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CHAPTER 2

Knowledge and Comprehension Problems:

Problem 2.1 Describe the laws of (a) multiple proportions and (b) mass conservation as related to atoms and their chemical properties.

Answer 2.1: (a) The law of multiple proportions states that atoms of one pure substance are different from the atoms of other pure substances and, when combined in specific simple fractions, form different compounds. (b) The law of mass conservation states that a chemical reaction is explained by separation, combination, or rearrangement of atoms, and that a chemical reaction does not lead to creation or destruction of matter.

Problem 2.2 How did scientists find out that atoms themselves are made up of smaller particles?

Answer 2.2: Henri Becquerel and Marie and Pierre Curie showed that some atoms spontaneously emit rays and named this phenomenon *radioactivity*. The radiation was shown to consist of α (alpha), β (Beta), and γ (gamma) rays. It was also shown that a and b particles have both charge and mass while g particles have no detectable mass or charge.

Problem 2.3 How was the existence of electrons first verified? Discuss the characteristics of electrons.

Answer 2.3: Joseph J. Thompson, using cathode ray tube experiments, concluded that atoms in all matter are made of smaller particles that are negatively charged. The negatively charged plate (cathode) emits an invisible ray that is attracted by the positively charged plate (anode). The invisible ray is called a cathode ray and is made up of electrons. He also calculated the ratio of mass to charge of these electrons to be 5.60 X 10-19 g/C where *Coulomb*, C, is the unit of electrical charge. Robert Millikan, in his oil-drop experiments, determined the fundamental quantity of charge or the charge of an electron (regardless of the source) to be 1.60×10^{-19} C. For an electron, this quantity of charge is represented by -1. Using the ratio of mass to charge of the electron measured by Thompson and the charge of the electron measured by Millikan, the mass of an electron was determined to be 8.96×10^{-28} g.

Problem 2.4 How was the existence of protons first verified? Discuss the characteristics of protons.

Answer 2.4: Ernest Rutherford bombarded a very thin foil of gold with positively charged a particles. He noticed that many of the a particles pass through the foil without deflection, some

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are slightly deflected, and a few are either largely deflected or completely bounce back. He concluded that 1) most of the atom must be made up of empty space (thus most particles pass through without deflection) and 2) a small neighborhood at the center of the atom, the *nucleus*, houses positively charged particles of its own. He suggested that those alpha particles that deflected intensely or bounced back must have interacted closely with the positively charged nucleus of the atom. The positively charged particles in the nucleus were called *protons*. It was later determined that the proton carries the same quantity of charge as an electron but opposite in sign and has a mass of 1.672×10^{-24} g (1840 times the mass of the electron). For a proton this quantity of charge is represented by +1. Also, since atoms are electrically neutral, they must have an equal number of electrons and protons.

Problem 2.5 What are the similarities and differences among protons, neutrons, and electrons? Compare in detail.

Answer 2.5: Using the information in Table 2.1, one can summarize that protons and neutrons have significantly higher mass, and basically constitute the total mass of the atom (the mass of electron is minimal in comparison). On the other hand, the charge of the atom comes equally from its electrons (negative) and protons (positive). Neutrons are not charged.

Particle	Mass (g)	Charge	
		Coulomb (C)	Charge Unit
Electron	9.10939×10^{-28}	-1.06022×10^{-19}	-1
Proton	1.67262×10^{-24}	$+1.06022 \times 10^{-19}$	+1
Neutron	1.67493×10^{-24}	0	0

Problem 2.6 One mole of iron atoms has a mass of 55.85 grams, without any calculations determine the mass in amu of one iron atom.

Answer 2.6: One mole of iron corresponds to the number of atoms needed to create a mass in units of grams (55.85 grams) numerically equal to the atomic mass in amu of the substance under consideration. Thus one atom of iron has an atomic mass of 55.85 amu.

Problem 2.7 One atom of oxygen has a mass of 16.00 amu, without any calculations determine the mass in grams of one mole of oxygen atoms.

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Answer 2.7: One mole of oxygen corresponds to the number of atoms needed to create a mass in units of grams (16.00 grams) numerically equal to the atomic mass in amu of the substance under consideration. Thus one mole of oxygen has a weight of 16 grams.

Problem 2.8 Define a) atomic number, b) atomic mass, c) atomic mass unit (amu), d) mass number, e) isotopes, f) mole, g) relative atomic mass, h) average relative atomic mass, and i) Avogadro's number.

Answer 2.8:

a) atomic number – the number of protons in the nucleus of an atom is the atomic number (Z).
b) atomic mass – the mass of one atom of a substance expressed in amu.
c) atomic mass unit (amu) - one amu is defined as exactly $1/12^{th}$ the mass of a carbon atom with 6 protons and 6 neutrons.
d) mass number - the sum of protons and neutrons in a nucleus of an atom.
e) isotopes – atoms with the same atomic number but different mass numbers.
f) mole - one mole or gram-mole (mol) of any element is defined as the amount of substance that contains 6.02×10^{23} atoms.
g) relative atomic mass - the mass in grams of one mole of an element is called the *relative atomic mass*, *molar mass*, or the *atomic weight*.
h) average relative atomic mass
i) Avogadro's number – number of atoms in one mole of an element.

Problem 2.9 Explain the law of chemical periodicity.

Answer 2.9: The law of chemical periodicity states that the properties of elements are functions of their atomic number in a periodic manner.

Problem 2.10 What is the nature of visible light? How is the energy released and transmitted in visible light?

Answer 2.10: Light is in the form of electromagnetic radiation. Energy is released and transmitted in the form electromagnetic waves.

Problem 2.11 (a) Rank the following emissions in increasing magnitude of wavelength: microwave oven emissions, radio waves, sun lamp emissions, x-ray emissions, and gamma ray emissions from the sun. (b) Rank the same emissions in terms of frequency. Which emission has the highest energy?

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Answer 2.11:

(a) Increasing wave length : Gamma Ray – x-ray – sun lamp – microwave – radio wave
(b) Increasing frequency of emission: Gamma Ray– x-ray– sun lamp – microwave – radio wave. The highest frequency emission, gamma ray, has the highest energy (E = hn).

Problem 2.12 Describe the Bohr model of the hydrogen atom. What are the shortcomings of the Bohr model?

Answer 2.12: Bohr suggested that electrons travel in circular paths around the nucleus with discrete angular momenta (a product of velocity and radius). Furthermore, he suggested that the energy of the electron is restricted to a specific energy level that places the electron at that fixed circular distance from the nucleus. He called this the orbit of the electron.

Bohr's model worked very well for a simple atom such as hydrogen but it did not explain the behavior of more complex (multi-electron) atoms and left many unanswered questions. Also, Bohr's model required that we know the position and speed (momentum) of a particle at a given instant. However, Werner Heisenberg proposed the uncertainty principle stating that "it is impossible to simultaneously determine the exact position and the exact momentum (product of speed and mass) of a body, for instance an electron. Heisenberg also rejected Bohr's concept of an "orbit" of fixed radius for an electron; he asserted that the best we can do is to provide the probability of finding an electron with a given energy within a given space.

Problem 2.13 Describe the Uncertainty Principle. How does this principle contradict Bohr's model of the atom?

Answer 2.13: The uncertainty principle states that it is impossible to simultaneously determine the exact position and the exact momentum (product of speed and mass) of a body. Any attempt at measurement of, for instance, position would alter the velocity and vice versa. For Bohr's theory to work, he needed the knowledge of the position and momentum of an electron simultaneously.

Problem 2.14 Describe the following terms (give a diagram for each): a) electron density diagram, b) orbital, c) boundary surface representation, and d) radial probability.

Answer 2.14:

a) Electron density diagram - An array of dots representing the probability of finding an electron (electron density) of a given energy level in a given region of space (see Figure 2.7 a).

b) Orbital – not to be confused with Bohr's "orbit" is a wave function that is the solution to the wave equation. An orbital has a characteristic energy level as well as a characteristic distribution of electron density (expressed geometrically in Figure 2.8).

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c) Boundary surface representation - Another way to probabilistically represent the location of an electron with a given energy level is by drawing the boundary inside which we have a 90% chance of finding that electron (see Figure 2.7 b).

d) Radial probability - radial probability also called total probability, considers the probability of the electron being at a spherical layer with respect to the volume of that layer (see Figure 2.7 c).

Problem 2.15 Name and describe all quantum numbers.

Answer 2.15:

1-The Principal Quantum Number, n - represents the principal energy level and only takes on integer values of one or greater than one, n = 1, 2, 3, ... Each principal energy level is also known as a shell representing a collection of subshells and orbitals with the same principal number, n. As n increases, so does the energy of the electron under consideration, indicating that the electron is less tightly bonded to the nucleus (easier to ionize).

2-The Subsidiary Quantum Number, l - within each principal shell, n, there exists a subshell. The shape of the electron cloud or the boundary space of the orbital is determined by this number. The quantum number l may be represented by an integer ranging from 0 to n-1, or by letters.

3-The Magnetic Quantum Number, m_l - represents the orientation of the orbitals within each subshell. The quantum number, m_l - will take on values ranging from + l to – l.

4-The Spin Quantum Number, *ms* – represents the direction of the spin of the electron. The spin quantum number can take on either +1/2 or -1/2.

Problem 2.16 Explain the Pauli's exclusion principle.

Answer 2.16: No more than two electrons can occupy the same orbital of an atom, and the two electrons must have opposite spins. In other words, no two electrons can have the same set of four quantum numbers.

Problem 2.17 Describe (a) the nucleus charge effect and (b) the shielding effect in multi-electron atoms.

Answer 2.17:

(a) The higher the charge of the nucleus (more protons), the higher the attraction force on an electron, and the lower the energy of the electron (a more stable system); this is called the nucleus charge effect.

