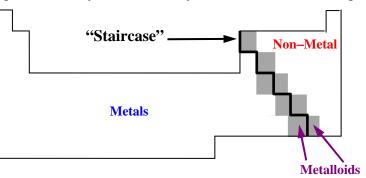
Unit 3: Quantum Theory, Periodicity and Chemical Bonding

Chapter 7: The Electronic Structure of Atoms (pg. 240 to 241)

- **48**. The shape of an *s*-orbital is a sphere. The shape of an *p*-orbital is a dumbbell. The shape of an *d*-orbital is a four-leave clover or a dumbbell with a donut in the middle. Using quantum numbers, n is the principle quantum number and it represents the energy level of an electron. ℓ is the angular momentum and it represents the type of atomic orbitals, such as s, p, d, and f subshells. m_{ℓ} is the magnetic angular momentum and it represents the orientation of these atomic orbitals (the *p*-orbital has three orientations, p_x , p_y and p_z , all pointing at different direction in a three-dimensional space).
- 57. A 2s orbital is larger than a 1s orbital. Both have the same spherical shape. The 1s orbital is lower in energy than the 2s.
- 61. There can be a maximum of two electrons occupying one orbital. (a) two (b) six (c) ten (d) fourteen
- 63. 3s: two 3d: ten 4p: six 4f: fourteen 5f: fourteen
- Equation (7.4) of the text gives the orbital energy in terms of the principal quantum number, n, alone (for **67**. the hydrogen atom). The energy does not depend on any of the other quantum numbers. If two orbitals in the hydrogen atom have the same value of *n*, they have equal energy. (a) 2s > 1s(c) equal (d) equal
- **(b)** 3p > 2p(e) 5s > 4f70. For hydrogen orbitals (increasing energy), 1s < (2s = 2p) < (3s = 3p = 3d) < (4s = 4p = 4d = 4f)
- 71. Electron configuration is a non-graphic notation that shows which orbitals the electrons are being occupied. The Pauli exclusion principle states that an atomic orbital can only have a maximum of two electrons due to their spin direction. Hund's rule specifies that for p, d, f, and higher orbitals, all electrons have to be unpaired in each orientation before they are paired.
- $4d^6$ means 6 electrons occupied in the 4d orbitals. 72.
- The ground state electron configuration of Cr is [Ar] $4s^{1}3d^{5}$, which is different than the expected 76. $[Ar]4s^23d^4$. This is because the energy level of the 4s and 3d orbitals are very similar and one of the electrons in the 4s orbital transfer into the remaining empty 3d orbital to achieve maximum number of unpaired electrons (6) in accordance to Hund's rule (arrangement for the lowest energy state). Similarly, Cu has an actual electron configuration of $[Ar]4s^{1}3d^{10}$, which is different than the expected $[Ar]4s^{2}3d^{9}$. At this point, the 3d orbitals has a slightly lower energy state than the 4s orbital. Hence, one of the electrons in the 4s orbital transfers into the 3d orbital's last remaining spot.
- The noble gas core is the electron configuration of the core electrons of an atom. For any elements with a 77. xenon core (elements Cs to Rn), their electron configurations can start with [Xe]. For example, Ba would have an electron configuration of $[Xe]6s^2$ B: $1s^22s^22p^1$ As: $[Ar]4s^23d^{10}4p^3$ V: $[Ar]4s^23d^3$ I: $[Kr]5s^24d^{10}5p^5$ Ni: $[Ar]4s^23d^8$ Au: $[Xe]6s^14f^{14}5d^{10}$ (this is one of those exceptions.)
- **83.** B: $1s^2 2s^2 2p^1$
- The Aufbau principle states that electrons must be "build-up" from orbitals of lower energy to orbitals of 87. higher energy.
- Transition metals have valence electrons in the d orbitals. Lathanides have valence electrons in the 4f88. orbitals and the actinides have valence electrons in the 5f orbitals.
- **89.** Again, the noble gas core represents the electron configuration of the core electrons. When we write electron configuration of elements with large atomic numbers, we can use the abbreviated form, starting with the [noble gas core] then follow by the list of orbitals and the number of electrons in the valence energy level.
- **91.** Se: [Ar] $4s^2 3d^{10} 4p^4$

