

d-Block Elements

Daily Tutorial Sheet	Level - 0
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- MnO_4^- : oxidation state of Mn = +7; Group No. = 7

CrO_4^{2-} : oxidation state of Cr = +6; Group No. = 6
- E.C. of transition elements $(n-1)d^{1-10}ns^{1-2}$

In transition element ultimate as well as penultimate orbit is incompletely filled whereas in representative element only ultimate orbit is incompletely filled.
- In lanthanoids the most predominant and stable O.S is +3. For certain elements +2, +3 also exist.
- Transition elements are able to form interstitial compounds when small atoms like H, C, or N are trapped inside the crystal lattice of metals. Due to similar size with these elements transition elements form interstitial compounds.
- The transition elements have a tendency to show variable oxidation state because of penultimate d-electrons to enter into chemical bond formation in addition to ns electrons as the energy of (n-1)d and ns orbitals are comparable.
- Lawrencium [Lr] is last element of actinoids

$\text{Lr} = 5f^{14}6d^17s^2$

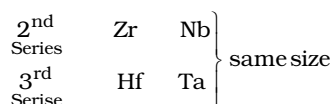
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- | | |
|---|--|
| <p>(i) $\text{Cr}^{3+} \longrightarrow 3d^3$</p> <p>(iii) $\text{Cu}^+ \longrightarrow 3d^{10}$</p> <p>(v) $\text{Co}^{2+} \longrightarrow 3d^7$</p> <p>(vii) $\text{Mn}^{2+} \longrightarrow 3d^5$</p> | <p>(ii) $\text{Pm}^{3+} \longrightarrow 4f^4$</p> <p>(iv) $\text{Ce}^{4+} \longrightarrow 4f^0 (\text{Ce} \rightarrow 4f^3 5d^2 6s^2)$</p> <p>(vi) $\text{Lu}^{2+} \longrightarrow 4f^{14}5d^1$</p> <p>(viii) $\text{Th}^{4+} \longrightarrow 6d^0 7s^0 (\text{Th} \longrightarrow 6d^2 7s^2)$</p> |
|---|--|
- $\text{Mn}^{2+}(3d^5)$ having half – filled stable configuration than $\text{Fe}^{2+}(3d^6)$.
- The transition elements are able to form alloy i.e. homogeneous mixture of two or more metal atoms because of their similar radii. Due to similar radii they are able to mutually substitute one another in their crystalline lattice.

MISCH METAL : It is an alloys of lanthanoid metal ($\approx 95\%$) and iron (5%) with traces of S, C, Ca and Al

It is used in Mg-based alloy to produce bullets, shell and lighter flint.
- The gradual and steady decrease in atomic/ionic radii along the lanthanoid series i.e. from La to Lu is called Lanthanoid contraction. It can be explained on the basis of poor shielding effect of f-orbitals due to which the effective nuclear charge increases regularly and hence size decreases regularly.

Consequences of Lanthanoid Contraction :

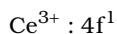
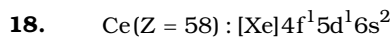
Due to lanthanoid contraction 2nd, 3rd T.S exhibit similar atomic radius



- 11.** A transition element is defined as the one which has incompletely filled d-orbitals in its ground state or in any one of its oxidation state.
Zn, Cd, Hg are not regarded as transition elements because they have fully – filled d^{10} configuration in ground state as well as in their most stable oxidation state.
- 12.** (i) Due to presence of unpaired electrons
(ii) Due to high interatomic attraction
(iii) Transition elements are coloured because when an electron from a lower energy d-orbital is excited to a higher energy d-orbitals with the d sub-shell then the energy of excitation lies in the visible region and the corresponding complementary colour is observed.
(iv) The transition element shows catalytic activity which can be attributed to their ability to show variable oxidation state and their tendency to form complexes.
- 13.** The inner transition elements are those in which the last electron enter f-subshells. The f-block elements are known as the inner transition elements in which the 4f and 5f orbitals are progressively filled. Elements having atomic number 59, 95 and 102 are inner transition elements.
- 14.** The stable oxidation states are predicted on the basis of electronic configuration. Up to Mn, the max. O.S. of stability correspond to sum of s & d-electrons. After Mn, there is decrease in the stability of higher oxidation states.
(i) $3d^3$: Stable oxidation state will be +5 due to outer electronic configuration $3d^3 4s^2$
(ii) $3d^5$: Stable oxidation state will be +7 due to outer electronic configuration $3d^5 4s^2$
(iii) $3d^8$: Stable oxidation state will be +2 due to outer electronic configuration $3d^8 4s^2$
(iv) $3d^4$: Stable oxidation state will be +6 due to outer electronic configuration $3d^4 4s^2$
➤ Though d^4 species does not exist but as it is given it must be chromium (Cr)
- 15.** Preparation of potassium dichromate
Step-I : $4FeCr_2O_4 + 8Na_2CO_3 + 7O_2 \longrightarrow 8Na_2CrO_4 + 2Fe_2O_3 + 8CO_2$
(yellow)
Step-II : $2Na_2CrO_4 + 2H^+ \longrightarrow Na_2Cr_2O_7 + 2Na^+ + H_2O$
chromate (yellow) Dichromate (Orange)
Step-III : $Na_2Cr_2O_7 + 2KCl \longrightarrow K_2Cr_2O_7 + 2NaCl$
(Orange crystals)
→ Chromate and dichromate ions are inter convertible depending upon the pH of the solution
(a) In acidic solution $2CrO_4^{2-} + 2H^+ \longrightarrow Cr_2O_7^{2-} + H_2O$
(yellow) (Orange)
(b) In basic solution $Cr_2O_7^{2-} + 2OH^- \longrightarrow 2CrO_4^{2-} + H_2O$
(Orange) (yellow)
- 16.** The ions which have incompletely filled d-orbitals will be coloured and those with fully filled or empty d-orbitals will be colourless.
 Ti^{3+} , V^{3+} , Mn^{2+} , Fe^{3+} , Co^{2+} are coloured because they have incompletely filled d-orbitals.
 $d^0 d^{10}$ will be colourless.
 $Ti^{3+} \longrightarrow 3d^1$; $V^{3+} \longrightarrow 3d^2$
 $Cu^+ \longrightarrow 3d^{10}$; $Sc^{3+} \longrightarrow 3d^0$

