



What you already know

- Atomic radii trend in d-block
- Ionic radii
- Isoelectronic species
- Ionic radii of isoelectronic species
- Ionisation energy
- Factors affecting ionisation energy



What you will learn

- Applications of ionisation energy
- Oxidation state
- Electron gain enthalpy
- Factors affecting electron gain enthalpy
- Electron affinity



Applications of Ionisation Energy



- **The trends of the metallic and non-metallic character of an element** can be explained by the ionisation energy. For example, metals have **low ionisation energy** and are more ready to form cations while **nonmetals have high ionisation energy** and prefer forming anions.
- **The knowledge of ionisation energy can be used to find the number of valence electrons in an atom.**

**For example, in the case of Li**, the value of  $I.E._1$  and  $I.E._2 = 5.4 \text{ eV}$  and  $75.6 \text{ eV}$  respectively. This indicates that the first electrons are much more readily removed than the other electrons. Thus, there is only one electron in the valence shell of a lithium atom.

- **Reducing power of an element**  
Lower the value of the ionisation energy of an element, greater is its reducing power. This is because a low value of ionisation energy means easier removal of electrons from the element which then can be used to reduce an oxidising agent.
- **Basic strength of an element**  
Lower the value of ionisation energy, easier to remove the electrons that means, greater will be the donor properties of the element. Thus, the basic strength of the elements increase considerably as the base is an electron donor.



- **Non-metals** have **higher** values of  $I.E._1$ ,  $I.E._2$  and  $I.E._3$  as compared to metals.
- **Alkaline earth metals** and **pnicogens (elements belonging to the nitrogen family)** have **higher** values of  $I.E._1$  as compared to the succeeding groups (trend observed upto 4<sup>th</sup> period).
- $I.E._3$  values of **alkaline earth metals** show exceptional **jump**.
- **Noble gases** have the highest  $I.E._1$  values in their respective period.



### Finding percentage composition of sample

One gram sample of Mg (g) is supplied with 50 kJ of energy. What will be the percentage composition of  $Mg^{2+}$  ions in the sample?

Given, first and second ionisation energies of Mg are 720 kJ/mol and 1440 kJ/mol respectively.

#### Solution

##### Step 1: Finding the moles of Mg (g)

$$\text{Moles of Mg} = \frac{\text{Mass}}{\text{Molar mass}} = \frac{1}{24}$$

##### Step 2: Calculating the energy required to convert into $Mg^+$ ion

Energy required for converting all of them to  $Mg^+$

$$= \frac{1}{24} \times 720 = 30 \text{ kJ}$$

Subtracting, 50 kJ - 30 kJ = 20 kJ

Now, we have 20 kJ of energy left.

##### Step 3: Calculating the energy required to convert into $Mg^{2+}$ ion

$$\text{Energy required to change } Mg^+ \text{ to } Mg^{2+} = \frac{1}{24} \times 1440 = 60 \text{ kJ}$$

However, we have only 20 kJ left. It means  $\frac{20}{60}$  of  $\frac{1}{24}$  will become  $Mg^{2+}$ .

$$= \frac{1}{72} \text{ moles will be } Mg^{2+}$$

##### Step 4: Calculating in percentage

$$\text{In percentage} = \left( \frac{1}{72} \right) \times 100 / \left( \frac{1}{24} \right) = 33.33 \%$$

Therefore, the percentage composition of  $Mg^{2+}$  ions in the sample is 33.33 %.



### Finding the correct statement about ionisation energy

Which of the following statement(s) is/are correct?

- The first ionisation energy of Al is less than the first ionisation energy of Mg.
- The second ionisation energy of Mg is greater than the second ionisation energy of Na.
- The second ionisation energy of Na is greater than the second ionisation energy of Mg.
- The third ionisation energy of Mg is greater than the third ionisation energy of Al.

### Solution

Statement **(a) is correct** because Mg has a **filled s-orbital**. So, the first ionisation energy of Al is less than that of Mg.

Statement **(b) is incorrect** because Na after losing one electron will attain the noble gas configuration and hence has exceptionally high second ionisation energy.

Statement **(c) is correct** because Na after losing one electron will attain the noble gas configuration and hence has much higher second ionisation energy than Mg which incidentally has a low value due to attainment of noble gas configuration after removal of the second electron.

Statement **(d) is correct** because the third ionisation energy of Mg is greater than the third ionisation energy of Al as a noble gas configuration is to be broken in Mg while Al attains one.

