CHEMISTRY

21st class Date : 08-10-2021

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Last class..

- Periodic properties
- Slater's rule

In this class….

- ❑ Slater's rule, continuation
- ❑ Applications

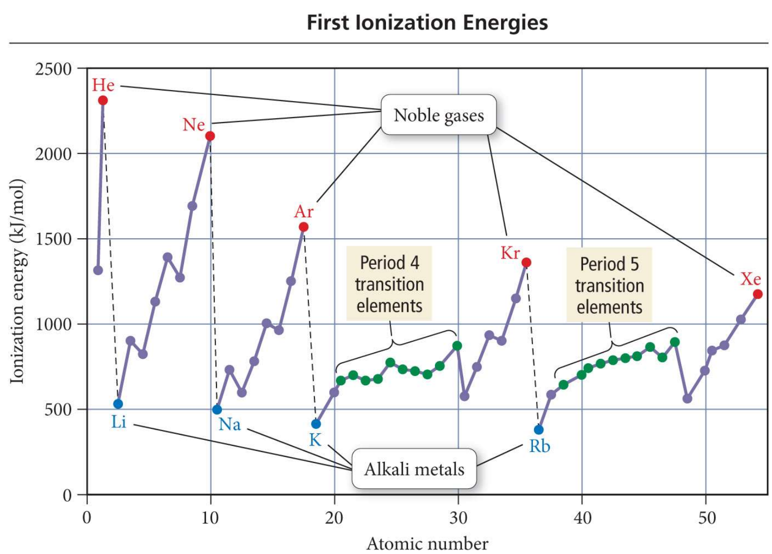
Ionization Energy (IE)

- ❑ Minimum energy needed to remove an electron from an neutral atom or ion
  - Valence electron easiest to remove, lowest IE
  - $M(g) + IE_1 \rightarrow M^{1+}(g) + 1\ e^-$
  - $M^{+1}(g) + IE_2 \rightarrow M^{2+}(g) + 1\ e^-$

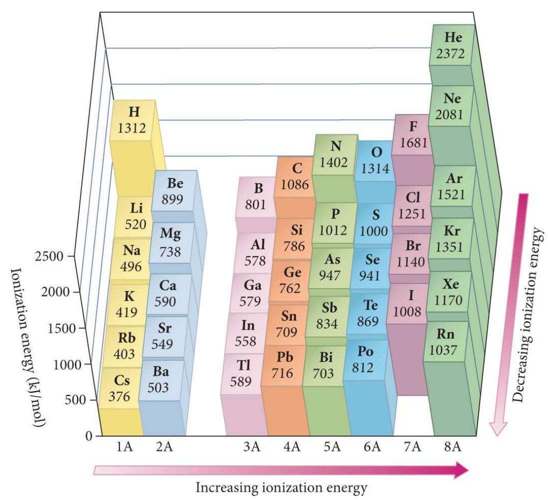
    - ➢ First ionization energy = energy to remove electron from neutral atom
    - ➢ Second IE = energy to remove from 1+ ion, etc.

General Trends in First Ionization Energy

- The **larger the effective nuclear charge on the electron, the more energy it takes to remove it**
- The **farther the most probable distance the electron is from the nucleus, the less energy it takes to remove it.**
- First IE generally **increases** across the period.
  - Effective nuclear charge increases
- First IE **decreases** down the group.
  - Valence electron farther from nucleus



Trends in First Ionization Energy

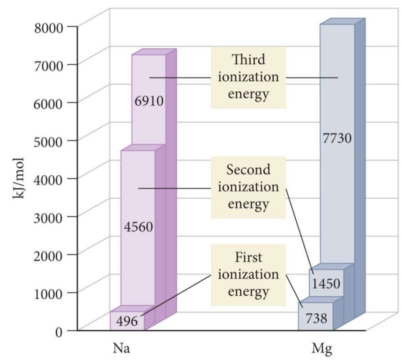


Explanation for the trends in First Ionization Energy

- The strength of attraction is related to the most probable distance the valence electrons are from the nucleus and the effective nuclear charge the valence electrons experience.
- **The larger the orbital an electron is in, the farther its most probable distance will be from the nucleus and the less attraction it will have for the nucleus.**
- Quantum-mechanics predicts the atom's **first ionization energy should get lower down a column**
- **Traversing across a period increases the effective nuclear charge on the valence electrons.**
- **Quantum-mechanics predicts the atom's first ionization energy should get larger across a period.**

Trends in Successive Ionization Energies

- Removal of each successive electron costs more energy.
  - Shrinkage in size due to having more protons than electrons
  - Outer electrons closer to the nucleus; therefore harder to remove
- There's a regular increase in energy for each successive valence electron.
- There's a large increase in energy when core electrons are removed.