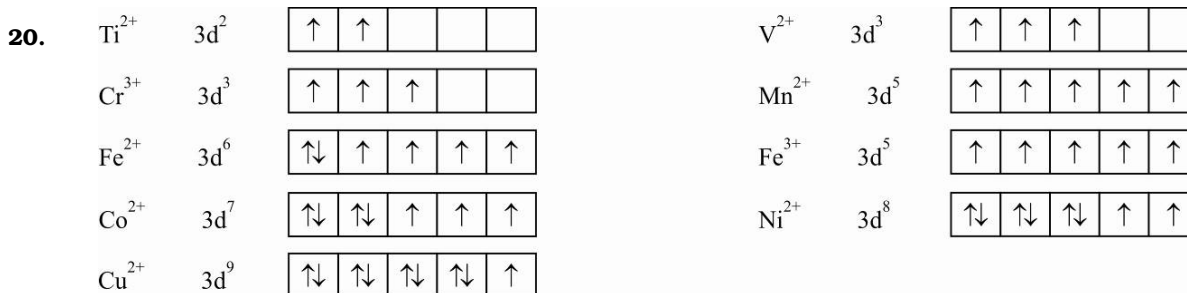
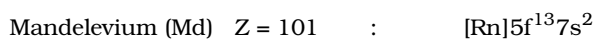
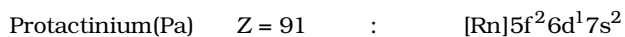
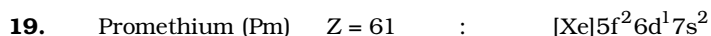


17. The actinoids show a wider range of O.S. which is partly attributed to the fact that the 5f, 6d and 7s levels are of comparable energies. The actinoids show in general +3 oxidation state.