**Hence, options (a), (c) and (d) are the correct.**

★ MAIN

★ BOARDS

### Oxidation State

It is the **imaginary charge that an atom of the element has or appears to have when present in the combined state with other atoms.**

Or

**The total charge acquired by the atom during the formation of a molecule** is also known as oxidation state. It can be thought of as the charge on an atom if all its bonds in the molecule are broken. Keep in mind that during this imaginary bond fission, bonded electrons would go with the more electronegative atom of the two bonded atoms.

**Oxidation number** represents the number of electrons lost by the atom when all its bonds are imagined to be broken as mentioned before. This number can be positive, when electrons are lost, or, negative, when electrons are gained. Oxidation state and oxidation number mostly have the same value except in cases that we will see going forward.

**For example**, the oxidation number of N in  $\text{HNO}_3$  is +5.

**It is always assigned a '+' or a '-' sign except for when it is zero.**

For example, the oxidation number of N in  $\text{NH}_3$  is -3 and that of H is +1.

**It can be a whole number or a fraction.**

For example, the oxidation number of Fe in  $\text{Fe}_3\text{O}_4$  is 8/3.

★ MAIN

★ ADVANCED

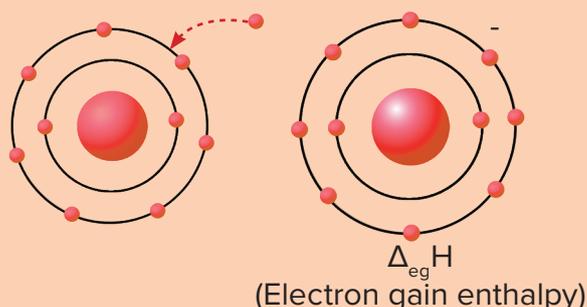
### Electron Gain Enthalpy

★ BOARDS

When an **electron is added** to an **isolated neutral gaseous atom** in its ground state, the **enthalpy change** accompanying the process is defined as the **electron gain enthalpy** ( $\Delta_{\text{eg}}H$ ).



It is represented by  $\Delta_{\text{eg}}H$  and is measured in  $\text{kJ/mol}$ .



**Fig. 1: Electron addition in Fluorine**

### Electron gain enthalpy

Positive

Negative

- When the **energy is supplied** to a gaseous atom while **adding an electron**, the electron gain enthalpy is **positive** ( $\Delta_{\text{eg}}H = +\text{ve}$ ).
- When the **energy is released** while **adding an electron** to a gaseous atom, the electron gain enthalpy is **negative** ( $\Delta_{\text{eg}}H = -\text{ve}$ ).

| Positive E.G.E.   | Negative E.G.E.  |
|---|--|
| For the <b>addition of an electron</b> , the energy needs to be <b>spent</b> , making $\Delta_{\text{eg}}H$ positive.               | The energy <b>released</b> on <b>adding an electron</b> is represented by negative values of $\Delta_{\text{eg}}H$ . |
| The atom is <b>reluctant</b> for the <b>addition of a new electron</b> in its valence shell and this drives it towards instability. | In order to <b>gain stability</b> , the atom tends to <b>gain electrons</b> .  |
| <b>Noble gases</b> and <b>alkaline earth metals</b> have <b>positive</b> $\Delta_{\text{eg}}H$ .                                    | <b>Halogens</b> have a <b>very high negative</b> $\Delta_{\text{eg}}H$ .   |

Table 1: Positive vs negative electron gain enthalpy

### Factors Affecting Electron Gain Enthalpy

- The magnitude of the electron gain enthalpy is inversely related to the atomic size.
- The magnitude of the electron gain enthalpy increases with increase in effective nuclear charge ( $Z_{\text{eff}}$ ).
- The magnitude of the electron gain enthalpy is inversely related to the screening effect.

Magnitude of  $\Delta_{\text{eg}}H$  decreases, when

Effective nuclear charge decreases

Electron is added to Half-filled or fully filled subshell

Atomic size increases

Screening effect increases

## Electron Gain Enthalpy: Trend

In general, the **electron gain enthalpy** becomes **more negative** on moving from the left to the right across a **period**, while it becomes **less negative** on moving from top to bottom in a group. However, the variation **does not show a perfectly regular trend** along a period or a group with a number of exceptions.

