CHEMISTRY STUDY MATERIALS FOR CLASS 12 (NCERT BASED QUESTIONS WITH ANSWERS)

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The d & f - Block Elements

Question 35: Compare the general characteristics of the first series of the transition metals with those of the second and third series metals in the respective vertical columns. Give special emphasis on the following points:

(i)electronic configurations, (ii)oxidation states,

(iii)ionisation enthalpies, and (iv)atomic sizes.

Solution 35:

(i)In the 1st, 2nd and 3rd transition series, the $3d$, $4d$ and $5d$ orbitals are respectively filled. We know that elements in the same vertical column generally have similar electronic configurations. In the first transition series, two elements show unusual electronic configurations:

$Cr(24) = 3d^5\,4s^1$ $Cr(29) = 3d^{10}\,4s^1$

Similarly, there are exceptions in the second transition series. These are:

$Mo(42) = 4d^5 5s^1$ $Tc(43) = 4d^6 5s^1$ $Ru(44) = 4d^7 5s^1$

$Rh(45) = 4d^8 5s^1$ $Pd\,(46) = 4d^{10} 5s^0$ $Ag(47) = 4d^{10} 5s^1$

There are some exceptions in the third transition series as well. These are:

$W(74) = 5d^4 6s^2$ $Pt(78) = 5d^9 6s^1$ $Au(79) = 5d^{10} 6s^1$

As a result of these exceptions, it happens many times that the electronic configurations of the elements present in the same group are dissimilar.

(ii)In each of the three transition series the number of oxidation states shown by the elements is the maximum in the middle and the minimum at the extreme ends. However, +2 and +3 oxidation states are quite stable for all elements present in the first transition series. All metals present in the first transition series form stable compounds in the +2 and +3 oxidation states. The stability of the +2 and +3 oxidation states decreases in the second and the third transition series, wherein higher oxidation states are more important.

(iii)In each of the three transition series, the first ionization enthalpy increases from left to right. However, there are some exceptions. The first ionization enthalpies of the third transition series are higher than those of the first and second transition series. This occurs due to the poor shielding effect of $4f$ electrons in the third transition series. Certain elements in the second transition series have higher first ionization enthalpies than elements corresponding to the same vertical column in the first transition series. There are also elements in the 2nd transition series whose first ionization enthalpies are lower than those of the elements corresponding to the same vertical column in the 1^{st} transition series.

(iv)Atomic size generally decreases from left to right across a period. Now, among the three transition series, atomic sizes of the elements in the second transition series are greater than those of the elements corresponding to the same vertical column in the first transition series. However, the atomic sizes of the elements in the third transition series are virtually the same as those of the corresponding members in the second transition series. This is due to lanthanoid contraction.

Question 37: Comment on the statement that elements of the first transition series possess many properties different from those of heavier transition elements.

Solution 37: The properties of the elements of the first transition series differ from those of the heavier transition elements in many ways.

(i) The atomic sizes of the elements of the first transition series are smaller than those of the heavier elements (elements of 2^{nd} and 3^{rd} transition series). However, the atomic sizes of the elements in the third transition series are virtually the same as those of the corresponding members in the second transition series. This is due to lanthanoid contraction.

(ii) +2 and +3 oxidation states are more common for elements in the first transition series, while higher oxidation states are more common for the heavier elements.

(iii)The enthalpies of atomization of the elements in the first transition series are lower than those of the corresponding elements in the second and third transition series.

(iv)The melting and boiling points of the first transition series are lower than those of the heavier transition elements. This is because of the occurrence of stronger metallic bonding (m—M bonding).

(v)The elements of the first transition series form low-spin or high-spin complexes depending upon the strength of the ligand field. However, the heavier transition elements form only low- spin complexes, irrespective of the strength of the ligand field.

Question 38:

Silver atom has completely filled d orbitals ($4d^{10}$) in its ground state. How can you say that it is a transition element?

Solution 38:

Ag has a completely filled 4d orbital in its ground state. Now, silver displays two oxidation states (+1 and +2). In the +1 oxidation state, an electron is removed from the s-orbital. However, in the +2 oxidation state, an electron is removed from the d-orbital. Thus, the d-orbital now becomes incomplete ($4d^9$). Hence, it is a transition element.

Question 39:

In the series Sc (Z = 21) to Zn (Z = 30), the enthalpy of atomization of zinc is the lowest, i.e. . 1 126KJ mol^{-1} Why?

Solution 39:

The extent of metallic bonding an element undergoes decides the enthalpy of atomization. The more extensive the metallic bonding of an element, the more will be its enthalpy of atomization. In all transition metals (except Zn, electronic configuration: $3d^{10}4s^2$), there are some unpaired electrons that account for their stronger metallic bonding. Due to the absence of these unpaired electrons, the inter-atomic electronic bonding is the weakest in Zn and as a result, it has the least enthalpy of atomization.

Question 40:

Which of the 3d series of the transition metals exhibits the largest number of oxidation states and why?

Solution 40:

$Mn(Z=25)$ - $3d^5 4s^2$

Mn has the maximum number of unpaired electrons present in the d-subshell (5 electrons). Hence, *Mn* exhibits the largest number of oxidation states, ranging from +2 to +7.

Question 41:

How would you account for the irregular variation of ionization enthalpies (first and second) in the first series of the transition elements?

Solution 41:

Ionization enthalpies are found to increase in the given series due to a continuous filling of the inner *d*-orbitals. The irregular variations of ionization enthalpies can be attributed to the extra stability of configurations such as d^0, d^5, d^{10}. Since these states are exceptionally stable, their ionization enthalpies are very high.

In case of first ionization energy, Cr has low ionization energy. This is because after losing one electron, it attains the stable configuration ($3d^5$). On the other hand, Zn has exceptionally high first ionization energy as an electron has to be removed from stable and fully-filled orbitals ($3d^{10} 4s^2$).

Second ionization energies are higher than the first since it becomes difficult to remove an electron when an electron has already been taken out. Also, elements like Cr and Cu have exceptionally high second ionization energies as after losing the first electron, they have attained the stable configuration (Cr^+ : $3d^5$ and Cu^+ : $3d^{10}$). Hence, taking out one electron more fromthis stable configuration will require a lot of energy.

Question 42:Why is the highest oxidation state of a metal exhibited in its oxide or fluoride only?

Solution 42: Both oxide and fluoride ions are highly electronegative and have a very small size. Due to these properties, they are able to oxidize the metal to its highest oxidation state.

Question 43:

Actinoid contraction is greater from element to element than lanthanoid contraction. Why?

Solution 43:

In actinoids, $5f$ orbitals are filled. These $5f$ orbitals have a poorer shielding effect than $4f$ orbitals (in lanthanoids). Thus, the effective nuclear charge experienced by electrons in valence shells in case of actinoids is much more that that experienced by lanthanoids. Hence, the size contraction in actinoids is greater as compared to that in lanthanoids.

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