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(b) The shielding effect takes place when there is more than one outer electron. In this case, the outer electrons repel each other because of their charge similarity. This repulsion energy works against the attraction energy between the nucleus and the electrons. As a result, it is easier to remove these electrons from the nucleus compared to a situation where only one outer electron exists.

Problem 2.18 Describe the terms a) metallic radius, b) covalent radius, c) first ionization energy, d) second ionization energy, e) oxidation number, f) electron affinity, g) metals, i) nonmetals, k) metalloids, and l) electronegativity.

Answer 2.18:

a) Metallic radius- is a measure of the size of an atom equal to half the distance between the nuclei of two adjacent atoms in a solid metallic element.

b) Covalent radius - is a measure of the size of an atom equal to half the distance between the nuclei of the identical atoms within the covalent molecule.

c) First ionization energy (IE1)- the energy required for the removal of the outermost electron in an atom.

d) Second ionization energy - the energy required for the removal of the second outermost electron in an atom after the first outermost electron has already been removed.

e) Oxidation number - the number of outer electrons that an atom can give up or receive through the ionization process.

f) Electron affinity – the tendency to easily accept an outermost electron.

g) Metals – those elements with atoms that have low ionization energies and little to no electron affinity (Groups 1A and 2A are exclusively metallic).

i) Nonmetals – elements with atoms that have a high ionization energy and very high electron affinity (Group 6A and 7A are exclusively nonmetallic).

k) Metalloids – elements that can behave either in a metallic or a nonmetallic manner (some elements in group 3A, 4A, and 5A; see the periodic table).

l) Electronegativity - indicates the degree by which an atom attracts electrons to itself.

Problem 2.19 Compare and contrast the three primary bonds in detail (draw a schematics for each). Explain what the driving force in the formation of such bonds or, in other words, why do atoms want to bond at all?

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Answer 2.19:

Ionic Bonds - metals and nonmetals bond through electron transfer and ionic bonding. Ionic bonding is typically observed between atoms with large differences in their electronegativities; for instance atoms of group 1A or 2A (reactive metals) with atoms of group 6A or 7A (reactive nonmetals). In short, one atom loses an electron and forms a cation, another atom gains the electron lost by the first atom and forms an anion. After the electron transfer process is completed, both atoms will have completed their outer electronic structure and take on the structure of a noble gas. The electrostatic attraction forces between the two ions will then hold the ions together to form an ionic bond.

Covalent Bonds - are typically observed between atoms with small differences in their electronegativities, and mostly between non-metals. At first, the nucleus of one atom attracts the electron cloud of the other; the atoms get closer to each other. As they get close, the two electron clouds interact, and both atoms start to take ownership of both electrons (share electrons). The atoms keep getting closer until they reach the equilibrium point in which the two atoms will form a bond by sharing their electrons, both completing their outer electronic structure, and reaching the lowest state of energy.

Metallic Bonds – during solidification, from a molten state, the atoms of a metal pack tightly together, in an organized and repeating manner. All the atoms contribute their valence electrons to a "sea of electrons" or the "electron charge cloud". These valence electrons (free electrons) are delocalized, move freely in the sea of electrons, and do not belong to any specific atom. The nuclei and the remaining core electrons of tightly packed atoms form a cationic or a positive core. What keeps the atoms together, in solid metals, is the attraction force between the positive ionic core (metal cations) and the negative electron cloud.

The driving for atoms to bond with other atoms through primary bonds is to lower their potential energy levels and become more stable.

Problem 2.20 Describe the factors that control packing efficiency (number of neighbors) in ionic and covalent solids. Give an example of each type of solid.

Answer 2.20: In ionic solids, the number of cations that can pack around an anion (packing efficiency) is determined by two factors: 1) their relative sizes and 2) charge neutrality. Example six Cl^- anions can pack around one Na^+ cation.

In covalent solids the number of neighbors (packing efficiency) around an atom will depend on the bond order (the number of shared pairs). The number of neighbors cannot be greater than four.

Problem 2.21 Describe the five stages leading to formation of an ionic solid. Explain which stages require energy and which stages release energy.

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Answer 2.21:

Stage 1: Solid metal to gaseous metal (atomization) – requires energy – DH^1

Stage 2: Nonmetal molecules to nonmetal atoms – requires energy – DH^2

Stage 3: Metal atoms, removing outer electrons – requires energy – DH^3

Stage 4: Nonmetal atoms, adding outer electrons – produces energy – DH^4

Stage 5: Formation of ionic solid from gaseous ions – produces energy – DH^5

Problem 2.22 Describe a) Hess law, b) lattice energy and b) heat of formation.

Answer 2.22:

(a) Hess Law states that the total heat produced during formation of an ionic solid is the sum of the heats required in each five stage: $DH^0 = DH^1 + DH^2 + DH^3 + DH^4 + DH^5$.
(b) Lattice energy, DH^5, is the energy released when gaseous ions form solid ions due to electrostatic attraction forces.
(c) The total heat, DH^0, is called the heat of formation.

Problem 2. 23 Describe the terms a) shared pair, b) bond order, c) bond energy, d) bond length, e) polar and non-polar covalent bonds, and f) network covalent solid.

Answer 2.23:

a) shared pair – the pair of electrons active in the bond between two covalently bonded atoms.

b) bond order – the number of shared pairs between covalently bonded atoms (maximum of four)

c) bond energy – the energy required to break the bonds between covalently bonded atoms.

d) bond length – the distance between the nuclei of two covalently bonded atoms at the equilibrium point (point of minimum energy).

e) polar and non-polar covalent bonds – if the difference between the electronegativities of the covalently bonded atoms is zero, the bond is non-polar (no dipole). As the difference in electronegativity between the atoms increases, the bonds become polar. This means the shared electron will lean toward the more electronegative element, thus creating a dipole.

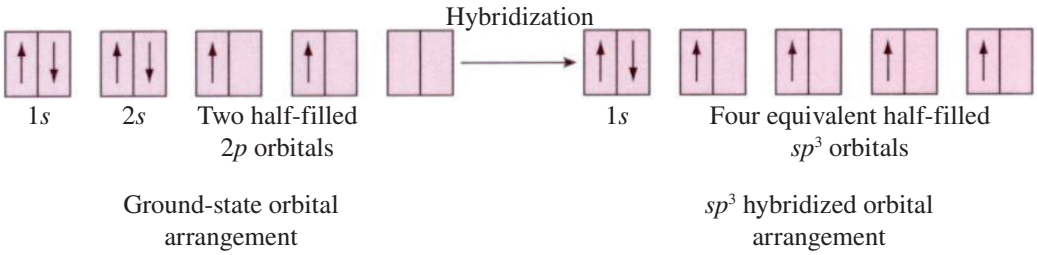
f) network covalent solid – when all atoms in a solid are bonded through covalent bonds in the form of an ordered network (example diamond).

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Problem 2.24 Explain the hybridization process in carbon. Use orbital diagrams.

Answer 2.24: The full 2S orbital is promoted to a 2p orbital to form 4 partially occupied hybrid SP^3 orbitals. Each hybrid orbital will be available for bonding with another atom for a maximum of 4.



Problem 2.25 Describe the properties (electrical, mechanical, etc…) of materials that are exclusively made up of a) ionic bonds, b) covalent bonds, and c) metallic bonds. Name a material for each type.

Answer 2.25:

a) ionic solids – will be hard (difficult to indent), strong (difficult to deform permanently or fail), stiff (difficult to deform elastically), brittle (deform little before they fail), electrically insulating (in the solid state), and have a high melting temperature. Examples are MgO and CsCl.

b) network covalent solids – will be hard (difficult to indent), strong (difficult to deform permanently or fail), stiff (difficult to deform elastically), brittle (deform little before they fail), have a low thermal conductivity, and have a high melting temperature. Examples are quartz and diamond.

c) metallic solids – in a pure state, they are generally more malleable (soft and deformable), and are less stiff than ionic or covalent networked materials. Strength can be increased through alloying. Highly conductive (both heat and electricity). Examples are copper and aluminum.

Problem 2.26 What are secondary bonds? What is the driving force for formation of such bonds? Give example of materials in which such bonds exist.

Answer 2.26: The bonding formed between molecules or atoms of noble gasses. Significantly weaker than primary bonds. The driving force is the electrostatic attraction between polar molecules and atoms.

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Problem 2.27 Discuss various types of mixed bonding.

Answer 2.27: Although different solids may be more inclined to form predominantly by a certain type of bond, other types of bonds will also be normally present. For instance, it is possible to have i) ionic-covalent, ii) metallic-covalent, and iii) metallic-ionic combinations.

Problem 2.28 Define the following terms: a) dipole moment, b) fluctuating dipole, c) permanent dipole, d) van der Waals bonds, and e) hydrogen bond.

Answer 2.28:

a) dipole moment – a moment that produces a temporary or permanent separation of positive and negative charge centers in an atom or a molecule (moment = q*d).

b) fluctuating dipole - Fluctuating dipole bonding is a secondary type of bonding between atoms which contain electric dipoles. These electric dipoles, formed due to the asymmetrical electron charge distribution within the atoms, change in both direction and magnitude with time. This type of bond is electrostatic in nature, and is very weak and nondirectional.

c) permanent dipole - Permanent dipole bonding is also a secondary type of bonding between molecules possessing permanent electric dipoles. The bonds, formed by the electrostatic attraction of the dipoles, are directional in nature. They are slightly stronger than the fluctuating dipole.

d) van der Waals bonds – all bonds involving dipoles are collectively called van der Waals bonds (forces).

e) hydrogen bond – a special class of permanent dipole bonds forming between polar molecules containing hydrogen.