### Electron gain enthalpy across a period

- As we move from **left to right across a period**,  $\Delta_{\text{eg}}H$  becomes **more negative**.
- The **effective nuclear charge increases**, which makes  $\Delta_{\text{eg}}H$  **more negative**.
- Consequently, it will be **easier to add** an electron to a **smaller atom**.

### Electron gain enthalpy down a group

- As we move **down a group**,  $\Delta_{\text{eg}}H$  becomes **less negative**.
- The **size of the atom increases**, making  $\Delta_{\text{eg}}H$  **less negative**.
- Also, the **added electron** would be at a **larger distance from the nucleus**.



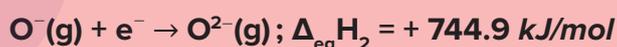
The electron gain enthalpy values are positive for the following:

- Inert gases
- Alkaline earth metals Be and Mg
- Nitrogen

The stability of half-filled and fully filled subshells is comparatively more and the addition of an extra electron is difficult.

### Successive electron gain enthalpy

- The **enthalpy change for the addition of a second electron** to an initially neutral atom is **invariably positive** because the electronic **repulsions between incoming electron and the target negative ion outweigh the nuclear attraction**.



Similarly,

$$\Delta_{\text{eg}}H_1 + \Delta_{\text{eg}}H_2 = +ve$$



### Notes

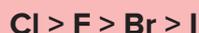
Second and subsequent electron gain enthalpies are always positive.

### Order of E.G.E. magnitude for halogens

- As we go **down the halogen group**, the size of the atom **increases**, thus suggesting the order to be as follows:



- However, in **reality** the trend is as follows:



### Order of E.G.E magnitude for chalcogens

- Similarly, as we go **down the chalcogen group**, the size of the atom **increases**, thus suggesting the order to be as follows:



- However, in **reality** the trend is as follows:

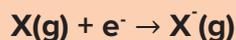


### Reason for such exceptions

- Fluorine and oxygen** have the **smallest size** in their respective groups.
- In the case of fluorine, the **valence shell** electronic configuration is  $2s^2 2p^5$ . On **adding another electron** externally to the valence shell, it causes **severe electron-electron repulsions** due to which the system becomes **comparatively unstable**.
- The same trend also occurs in the case of oxygen.
- It is quite **easy to add an electron** to Cl and S, because of their **larger size**, which is due to the **large size of their third shell**.
- Hence, the order is different from the actual orders.
- Cl** has the **highest negative electron gain enthalpy** value in the entire periodic table.

### Electron Affinity (E.A.)

It is defined as the **energy released** when an **electron is added to a neutral** isolated gaseous atom in its ground state.



Generally, the order of **E.A.** will be the **same as negative E.G.E.**, whereas the **order of E.G.E.** will be the **opposite of E.A.**



### Notes

The smallest value of I.E. of an element (Cs) is also greater than the highest value of E.A. of an element (Cl).



### Finding the order of electron affinity

Select the correct order(s) of magnitude of electron affinity.

- (a)  $\text{Mg} < \text{P} < \text{Al}$       (b)  $\text{Si} < \text{S} < \text{Cl}$       (c)  $\text{Ar} < \text{P} < \text{Na}$       (d)  $\text{Si} < \text{Na} < \text{Al}$

#### Solution

Option **(a) is incorrect**. The correct order will be  $\text{Mg} < \text{Al} < \text{P}$ .

Option **(b) is correct**. The correct order is  $\text{Si} < \text{S} < \text{Cl}$ . On going from left to right, electron gain enthalpy magnitude increases due to increase in effective nuclear charge.

Option **(c) is incorrect**. The correct order will be  $\text{Na} < \text{P} < \text{Ar}$ .

Option **(d) is incorrect**. The correct order will be  $\text{Na} < \text{Al} < \text{Si}$ .

**Hence, option (b) is the correct answer.**



### Based on electron gain enthalpy

Out of  $\text{Cs}^+$  (g) and  $\text{Cl}$  (g) which atom will release more energy upon the electron gain?

#### Solution

$\text{Cs}^+$  will be the answer.

$\text{Cs}^+ + e = \text{Cs}$  (magnitude of energy released will be same as **ionisation energy**)

$\text{Cl} + e = \text{Cl}^-$  (magnitude of energy released will be same as that of **Electron gain enthalpy**)

The ionisation energy of Cs is the least in the periodic table. Even then, the **lowest ionisation energy** is still **higher than** the **highest electron affinity**. Hence,  **$\text{Cs}^+$**  is the answer.