Chapter 8: The Periodic Table (pg. 272 to 274)

- 1. Mendeleev's Periodic Table is significant because it organizes the elements based on their chemical properties and it is possible to make predictions on elements that had yet been discovered.
- **3.** The modern layout of the Periodic Table of Elements not only retains the spirit of Mendeleev's work of group the elements with similar chemical properties in columns, it also blocked the elements by their atomic orbitals (*s* and *p*-orbitals into the representative elements A groups, *d*-orbitals into the transition metals B groups and the inner-transition metals of the *f*-orbitals as outlined by the lanthanides and actinides series at the bottom of the table).
- 4. The most important relationship of the elements in the same group of the table is their similar chemical properties as they have relatively the same electron configuration at the valence energy level.
- 7.

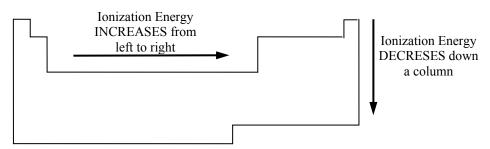


- **11.** We can test whether the substance conduct electricity. As iodine is a non-metal, it would not conduct any electricity.
- **13.** (a) Alkali Metals ns^1 (b) Alkaline Earths ns^2 (c) Halogens ns^2np^5 (d) Noble Gases ns^2np^6
- **15.** Hydrogen forms the H^+ ion (resembles the alkali metals) and the H^- ion (resembles the halogens).
- **19.** (a) $1s^2 2s^2 2p^5$ (halogen) (c) $[Ar]4s^2 3d^6$ (transition metal) (d) $[Ar]4s^2 3d^{10}4p^3$ (Group 5A)
- 23. The electron configurations of stable cations of the representative elements are the same as their core electrons (their previous noble gas). The electron configurations of stable anions of the representative elements are the same as their subsequent noble gas.
- 24. Isoelectronic means that ions or an atom having the same electron configuration.
- **25.** No two atoms can have the same electron configuration.
- **26.** Using Figure 4.10 on pg. 110, the first-row transition metal ions that have the same electron configuration as the argon core are Sc³⁺, Ti⁴⁺, V⁵⁺, Cr⁶⁺ and Mn⁷⁺.
- 34. (a) Atomic radius generally decreases from left to right across the period.(b) Atomic radius increases top to bottom in a group.
- **36.** For isoelectronic ions, the cations tend to have more protons in their nuclei than their isoelectronic anions while they all have the same number of electrons. The higher number of protons allows these cations to pull the electrons more effectively than the anions. Hence, isoelectronic anions are larger than cations.
- **43.** (a) Cl is smaller than Cl^{-} . An atom gets bigger when more electrons are added.
 - (b) Na^+ is smaller than Na. An atom gets smaller when electrons are removed.
 - (c) O^{2^-} is smaller than S^{2^-} . Both elements belong to the same group, and ionic radius increases going down a group.
 - (d) Al^{3+} is smaller than Mg^{2+} . The two ions are isoelectronic and in such cases the radius gets smaller as the charge becomes more positive.
 - (e) Au^{3+} is smaller than Au^{+} for the same reason as part (b).
- **45.** The Cu^+ ion is larger than Cu^{2+} because it has one more electron.
- **47.** Bromine is liquid; all the others are solids.

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50.

49. Ionization energy is the minimal amount of energy needed to completely remove a valence electron of a gaseous atom from its ground state. Gaseous atoms are specified in the definition because atoms in gas phase do not have any intermolecular interactions with adjacent atoms. Hence, the amount of energy measured for the ionization process is more accurate. The Second Ionization Energy is always greater than the First Ionization Energy because the number of protons remain the same at each stages of ionization. Therefore, as more electrons are removed, the difference between the electric charges increases and more energy are required to remove any successive electrons.