Problem 2.29 The diameter of a soccer ball is approximately 0.279 m (11 inches). The diameter of the moon is 3.476 x 10^6 m. Give an "estimate" of how many soccer balls it will take to cover the surface of the moon (assume moon is a sphere with a flat terrain). Compare this number to Avogadro's number. What is your conclusion?

Solution 2.29

Surface area of the moon = $4\pi R^2$ where R is the radius of the moon

$$A_{s,moon} = 4\pi\left(\frac{3.476}{2}\times 10^6\right)^2 = 3.79\times 10^{13}\,m^2$$

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Cross-sectional area of soccer ball = πR^2

$$A_{cs,ball} = \pi\left(\frac{0.279}{2}\right)^2 = 0.0611 m^2$$

Number of soccer balls required to cover the surface of the moon

$$= \frac{3.79 \times 10^{13}\, m^2}{0.0611 m^2} = 6.22 \times 10^{14} \text{ balls}$$

Avogadro's number is $\sim$ 1 billion times larger.

Problem 2.30 Each quarter produced by the US mint is made up of a copper and nickel alloy. In each coin, there is 0.00740 moles of Ni and 0.0886 moles of copper. (a) What is the total mass of a quarter? (b) What percentage of the mass of a quarter is nickel and what percentage is copper?

Solution 2.30

In each coin:

0.00740 moles of Ni

0.0886 moles of Cu

The masses of Ni & Cu are

$$0.0074 \text{ moles} \times \frac{58.69 \text{ gr}}{\text{mole}} = 0.434 \text{ gr Ni}$$

$$0.0886 \text{ moles} \times \frac{63.55 \text{ gr}}{\text{mole}} = 5.63 \text{ gr Cu}$$

Total mass = 0.434 + 5.63 = 6.06 gr

$$\% \text{ Ni} = \frac{0.434}{6.06} \times 100 = 7.16\%$$

$$\% \text{ Cu} = \frac{5.63}{6.06} \times 100 = 92.9\%$$

Problem 2.31 Sterling silver contains 92.5 wt% silver and 7.5 wt% copper. Copper is added to silver to make the metal stronger and more durable. A small sterling silver spoon has a mass of 100 grams. Calculate the number of copper and silver atoms in the spoon.

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Solution 2.31

Sterling silver: 92.5 wt % Ag + 7.5 wt % Cu

Mass of spoon = 100 gr

Mass of silver = m_{Ag} = 92.5 gr $\Rightarrow$ number of silver atoms $= \dfrac{6.02\times10^{23}\ \text{atoms}/\text{mol}}{107.9\ \text{gr}/\text{mol}} \times 92.5\ \text{g}$

$= 5.2\times10^{23}$ atoms (Ag)

Mass of copper = m_{Cu} = 7.5 gr $\Rightarrow$ number of copper atoms $= \dfrac{6.02\times10^{23}\ \text{atoms}/\text{mol}}{63.55\ \text{gr}/\text{mol}} \times 7.5\ \text{g}$

$= 7.1\times10^{22}$ atoms (Cu)

Total number of atoms in the spoon = 5.91×10^{23} atoms

Note: it is smaller than N_A

Problem 2.32 There are two naturally occurring isotopes for boron with mass numbers 10 (10.0129 amu) and 11 (11.0093 amu); The %abundances are 19.91 and 80.09 respectively. (a) Find the average atomic mass and (b) the relative atomic mass (or atomic weight) of boron. (c) Compare your value with that presented in the periodic table.

Solution 2.32

Boron isotopes : ^{10}B – 10.0129 amu 19.91%

^{11}B – 11.0093 amu 80.09%

Average atomic mass = $\left[(10.0129\times0.1991)+(11.0093\times0.8009)\right]$

$= \left[1.993+8.817\right] = 10.81$ amu

Relative atomic mass = 10.81

Comparing with the value in the periodic table for B, we have a match.

Problem 2.33 A monel alloy consists of 70 wt % Ni and 30 wt % Cu. What are the atom percentages of Ni and Cu in this alloy?

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Solution 2.33 Using a basis of 100 g of alloy, there are 70 g of Ni and 30 g of Cu. The number of gram-moles of each element is thus,

$$\text{No. of gram-moles of Cu} = \frac{30\text{ g}}{63.54\text{ g/mol}} = 0.472\text{ mol}$$

$$\text{No. of gram-moles of Ni} = \frac{70\text{ g}}{58.71\text{ g/mol}} = \underline{1.192\text{ mol}}$$

$$\text{Total gram-moles} = \mathbf{1.664\text{ mol}}$$

The atomic percentages may then be calculated as,

$$\text{Atomic \% Cu} = \left[\frac{0.472\text{ mol}}{1.664\text{ mol}}\right](100\%) = \mathbf{28.4\ \ at\%}$$

$$\text{Atomic \% Ni} = \left[\frac{1.192\text{ mol}}{1.664\text{ mol}}\right](100\%) = \mathbf{71.6\ \ at\%}$$

Problem 2.34 What is the chemical formula of an intermetallic compound that consists of 15.68 wt % Mg and 84.32 wt % Al?

Solution 2.34 The chemical formula, Mg_xAl_y, may be determined based on the gram-mole fractions of magnesium and aluminum. Using a basis of 100 g of intermetallic compound,

$$\text{No. of gram-moles of Mg} = \frac{15.68\text{ g}}{24.31\text{ g/mol}} = 0.645\text{ mol}$$

$$\text{No. of gram-moles of Al} = \frac{84.32\text{ g}}{26.98\text{ g/mol}} = \underline{3.125\text{ mol}}$$

$$\text{Total gram-moles} = \mathbf{3.770\text{ mol}}$$

$$x = \text{Gram-mole fraction of Mg} = \left[\frac{0.645\text{ mol}}{3.770\text{ mol}}\right] = \mathbf{0.17}$$

$$y = \text{Gram-mole fraction of Al} = \left[\frac{3.125\text{ mol}}{3.770\text{ mol}}\right] = \mathbf{0.83}$$

Thus we have $Mg_{0.17}Al_{0.83}$ or, multiplying by 6, $\mathbf{MgAl_5}$.

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Problem 2.35 In order to raise the temperature of 100 grams of water from room temperature (20°C) to boiling temperature (100°C), an energy input of 33,440.0 J is required. If one uses a microwave oven (l, of radiation of 1.20 cm) to achieve this, how many photons of the microwave radiation are required?

Solution 2.35

33,440 joules of energy to raise water temp from 20°C to 100°C

λ microwave = 1.20 cm = 0.012 m

$$E_{mw\ photon} = \frac{h_c}{\lambda_{mw\ photon}} = \frac{\left(6.63\times10^{-34}\ J\cdot sec\right)\left(3.00\times10^{8}\ {}^{m}/_{sec}\right)}{0.012\ m}$$

$E_{mw\ photon} = 1.66 \times 10^{-23}$ J

$$\Rightarrow \text{Number of photons needed} = \frac{33{,}440\ J}{1.66\times10^{-23}\ J} = 2.0\times10^{27}$$

Note: number is greater than N_A by $\sim$ 10,000 times.

Problem 2.36 For problem 2.35, determine the number of photons to achieve the same increase in temperature if (a) ultraviolet (l = 1.0 x 10-8 m), visible (l = 5.0 x 10-7 m), and infrared (l = 1.0 x 10-4 m) lights were used. What important conclusions can you draw from this exercise?

Solution 2.36

Repeating problem 2.35 for UV and visible red lights

a) Ultraviolet, $\lambda = 1\times10^{-8}$ m

$$E_{UV\ photon} = \frac{\left(6.63\times10^{-34}\ J\cdot sec\right)\left(3.00\times10^{8}\ {}^{m}/_{sec}\right)}{1.0\times10^{-8}\ m}$$

$E_{UV\ photon} = 1.989\times10^{-17}$ J

$$\text{number of UV photons needed} = \frac{33{,}440\ J}{1.98\times10^{-17}\ J} = 1.68\times10^{21}$$

b) Visible, $\lambda = 5.0\times10^{-7}$ m

$$E_{vis\ photon} = \frac{\left(6.63\times10^{-34}\ J\cdot sec\right)\left(3.00\times10^{8}\ {}^{m}/_{sec}\right)}{5.0\times10^{-7}\ m}$$

$E_{vis\ photon} = 4.0\times10^{-19}$ J

$$\text{number of vis photons needed} = \frac{33{,}440\ J}{4.0\times10^{-19}\ J} = 8.36\times10^{22}$$

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c) Infrared

$\lambda = 1 \times 10^{-4}$ m

$$E_{IR}\ \text{photon} = \frac{\left(6.63 \times 10^{-34}\ \text{J}\cdot\text{sec}\right)\left(3.00 \times 10^{8}\ \text{m/sec}\right)}{1.0 \times 10^{-4}\ \text{m}}$$

$$E_{IR}\ \text{photon} = 2.0 \times 10^{-21}\ \text{J}$$

$$\text{number of IR photons needed} = \frac{33{,}440\ \text{J}}{2.0 \times 10^{-21}\ \text{J}} = 1.6 \times 10^{25}$$

Note: $E_{UV} > E_{vis} > E_{IR} > E_{mw}$

Problem 2.37 In order for the human eye to detect the visible light, its optical nerves must be exposed to a minimum energy of 2.0 x 10-17 J. (a) Calculate the number of photons of red light needed to achieve this (I = 700 nm). (b) Without any additional calculations, determine if you would need more or less photons of blue light to excite the optical nerves?

Solution 2.37

a) Energy for detection of light by optic nerve = 2.0×10^{-17} J

number of photons of red light needed (λ = 700 nm)

$$\text{Ered} = \frac{\left(6.63 \times 10^{-34}\ \text{J}\cdot\text{sec}\right)\left(3.00 \times 10^{8}\ \text{m/sec}\right)}{700 \times 10^{-9}\ \text{m}} = 2.84 \times 10^{-19}\ \text{J}$$

$$\text{number of red photons} = \frac{2.0 \times 10^{-17}\ \text{J}}{2.84 \times 10^{-19}\ \text{J}} \approx 70.4 \quad \text{photons}$$

(very little energy is needed).

b) Blue light has a lower wavelength 450-495 nm. Thus, each photon of blue light will have more energy. You would need less photons to detect blue light.