### Finding the stability

Identify the least stable ion amongst the following:

- (a)  $\text{Li}^-$       (b)  $\text{Be}^-$       (c)  $\text{B}^-$       (d)  $\text{C}^-$

#### Solution

This question can be answered by thinking about which species will readily give up the extra electron. Since, all given options are mono negative ions, the energy associated with the removal of one electron will be the same as the electron affinity of the respective atoms. This is because electron affinity is defined as the energy released when an electron is added to the atom. The order of electron affinity here is:  $\text{Be} < \text{Li} < \text{B} < \text{C}$ . Be has the minimum electron affinity among the four as it has to gain energy to accept an electron.

Hence, we can see that  **$\text{Be}^-$  releases energy on removal of an electron** while other anions absorb energy before giving up an electron. Hence  **$\text{Be}^-$**  is least stable and readily releases an electron.

Thus,  **$\text{Be}^-$  is the least stable.**

**Hence, option (b) is the correct answer.**



### Calculating the energy released of an element

The electron gain enthalpy of a hypothetical element 'A' is  $-3 \text{ eV/atom}$ . How much energy in  $\text{kcal}$  is released when  $10 \text{ g}$  of 'A' is completely converted to  $\text{A}^-$  ions in gaseous state? (Take  $1 \text{ eV/atom} = 23 \text{ kcal/mol}$ , molar mass of A =  $30 \text{ grams}$ )

#### Solution

$$\text{Moles of A} = \frac{\text{Mass}}{\text{Molar mass}} = \frac{10}{30} = \frac{1}{3}$$



Energy released by one atom =  $3 \text{ eV/atom} = 3 \times 23 \text{ kcal/mol}$

Energy released by  $\frac{1}{3}$  mole of atom =  $3 \times 23 \times \frac{1}{3} = \mathbf{23 \text{ kcal/mol}}$



### Predicting the possible compounds

Consider the following values of I.E. (eV) for the elements W and X.

| Element | I.E. <sub>1</sub> | I.E. <sub>2</sub> | I.E. <sub>3</sub> | I.E. <sub>4</sub> |
|---------|-------------------|-------------------|-------------------|-------------------|
| W       | 10.5              | 15.5              | 24.9              | 79.8              |
| X       | 8                 | 14.8              | 78.9              | 105.8             |

Other two elements Y and Z have an outermost electronic configuration,  $ns^2 np^4$  and  $ns^2 np^5$ , respectively. Then, according to the given information, which of the following compounds are **not possible**?

- (a)  $\text{W}_2\text{Y}_3$                       (b)  $\text{X}_3\text{Y}_2$                       (c)  $\text{YZ}_2$                       (d)  $\text{XZ}_2$

#### Solution

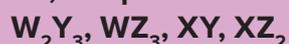
**For W** atoms, there are three times the ionisation energy from 3 to 4. So, the maximum oxidation state = + 3 or  $\text{W}^{3+}$ .

**For an X** atom, there are five times the ionisation energy from 2 to 3. So, the maximum oxidation state = + 2 or  $\text{X}^{2+}$ .

**Y** will form  $\text{Y}^{2-}$ .

**And Z** will form  $\text{Z}^-$ .

**So, the possible compounds are as follows:**



**So,  $\text{W}_2\text{Y}_3$  and  $\text{XZ}_2$  in (a) and (d) are possible compounds.**

**Hence, options (b) and (c) are the correct answers.**

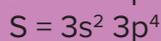
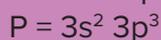
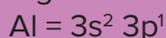
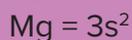


### Predicting ionisation energy trend with respect to the sample given

| Element | n | l | m  | s              | Magnetic moment ( $\mu$ ) | Valence electron |
|---------|---|---|----|----------------|---------------------------|------------------|
| Mg      | 3 | 0 | 0  | $+\frac{1}{2}$ | 0                         | 2                |
| Al      | 3 | 1 | +1 | $-\frac{1}{2}$ | $\sqrt{3}$                | 3                |
| P       | 3 | 1 | -1 | $+\frac{1}{2}$ | $\sqrt{15}$               | 5                |
| S       | 3 | 1 | 0  | $-\frac{1}{2}$ | $\sqrt{8}$                | 6                |

Consider the value of all four quantum numbers of the last electrons and magnetic moment and valence electrons of elements **Mg**, **Al**, **P**, and **S** in their ground state.

Given that,



Which of the following statement(s) will be correct?