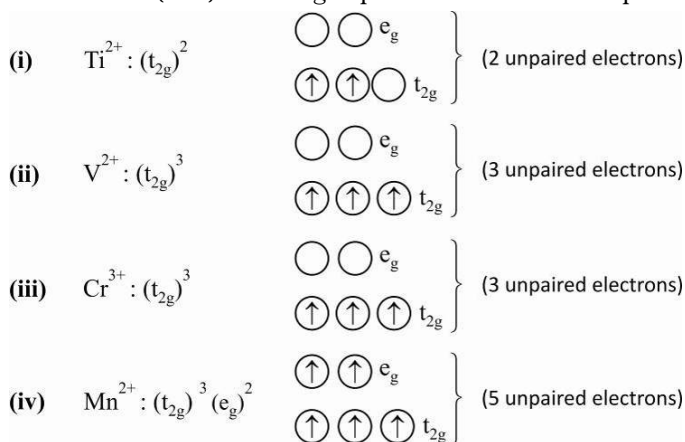


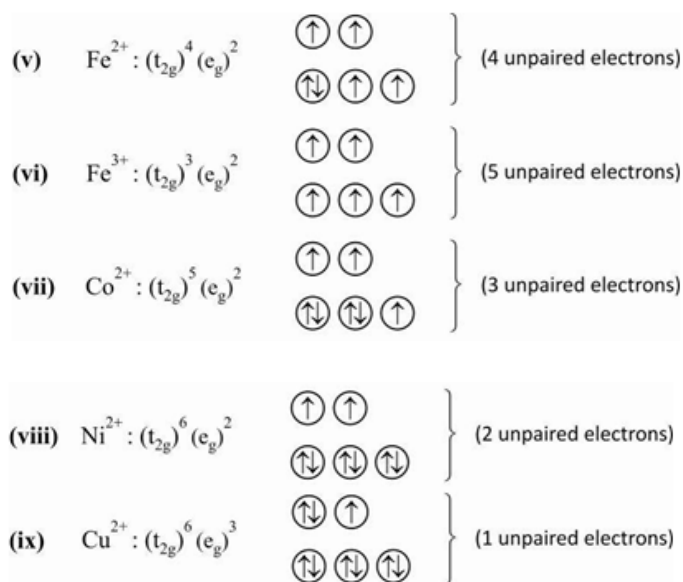
No. of unpaired electrons = 1

$$\mu_s = \sqrt{n(n+2)} = \sqrt{1(1+2)} = \sqrt{3} = 1.73 \text{ BM}$$

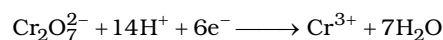


Note : Water (H_2O) forms high spin or outer orbital complexes.

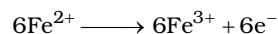
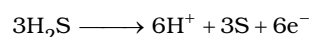
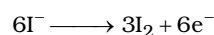




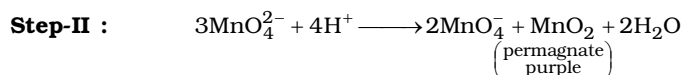
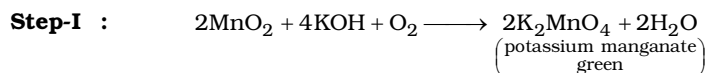
21. $\text{K}_2\text{Cr}_2\text{O}_7$ is a very good oxidizing agent in acidic medium and is reduced to Cr^{3+} .



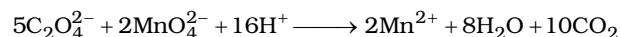
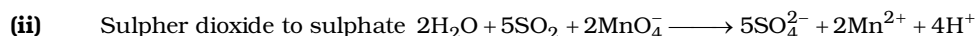
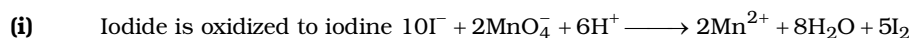
It oxidizes iodides to iodine, sulphides to sulphur, ferrous to ferric



22. Preparation of KMnO_4 .



Oxidizing property

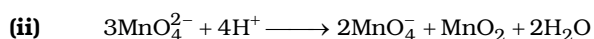
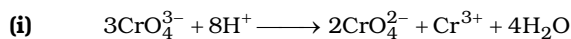


23. (a) $E^\ominus$ values for $\text{Cr}^{3+}/\text{Cr}^{2+}$ is negative (-0.41V) and for $\text{Mn}^{3+}/\text{Mn}^{2+}$ is positive ($+1.57\text{V}$). Thus, Cr^{2+} can undergo oxidation and therefore, is reducing agent. On the other hand, Mn^{3+} can undergo reduction, and therefore, acts as an oxidising agent.
- (b) In the presence of complexing agents, cobalt gets oxidised from +2 to +3 state because Co^{3+} is more stable than Co^{2+} .

(c) After loss of ns , d^1 electron can easily be lost to give a stable configuration. Therefore, the elements having d^1 configuration are either reducing or undergo disproportionation.

24. A reaction in which same atom is oxidised and reduced at the same time is called as the disproportionation reaction.

Example :



25. Mn^{2+} has $4s^0 3d^5$ electronic configuration $\mu = \sqrt{n(n+2)} = \sqrt{1 \times 3} = 1.732$ B.M.

$\text{K}_4[\text{Mn}(\text{CN})_6]$ is low spin complex with one unpaired electron.

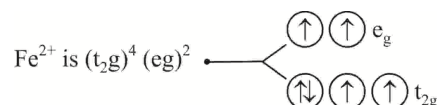
Mn^{2+} is $(t_{2g})^5$  [either there can be 1 unpaired electron or 3 or 5

if $n = 1$, $\mu = 1.73$

$n = 3$, $\mu = 3.9$

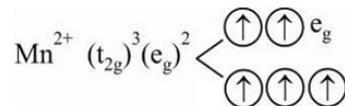
So, the nearest possible value is 1.73]

$[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$; Fe^{2+} : $4s^0 3d^6$, $\mu = \sqrt{4 \times 6} = \sqrt{24} = 4.9$ B.M.



It has four unpaired electrons because H_2O is weak field ligand. It is high spin complex.

In $\text{K}_2[\text{MnCl}_4]$, Mn^{2+} has 5 unpaired electrons, $\mu = \sqrt{5 \times 7} = \sqrt{35} = 5.9$ B.M.



It is because Cl^- is weak field ligand therefore, it is high spin complex.