Problem 2.38 Represent the wave length of the following rays by comparing each to the length of a physical object (example: a ray with a wavelength of 1m (100 cm) would be approximately that of a baseball bat) : a) rays from a dental ray, b) rays in a microwave oven, c) rays in a sun lamp, d) rays in a heat lamp, and e) an FM radio wave.

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Solution 2.38

Dental X-ray : $\lambda \sim 10^{-1}$ nm (100 times the diameter of an atom)

Micro wave : $\lambda \sim 1\,\text{mm}$ to $1\,\text{m}$ (thickness of 10 sheets of paper to the length of a baseball bat)

Heat lamp : $\lambda \sim 750\,\text{nm}$ to $1\,\text{mm}$ (a bacterial cell to thickness of 10 sheets of paper)
(Infrared)

Sun lamp : $\lambda \sim 400\,\text{nm}$ to $10\,\text{nm}$ (size of a virus)
(UV)

FM radio : $\lambda \sim 1\,\text{m}$ to $10\,\text{m}$ (baseball bat to a flagpole)
(radio wave)

Problem 2.39 For the rays in problem 2.38, without any calculations, rank them in increasing order of the energy of the radiation.

Solution 2.39

As wavelength increases, energy decreases

As wavelength decreases, energy increases

FM radio → microvave → heat lamp → sun lamp → X ray

(low energy) (high energy)

Problem 2.40 In a commercial x-ray generator, a stable metal such as copper (Cu) or tungsten (W) is exposed to an intense beam of high-energy electrons. These electrons cause ionization events in the metal atoms. When the metal atoms regain their ground state they emit x-rays of characteristic energy and wavelength. For example, a "tungsten" atom struck by a high-energy electron may lose one of its K shell electrons. When this happens, another electron, probably from the tungsten L shell will "fall" into the vacant site in the K shell. If such a 2p → 1s transition occurs in tungsten, a tungsten K_α x-ray is emitted. A tungsten K_α x-ray has a wavelength λ of 0.02138 nm. What is its energy? What is its frequency?

Solution 2.40

$$E = \frac{hc}{\lambda} = \frac{(6.63\times10^{-34}\ \text{J}\cdot\text{s})(3.00\times10^{8}\ \text{m/s})}{(0.02138\ \text{nm})(10^{-9}\ \text{m/nm})} = \mathbf{9.30\times10^{-15}\ J}$$

$$\nu = \frac{\text{E}}{\text{h}} = \frac{9.30\times10^{-15}\ \text{J}}{6.63\times10^{-34}\ \text{J}\cdot\text{s}} = \mathbf{1.40\times10^{19}\ Hz}$$

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Problem 2.41 A hydrogen atom exists with its electron in the $n = 4$ state. The electron undergoes a transition to the $n = 3$ state. Calculate (*a*) the energy of the photon emitted, (*b*) its frequency, and (*c*) its wavelength in nanometers (nm).

Solution 2.41

(a) Photon energy emitted is:

$$\Delta E = \Delta\left[\frac{-13.6}{n^2}\right] = \left[\frac{-13.6}{4^2}\right] - \left[\frac{-13.6}{3^2}\right] = \mathbf{0.66\ eV = 1.06 \times 10^{-19}\ J}$$

(b) Photon frequency is found as:

$$\nu = \frac{\Delta E}{h} = \frac{1.06 \times 10^{-19}\ \text{J}}{6.63 \times 10^{-34}\ \text{J}\cdot\text{s}} = \mathbf{1.6 \times 10^{14}\ Hz}$$

(c) The wavelength is given as:

$$\lambda = \frac{hc}{\Delta E} = \frac{(6.63 \times 10^{-34}\ \text{J}\cdot\text{s})(3.00 \times 10^{8}\ \text{m/s})}{(1.06 \times 10^{-19}\ \text{J})(10^{-9}\ \text{m/nm})} = \mathbf{1876\ nm}$$

Problem 2.42 A hydrogen atom exists with its electron in the $n = 6$ state. The electron undergoes a transition to the $n = 2$ state. Calculate (*a*) the energy of the photon emitted, (*b*) its frequency, and (*c*) its wavelength in nanometers.

Solution 2.42

(a) Photon energy emitted is:

$$\Delta E = \Delta\left[\frac{-13.6}{n^2}\right] = \left[\frac{-13.6}{6^2}\right] - \left[\frac{-13.6}{2^2}\right] = \mathbf{3.02\ eV = 4.84 \times 10^{-19}\ J}$$

(b) Photon frequency is found as:

$$\nu = \frac{\Delta E}{h} = \frac{4.84 \times 10^{-19}\ \text{J}}{6.63 \times 10^{-34}\ \text{J}\cdot\text{s}} = \mathbf{7.3 \times 10^{14}\ Hz}$$

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(c) The wavelength is given as:

$$\lambda = \frac{hc}{\Delta E} = \frac{(6.63\times10^{-34}\ \text{J}\cdot\text{s})(3.00\times10^{8}\ \text{m/s})}{(4.84\times10^{-19}\ \text{J})(10^{-9}\ \text{m/nm})} = \mathbf{410\ nm}$$

Problem 2.43 Using the information given in Examples 2.4 and 2.5 determine the uncertainty associated with the electron's position if the uncertainty in determining its velocity is 1%. Compare the calculated uncertainty in the position with the estimated diameter of the atom. What is your conclusion?

Solution 2.43

Speed of electron = 16.67 % of speed of light

$$= 0.166 \times 3 \times 10^{8} = 50.0 \times 10^{6}\ \text{m/sec}$$

1% uncertainty in measurement of speed = $0.01 \times 50.0 \times 10^{6} = 500 \times 10^{3}$

Uncertainty in position $\Delta x \geq \dfrac{h}{4\pi\, m\, \Delta u} = \dfrac{6.62\times10^{-34}\ \text{kg.m}^2/\text{s}}{4\,\pi\left(9.11\times10^{-31}\ \text{kgr}\right)\times(500\times10^{3}\ \text{kgr})}$

$\Delta x \geq 1.15 \times 10^{-10}\ \text{m} \approx 0.115\ \text{nm}$

Note: diameter of atom is $\sim$ 0.1 nm. Uncertainty in the position of electron will be close to the size of the atom.

Problem 2.44 Repeat problem 2.43 to determine the uncertainty associated with the electron's position if the uncertainty in determining its velocity is 2%. Compare the calculated uncertainty in the position with that of problem 2.37. What is your conclusion?

Solution 2.44

2% uncertainty associated with speed

$= 0.02 \times 50.0 \times 10^{6}\ \text{m/s} = 1000 \times 10^{3}\ \text{m/s}$

$\Rightarrow$ The corresponding uncertainty in position will be $\Delta x \geq \dfrac{6.62\times10^{-34}\ \text{kg.m}^2/\text{s}}{4\,\pi\left(9.11\times10^{-31}\ \text{kgr}\right)\left(1000\times10^{3}\text{m/s}\right)}$

$\Delta x \geq 5.268\times10^{-11}\ \text{m} \approx 0.0526\ \text{nm}$

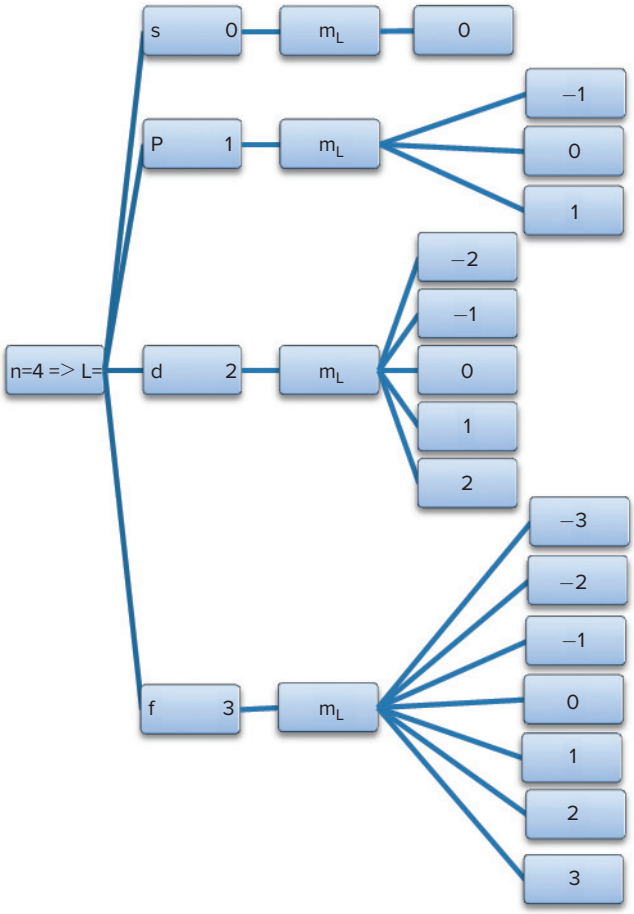
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Note: the uncertainty in position decreases to the radius of the atom as the uncertainty in the speed of electron increases to 2%.

Problem 2.45 For the principal quantum number, n, of value 4, determine all other possible quantum numbers for l and m_l.

Solution 2.45



Problem 2.46 For each pair of n and l given below, give the sublevel name, possible values of m_l, and the corresponding # of orbitals.