- **51.** Apart from the small irregularities, the ionization energies of elements in a period increase with increasing atomic number. We can explain this trend by referring to the increase in effective nuclear charge from left to right. A larger effective nuclear charge means a more tightly held outer electron, and hence a higher first ionization energy. Thus, in the third period, sodium has the lowest and neon has the highest first ionization energy.
- **59.** (a) Electron Affinity is the negative of the energy change that occurs when an electron is accepted by a gaseous atom.
 - (b) Electron affinity is made with gaseous atom because like ionization energy, we want to minimize effect of intermolecular forces when measuring electron affinity.
 - (c) Ionization is always a positive energy because electrons absorb energy to move to higher orbitals. Since ionization is an act of remove an electron of an atom from its ground state, it will always be associated with positive energy. Electron affinity is a process when an atom accepts an electron. This is the reverse of ionization, and hence energy is usually given off in this process. Therefore, electron affinity is usually associated with negative energy. Its energy can be positive in cases when placing an electron in a filled energy level – such as putting an extra electron into the valence energy level of a noble gas atom.
- **60.** There is a generally increasing trend for electron affinity from aluminum to chlorine, with the exception of Si. This is because Si has 2 unpaired electrons in its 3*p* orbital and an extra electron would be an arrangement with minimum energy according to Hund's rule. Hence, Si has a higher electron affinity than P despite the general increasing trend.
- **59.** (a) K < Na < Li (b) I < Br < F < Cl
- **61.** Based on electron affinity values, we would not expect the alkali metals to form anions. A few years ago most chemists would have answered this question with a loud "No"! In the early seventies a chemist named J.L. Dye at Michigan State University discovered that under very special circumstances alkali metals could be coaxed into accepting an electron to form negative ions! These ions are called alkalide ions.

Chapter 9: The Periodic Table (pg. 306 to 308)

1. Lewis dot symbol shows the valence electrons of the *s* and *p* orbitals. Lewis dot symbol is effective when it applies to representative (A) group elements.

5. (a) (b)
$$\begin{bmatrix} \cdot \cdot \cdot \\ \cdot \cdot \end{bmatrix}^{-}$$
 (c) (c) (d) $\begin{bmatrix} \cdot \cdot \cdot \\ \cdot \cdot \end{bmatrix}^{2^{-}}$ (e) (f) $\begin{bmatrix} \cdot \cdot \\ \cdot \\ \cdot \end{bmatrix}^{3^{-}}$ (g) Na

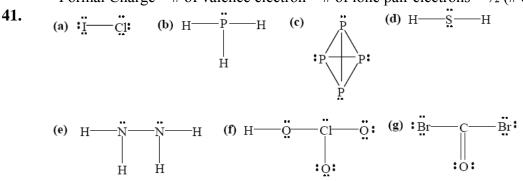
(h)
$$[Na]^+$$
 (i) •Mg• (j) $[Mg]^{2+}$ (k) •AI• (l) $[Al]^{3+}$ (m) • Pb• (n) $[Pb]^{2+}$

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Selected Honour Chemistry Assignment Answers

