

3.6 IONS

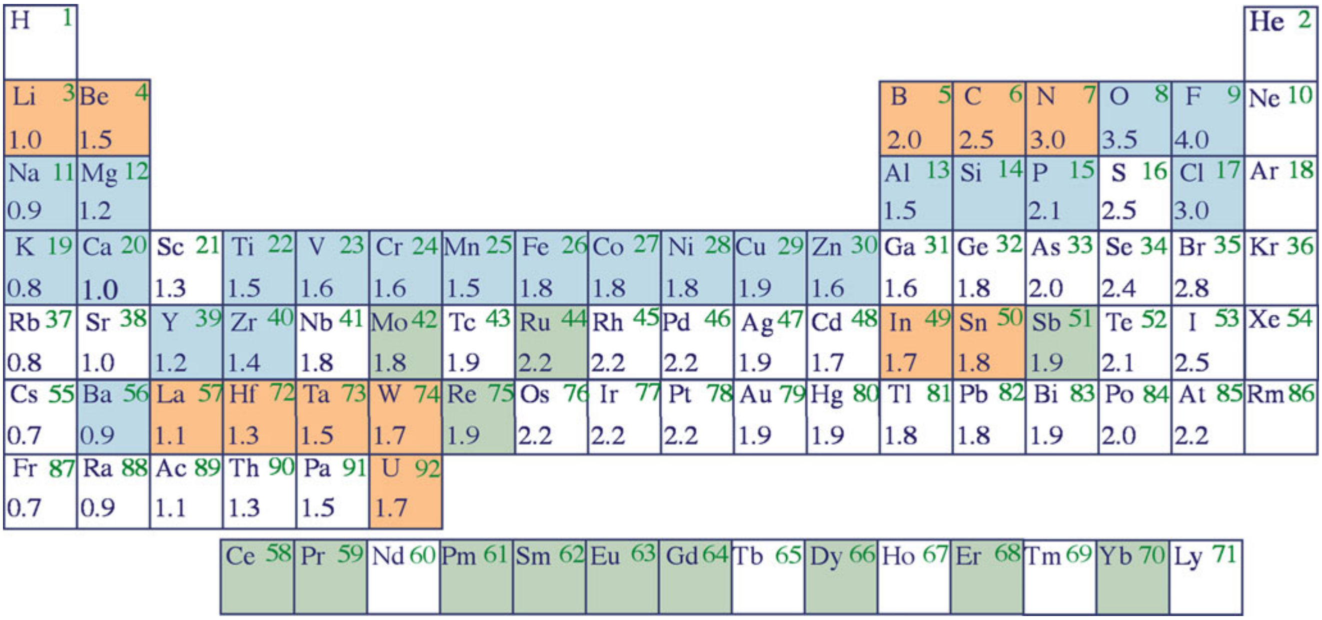
In ceramics we are usually dealing with materials that have a significant fraction of ionic character in their bonding. The requirements for ionic bonding are simple.

- 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.