(a) n=1, l=0

(b) n=2, l=1

(c) n=3, l=2

(d) n=4, l=3

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Solution 2.46

				Sublevel name	m_l	number of orbitals
a)	n=1,	l=0	⇒	1s	0	1
b)	n=2,	l=1	⇒	2p	-1,0,+1	3
c)	n=3,	l=2	⇒	3d	-2,-1,0,+1,+2	5
d)	n=4,	l=3	⇒	4f	-3,-2,-1,0,+1,+2,+3	7

Problem 2.47 Determine if the following combinations of quantum numbers are acceptable.

(a) n=3, l=0, m_l=+1

(b) n=6, l=2, m_l=-3

(c) n=3, l=3, m_l=-1

(d) n=2, l=1, m_l=+1

Solution 2.47

a)	n=3,	l=0	m_l = +1 :	not possible,	m_l = 0
b)	n=6,	l=2	m_l = -3 :	not possible,	-2 < m_l < +2
c)	n=3,	l=3	m_l = -1:	not possible,	l = 0,1,2 for n=3
d)	n=2	l=1	m_l = +1 :	possible	

Problem 2.48 In each row (a through d) there is only one piece of information that is wrong, highlight the information that is wrong (explain why).

	n	l	**m_l**	**Name**
(a)	**3**	**0**	**1**	**3s**
(b)	**2**	**1**	**-1**	**2s**
(c)	**3**	**1**	**+2**	**3d**
(d)	**3**	**3**	**0**	**4f**

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Solution 2.48

(Note: only one entry is wrong)

	n	l	m_l	name		
a)	3	0	[1]	3s	:	$m_l \rightarrow$ 0 since l=0
b)	2	1	-1	[2s]	:	name $\rightarrow$ 2p since l=1
c)	3	[1]	+2	3d	:	l $\rightarrow$ 2 since m_l > +2 and name is 3d
d)	[3]	3	0	4f	:	n $\rightarrow$ 4 since l=3 and name is 4f

Problem 2.49 Determine the four quantum numbers for the 3rd, 15th, and 17th electrons of the Cl atom.

Solution 2.49

Cl has 17 electrons

3rd electron of Cl atom: n = 2, l = 0, s, $m_l = 0$ $m_s = +1/2$

15th electron of Cl atom: n = 3, l = 1, p, $m_l = +1$ $m_s = +1/2$

17th electron of Cl atom: n = 3,l = 1,p, $m_l = 0$ $m_s = -1/2$

Problem 2.50 Determine the electron configuration and group number of the atom in the ground state based on the given partial (valence level) orbital diagram. Identify the element.

Solution 2.50

The outer electron structure is $4s^2p^1$.

This means 28 subvalent electrons.

Total number of electrons will be 31.

The element is Ga (Gallium)

(Alternatively, the element is in the 3rd column since it has 3 outer electrons and fourth period since $4s^24p^7 \rightarrow$ Ga)

Problem 2.51 Write the electron configurations of the following elements by using *spdf* notion:

(*a*) yttrium, (*b*) hafnium, (*c*) samarium, (*d*) rhenium.

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Solution 2.51

(a) Y (Z = 39): [Kr] $4d^1 5s$ (c) Sm (Z = 62): [Xe] $4f^6 6s^2$
(b) Hf (Z = 72): [Xe] $4f^{14} 5d^2 6s^2$ (d) Re (Z = 75): [Xe] $4f^{14} 5d^5 6s^2$

Problem 2.52 Write the electron configuration of the following ions by using *spdf* notation:

(*a*) Cr^{2+}, Cr^{3+}, Cr^{6+}; (*b*) Mo^{3+}, Mo^{4+}, Mo^{6+}; (*c*) Se^{4+}, Se^{6+}, Se^{2-}.

Solution 2.52

(a)	Cr	[Ar] $3d^5 4s^1$	(b)	Mo	[Kr] $4d^5 5s^1$	(c)	Se	[Ar] $3d^{10} 4s^2 4p^4$
	Cr^{2+}	[Ar] $3d^4$		Mo^{3+}	[Kr] $4d^3$		Se^{4+}	[Ar] $3d^{10} 4s^2$
	Cr^{3+}	[Ar] $3d^3$		Mo^{4+}	[Kr] $4d^2$		Se^{6+}	[Ar] $3d^{10}$
	Cr^{6+}	[Ar]		Mo^{6+}	[Kr] $4d^3$		Se^{2-}	[Ar] $3d^{10} 4s^2 4p^6$

Problem 2.53 Rank the following atoms in (a) increasing atomic size and (b) decreasing first ionization energy, IE1. Use only the periodic table to answer the questions. Check your answer using Figures 2.10 and 2.11.

i) K, Ca, Ga
ii) Ca, Sr, Ba
iii) I, Xe, Cs

Solution 2.53

i)

a) Atomic size (increasing)

As we move to the left in a period, the atomic size increases

Ga : period 4 group 3
Ca: period 4 group 2
K: period 4 group 1

$\Rightarrow$ Ga, Ca, K (increasing order)

b) Ionization energy (decreasing)

As we move to the left in a period, the ionization energy increases.

Ga, Ca, K (decreasing order)

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ii)

a) Atomic size (increasing)

Ca : period 4 group 2

Sr: period 5 group 2

Ba: period 6 group 2

As we move down in a group, atomic size increases

$\Rightarrow$ Ca, Sr, Ba (increasing size)

b) Ionization energy (decreasing)

Ionization energy will have the opposite trend as that of atomic size.

(as we move down in a group, ionization energy decreases)

Thus, Ca, Sr, Ba (decreasing)

iii)

a) Atomic size (increasing)

I : period 5 group 7

Xe: period 5 group 8

Cs: period 6 group 1

In period 5, Xe (group 8) will have a smaller radius than I (group 7).

Cs in period 6 will be larger than both.

Cs, I, Xe (increasing size)

b) Ionization energy (decreasing)

In period 5, I will have a lower ionization energy than Xe.

Cs, in period 6, will have the lowest ionization energy.

Xe, I, Cs (decreasing)

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Problem 2.54 Rank the following atoms in (a) increasing atomic size and (b) decreasing first ionization energy, IE1. Use only the periodic table to answer the questions. Check your answer using Figures 2.10 and 2.11.

i) Ar, Li, F, O, Cs C

ii) Sr, H, Ba, He, Mg, Cs

Solution 2.54

a) Increasing atomic size

i)

Ar	:	period 3,	group 8
Li	:	period 2,	group 1
F	:	period 2,	group 7
O	:	period 2,	group 6
Cs	:	period 6,	group 1
C	:	period 2,	group 4

Period 2 elements will be smaller than period 3, and both will be smaller than period 6.

	period 2	Li, F, O, C	↓
1st organization	period 3	Ar	Increasing size
	Period 6	Cs	

Within each period, the size decreases as you move to the right

2nd organization	Li	F
	C,	O
Increasing size ↓	O,	C
	F,	Li

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Argon (Ar), the last element in period 3, will be smaller than Li but larger than F

F

O

C

Ar

Li

Cs

Cs, will be the largest since it is in period 6.

Problem 2.55 The first ionization energies of two atoms with electronic configurations (a) $1S^2 2s^2 2p^6$ and (b) $1s^2 2s^2 2p^6 3s^1$ are given to be 2080 kJ/mol and 496 kJ/mol. Determine which IE1 belongs to which electronic structure and justify your answer.

Solution 2.55

$1s^2 2s^2 2p^6$	This atom belongs to group VIII. Its outer electron structure is complete. It will be difficult to ionize this atom. Thus, it must have a high IE_1.
$1s^2 2s^2 2p^6 3s^1$	This atom belongs to group I, period III. There is a single electron in n=3. It will be easier to ionize, so it must have a lower IE_1.

Problem 2.56 The first ionization energies of three atoms with electronic configurations (a) $[He]2s^2$, (b) $[Ne]3s^1$, and (c) $[Ar]4s^1$ and (d) $[He]2S^1$ are given to be 496 kJ/mol, 419 kJ/mol, 520 kJ/mol, and 899 kJ/mol. Determine which IE1 belongs to which electronic structure and explain your answer.

Solution 2.56

$[He]\ 2s^2$

$[Ne]3s^1$

$[Ar]4s^1$

$[He]2s^1$

$[He]2s^1$, $[Ne]3s^1$ and $[Ar]4s^1$ all belong to group I. The atom that is located in the lowest period will have the lowest IE_1. Thus,

$IE_1\ [Ar]4s^1 = 419$ KJ/mol

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IE_1 $[Ne]3s^1$ = 496 KJ/mol

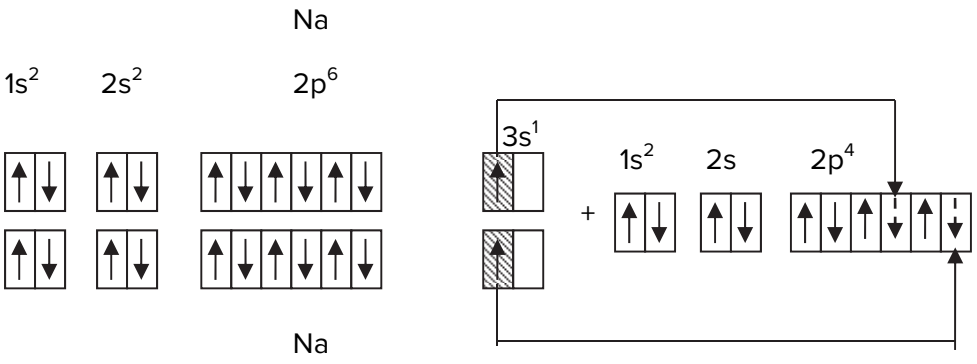
IE_1 $[He]2s^1$ = 520 KJ/mol

$[He]2s^2$ belongs to the second group in period II. Thus, its IE_1 must be higher than $[HE]2s^1$. And so, IE_1 $[He]2s^1$ = 899 KJ/mol

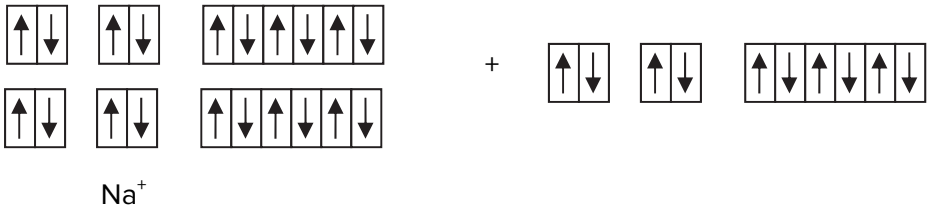
Problem 2.57 Similar to Figure 2.15 use (a) orbital diagrams and (b) Lewis symbols to explain the formation of Na^+ and O^{2-} ions and the corresponding bonding. What is the formula of the compound?

