Worksheet 12 - Periodic Trends

A number of physical and chemical properties of elements can be predicted from their position in the **Periodic Table**. Among these properties are **Ionization Energy**, **Electron Affinity** and **Atomic/Ionic Radii**.

These properties all involve the **outer shell** (valence) **electrons** as well as the **inner shell** (shielding) **electrons**. Electrons are held in the atom by their electrostatic attraction to the positively charged protons, the nuclear charge, Z. However, not all electrons in an atom experience the same nuclear charge. Those closest to the nucleus experience the full nuclear charge and are held most strongly. As the number of electrons between the nucleus and the valence electrons increases, the apparent nuclear charge decreases, due to the "screening" of these inner shell electrons. The charge felt by the valence electrons is called the **effective nuclear charge**, **Z**_{eff}.

Going **down** a **group** increases the value of **n**, and increases the number of inner shell electrons. This leads to better shielding and a weaker attraction between the nucleus and the outer shell electrons.

Going **across** a **period** leads to a **larger nuclear charge**, as the number of protons increases. There is also an increase in the number of valence electrons, but electrons in the same shell are poor at shielding each other. Going across a row generally leads to a **stronger** interaction between the nucleus and the valence electrons.

The **type of orbital** holding the shielding electrons is also important. The s orbitals are said to be **penetrating** - they have electron density close to the nucleus. The best shielding comes from s orbitals, followed by p, d and f.

Ionization Energy

Ionization energy is the energy required to remove an electron from a gaseous atom in its ground state. This is related to how "tightly" the electron is held by the nucleus. The higher the ionization energy, the more difficult it is to remove the electron. For a many-electron atom, the energy required for the reaction:

energy +
$$X(g) \rightarrow X^{+}(g) + e^{-}$$

is called the **first ionization energy** (I_1). Since this requires an input of energy, it is an **endothermic reaction**, with a positive energy value. The energy required for the reactions

energy +
$$X^{+}(g) \rightarrow X^{2+}(g) + e^{-}$$

energy + $X^{2+}(g) \rightarrow X^{3+}(g) + e^{-}$

are the second (I_2) and third (I_3) ionization energies.

When an electron is removed from an atom the repulsion between the remaining electrons decreases. The nuclear charge remains constant, so more energy is required to remove another electron from the positively charged ion. This means that, $I_1 < I_2 < I_3 < ...$, for any given atom.

Going **down** a **group** the electrons become increasingly easy to remove, since they are at an increasing distance from the nucleus, with increasing numbers of shielding inner electrons. So, the ionization energies **decrease**.

Going **across** a **period** the ionization energies **generally** increase. Electrons in the same set of orbitals do not shield each other very well but the nuclear charge increases, making the electrons more difficult to remove.

Ζ	Atom	electron configuration	I₁ (kJ/mol)
3	Li	1s ² 2s ¹	520
4	Be	$1s^2 2s^2$	899

This trend is observed for Li and Be. The **1s** electrons are the screening electrons for both Li and Be. The nuclear charge for Li is +3. The nuclear charge for Be is +4 and the 2s electrons in Be doesn't screen the nuclear charge very effectively. So an electron in Be is harder to remove than an electron in Li.

However, there are some notable **exceptions** to this trend.

Z	Atom	electron configuration	I₁ (kJ/mol)
3	Li	$1s^2 2s^1$	520
4	Be	$1s^2 2s^2$	899
5	В	$1s^2 2s^2 2p^1$	800

It is **easier** to remove an electron from B (Z = +5) than from Be (Z = +4).

Why? (Hint: what type of electron is being removed?)

For the next few elements the trend is followed. As Z increases, the I₁ increases.

Ζ	Atom	electron configuration	I₁ (kJ/mol)
3	Li	$1s^2 2s^1$	520
4	Be	$1s^2 2s^2$	899
5	В	$1s^2 2s^2 2p^1$	800
6	С	$1s^2 2s^2 2p^2$	1090
7	N	$1s^2 2s^2 2p^3$	1400
8	0	$1s^2 2s^2 2p^4$	1310

There is another break between N and O.

Fill in the energy diagram for each of these atoms:

N
$$\frac{}{1s} \frac{}{2s} \frac{}{2p_x} \frac{}{2p_y} \frac{}{2p_z}$$

O
$$\frac{1}{1s} \frac{1}{2s} \frac{1}{2p_x} \frac{1}{2p_y} \frac{1}{2p_z}$$

How do the electrons being removed differ from each other?

The final two elements in this period follow the trend as Z increases, I₁ increases.

Ζ	Atom	electron configuration	I₁ (kJ/mol)
9	F	$1s^2 2s^2 2p^5$	1680
10	Ne	$1s^2 2s^2 2p^6$	2080

The metals have relatively low I₁ values (electrons are relatively easy to remove). Cs has the lowest I₁ (382 kJ/mol) and He has the highest I₁ (2370 kJ/mol).