Trends in Second and Successive Ionization Energies

TABLE 8.1 Successive Values of Ionization Energies for the Elements Sodium through Argon (kJ/mol)

Element	IE_1	IE_2	IE_3	IE_4	IE_5	IE_6	IE_7
Na	496	4560					
Mg	738	1450	7730		Core electrons		
Al	578	1820	2750	11,600			
Si	786	1580	3230	4360	16,100		
P	1012	1900	2910	4960	6270	22,200	
S	1000	2250	3360	4560	7010	8500	27,100
Cl	1251	2300	3820	5160	6540	9460	11,000
Ar	1521	2670	3930	5770	7240	8780	12,000

Trends in Second and Successive IEs

Boron (B), electron configuration $1s^22s^22p^1$

$B(g) \rightarrow B^+(g) + e^-$	IE(1) = 801 kJ/mol	Valence electrons
$B^+(g) \rightarrow B^{2+}(g) + e^-$	IE(2) = 2,427 kJ/mol	
$B^{2+}(g) \rightarrow B^{3+}(g) + e^-$	IE(3) = 3,660 kJ/mol	
$B^{3+}(g) \rightarrow B^{4+}(g) + e^-$	IE(4) = 25,025 kJ/mol	Core electrons
$B^{4+}(g) \rightarrow B^{5+}(g) + e^-$	IE(5) = 32,822 kJ/mol	

Exceptions in the First IE Trends

- First ionization energy generally increases from left to right across a period
- **Except from 2A to 3A (Be & B), 5A to 6A (N & O)**

	1*s*	2*s*	2*p*
Be	↑↓	↑↓	[ ][ ][ ]
B	↑↓	↑↓	[↑][ ][ ]
N	↑↓	↑↓	[↑][↑][↑]
O	↑↓	↑↓	[↑↓][↑][↑]

Exceptions in the First Ionization Energy Trends, Be and B

	1*s*	2*s*	2*p*		
Be	↑↓	↑↓			
Be^+	↑↓	↑			

To ionize Be, you must break up a full sublevel, which costs extra energy.

	1*s*	2*s*	2*p*		
B	↑↓	↑↓	↑		
B^+	↑↓	↑↓			

When you ionize B, you get a full sublevel, which costs less energy.

Exceptions in the First Ionization Energy Trends, N and O

	1*s*	2*s*	2*p*		
N	↑↓	↑↓	↑	↑	↑
N^+	↑↓	↑↓	↑	↑	

To ionize N, you must break up a half-full sublevel, which costs extra energy.

	1*s*	2*s*	2*p*		
O	↑↓	↑↓	↑↓	↑	↑
O^+	↑↓	↑↓	↑	↑	↑

When you ionize O, you get a half-full sublevel, which costs less energy.

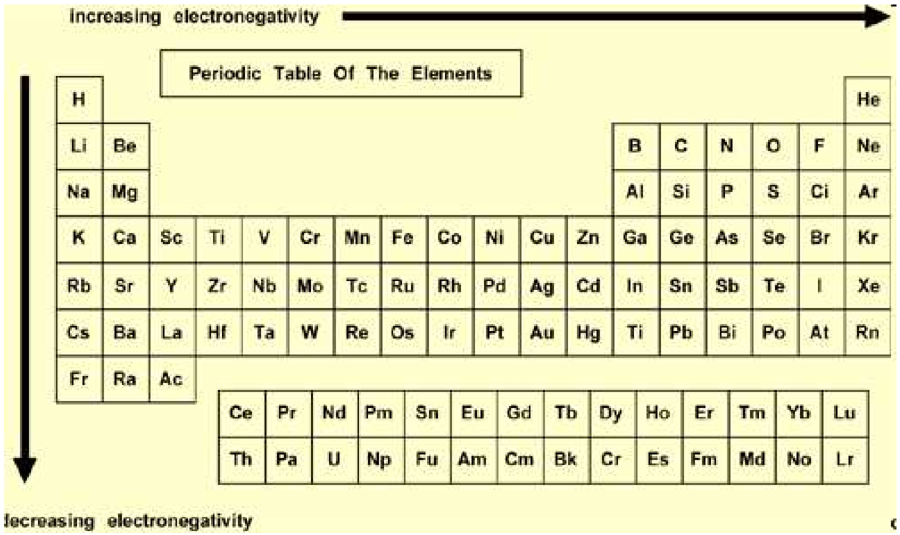
First IE of Al is lower than Mg – Explain

- Magnesium electron configuration will be $1s^2 2s^2 2p^6 3s^2$
- Aluminium electron configuration will be $\mathbf{1s^2 2s^2} 2p^6 \mathbf{3s^2} 3p^1$
- Al **has one unpaired electron** in it's highest energy orbital (3p), and Mg's highest energy orbital (3s) the electrons are paired.
- It is **energetically favourable for all the electrons in an orbital to be paired**, which means that breaking up this pair would require more energy.