Solution 2.57

a) Orbital diagram



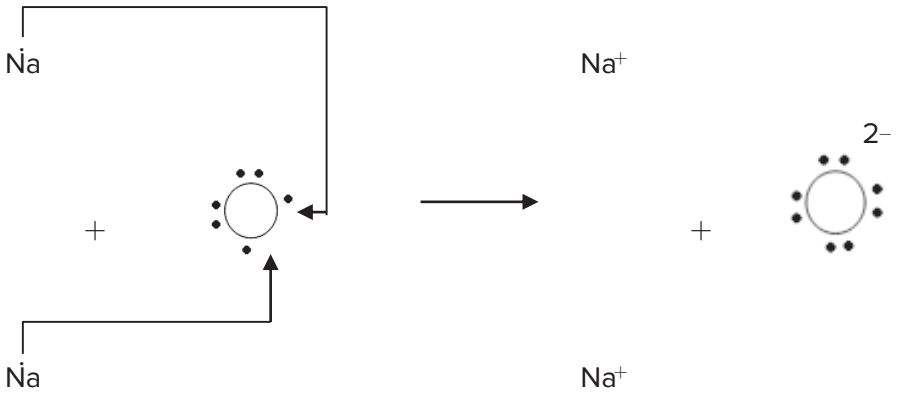
⇒ Na^+ O^{2-}



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b) Lewis symbols



Chemical formula = Na_2O

Problem 2.58 Calculate the attractive force $(\bullet \rightarrow\leftarrow \bullet)$ between a pair of Ba^{2+} and S^{2-} ions that just touch each other. Assume the ionic radius of the Ba^{2+} ion to be 0.143 nm and that of the S^{2-} ion to be 0.174 nm.

Solution 2.58 The attractive force between the ion pair is found by applying Coulomb's law,

$$F_{\text{attractive}} = \frac{-Z_1 Z_2 e^2}{4\pi\varepsilon_o a_o^2}$$

Where $Z_1 = +2$ for Ba^{2+}, $Z_2 = -2$ for S^{2-}, and

$$a_o = r_{Ba^{2+}} + r_{S^{2-}} = 0.143\text{ nm} + 0.174\text{ nm} = 0.317\text{ nm} = 3.17 \times 10^{-10}\text{ m}$$

Substituting,

$$F_{\text{attractive}} = \frac{-(+2)(-2)(1.60 \times 10^{-19}\text{ C})^2}{4\pi(8.85 \times 10^{-12}\text{ C}^2/\text{N}\cdot\text{m}^2)(3.17 \times 10^{-10}\text{ m})^2} = \mathbf{9.16 \times 10^{-9}\ N}$$

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Problem 2.59 Calculate the net potential energy for a Ba^{2+} S^{2-} ion pair by using the *b* constant calculated from Prob. 2.58. Assume $n = 10.5$.

Solution 2.59 The repulsive energy constant *b* is:

$$b = \frac{-F_{\text{Repulsive}} a_o^{\,n+1}}{n} = \frac{-(-F_{\text{Attractive}}) a_o^{\,n+1}}{n} = \frac{-(-9.16\times10^{-9}\ \text{N})(3.17\times10^{-10}\ \text{m})^{11.5}}{10.5}$$
$$= 5.045\times10^{-119}\ \text{N}\cdot\text{m}^{10}$$

Thus the net potential energy between the ions is,

$$E_{Ba^{2+}S^{2-}} = \frac{+Z_1 Z_2 e^2}{4\pi\varepsilon_o a_o} + \frac{b}{a_o^n}$$
$$= \frac{+(+2)(-2)(1.60\times10^{-19}\ \text{C})^2}{4\pi(8.85\times10^{-12}\ \text{C}^2/(\text{N}\cdot\text{m}^2))(3.17\times10^{-10}\ \text{m})} + \frac{5.045\times10^{-119}\ \text{N}\cdot\text{m}^{10}}{(3.17\times10^{-10}\ \text{m})^{10.5}}$$
$$= (-2.905\times10^{-18}\ \text{J}) + (2.765\times10^{-19}\ \text{J}) = \mathbf{-2.63\times10^{-18}\ J}$$

Problem 2.60 If the attractive force between a pair of Cs^+ and I^- ions is 2.83×10^{-9} N and the ionic radius of the Cs^+ ion is 0.165 nm, calculate the ionic radius of the I^- ion in nanometers.

Solution 2.60 From Coulomb's law,

$$a_o = \sqrt{\frac{-Z_1 Z_2 e^2}{4\pi\varepsilon_o F_{\text{Attractive}}}} = \sqrt{\frac{-(+1)(-1)(1.60\times10^{-19}\ \text{C})^2}{4\pi(8.85\times10^{-12}\ \text{C}^2/(\text{N}\cdot\text{m}^2))(2.83\times10^{-9}\ \text{N})}}$$
$$= 2.852\times10^{-10}\ \text{m} = 0.2852\ \text{nm}$$

The ionic radius of iodine is thus,

$$r_{I^-} = a_o - r_{Cs^+} = 0.285\ \text{nm} - 0.165\ \text{nm} = \mathbf{0.120\ nm}$$

Problem 2.61 For the each pair of compounds presented below, determine which has the higher lattice energy (more negative). Explain your answer. Also, which of the five ionic compound do you think has the highest melting temperature and why? Verify your answers.

(a) LiCl and CsCl
(b) CsCl and RbCl
(c) LiF and MgO
(d) MgO and CaO

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Solution 2.61

a) LiCl CsCl : Cl is common to both compounds. As the size of the cation increases (Cs > Li), the lattice energy decreases. Thus, LiCl will have higher lattice energy than CsCl.

b) CsCl RbCl : Cl is common to both compounds. The size of Cs is larger than Rb (Cs >Rb). Thus, RbCl has higher lattice energy than CsCl.

c) LiF MgO : Mg^{++} and O^{--} have a higher ionic charge than Li^{+} and F^{-}. Thus, MgO will have higher a lattice energy.

d) MgO CaO : O is common to both compounds. All ions have an ionic charge of 2: Mg^{++}, O^{--} and Ca^{++}. However, Ca^{++} is larger in radius than Mg^{++}. Thus, MgO will have higher lattice energy.

Overall, MgO will have the highest lattice energy, and therefore has the highest melting point.

Problem 2.62 Calculate the lattice energy for the formation of solid NaF if the following information is given. What does the calculated lattice energy tell you about the material?

109 kJ is required to convert solid Na to gaseous Na

243 kJ is required to convert gaseous F2 to two monatomic F atoms

496 kJ is required to remove the 3s1 electron of Na (form Na+ cation)

-349 kJ of energy (energy is released) to add an electron to the F (form Na- anion)

-411 kJ of energy to form gaseous NaF (heat of formation of NaF)

Solution 2.62

NaF

Atomization of Na,	ΔH^1	=	+109kJ	(energy input)
Atomization of F_2,	ΔH^2	=	+243kJ	(energy input)
Removing $3s^1$ electrons,	ΔH^3	=	+496kJ	(energy input)
Adding electron to F,	ΔH^4	=	-349 kJ	(energy released)
To form ionic solid from gaseous NaF,	ΔH^5	=	lattice energy	(unknown)
Heat of formation for NaF		=	-411 kJ (ΔH^0)	

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$\Delta H^0 = \Delta H^1 + \Delta H^2 + \Delta H^3 + \Delta H^4 + \Delta H^5$

$-411 = +109 + 243 + 496 - 349 + \Delta H^5$

$\Rightarrow \Delta H^5 = -910$ kJ

As solid NaF is formed, 910 kJ is released.

Problem 2.63 Calculate the lattice energy for the formation of solid NaCl if the following information is given. What does the calculated lattice energy tell you about the material?

109 kJ is required to convert solid Na to gaseous Na

121 kJ is required to convert gaseous Cl^2 to two monatomic Cl atoms

496 kJ is required to remove the $3s^1$ electron of Na (form Na+ cation)

-570 kJ of energy (energy is released) to add an electron to the Cl

-610 kJ of energy to form gaseous NaCl (heat of formation of NaCl)

Solution 2.63

NaCl

Atomization of Na,	ΔH^1	=	+109kJ	(energy input)
Atomization of Cl_2,	ΔH^2	=	+121kJ	(energy input)
Removing $3s^1$ electrons,	ΔH^3	=	+496kJ	(energy input)
Adding electron to Cl,	ΔH^4	=	-570 kJ	(energy released)
To form ionic solid from gaseous NaCl,	ΔH^5	=	lattice energy	(unknown)
Heat of formation for NaCl		=	-610 kJ (ΔH^0)	

$\Delta H^0 = \Delta H^1 + \Delta H^2 + \Delta H^3 + \Delta H^4 + \Delta H^5$

$-610 = +109 + 121 + 496 - 570 + \Delta H^5$

$\Rightarrow \Delta H^5 = -766$ kJ

As solid NaF is formed, 766 kJ is released.