- 7. When atoms with small ionization energy (especially groups 1A and 2A metals) combine with atoms that have large electron affinity (especially groups 6A and 7A nonmetals), they will form ionic compound. This is because it would be easier for the electron to leave the metal atom and join the nonmetal atom where large energy is given off. Hence, it would achieve a more favorable energy state.
- Any ionic compounds with ammonia as cations. Example: NH₄Cl 9.
- Answers may vary. Examples: NH₄OH, (NH₄)₂CO₃ 10.
- (a) NaCl_(s) would not conduct electricity because its ions are locked in a lattice structure. 13.
 - (b) NaCl_(l) would conduct electricity because the lattice structure is broken down and the ions are free to move about.
 - (c) NaCl_(aq) would conduct electricity because water molecules would carry the ions to move around in the solution.
- 29. For HBr, bromine has 3 lone pairs. For H₂S, sulfur has two lone pairs. For CH₄, carbon has no lone pairs.
- 30. Single bond has two electrons between the atoms of the covalent bond, as in the case of CH₄. Double bond has four electrons between the atoms of the covalent bond, as in the case of CO₂. Triple bond has six electrons between the atoms of the covalent bond, as in the case of CO. Bond length decreases with increasing multiple bonds. Hence, triple bond is shorter than double bond, and double bond is shorter than single bond.
- A polar covalent bond is a covalent bond with two atoms of different electronegativity. This can cause 32. electrons to be closer to one atom instead of the other, creating a non-uniform electron density within the covalent bond. As such, one side of the covalent bond is more negatively charged than the other side.
- DG < EG < DF < DE35.
- 37. (a) The two carbon atoms are the same. The bond is covalent.
 - (b) The electronegativity difference between K and I is 2.5 0.8 = 1.7. The bond is polar covalent.
 - (c) The electronegativity difference between N and B is 3.0 2.0 = 1.0. The bond is polar covalent.
 - (d) The electronegativity difference between C and F is 4.0 2.5 = 1.5. The bond is polar covalent.
- The formal charge of an atom is the electrical charge difference between the valence electrons in an **40**. isolated atom and the number of electron assigned to that atom in a Lewis structure.

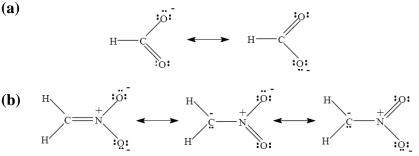
Formal Charge = # of valence electron – # of lone pair electrons – $\frac{1}{2}$ (# of bonding electrons)



- (a) The structure has too many electrons. The correct structure is H-C=N: **43**.
 - (b) Hydrogen atoms do not form double bond. The correct structure is H-C=C-H(c) Too few electrons. The correct structure is O=Sn=O (f) Oxygen does not have an The correct structure is
 - The correct structure is
 - (d) Too many electrons. The correct structure is
- (e) Fluorine has more than an octet. The correct structure is H-O-F:

- (f) Oxygen does not have an octet.
 - The correct structure is
- (g) Too few electrons. The correct structure is

- **49**. The resonance structures are:

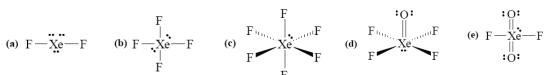


51. The structures of the most important resonance forms are:

$$H \xrightarrow{\hspace{0.1cm}} N \xrightarrow{\hspace{0.1cm}}$$

53. Three reasonable resonance structures are:

- Atoms in the third period and beyond tend to exceed the octet rule. This is because the adjacent *d*-55. orbitals are available for borrowing starting at n = 3. Hence, these central atoms can have dsp^3 and d^2sp^3 hybridizations (sometimes even d^3sp^3).
- 57. F can only form a single bond. In order to exceed the octet rule, the atom must be able to borrow from any adjacent *d*-orbitals. Since fluorine has an electron configuration of $[He]2s^22p^5$, and *d*-orbitals start appearing in n = 3, it cannot exceed the octet rule. Hence, compounds like FH₇ and FCl₇ (both would mean F follow the 14-electron rule) cannot be synthesized
- For simplicity, the three lone-pairs around the fluorine atoms are omitted. Note that all central atoms 61. exceed the octet rule.

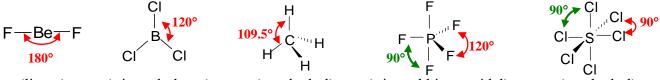


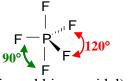
63. For simplicity, the three lone-pairs around the fluorine atoms are omitted. In each case the octet rule did not satisfy for Se.