- (a) The ionisation energy of **Mg** is greater than the ionisation energy of **Al**.
- (b) The ionisation energy of **P** is greater than the ionisation energy of **S**.
- (c) The ionisation energy of **Al** is greater than the ionisation energy of **Mg**.
- (d) The ionisation energy of **S** is greater than the ionisation energy of **P**.

#### Solution

**Option (a) is correct.** The ionisation energy of **Mg** is greater than **Al** because **Al**, after losing one electron, attains a stable fully filled configuration and **Mg** has a stable fully filled configuration. Therefore, it is easier to remove an electron from **Al** and difficult to remove from **Mg**. Thus, the ionisation potential of **Mg** > **Al**. The first ionisation energy of aluminum is smaller than magnesium.

**Option (b) is correct.** The ionisation energy of **P** is greater than **S** as **P** has half filled electronic configuration, so it is more stable hence more ionisation energy.

**Option (c) is incorrect.** The ionisation energy of **Mg** is greater than **Al** because **Al**, after losing one electron, attains a stable fully filled configuration and **Mg** has a stable fully filled configuration. Therefore, it is easier to remove an electron from **Al** and difficult to remove from **Mg**. Thus, the ionisation potential of **Mg** > **Al**.

**Option (d) is incorrect** because The ionisation energy of **P** is greater than **S** as **P** ( $1s^2 2s^2 2p^6 3s^2 3p^3$ ) has half filled electronic configuration, so it is more stable hence more ionisation energy. Thus, **P** is having more ionisation energy than sulphur.

Hence, options (a) and (b) are the correct.



## Summary

### 1. Application of ionisation energy

- **The trends of the metallic and non-metallic characters** of an element can be explained by the ionisation energy.
- The knowledge of the ionisation energy can be used to **find the number of valence electrons in an atom**.
- **Lower** the value of the **ionisation energy** of an element, **greater** is its **reducing power**. This is because a low value of ionisation energy means easier removal of electrons from the element which then can be used to reduce an oxidising agent.
- Lower the value of ionisation energy, easier to remove the electrons that means, greater will be the donor properties of the element. Thus, the basic properties of the elements increase considerably as the base is an electron donor.

### 2. Oxidation state

It is the **charge that an atom of the element has or appears to have when present in the combined state with their atoms**.

Or

**The total charge acquired by the atom during the formation of a molecule** is also known as oxidation state.

### 3. Electron gain enthalpy

When an **electron is added** to an **isolated neutral gaseous atom**, the **enthalpy change accompanying** the process is defined as the **electron gain enthalpy ( $\Delta_{eg}H$ )**.

- When an **energy is to be supplied** to a gaseous atom while **adding an electron**, the electron gain enthalpy is **positive ( $\Delta_{eg}H = +ve$ )**.
- When an **energy is released** while **adding an electron** to a gaseous atom, the electron gain enthalpy is **negative ( $\Delta_{eg}H = -ve$ )**.

### 4. Electron gain enthalpy: Trend

In general, the **electron gain enthalpy** becomes **more negative** on moving from left to right across a **period**, while it becomes **less negative** on moving from top to bottom in a **group**.

However, the variation **does not show a perfectly regular trend** along a period or a group with a number of exceptions.

### 5. Electron gain enthalpy across a period

- As we move from **left to right across a period**,  **$\Delta_{eg}H$**  becomes **more negative**.
- The **effective nuclear charge increases**, which makes  **$\Delta_{eg}H$**  **more negative**.
- Consequently, it will be **easier to add** an electron to a **smaller atom**.

### 6. Electron gain enthalpy down a group

- As we move **down a group**,  **$\Delta_{eg}H$**  becomes **less negative**.
- The **size of the atom increases**, making  **$\Delta_{eg}H$**  **less negative**.
- Also, the **added electron** would be at a **larger distance from the nucleus**.

## 7. Factors affecting electron gain enthalpy

- The magnitude of electron gain enthalpy is inversely related to the atomic size.
- The magnitude of electron gain enthalpy is directly related to the effective nuclear charge ( $Z_{\text{eff}}$ ).
- The magnitude of electron gain enthalpy is inversely related to the screening effect.

## 8. Electron affinity (E.A.)

It is defined as the **energy released** when an **electron is added to a neutral** isolated gaseous atom in its ground state.

The order of **E.A.** will be the **same as negative E.G.E**, whereas the **order of E.G.E** will be the **opposite of E.A.**

The smallest value of I.E. of an element (Cs) is also greater than the highest value of E.A. of an element (Cl).