

Question 16. Among the second period elements, the actual ionization enthalpies are in the order: Li < B < Be < C < O < KI < F< Ne

Explain why

- (i) Be has higher ΔH_1 than B?
- (ii) O has lower $\Delta_i H_1$ than N and F?

Answer:

- (i) In case of Be (1s 2 2s 2) the outermost electron is present in 2s-orbital while in B (1s 2 2s 2 2p 1) it is present in 2p-orbital. Since 2s electrons are more strongly attracted by the nucleus than 2p-electrons, therefore, lesser amount of energy is required to knock out a 2p-electron than a 2s electron. Consequently, At of Be is higher than that Δ_iH_1 of B.
- (ii) The electronic configuration of

$$N_7 = 1s^2 2s^2 2p_x^{-1} 2p_u^{-1} 2p_z^{-1}$$

$$O_8 = 1s^2 2s^2 2p_x^{1} 2p_u^{1} 2p_z^{1}$$

We can see that in case of nitrogen 2p-orbitals are exactly half filled. Therefore, it is difficult to remove an electron from N than from O. As a result $\Delta_i H_1$ of N is higher than that of O.

Question 17. How would you explain the fact that the first ionization enthalpy of sodium is lower than that of magnesium but its second ionization enthalpy is higher than that of magnesium?

Electronic configuration of Na and Ma are

$$Na = 1s^2 2s^2 2p^6 3s^1$$

$$Ma = 1s^2 2s^2 2p^6 3s^2$$

First electron in both cases has to be removed from 3s-orbital but the nuclear charge of Na (+ 11) is lower than that of Mg (+ 12) therefore first ionization energy of sodium is lower than that of magnesium.

After the loss of first electron, the electronic configuration of

$$Na^{+} = 1s^{2} 2s^{2} 2p^{6}$$

$$Mg^+ = 1s^2 2s^2 2p^6 3s^1$$

Here electron is to be removed from inert (neon) gas configuration which is very stable and hence removal of second electron requires more energy in comparison to Mg.

Therefore, second ionization enthalpy of sodium is higher than that of magnesium.

Question 18. What are the various factors due to which the ionization enthalpy of the main group elements tends to decrease down the group?

Answer

Atomic size: With the increase in atomic size, the number of electron shells increase. Therefore, the force that binds the electrons with the nucleus decreases. The ionization enthalpy thus decreases with the increase in atomic size.

Screening or shielding effect of inner shell electron: With the addition of new shells, the number of inner electron shells which shield the valence electrons increases. As a result, the force of attraction of the nucleus for the valence electrons further decreases and hence the ionization enthalpy decreases.

Question 19. The first ionization enthalpy values (in kJ mol⁻¹) of group 13 elements are:

B Al Ga In TI 801 577 579 558 589

How would you explain this deviation from the general trend? Answer:

The decrease in $\Delta_i H_1$ value from B to Al is due to the bigger size of Al.

In Ga there is 10 3d electrons which do not screen as is done by S and P electrons. Therefore, there is an unexpected increase in the magnitude of effective nuclear charge resulting in increased $\Delta_i H_1$ values. The same is with into Tl. The later has fourteen Δf electrons with very poor shielding effect. This also increases, the effective nuclear charge thus the value of $\Delta_i H_1$ increases.

Question 20. Which of the following pairs of elements would have a move negative electron gain enthalpy? (i) O or F (ii) F or Cl. Answer:

(i) O or F. Both O and F lie in 2nd period. As we move from O to F the atomic size decreases.

Due to smaller size of F nuclear charge increases.

Further, gain of one electron by

 $F \rightarrow F^{-}$

 $F^{\text{-}}$ ion has inert gas configuration, While the gain of one electron by O \rightarrow O $^{\text{-}}$

gives CT ion which does not have stable inert gas configuration, consequently, the energy released is much higher in going from

than going from $O \rightarrow O^{-}$

In other words electron gain enthalpy of F is much more negative than that of oxygen.

(ii) The negative electron gain enthalpy of CI (Δ eg H = - 349 kj mol⁻¹) is more than that of F (Δ eg H = - 328 kJ mol⁻¹).

The reason for the deviation is due to the smaller size of F. Due to its small size, the electron repulsions in the relatively compact 2p-subshell are comparatively large and hence the attraction for incoming electron is less as in the case of Cl.

Question 21. Would you expect the second electron gain enthalpy of O as positive, more negative or less negative than the first? Justify your answer.

Answer: For oxygen atom:

O (g) +
$$e^- \rightarrow O^-$$
 (g) (Δ eg H = -141 kJ mol⁻¹)

 $O^{-}(g) + e^{-} \rightarrow O^{2-}(g) (\Delta eg H = +780 \text{ kJ mol}^{-1})$

The first electron gain enthalpy of oxygen is negative because energy is released when a gaseous atom accepts an electron to form monovalent anion. The second electron gain enthalpy is positive because energy is needed to overcome the force of repulsion between monovalent anion and second incoming electron.

Question 22. What is basic difference between the terms electron gain enthalpy and electro negativity?

Answer: Electron gain enthalpy refers to tendency of an isolated gaseous atom to accept an additional electron to form a negative ion. Whereas electronegativity refers to tendency of the atom of an element to attract shared pair of electrons towards it in a covalent bond.

23. How would you react to the statement that the electronegativity of N on Pauling scale is 3.0 in all the nitrogen compounds? Ans. On Pauling scale, the electronegativity of nitrogen, (3.0) indicates that it is sufficiently electronegative. But it is not correct to say that the electronegativity of nitrogen in all the compounds is 3.

It depends upon its state of hybridisation in a particular compound, greater the percentage of s-character, more will be the electronegativity of the element. Thus, the electronegativity of nitrogen increases in moving from $\rm sp^3$ hybridised orbitals to sp hybridised orbitals i.e., as $\rm sp^3 < sp^2 < sp$.

Question 24. Describe the theory associated with the radius of an atom as it:

(a) gains an electron (b) loses an electron? Answer:

- Gain of an electron leads to the formation of an anion. The size of an anion will be larger than that of the parent atom because the addition of one or more electrons would result in increased repulsion among electrons and decrease in effective nuclear charge.
 - This the ionic radius of fluoride ion (F^-) is 136 pm whereas atomic radius of Fluorine (F) is only 64 pm.
- Loss of an electron from an atom results in the formation of a cation. A cation is smaller than its parent atom because it has fomer electrons while its nuclear charge remains the same.
 For example, The atomic radius of sodium (Na) is 186 pm and atomic radius of sodium ion (Na⁺) = 95 pm.

Question 25. Would you expect the first ionization enthalpies of two isotopes of the same element to be the same or different? Justify your answer.

Answer: Ionization enthalpy, among other things, depends upon the electronic configuration (number of electrons) and nuclear charge (number of protons). Since isotopes of an element have the same electronic configuration and same nuclear charge, they have same ionization enthalpy.