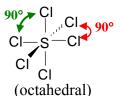


Chapter 10: Chemical Bonding II: Molecular Geometry (pg. 349 to 350)

- 2. Lewis dot symbol shows the valence electrons of the s and p orbitals. Lewis dot symbol is effective
- 3. tetrahedral -4 atoms bonded to a central atom; trigonal bipyramidal -5 atoms bonded to a central atom; octahedral - 6 atoms bonded to a central atom
- 4.







(trigonal planar) (linear)

(tetrahedral) (trigonal bipyramidal)

- 5. If there are any lone-pairs on a trigonal bipyramidal central atom, it would occupy the equatorial position because the angle there is bigger than the axial bond angle (120° compares to 90°).
- 7. (a) PCl₃ (trigonal pyramid) (b) CHCl₃ (tetrahedral) (c) SiH₄ (tetrahedral) (d) TeCl₄ (see-saw)

- 9. (a) The lone-pairs on Br atoms have been omitted for simplicity. Br-Hg-Br (HgBr₂ is linear). (b) N₂O is linear. $N \equiv N = N = O$. (c) SCN⁻ is linear. S = C = N = O.
- $:N \equiv N Q:$ $:S = C \equiv N:$ 11. The Lewis structure is: $:\stackrel{H}{\underset{H \to C}{\overset{O:}{\leftarrow}} \stackrel{H}{\underset{H \to C}{\overset{H \to C}{\leftarrow}} \stackrel{H}{\underset{H \to C}{\overset{H \to C}{\leftarrow} \stackrel{H}{\underset{H \to C}{\overset{H \to C}{\leftarrow}} \stackrel{H}{\underset{H \to C}{\overset{H \to C}{\leftarrow}} \stackrel{H}{\underset{H \to C}{\overset{H \to C}{\leftarrow} \stackrel{H}{\underset{H \to C}{\overset{H \to C}{\leftarrow} \stackrel{H}{\underset{H \to C}{\overset{H \to C}{\leftarrow} \stackrel{H \to C}{\underset{H \to C}{\overset{H \to C}{\underset{H \to C}{\underset{H \to C}{\overset{H \to C}{\underset{H \to C}{$
- 14. Dipole Moment and Bond Moment are essentially the same thing. It is the relative difference between the electronegativities of the two atoms that form a chemical bond. The greater this difference, the more polar is the bond. It is necessary to know that even though a molecule has many dipole moments, it can still be a non-polar molecule. This is true when all the dipole moment vectors cancel each other out when added.
- **15.** It takes two atoms bonding together to form a dipole. A single atom cannot have a permanent dipole moment. (It can, however, have a temporary dipole moment because electrons can momentary gathered on one side of the atom, making that side temporary more negative. It is called London-Dispersion Force more of this in Chapter 12.)
- 21. Molecule (b) will have a higher dipole moment. In molecule (a), the trans- arrangement cancels the bond dipoles and the molecule is non-polar.

Chapter 12: Intermolecular Forces (pg. 418 to 422 and pg. 448)