TABLE 3.4 Electron Configurations of the Elements

Z	*Element*	*Electron configuration*
1	H	1s
2	He	1s^{2}
3	Li	[He]2s
4	Be	[He]2s^{2}
5	B	[He]2 s^{2}2p
6	C	[He]2 s^{2}2p^{2}
7	N	[He]2 s^{2}2p^{3}
8	O	[He]2 s^{2}2p^{4}
9	F	[He]2s^{2}2p^{5}
10	Ne	[He]2s^{2}2p^{6}
11	Na	[Ne]3s
12	Mg	[Ne]3s^{2}
13	Al	[Ne]3 s^{2}3p
14	Si	[Ne]3 s^{2}3p^{2}
15	P	[Ne]3 s^{2}3p^{3}
16	S	[Ne]3 s^{2}3p^{4}
17	Cl	[Ne]3s^{2}3p^{5}
18	Ar	[Ne]3s^{2}3p^{6}
19	K	[Ar]4s
20	Ca	[Ar]4s^{2}
21	Sc	[Ar]3d4s^{2}
22	Ti	[Ar]3d^{2}4s^{2}
23	V	[Ar]3d^{3}4s^{2}
24	Cr	[Ar]3d^{5}4s
25	Mn	[Ar]3d^{5}4s^{2}
26	Fe	[Ar]3d^{6}4s^{2}
27	Co	[Ar]3d^{7}4s^{2}
28	Ni	[Ar]3d^{8}4s^{2}
29	Cu	[Ar]3d^{10}4s
30	Zn	[Ar]3d^{10}4s^{2}
31	Ga	[Ar]3d^{10}4s^{2}4p
32	Ge	[Ar]3d^{10}4s^{2}4p^{2}
33	As	[Ar]3d^{10}4s^{2}4p^{3}
34	Se	[Ar]3d^{10}4s^{2}4p^{4}
35	Br	[Ar]3d^{10}4s^{2}4p^{5}
36	Kr	[Ar]3d^{10}4s^{2}4p^{6}
37	Rb	[Kr]5s
38	Sr	[Kr]5s^{2}
39	Y	[Kr]4d5s^{2}
40	Zr	[Kr]4d^{2}5s^{2}
41	Nb	[Kr]4d^{4}5s
42	Mo	[Kr]4d^{5}5s
43	Tc	[Kr]4d^{5}5s^{2}
44	Ru	[Kr]4d^{7}5s
45	Rh	[Kr]4d^{8}5s
46	Pd	[Kr]4d^{10}
47	Ag	[Kr]4d^{10}5s
48	Cd	[Kr]4d^{10}5s^{2}
49	In	[Kr]4d^{10}5s^{2}5p
50	Sn	[Kr]4d^{10}5s^{2}5p^{2}
51	Sb	[Kr]4d^{10}5s^{2}5p^{3}
52	Te	[Kr]4d^{10}5s^{2}5p^{4}
53	I	[Kr]4d^{10}5s^{2}5p^{5}
54	Xe	[Kr]4d^{10}5s^{2}5p^{6}
55	Cs	[Xe]6s
56	Ba	[Xe]6s^{2}
57	La	[Xe]5d6s^{2}
58	Ce	[Xe]4f5d6s^{2}
59	Pr	[Xe]4f^{3}6s^{2}
60	Nd	[Xe]4f^{4}6s^{2}
61	Pm	[Xe]4f^{5}6s^{2}
62	Sm	[Xe]4f^{6}6s^{2}
63	Eu	[Xe]4f^{7}6s^{2}
64	Gd	[Xe]4f^{7}5d6s^{2}
65	Tb	[Xe]4f^{9}6s^{2}
66	Dy	[Xe]4f^{10}6s^{2}
67	Ho	[Xe]4f^{11}6s^{2}
68	Er	[Xe]4f^{12}6s^{2}
69	Tm	[Xe]4f^{13}6s^{2}
70	Yb	[Xe]4f^{14}6s^{2}
71	Lu	[Xe]4f^{14}5d6s^{2}
72	Hf	[Xe]4f^{14}5d^{2}6s^{2}
73	Ta	[Xe]4f^{14}5d^{3}6s^{2}
74	W	[Xe]4f^{14}5d^{4}6s^{2}
75	Re	[Xe]4f^{14}5d^{5}6s^{2}
76	Os	[Xe]4f^{14}5d^{6}6s^{2}
77	Ir	[Xe]4f^{14}5d^{7}6s^{2}
78	Pt	[Xe]4f^{14}5d^{9}6s
79	Au	[Xe]4f^{14}5d^{10}6s
80	Hg	[Xe]4f^{14}5d^{10}6s^{2}
81	Tl	[Xe]4f^{14}5d^{10}6s^{2}6p
82	Pb	[Xe]4f^{14}5d^{10}6s^{2}6p^{2}
83	Bi	[Xe]4f^{14}5d^{10}6s^{2}6p^{3}
84	Po	[Xe]4f^{14}5d^{10}6s^{2}6p^{4}
85	At	[Xe]4f^{14}5d^{10}6s^{2}6p^{5}
86	Rn	[Xe]4f^{14}5d^{10}6s^{2}6p^{6}
87	Fr	[Rn]7s
88	Ra	[Rn]7s^{2}
89	Ac	[Rn]6d7s^{2}
90	Th	[Rn]6d^{2}7s^{2}
91	Pa	[Rn]5f^{2}6d7s^{2}
92	U	[Rn]5f^{3}6d7s^{2}
93	Np	[Rn]5f^{4}6d7s^{2}
94	Pu	[Rn]5f^{6}7s^{2}
95	Am	[Rn]5f^{7}7s^{2}
96	Cm	[Rn]5f^{7}6d7s^{2}
97	Bk	[Rn]5f^{9}7s^{2}
98	Cf	[Rn]5f^{10}7s^{2}
99	Es	[Rn]5f^{11}7s^{2}
100	Fm	[Rn]5f^{12}7s^{2}
101	Md	[Rn]5f^{13}7s^{2}
102	No	[Rn]5f^{14}7s^{2}
103	Lr	[Rn]5f^{14}6d7s^{2}

In both cases the “3” is rare, and it must not involve too much energy exchange. The ionization energy (IE) 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 a charge of +1.