- 1. Choose the orbital in which an electron would experience the highest Z_{eff}, effective nuclear charge (least shielded), and the highest I₁.
 - Na (3s) Mg (3s)
- Al (3p)
- P(3p)
- S(3p)
- 2. Match the following electron configurations with the appropriate ionization energies (I_1) .
 - a) $1s^2 2s^2 3p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^1$
- i) 1356 kJ/mol

- ii) 595 kJ/mol
- b) $1s^2 2s^2 3p^6 3s^2 3p^6 4s^2$ c) $1s^2 2s^2 3p^6 3s^2 3p^6 4s^2 3q^{10} 4p^6$
- iii) 409 kJ/mol
- 3. Which of the following would have the largest I_1 ?
 - Na
- Κ
- Shown below are I₁ (in kJ/mol) values for sequential elements in period 3. 4. Assign elements to these values based on the trends discussed above.
 - 740
- 578
- 786

Li

1012

Cs

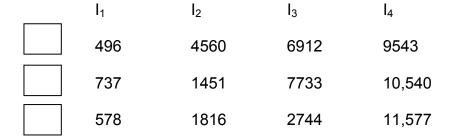
999

The **second**, **third** and subsequent ionization energies increase for any element, but again, there are jumps in these values.

Ζ	Atom		I_1	I_2	I_3	I_4	l ₅
3	Li	$1s^2 2s^1$	520	7300	11,815		
4	Be	1 <i>s</i> ² 2 <i>s</i> ²	899	1757	14,850	21,000	
5	В	1 <i>s</i> ² 2 <i>s</i> ² 3 <i>p</i> ¹	800	2430	3660	25,000	32,820
6	С	$1s^2 2s^2 3p^2$	1090	2350	4620	6220	38,000

These data show that the removal of **valence shell** electrons is much easier than the removal of **core** electrons.

5. Shown below are the ionization energies for three elements in the third period. Label each box with the correct element:



- 6. The first four ionization energies for element X (not in kJ/mol) are 170, 350, 1800, 2500. The first four ionization energies for element Y are 200, 400, 3500 and 5000. Identify elements X and Y. There may be more than one correct answer
- 7. Which of the following has the largest I_2 ? (Transition metals lose their s electrons before the *d* electrons)

K Ca Sc Fe

- 8. Which species of each pair has the higher ionization energy?
 - a) Mg or Mg²⁺

b) O or O²-

c) K⁺ or Cl⁻

d) P^{3-} or S^{2-}

Atomic and Ionic Radii

Similar periodic trends are seen in the radii of the elements. Moving **down** a **group increases** atomic radii. As n increases, the sizes of the orbitals increase.

Moving **across** a **period** leads to a **decrease** in the atomic radii. This is again due to the **increase** in atomic charge (Z) with the poor shielding by outer shell electrons.

9. Arrange the following atoms in order of decreasing atomic radius.

Na Al P Cl Mg

10. Which is the largest atom in Group IV?

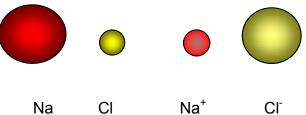
Which is the smallest atom in Group VII?

Which is the smallest atom in period 5?

The **ionic radius** is the radius of an anion or cation. When neutral atoms are ionized, there is a change in their sizes.

If the atom forms an **anion** the size **increases**, because the nuclear charge (Z) is unchanged but the electron-electron repulsion increases, due to the added electron, enlarging the electron cloud.

If the atom forms a **cation**, the size **decreases**. The nuclear charge is unchanged and the decreased electron-electron repulsion shrinks the electron cloud.



For ions derived from elements in different groups, a comparison of sizes is possible only in an **isoelectronic series**, a series of ions containing the same number of electrons.

11. Which of the ions listed below are **isoelectronic** with krypton?

 Ag^{+} Br^{-} Cd^{2+} Sc^{3+} Se^{2-} Sr^{2+} Ti^{2+} Zn^{2+}

12. Pick a noble gas, write its shorthand e⁻ configuration and determine its number of electrons. Then find the halogen, alkali metal and alkaline earth metal with the same number of electrons. Write these as their most stable ion. They will constitute an isoelectronic series

	noble gas	halogen	alkali metal	alkaline earth
species				
e ⁻ configuration				
Z, nuclear charge				
# electrons				

Order them by **increasing** atomic or ionic radius. (Hint: Compare the positive and negative charges)

- 13. For each of the following pairs, which of the two species is larger?
 - a) N^{3-} or F^{-}
- b) Mg^{2+} or Ca^{2+} c) Fe^{2+} or Fe^{3+}
- 14. For each of the following pairs, which of the two species is smaller?
 - a) K⁺ or Li⁺
- b) Au⁺ or Au³⁺
- c) P³⁻ or N³⁻
- 15. Order the following groups from largest to smallest radii.
 - a) Ar, Cl⁻, K⁺, S²⁻
 - b) C, Al, F, Si
 - c) Na, Mg, Ar, P
 - d) I⁻, Ba²⁺, Cs⁺, Xe
- 16. Which species of each pair has the larger radius?
 - a) Mg or Mg²⁺

b) O or O²

c) K⁺ or Cl⁻

d) P^{3} or S^{2}

Electron Affinity

Electron affinity is defined as the energy released when the following reaction occurs:

$$X(g) + e^{-} \rightarrow X^{-}(g) + energy$$

These reactions are **exothermic** (negative energy) since energy is given off.

Second and third electron affinities also exist, but these are all very difficult to measure experimentally.

This is also a periodic property. Electron affinity tends to **increase** going across a period, from left (metals) to right (non-metals). And, with exceptions, electron affinity **decreases** as we down a group.

These are the same general trends that are seen when looking at **electronegativity**. This is a measure of the ability of a bonded atom to attract the bonding electrons to itself and away for the other atoms bonded to it. The element with the highest electronegativity value is F. The electronegativity decreases going down and across the periodic table. The least electronegative element is Cs.