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Problem 2.64 For each bond in the following series of bonds, determine the bond order, rank bond length, and rank bond strength. Use only the periodic table. Explain your answers.

(a) S-F; S-Br; S-Cl

(b) C-C; C=C; $C=C^-$

Solution 2.64

a) S-F; S-Br; S-Cl

Note, S is the common element. All bonds have order "one" since all have one shared pair.

Since the diameter of Br is larger than Cl, and Cl is larger than F, the bond length of S-Br will be greater than S-Cl, and these will be greater than S-F.

Bond strength will have an inverse relation with bond length.

Thus, S-F is stronger than S-Cl, and both are stronger than S-Br

b) C ≡ C; C = C; C-C

The bond order is directly related to number of shared pairs.

C ≡ C, bond order of +3

C = C, bond order of +2

C – C, bond order of +1

As the bond order increases, bond length decreases.

Thus, C ≡ C has a smaller bond length than C = C, and both are smaller than than C – C.

Bond strength is inversely related to bond length. Therefore, C ≡ C is the strongest, and C – C is the weakest.

Problem 2.65 Rank the following covalently bonded atoms according to the degree of polarity:

C-N; C-C; C-H; C-Br.

Solution 2.65

Note: the electronegativities below the symbol

C – C non polar, no difference in electronegativities
2.5 2.5

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C – N high polarity – electron shared more by N
2.5 3.0

C – H some polarity – electon shared by C
2.5 2.1

C – Br high polarity – electron shared more by C
2.5 2.0

Polarity Increasing

C – C → C – H → C – N → C – Br

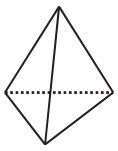
Problem 2.66 List the number of atoms bonded to a C atom that exhibits sp^3, sp^2, and *sp* hybridization. For each, give the geometrical arrangement of the atoms in the molecule.

Solution 2.66 sp^3 hybridization: Four atoms are bonded to a central carbon atom in a tetrahedral arrangement. An example is methane, CH_4.

sp^2 hybridization: Three atoms are bonded to a carbon atom in a planar arrangement. An example is ethylene, CH_2: CH_2.

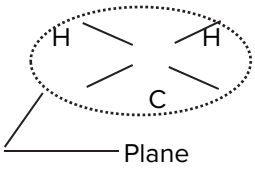
sp hybridization: Two atoms are bonded to a carbon atom in a linear arrangement. An example is acetylene, CH:CH.

Methane



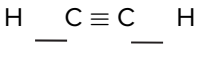
Tetrahedron

Ethylene



Plane

Acetylene



Linear

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Problem 2.67 Is there a correlation between the electron configurations of the elements potassium

(Z = 19) through copper (Z = 29) and their melting points? (See Tables 2.7).

Solution 2.67 A possible correlation between the melting points and the electron configurations of the elements from scandium (Z = 21) through copper (Z = 29) is that unpaired 3*d* electrons cause covalent hybridized bonds, and hence give higher melting points to these transition metals.

Problem 2.68 Compare the percentage ionic character in the semiconducting compounds CdTe and InP.

Solution 2.68 Applying Pauling's equation to CdTe and InP compounds can help calculate ionic character. This equation is:

$$\%ionic\,character = \left(1 - e^{-0.25(X_a - X_b)^2}\right)(100\%)$$

where Xa and Xb represent the electronegativities of the atoms. Looking at Figure 2.14, we see the eletronegativities are as follows:

Cd= 1.7, Te= 2.1, In= 1.7, P= 2.1

Therefore, when solving the equation using these electronegativities, the %ionic character would be the same for the two compounds.

$$\%ionic\,character = \left(1 - e^{-0.25(1.7-2.1)^2}\right)(100\%) = 4\%$$

Problem 2.69 ^{39}K, ^{40}K, and ^{41}K are the three isotopes of potassium. If ^{40}K has the lowest %abundance, which other isotope has the highest?

Solution 2.69
Note, from the periodic table, that the relative atomic mass of K is 39.10 grams. This number is much closer to 39_K than to 40_K. Thus, given that 41_K is the last abundant, 39_K must be the most abundant.

Problem 2.70 Most modern scanning electron microscopes (SEMs) are equipped with energy dispersive x-ray detectors for the purpose of chemical analysis of the specimens. This x-ray analysis is a natural extension of the capability of the SEM because the electrons that are used to form the image are also capable of creating characteristic x-rays in the sample. When the

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electron beam hits the specimen, x-rays specific to the elements in the specimen are created. These can be detected and used to deduce the composition of the specimen from the well-known wavelengths of the characteristic x-rays of the elements. For example:

Element	Wavelength of K_α x-rays
Cr	0.2291 nm
Mn	0.2103 nm
Fe	0.1937 nm
Co	0.1790 nm
Ni	0.1659 nm
Cu	0.1542 nm
Zn	0.1436 nm

Suppose a metallic alloy is examined in an SEM and three different x-ray energies are detected. If the three energies are 7492, 5426, and 6417 eV, what elements are present in the sample? What would you call such an alloy? (Look ahead to Chap. 9 in the textbook.)

Solution 2.70 The elements may be identified by calculating their respective wavelengths.

$$\text{(a)} \quad \lambda = \frac{hc}{E} = \frac{(6.63\times10^{-34}\ \text{J}\cdot\text{s})(3.00\times10^{8}\ \text{m/s})}{(7492\ \text{eV})(1.60\times10^{-19}\ \text{J/eV})}$$
$$= 1.659\times10^{-10}\ \text{m} = 0.1659\ \text{nm} \quad \Rightarrow \quad \textbf{Ni}$$

From the table provided, a wavelength of 0.1659 nm corresponds to nickel, Ni.

$$\text{(b)} \quad \lambda = \frac{hc}{E} = \frac{(6.63\times10^{-34}\ \text{J}\cdot\text{s})(3.00\times10^{8}\ \text{m/s})}{(5426\ \text{eV})(1.60\times10^{-19}\ \text{J/eV})}$$
$$= 2.291\times10^{-10}\ \text{m} = 0.2291\ \text{nm} \quad \Rightarrow \quad \textbf{Cr}$$

From the table provided, a wavelength of 0.2291 nm corresponds to chromium, Cr.

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(c) $$\lambda = \frac{hc}{E} = \frac{(6.63\times10^{-34}\ \text{J}\cdot\text{s})(3.00\times10^{8}\ \text{m/s})}{(6417\ \text{eV})(1.60\times10^{-19}\ \text{J/eV})}$$
$$= 1.937\times10^{-10}\ \text{m} = 0.1937\ \text{nm} \quad \Rightarrow \quad \textbf{Fe}$$

From the table provided, a wavelength of 0.1937 nm corresponds to iron, Fe.

The elements present, nickel, chromium, and iron, are the primary constituents of the austenitic stainless steels.

Problem 2.71 According to section 2.5.1, in order to form monatomic ions from metals and nonmetals, energy must be added. However, we know that primary bonds form because the involved atoms want to lower their energies. Why then do ionic compounds form?

Solution 2.71
Although energy is added during atomization of metals and non metals, when solid ionic materials are formed, a significant amount of energy is released. The activity will result in a net release of energy (lattice energy). Thus, the energy of the involved atoms is lowered.

Problem 2.72 Of the noble gases Ne, Ar, Kr, and Xi, which should be the most chemically reactive?

Solution 2.72 Xenon should be most reactive since its outermost electrons ($5s^2 6p^6$) are further away from the nucleus than the other noble gases, and thus easier to remove.

Problem 2.73 The melt temperature of Na is (89°C) is higher than the melt temperature of K (63.5°C). Can you explain this in terms of the differences in electronic structure?

Solution 2.73
The electronic structure of Na is $1s^2\ 2s^2\ 2p^6\ 3s^1$ while that of K is $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^1$.
The outer electrons in K are farther from the nucleus and thus easier to remove. For this reason, K has a lower melting temp than Na.

Problem 2.74 The melt temperature of Li (180°C) is significantly lower than the melt temperature of its neighbor Be (1287°C). Can you explain this in terms of the differences in electronic structure?

Solution 2.74 The electronic structure of Li is $1s^2\ 2s^1$ and that of Be is $1s^2\ 2s^2$. There are more + particles in the nucleus of Be than in Li. Thus, the attraction force between the valence electrons and the nucleus is larger in Be than in Li. Therefore, the melt temperature of Be is higher due to its higher nucleus charge.

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Problem 2.75 The melting point of the metal potassium is 63.5°C, while that of titanium is 1660°C. What explanation can be given for this great difference in melting temperatures?

Solution 2.75 Both K & Ti are located in period IV of the periodic table. The electronic structure of K is $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^1$ and that of Ti is $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^2 4s^2$. First, as the number of valence electrons increases, such as in Ti, the attraction force between the electron and the nucleus also increases. As 3d electrons are introduced (in Ti), the melt temperature further increases. This is due to more covalent bonding being introduced.

Problem 2.76 Cartridge brass is an alloy of two metals: 70 wt% copper and 30 wt% zinc. Discuss the nature of the bonds between copper and zinc in this alloy.

Solution 2.76
Both Copper and Zinc are in period IV of the periodic table.
The electronic structure of Copper is $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3d^{10} 4s^1$ and that of Zn is $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10} 4s^2$. The 3d and 4s orbitals of Zinc are full. Thus, it has significantly less tendency for covalent bonding. When Cu is replaced by Zn, the overall percentage of covalent bonds is dropped. Thus, brass (70 wt % Cu – 30 wt % Zi) will have a higher percentage of metallic bonds when compared to Cu. Therefore, Brass will have a lower melt temperature than Cu, and a higher melt temperature than Zn.