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. Periodic table of elements as viewed by a ceramist showing atomic numbers and electronegativity. Different colors show the groupings of some of the most important components of traditional ceramics (*blue*) and advanced ceramics (*orange*). Elements that are becoming increasingly important in a number of emerging applications for ceramics are shown in *green*. Other elements, such as Pb (as in PZT), deserve color today but we hope not in the future.

The noble gases, which have a complete shell of outer electrons, have very high ionization energies; whereas the elements in group I (e.g., Na and K), which have an outer ns^1 orbital, 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 decreases, and the net attraction between the electrons and the nucleus increases (Table 3.5).

IONIZATION ENERGY

$$\text{Atom (g)} + \text{IE}_1 \rightarrow \text{Ion}^+ \text{ (g)} + e^-$$

This reaction is always endothermic ($\text{IE}_1 > 0$). The sign is a convention of thermodynamics; some fields use the opposite convention.

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

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 (e.g., 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 orbitals (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'll 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 costs some, but not too much, energy.

Recap:

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

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
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				

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 (e.g., F and Cl) are strongly electronegative and readily accept electrons. However, atoms with nearly empty outer shells (e.g., Li and Na) readily give up electrons and are strongly electropositive. Higher *Z* elements also have 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; four and the other elements are then based on this value. The differences in the

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

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

Source: Berry RS (1969) Chem Rev 69: 533, except
[a] Edlen B (1960) J. Chem. Phys 33: 98
[b] Baughan EC (1961) Trans. Faraday Soc 57: 1863
[c] Ginsberg AP, Miller JM (1958) J Inorg Nucl Chem 7: 351
[d] Politzer P (1968) Trans. Faraday Soc 64: 2241

electronegativities of two atoms in a molecule can be used to estimate bond strengths and bond ionicities (i.e., the percentage of ionic characters in the bond—the extent of "mixed" bonding) (see Section 4.6 for numerical examples).

3.8 THERMODYNAMICS: 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 is discussed in several other chapters, such as in regard to point defects in Chapter 11 and to surfaces in Chapter 13. The primary role of thermodynamics in ceramics is to tell us whether a system is stable and what conditions (usually changes in temperature or pressure) can 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.

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

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

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.mol
C_v	Heat capacity at constant volume	J/K
c_v	Molar heat capacity at constant volume	J/K.mol
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

3.8.1 Thermodynamic Stability

Gibbs free energy (G) is a property that provides a convenient measure of the driving force of a reaction, and it 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

$$\mathrm{A} \rightarrow \mathrm{B}$$

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

$$\Delta G = G_{\mathrm{B}} - G_{\mathrm{A}}$$

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

CONVENIENT FORMS OF ΔG

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

$$\Delta G = RT(X_{\mathrm{A}} \ln a_{\mathrm{A}} + X_{\mathrm{B}} \ln a_{\mathrm{B}})$$

Oxidation of a metal to form a ceramic

$$\Delta G = RT \ln p\mathrm{O}_2$$

Electrochemical process (such as in a fuel cell)

$$\Delta G = -zFE = RT \ln p\,\mathrm{O}_2$$

In many processes, particularly those that occur in ceramics, there is little if any volume change, so $P\Delta V = 0$. Because the sign of ΔG is dependent on 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 eventually becomes negative relative to some other structure and a phase transition occurs. This may be a transition from one crystal structure to another (e.g., 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 a reduction in the total grain boundary area), or it could be when we melt a solid to form a liquid.

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

3.8.2 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 to account for this.

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

The subscript indicates that the values are given at 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 equation 3.4 in Chapter 34 to determine the c_{p} value 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 of the heat supplied goes into internal energy; and we can approximate ΔH_T by ΔE_T. Values of ΔH_{298} are already tabulated. The variation of ΔG with temperature is illustrated in Figure 3.5.

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 equation 3.1 equal to 0 and solving for T.

