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d-BLOCK ELEMENTS

1. INTRODUCTION

d-block elements/Transition Elements-

The elements in which the last electron enters (n – 1)d orbitals of the atom are called d-block elements. Also, these elements lie in between s and p block elements in the long form of the periodic table. So, they are also called transition elements.

2. ELECTRONIC CONFIGURATION AND IRREGULARITIES

The valence shell configurations of these elements can be represented by $(n-1)d^{1-10}ns^{0,1,2}$. All the d-block elements are classified into four series viz 3d, 4d, 5d and 6d orbitals of $(n-1)^{th}$ main shell. Each series has 10 elements. Cr($3d^5$, $4s^1$), Cu($3d^{10}$, $4s^1$), Mo($4d^5$, $5s^1$), Pd($4d^{10}$, $5s^0$), Ag($4d^{10}$, $5s^1$) and Au($5d^{10}$, $6s^1$) clearly show irregularities in the configurations. These are explained on the basis of the concept that half-filled and completely filled d-orbitals are relatively more stable than other d-orbitals.

PLANCESS CONCEPTS

It should be noted here that when atoms of these elements form cations, electrons are removed from the outermost s-subshell instead of the penultimate d-subshell, although the former was filled earlier.

Note: $_{25}Mn$: [Ar] $3d^5$, $4s^2$ Mn^{2+} ; [Ar]$3d^5$
$_{26}Fe$: [Ar]$3d^6$, $4s^2$ Fe^{2+} ; [Ar] $3d^6$

■Vaibhav Krishnan
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Illustration 1: To what extent do the electronic configurations decide the stability of oxidation states in the first series of the transition elements? Illustrate your answer with example.

(JEE MAIN)

Sol:

Methodology:

Half-filled and completely filled orbitals have extra stability

e.g., Mn^{2+} = [Ar]$3d^5$, Sc^{3+} = [Ar], Zn^{2+} = [Ar] $3d^{10}$

Illustration 2: What may be the stable oxidation state of the transition element with the following d-electron configurations in the ground state of their atoms: $3d^3$, $3d^5$, $3d^8$ and $3d^4$?

(JEE ADVANCED)

Sol:

Ground state configuration	Stable oxidation state
$3d^3$	+5
$3d^5$	+2, + 7
$3d^8$	+2
$3d^4$	$3d^4$ does not exist

3. GENERAL PROPERTIES OF THE TRANSITION METALS

3.1 Atomic and Ionic Radii

(a) The atomic and ionic radii for transition elements are smaller than their corresponding s-block elements and are greater than their corresponding p-block elements.

(b) The atomic and ionic radii for transition elements for a given series show a decreasing trend for the first five elements and then becomes almost constant for next five elements of the series.

For example, in in 3d-series atomic radius decreases from $_{21}Sc$ to $_{25}Mn$ and then becomes constant for next five i.e. $_{26}Fe$ to $_{30}Zn$

Explanation: This is due to the combined effect of the increasing effective nuclear charge, (ENC) and increasing screening effect along the period. An increase in ENC favors a decrease in atomic radii, whereas increase in number of d-elements increases the screening effect and thus increases the atomic radii. Thus both ENC and screening effect act opposite to each other and therefore the atomic size is governed by the net influence of these two.

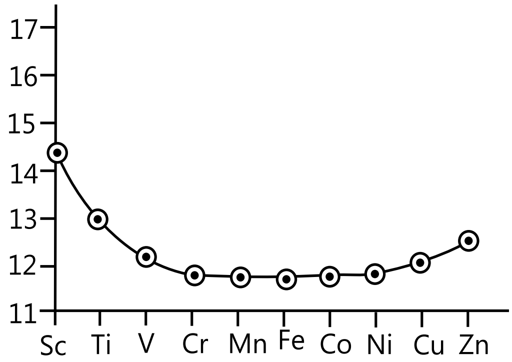

Figure 1: Atomic radii of elements of 3d-

(c) The atomic and ionic radii of the elements of 4d-series are higher than 3d-series as the number of shells increases down the group. However, the elements of 4d-series and 5d-series on moving down the group reveal almost constant value. For example, Zirconium and Hafnium, the members of 4d and 5d-series, respectively have the almost same size i.e., 145 pm. Similarly, Zr^{4+} and Hf^{4+} have almost the same size i.e., 145 pm. Similarly, Zr^{4+} and Hf^{4} have their atomic radii as 80 pm and 81 pm respectively. This is due to the Lanthanoid contraction.

(d) The ionic radii decreases as charge on the cation increases (i.e., higher oxidation state). e.g.,

$Ti^{2+} > Ti^{3+} > Ti^{4+}$

$Cr^{2+} > Cr^{3+} > Cr^{5+} > Cr^{6+}$

$Fe^{2+} > Fe^{3+}$

(c) For ions having same oxidation states, the ionic radii decreases with increase in atomic number e.g.,

For 3d-series

Sc^{2+} >	Ti^{2+} >	V^{2+} >	Cr^{2-} >	Mn^{2+} >	Fe^{2+} >	Co^{2+} >	Ni^{2+} >	Cu^{2+}
0.95	0.90	0.88	0.84	0.80	0.76	0.74	0.72	0.69

Ionic radii (in Å)

Illustration 3: In a transition series, with an increase in atomic number, the atomic radius does not change very much. Why is it so? **(JEE MAIN)**

Sol:

With increase in atomic number along a transition series, the nuclear charge increases which tends to decrease the size of the atom. But, the addition of electrons in the d-subshell increases the screening effect which counterbalances the increased nuclear charge. Hence, along a transition series the atomic radius does not change very much.

3.2 Atomic Volume and Density

(a) The size decreases along the period and, therefore, atomic volume also decreases along the period.

(b) Atomic volumes are smaller than group 1 and 2 members i.e., s-block elements.

(c) The density, however, increases along the period.

3.3 Melting and Boiling Points

(a) All the transition elements have a higher melting point as compared to s-block elements due to strong metallic bonding as well as unpaired d-electrons leading to covalence.