Problem 2.77 After ionization, why is the sodium ion smaller than the sodium atom? After ionization, why is the chloride ion larger than the chlorine atom?

Solution 2.77 After ionization to the Na^+, the Na atom becomes smaller because the electron-to-proton ratio of the Na atom is decreased when the Na^+ ion forms. Also, the outer third shell no longer exists once the $3s^1$ electron is lost by the Na atom.

After ionization, the Cl^- ion is larger because the electron-to-proton ratio of the chlorine atom is decreased by the ionization process.

Problem 2.78 Regardless of the type of primary bond, why does this tendency exist for atoms to bond?

Solution 2.78 The tendency of an atom to bond with other atom is to lower its energy level, and to exist in the most stable state.

Problem 2.79 Pure aluminum is a ductile metal with low tensile strength and hardness. Its oxide Al_2O_3 (Alumina) is extremely strong, hard, and brittle. Can you explain this difference from an atomic bonding point of view?

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Solution 2.79
Pure aluminum is a metal with mostly metallic bonds. Alumina (Al_2O_3) is a ceramic with mostly ionic bonds in a 3-d network. The strength of the ionic bonds is significantly higher than the metallic bonds. Thus, more energy is required to break the bonds between Al and O than between Al and Al.

Problem 2.80 Graphite and diamond are both made from carbon atoms. a) List some of the physical characteristics of each. b) Give one application for graphite and one for diamond. c) If both materials are made of carbon, why does such a difference in properties exist?

Solution 2.80

a) Graphite: Dark color that can have powder (flake-like) form or fiber form. It is an electrical conductor. Strength is high in transverse plane but not high in other directions (anisotropic). It has a layered hexagonal structure. The bonds inside the layer are covalent, and the bonds between the layers are of secondary (electrostatic) nature.
   Diamond: Transparent, hard, strong, very high melt temperature. It is an electrical insulator. It has a 3-D networked structure. All bonds are covalent.
b) Graphite is used as a lubricant because various layers are weakly bonded and can slide on top of each other.
   Diamond (synthetic type) is used as abrasive and cutting tool materials.
c) The bonding structure for diamond is 3-D covalent network (very strong) but graphite is layered with very weak forces between the layers.

Problem 2.81 Silicon is extensively used in the manufacturing of integrated circuit devices such as transistors and light emitting diodes. It is often necessary to develop a thin oxide layer (SiO_2) on silicon wafers. a) What are the differences in properties between the silicon substrate and the oxide layer? b) Design a process that produces the oxide layer on a silicon wafer. c) Design a process that forms the oxide layer only in certain desired areas.

Solution 2.81

a) Si is a metalloid (refer to the periodic table, page 32). It has a structure similar to diamond (fig 2.2). It has excellent semiconductor characteristics. SiO_2 is a ceramic. It has excellent insulative characterstics. The bonding is mostly ionic.
b) Exposing Si to an oxygen atmosphere at high temperatures will create a thin oxide layer on the surface of Si.
c) After oxidation, we can expose certain regions to chemical etchants and remove the oxide material. This is often done by applying a mask with a specific pattern to the surface of Si (see figure 14.44).

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Problem 2.82 How can the high electrical and thermal conductivities of metals be explained by the "electron cloud" model of metallic bonding? Ductility?

Solution 2.82 The high electrical and thermal conductivities of metals are explained by the mobility of their outer valence electrons in the presence of an electrical potential or thermal gradient. The ductility of metals is explained by the bonding "electron gas" which enables atoms to pass over each other during deformation, without severing their bonds.

Problem 2.83 Describe fluctuating dipole bonding among the atoms of the noble gas neon. Of a choice between the noble gases krypton and xenon, which noble gas would be expected to have the strongest dipole bonding and why?

Solution 2.83 A fluctuating electric dipole exists in the atoms of noble gases, such as neon, because there is, at any instant, an asymmetrical distribution of electrical charge among their electrons. The noble gas xenon would be expected to have a stronger fluctuating dipole moment than krypton since it has an additional electron shell; the krypton atom has four electron shells while the xenon atom has five. The electrons of this fifth shell, being further away from the xenon nucleus, are able to fluctuate more and, thus, create greater asymmetry of charge.

Problem 2.84 Carbon tetrachloride (CCl_4) has a zero dipole moment. What does this tell us about the C—Cl bonding arrangement in this molecule?

Solution 2.84 Since the molecule CCl_4 has a zero dipole moment, the C—Cl bonding arrangement must be symmetrical about the carbon nucleus.

Problem 2.85 Methane (CH_4) has a much lower boiling temperature than does water (H_2O). Explain why this is true in terms of the bonding between molecules in each of these two substances.

Solution 2.85 The methane molecules are bonded together by weak –C–H dipoles. The water molecules are bonded together by the much stronger –O–H hydrogen bonded dipoles.

Problem 2.86 For each of the following compounds, state whether the bonding is essentially metallic, covalent, ionic, van der Waals, or hydrogen: (a) Ni, (b) ZrO_2, (c) graphite, (d) solid Kr, (e) Si, (f) BN, (g) SiC, (h) Fe_2O_3, (i) MgO, (j) W, (k) H_2O within the molecules, (l) H_2O between the molecules. If ionic and covalent bonding are involved in the bonding of any of the compounds listed, calculate the percentage ionic character in the compound.

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Solution 2.86

(a) Ni:	Nickel bonding is primarily metallic.
(b) ZrO_2:	From Pauling's equation, the Zr–O bond is 73.4% ionic and 26.6% covalent, where x_A and x_B are the electronegativities of zirconium and oxygen, respectively.
(c) Graphite:	The bonding is covalent within the layers and secondary between the layers.
(d) Solid Kr:	The bonding represents van der Waals due to fluctuating dipoles.
(e) Si:	Silicon bonding is covalent.
(f) BN:	The B–N bond, from Pauling's equation, is 26.1% ionic and 73.9% covalent.
(g) SiC:	The Si–C bond is 11% ionic and 89% covalent.
(h) Fe_2O_3:	The Fe-O bond is 55.5% ionic and 44.5% covalent.
(i) MgO:	The Mg-O bond is 70.2% ionic and 29.8% covalent.
(j) W:	Tungsten bonding primarily consists of metallic bonding with some covalent character.
(k) H_2O within the molecules:	The H–O bond is 38.7% ionic and 61.3% covalent.
(l) H_2O between the molecules:	Hydrogen bonding exists between H_2O molecules.

Problem 2.87 In the manufacturing of a light bulb, the bulb atmosphere is evacuated and then filled with argon gas. What is the purpose of this?

Solution 2.87 Because, the tungsten filament in a light bulb becomes hot, it can react (form bonds) with impurities in the atmosphere of a light bulb. This will weaken and damage the filament. Argon is a noble gas and is non-reactive (inert). It does not react with tungsten and keeps the integrity of the wire.

Problem 2.88 Stainless steel is a corrosion resistant metal because it contains large amounts of chromium in its composition. How does chromium protect the metal from corrosion? Hint: Chromium reacts with oxygen.

Solution 2.88

Chromium easily reacts with oxygen in the atmosphere, and it forms chromium oxide Cr_2O_3. Chromium oxide is a ceramic with high hardness. The chromium on the surface forms a thin protective ceramic layer that is chemically stable and protects material inside. This is called a passivity layer.

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Problem 2.89 Robots are used in auto industries to weld two components at specific locations. Clearly, the end-position of the arm must be determined accurately in order to weld the components at the precise position. a) In selecting the material for the arm of such robots, what factors must be considered? b) Select a proper material for this application.

Solution 2.89

a) One would have to choose materials that are very stiff (little elastic deformation under load).
   The stronger the bonds are between the atoms in the material, the stiffer the material will behave.
b) Thus, ceramics, advanced composites and some metals will be good choices (economic considerations are important).

Problem 2.90 A certain application requires a material that is lightweight, an electrical insulator, and has some flexibility. a) Which class of materials would you search for this selection?
b) Explain your answer from a bonding point of view.

Solution 2.90

a) The characteristics required are found in polymers.
b) Polymers are insulators because all valence electrons are involved in covalent bonds within the polymeric molecule.
   - The bonding between molecules however is of secondary type (electrostatic attraction). This allows the material to be flexible.
   - Polymers are also low density because there exist large empty spaces (gaps) in the structure between molecules.

Problem 2.91 A certain application requires a material that is electrically non-conductive (insulator), extremely stiff, and lightweight. Which classes of materials would you search for this selection? b) Explain your answer from a bonding point of view.

Solution 2.91

a) The only class of materials that possess the properties is structural ceramics.
b) Structural ceramics are mostly made of ionically-bonded atoms in a 3-D network (there is often a mix of ionic and covalent). They are insulators because valence electrons are tightly held in ionic bonds. Ionic bonds are very strong and require high temperatures for melting.

Problem 2.92 Solid potassium and solid calcium have densities $0.862 g/cm^3$ and $1.554 g/cm^2$. Compare the mass of individual potassium and calcium atoms; what is your observation? How do you explain the difference in the solid density between the two elements?

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Solution 2.92
Potassium and calcium are in the same period, but calcium has a higher atomic number. Calcium has 2 electrons in its 4s orbital , whereas potassium only has 1.

potassium: 39g/mol

$$\frac{39g}{mol} \times \frac{mol}{6.022x10^{23}\,atoms} = \frac{6.48x10^{-23}\,g}{atom} of\ potassium$$

Calcium: 40g/mol

$$\frac{40g}{mol} \times \frac{mol}{6.022x10^{23}\,atoms} = \frac{6.64x10^{-23}\,g}{atom} of\ calcium$$

Atoms of calcium weight more than atoms of potassium due to having a higher atomic number (an additional electron and proton).
Calcium has a higher density because the calcium has smaller atomic radii due to having a larger nuclear charge (more protons in the nucleus).

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