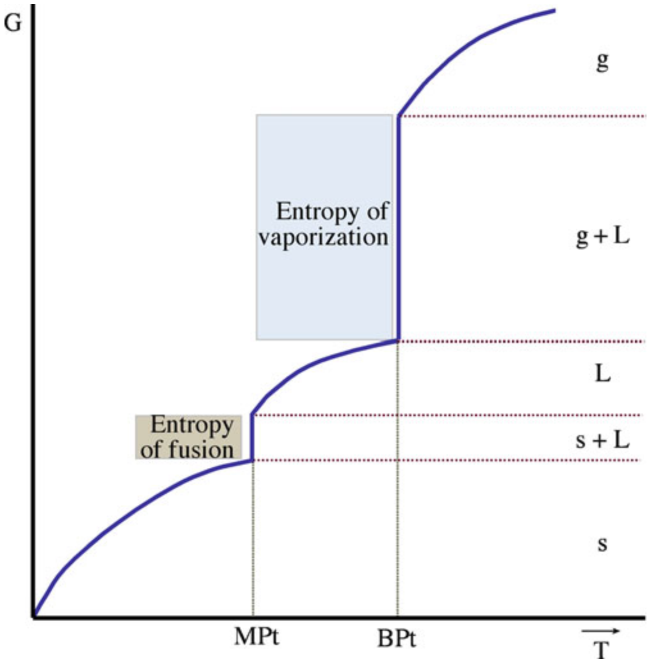


FIGURE 3.5. Variation in Gibbs free energy as a function of temperature. The vertical segments are associated with phase transformations.

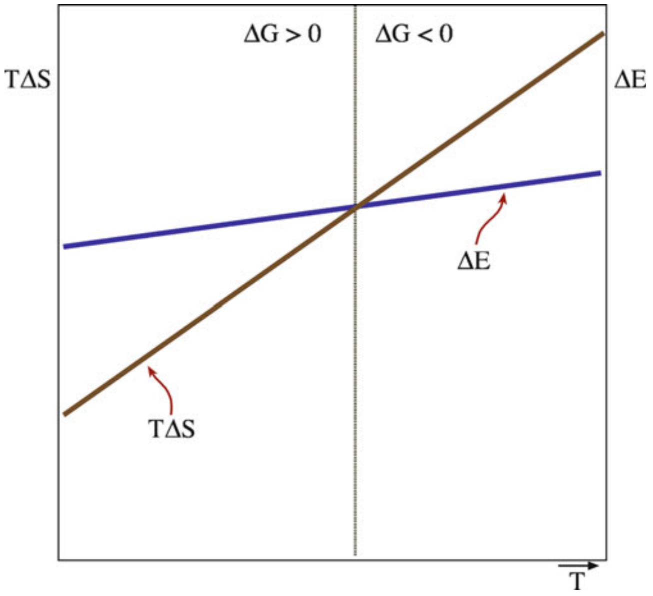


FIGURE 3.6. Effect of temperature on reaction spontaneity. The two lines cross when the energy contribution becomes less than the entropy contribution.

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

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

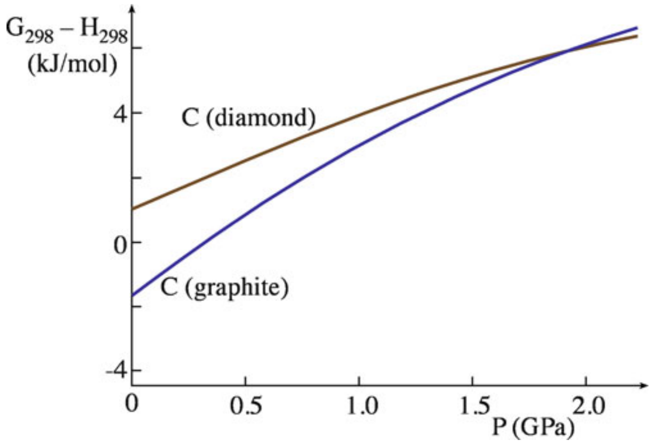


FIGURE 3.7. Pressure dependence of Gibbs free energies of carbon in graphite and diamond. Diamond becomes more stable at high pressures.

3.8.3 Effect of Pressure

Higher pressures favor structures that have a higher density. Their formation involves a decrease in volume (negative ΔV). For instance, diamond ($\rho = 3.51$ g cm^{-3}) is more stable than graphite ($\rho = 2.26$ g cm^{-3}) at very high pressures. At room temperature, graphite transforms 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

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

3.8.4 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 and Al_2O_3 that react to form a spinel. Equilibrium, at constant T and P, is reached in these systems when the chemical potential, μ_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, we get a reaction, the rate of which is determined by kinetics.