Electronegativity

- Measure of the ability of an atom to attract an electron towards itself
- **What happens down a group?**
  - **Decreases;** since the electrons are further from the nucleus, there is a weaker attraction
- **What happens across a period?**
  - **Increases;** since there is an increase in core charge, there is a greater attraction of the outer shell electrons to the nucleus.

Electronegativity



Electron Affinity

- Energy is released when an neutral atom gains an electron.
  - Gas state
  - $M(g) + 1e^- \rightarrow M^{1-}(g) + EA$
- The more energy that is released, the larger the electron affinity.
  - **The more negative the number, the larger the EA.**

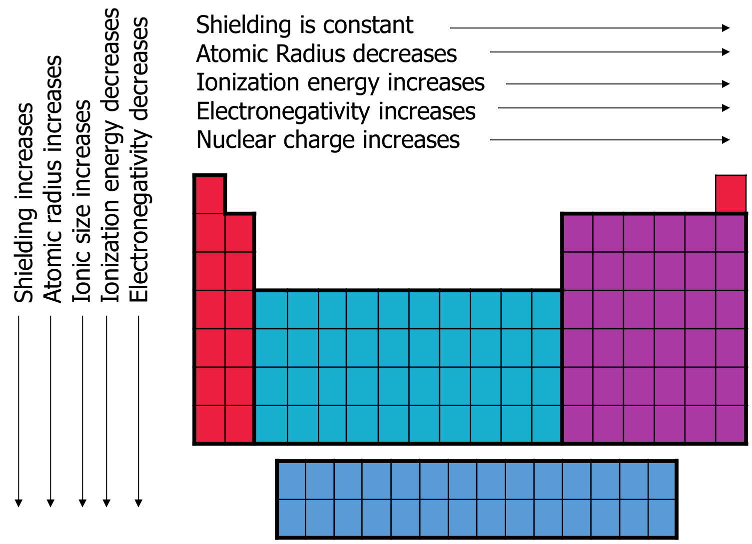
Trends in Electron Affinity

- **Alkali metals <u>show decrease</u> in the electron affinity down the column**
  - But not all groups do
  - Generally irregular increase in EA from second period to third period
- **"Generally" <u>increases across period</u>**
  - Becomes more negative from left to right
  - Not absolute
  - Group 5A generally lower EA than expected because extra electron must pair
  - Groups 2A and 8A generally very low EA because added electron goes into higher energy level or sublevel
- **Highest EA in any period = halogen**

Electron Affinities (kJ/mol)

1A	2A	3A	4A	5A	6A	7A	8A
H −73							He >0
Li −60	Be >0	B −27	C −122	N >0	O −141	F −328	Ne >0
Na −53	Mg >0	Al −43	Si −134	P −72	S −200	Cl −349	Ar >0
K −48	Ca −2	Ga −30	Ge −119	As −78	Se −195	Br −325	Kr >0
Rb −47	Sr −5	In −30	Sn −107	Sb −103	Te −190	I −295	Xe >0

Summary



8 October 2021 21 21CYB101J

Determine the Z_{eff} difference for a 3p and 2s electron in Phosphorous, Z=15 ?

$1s^2 2s^2 2p^6 3s^2 3p^3$; If we consider an electron in 3p, Z_{eff} = 4.8; however, we are asked to consider a 2s electron. The other electrons to the right do not shield, and are removed from the calculation (n_0= 2, we start the calculations at $1s^2 2s^{2-1}$ for our grouping (15 – [2x 0.85 + 0.35]) Z_{eff} = 12.95.

Difference in Z_{eff} is 12.95 – 4.8 = 8.15

8 October 2021 22 21CYB101J

Which electron will be removed when Zinc is ionised? Explain using slater's rule

Determine the electron configuration for Zn

$(1s)^2(2s, 2p)^8(3s, 3p)^8(3d)^{10}(4s)^2$

For a 4s electron:

Establish the screening constant for the 4s electron

$\sigma = (1 \times 0.35) + (18 \times 0.85) + (10 \times 1.00) = 25.65$

Calculate the effective nuclear charge

$Z^* = Z - \sigma = 30 - 25.65 = 4.35$

For a 3d electron:

Establish the screening constant for the 3d electron

$\sigma = (9 \times 0.35) + (18 \times 1.00) = 21.15$

– **Calculate the effective nuclear charge**

$Z^* = Z - \sigma = 30 - 21.15 = 8.85$

From this example, you can see that the 3d electrons experience a much greater positive charge than the 4s electron and would be held more tightly. Thus, the 4s electrons will be the first removed when Zn is ionized.

Which statement is correct?