- 2. "Polarizability" means the ability to create a molecule with high polarity. Bonds that consist of atoms with large dipole moment (large difference in electronegativities) tend to have high "polarizability". The stronger the molecule's overall "polarizability", the stronger are their intermolecular forces.
- 3. Temporary dipole moment, such as London dispersion force, is the result of electron "sloshing" in their mixed orbitals. Due to their non-permanent nature, the intermolecular forces results are not strong. Permanent dipole moments of polar molecules are the result large difference in electronegativities of the adjacent bond atoms, and their molecular geometry. The resulting intermolecular forces are very strong as these dipole moments are permanent.
- 6. Hydrogen bonds will result when H atoms are bonded with O, N, F or Cl atoms.
- 7. ICl has a dipole moment and Br_2 does not. The dipole moment increases the intermolecular attractions between ICl molecules and causes that substance to have a higher melting point than bromine.
- **9.** All are tetrahedral (AB₄ type) and are nonpolar. Therefore, the only intermolecular forces possible are dispersion forces. Without worrying about what causes dispersion forces, you only need to know that the strength of the dispersion force increases with the number of electrons in the molecule (all other things being equal). As a consequence, the magnitude of the intermolecular attractions and of the boiling points should increase with increasing molar mass.
- **13.** CO_2 is a non-polar molecular compound. The only intermolecular force present is a relatively weak dispersion force (small molar mass). CO_2 will have the lowest boiling point. CH_3Br is a polar molecule. Dispersion forces (present in all matter) and dipole-dipole forces will be present. This compound has the next highest boiling point. CH_3OH is polar and can form hydrogen bonds, which are especially strong dipole-dipole attractions. Dispersion forces and hydrogen bonding are present to give this substance the next highest boiling point. RbF is an ionic compound. Ion-ion attractions are much stronger than any intermolecular force. RbF has the highest boiling point. (mp: $CO_2 < CH_3Br < CH_3OH < RbF$)
- 15. (a) O₂: it has more electrons the N₂ (both are non-polar) and therefore has stronger dispersion forces.
 (b) SO₂: it is polar (most important) and also has more electrons than CO₂ (non-polar). More electrons imply stronger dispersion forces.

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- (c) HF: although HI has more electrons and should therefore exert stronger dispersion forces, HF is capable of hydrogen bonding and HI is not. Hydrogen bonding is the stronger attractive force
- 17. (a) CH_4 has a lower boiling point because NH_3 is polar and can form hydrogen bonds; CH_4 is non-polar and can only form weak attractions through dispersion forces.
 - (b) KCl is an ionic compound. Ion-ion forces are much stronger than any intermolecular forces. I₂ is a non-polar molecular substance; only weak dispersion forces are possible.
- 19. The linear structure (n-butane, the molecule on the left) has a higher boiling point $(-0.5^{\circ}C)$ than the branched structure on the right (2-methylpropane, boiling point $-11.7^{\circ}C$) because the linear form can be stacked together more easily.
- **31.** Ethanol molecules can attract each other with strong hydrogen bonds; dimethyl ether molecules cannot (it does not have hydrogen bonds, only dipole-dipole force). The surface tension of ethanol is greater than that of dimethyl ether because of stronger intermolecular forces (the hydrogen bonds). Note that ethanol and dimethyl ether have identical molar masses and molecular formulas so attractions resulting from dispersion forces will be equal.
- **63.** The stronger the intermolecular forces in a liquid, the higher its boiling point and critical temperature. Water has a higher critical temperature than most other substances because it is very polar (V-shape and consists of strong hydrogen bonds).
- **64.** The boiling point and melting point of water does not change very much with change in pressure. This is due to water's strong intermolecular forces (it has hydrogen bonds). Hence, a very large pressure change is needed to bring about a change in water's boiling and melting point. CCl₄ is non-polar. It only has dispersion forces as its intermolecular force. Therefore, a small change in pressure can have a large effect on the boiling point and melting point of CCl₄.
- **101.** (a) False. Permanent dipoles are usually much stronger than temporary dipoles.
 - (b) False. The hydrogen atom must be bonded to N, O, or F.
 - (c) True.
 - (d) False. The magnitude of the attraction depends on both the ion charge and the polarizability of the neutral atom or molecule.
- 9. (pg. 448) The order of increasing solubility is: $O_2 < Br_2 < LiCl < CH_3OH$. Methanol is miscible with water because of strong hydrogen bonding. LiCl is an ionic solid and is very soluble because of the high polarity of the water molecules. Both oxygen and bromine are nonpolar and exert only weak dispersion forces. Bromine is a larger molecule and is therefore more polarizable and susceptible to dipole-induced dipole attractions.