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

$$\partial G = V\partial P - S\partial T + \Sigma\mu_i\partial n_i \qquad (3.10)$$

The importance of equation 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: 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

$$k = A\exp - (E_a/RT) \qquad (3.11)$$

where R is the gas constant (8.314 $\mathrm{JK^{-1}\ mol^{-1}}$); 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.

$$\ln k = \frac{E_a}{RT} + \ln A \qquad (3.12)$$

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 (i.e., occur appreciably in minutes or hours) have values of E_a between 50 and 100 kJ. For such reactions, you can use equation 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.

$$D = D_0\exp(-E_a/RT) \qquad (3.13)$$

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

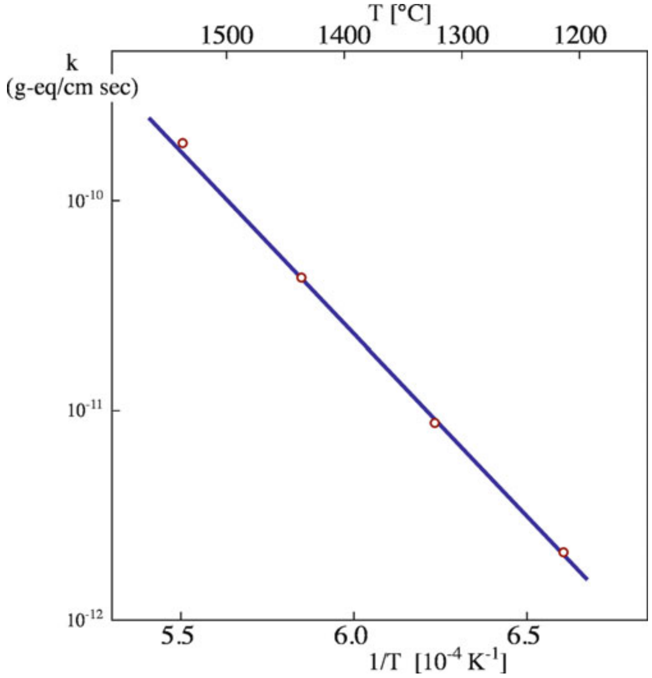


FIGURE 3.8. Arrhenius plot. The slope of the line indicates the activation energy for the process.

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

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 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 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 underpin 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 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 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 with economics. Processes that are slow are usually expensive.

PEOPLE AND HISTORY

Arrhenius, Svante August. He 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 aged 68.

Barkla, Charles Glover (1877–1944). He 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, he proposed an atomic model where electrons could only move in certain stable orbits. He won the Nobel Prize in Physics in 1922 and died in 1962 at age 77.

Boltzmann, Ludwig Eduard. He was born in Vienna in 1844 and died aged 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*. They were working at Bell Labs at the time of their discovery of electron diffraction. Davisson died in 1958 aged 76. Germer died in 1971 at age 75.

de Broglie, Louis. In 1924, he 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). He was born in Würzburg, Germany. He obtained his Ph.D. in 1923 at the University of Munich. His theory of quantum mechanics was published at age 23, and he was awarded the 1932 Nobel Prize in Physics for this theory. 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 aged 74.

Pauli, Wolfgang (1900–1958). 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 at 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. Pauling won the Noble Prize for Chemistry in 1954 and for Peace in 1962. He died in 1994 at age 93.

Schrödinger, Erwin. He was born in Vienna, Austria in 1887. His great discovery, Schrödinger's wave equation, was made in 1926. He won the Nobel Prize in Physics in 1933 for that work. When Hitler came to power in Germany (1933), he moved to England. He 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*. These men were father and son. Rutherford was J.J.'s student at Cambridge. The elder Thomson discovered the electron in 1897 and won the Nobel Prize in Physics in 1906. His son, G.P. Thomson, won the same Nobel Prize in 1937 together with Davisson. He died in 1976 (born 1892). Thus, the father "proved" that electrons were particles, and the son "proved" they were waves.

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.

3.11 In Table 3.3 we highlighted the electron configurations of Cr and Cu. What is special about the electron configurations of these particular elements?

3.12 As you go down a column in the periodic table, you generally find that the electronegativity decreases for the main group elements. In contrast, as you go down a column of transition metal atoms, there is no consistent trend in electronegativity values. Why?

3.13 The Gibbs free energy of formation of Ag_2O at room temperature is -11 kJ and for Cu_2O the corresponding value is -142 kJ. What do these numbers imply about these two oxides?

3.14 Why is temperature so important in ceramics?

3.15 The activation energy for migration of gold nanoparticles on gallium nitride has been determined to be 27 kJ/mol. (1) Convert this number to eV. (2) Would you expect the activation energy to be the same for gold nanoparticles on all ceramics? Briefly justify your answer.

3.16 Discuss the sign used for E that says the reaction is exothermic when EA is positive.

3.17 Using the four journals in question 1.20, give 10 exceptions to the "shading rule" in Figure 3.4.

3.18 Is the crossover in Figure 3.7 what and where you would expect?

3.19 When is 50 kJ/mol approximately equal to 0.5 eV/atom?

3.20 We say that "a useful rule of thumb is that the rate doubles for every 10 K increase in temperature." Discuss this statement.

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