(A) Radius of Cl atom is 0.99 Å, while that of Na^+ ion is 1.54 Å

(B) Radius of Cl atom is 0.99 Å while that of Na atom is 1.54 Å

(C) The radius of Cl atom is 0.95 Å while that of Cl^- ion is 0.81 Å

(D) Radius of Na atom is 0.95 Å, while that of Na^+ ion is 1.54 Å

PROBLEM: Rank each set of ions in order of *decreasing* size, and explain your ranking:

(a) Ca^{2+}, Sr^{2+}, Mg^{2+} (b) K^{+}, S^{2-}, Cl^{-} (c) Au^{+}, Au^{3+}

PLAN: Compare positions in the periodic table, formation of positive and negative ions and changes in size due to gain or loss of electrons.

SOLUTION:

(a) $Sr^{2+} > Ca^{2+} > Mg^{2+}$ These are members of the same Group (2A/2) and therefore decrease in size going up the group.

(b) $S^{2-} > Cl^{-} > K^{+}$ These ions are isoelectronic; S^{2-} is an anion with the smallest Z_{eff} and is the largest K^{+} is a cation with a large Z_{eff} and is the smallest.

(c) $Au^{+} > Au^{3+}$ The higher the + charge, the smaller the ion.

What is the Zeff experienced by the valence electrons in the three isoelectronic species: fluorine anion (F^{-}), neutral neon atom (Ne), and sodium cation (Na^{+})?

Each species has 10 electrons, and the number of core electrons is 2 (10 total electrons - 8 valence), but the effective nuclear charge varies because each has a different atomic number (Z).

The approximate Zeff can be found with Slater's Rules. For all of these species, we would calculate the same sigma or S value:

- Calculating σ : (1s)(2s,2p), $\sigma=2(0.85)+7(0.35)=1.7+2.45=4.15$
- ***Fluorine anion: Zeff = 9−σ = 9−4.15 = 4.85***
- ***Neon atom: Zeff = 10−σ = 10−4.15 = 5.85***
- ***Sodium Cation: Zeff = 11−σ = 11−4.15 = 6.85***
- So, the sodium cation has the greatest effective nuclear charge.

Which would have a higher second ionization energy: sodium or calcium? Explain your reasoning.

- **Na : $1s^22s^22p^63s^1$ Ca : $1s^22s^22p^63s^23p^64s^2$**
- Sodium would be expected to have a higher second ionization energy than calcium.
- A second ionization brings calcium to the favorable electron configuration of the noble gas argon as it removes the last valence electron.
- For sodium, the first ionization accomplished a noble gas configuration, removing its lone valence electron.
- Removal of a second electron then means that a core electron has to be removed, which is a much higher energy reaction and creates a less favorable configuration.

In general, ionization energies increase across a period from left to right. Explain why the second ionization energy of chromium is higher, not lower, than that of manganese.

The reactions associated with the second ionization potentials are:

$Cr^{+}(g) \rightarrow Cr^{2+}(g) + e^{-}$ (IP_2 for Cr)

and

$Mn^{+}(g) \rightarrow Mn^{2+}(g) + e^{-}$ (IP_2 for Mn)

The electron configurations for each species is:

Cr^{+}: $[Ar]3d^5 \rightarrow Cr^{2+}$: $[Ar]3d^4$

Mn^{+} : $[Ar]3d^5 4s^1 \longrightarrow Mn^{2+}$: $[Ar]3d^5$

- ❑ In the case of Cr, the reactant is half-filled, imparting extra stability and requiring more energy for ionization.
- ❑ In the case of Mn, the product is half-filled, giving extra stability to the product and requiring less energy for ionization.
- ❑ The two effects together lead to $IP_2(Cr) > IP_2(Mn)$.

From their locations in the periodic table, predict which of these elements has the highest fourth ionization energy: B, C, or N.

These elements all lie in the second row of the periodic table and have the following electron configurations:

•B: [He]2$s^2$2p^1
•C: [He]2$s^2$2p^2
•N: [He]2$s^2$2p^3

The fourth ionization energy of an element (I4) is defined as the energy required to remove the fourth electron:

$$E^{3+}(g) \rightarrow E^{4+}(g)+e^{-}$$

- Because carbon and nitrogen have four and five valence electrons, respectively, their fourth ionization energies correspond to ***removing an electron from a partially filled valence shell.***
- The fourth ionization energy for boron, however, corresponds to ***removing an electron from the filled 1s² subshell***.
- This should require much more energy.
- The actual values are as follows: ***B, 25,026 kJ/mol; C, 6223 kJ/mol; and N, 7475 kJ/mol.***

Thank you all for your attention

Information presented here were collected from various sources – textbooks, articles, manuscripts, internet and newsletters. All the researchers and authors of the above mentioned sources are greatly acknowledged.